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UNIVERSITY OF SOUTHAMPTON

FACULTY OF ENGINEERING AND PHYSICAL SCIENCES

Chemistry

**Applications of Metal Nitride Nanostructures in Stabilising High Energy and High
Capacity Battery Systems**

by

Min Zhang

Thesis for the degree of Doctor of Philosophy

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ABSTRACT

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Applications of Metal Nitride Nanostructures in Stabilising High Energy and High Capacity Battery Systems

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Applications of metal nitride nanostructures in stabilising high energy and high capacity battery systems were investigated. Sol-gel synthesis routes using *tetrakis(dimethylamido)titanium(IV)* and a propylamine or ammonia cross linking agent, followed by thermal treatment under NH_3 or H_2+N_2 , were developed to produce TiN powders of small crystallite size (<10 nm). The TiN with good conductivity were coated on LiFePO_4 cathodes in lithium-ion batteries, which exhibited significantly improved electrochemical performance with a discharge capacity of 159 mA h g^{-1} at 0.1 C , that is $\sim 93\%$ of the theoretical capacity. A literature review of various synthetic routes such as solid-state reactions, hydrothermal/solvothermal synthesis and sol-gel process to produce LiCoPO_4 was performed, and various strategies such as surface modification, ion doping, size reduction and morphology control to improve the electrochemical performance of LiCoPO_4 were summarised. Olivine-structured LiCoPO_4 was prepared via a facile solvothermal synthesis, using various ratios of water/diethylene glycol co-solvent, followed by thermal treatment under Ar, air, $5\% \text{H}_2/\text{N}_2$ or NH_3 . The LiCoPO_4 prepared after heating in Ar exhibited high initial discharge capacity of 147 mA h g^{-1} at 0.1 C with capacity retention of 70% after 40 cycles. This is attributed to the enhanced electronic conductivity of LiCoPO_4 due to the presence of Co_2P after firing under Ar. In addition, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesized via solid-state reaction with 2% Li excesses were found to have minimum TiO_2 impurities, which delivered an initial capacity of 165 mA h g^{-1} . TiN were coated onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes in lithium-ion batteries, which exhibited improved initial capacity of 174 mA h g^{-1} . Finally, nanostructured TiN were prepared by a cross-linked sol-gel method with HDA or P123 as a surfactant, or evaporation induced self-assembly method with PEO-b-PS as a surfactant, and heated under NH_3 at a variety of processing conditions. Mesoporous TiN with worm-like morphology and pore size of ~ 20 nm were obtained, and selected TiN samples have been used as host materials for sulfur cathodes in lithium-sulfur batteries.

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DECLARATION OF AUTHORSHIP

I, Min Zhang declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

Applications of Metal Nitride Nanostructures in Stabilising High Energy and High Capacity Battery Systems

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 - (2) Understanding and development of olivine LiCoPO₄ cathode materials for lithium-ion batteries
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 - (3) Solvothermal water-diethylene glycol synthesis of LiCoPO₄ and effects of surface treatments on lithium battery performance
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Date:

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Definitions and Abbreviations

BET	Brunauer-Emmett-Teller
CV	Cyclic voltammetry
DEG	Diethylene glycol
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EDX	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EMC	Ethyl methyl carbonate
EV	Electric vehicle
HDA	Hexadecylamine
HEV	Hybrid electric vehicle
HT	Hydrothermal synthesis
LIB	Lithium-ion battery
LiPF ₆	Lithium hexafluorophosphate
LSB	Lithium-sulfur battery
NMP	N-methyl-2-pyrrolidone
P123	Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethane oxide)
PEO-b-PS	Poly(ethylene oxide)-block-polystyrene
PTFE	Polytetrafluoroethylene
PVDF	Poly(vinylidene fluoride)
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
ST	Solvothermal synthesis
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
VMP	Variable multi-channel potentiostat
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1: Introduction

Development of environmentally friendly, sustainable and renewable energy supplies is vital to meet the increasing energy demand of modern society and emerging ecological concerns.¹⁻³ Due to their high energy density, high power density, and light weight compared to conventional batteries,⁴⁻⁶ lithium-ion batteries (LIBs) and lithium-sulfur batteries (LSBs) are promising reversible energy storage devices for large scale industrial application.⁵⁻¹¹

Metal nitrides have been studied as electrode materials for batteries and supercapacitors in their own right for some years.¹² However, they have also been combined with other electrode materials to form structured composites with improved conductivity and stability relative to the active electrode material itself.¹³⁻¹⁶ TiN is suitable for these purposes as it possesses good electrical conductivity, low cost, and good chemical and thermal stability.^{17, 18}

1.1 Aims and objectives

The aim of this project was to investigate the applications of metal nitride nanostructures in stabilising high energy and high capacity battery systems. This work will mainly focus on the research of the following two potentially important areas.

(1) The application of TiN conductive coating onto electrode materials such as LiFePO_4 and LiCoPO_4 cathodes, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for lithium-ion batteries, where the higher stability of TiN relative to carbon at high potentials may improve the cycling life of these materials, resulting in electrochemical performance improvements.

(2) TiN possesses good electrical conductivity and good chemical and thermal stability, and there are opportunities to employ porous TiN in lithium-sulfur batteries as a highly efficient immobilizer to trap polysulfides, which may improve the electrical conductivity and reduce the shuttle effect in lithium-sulfur batteries.

1.2 Lithium-ion batteries

As a promising reversible energy storage system, lithium-ion batteries are not only widely used in portable electronic devices such as laptops, cameras and smart phones, but also to power emerging large-scale applications such as electric vehicles and hybrid electric vehicles.⁵⁻⁸

1.2.1 Principles of lithium-ion batteries

The schematic of Li-ion batteries is shown in Figure 1-1, with a LiCoO_2 cathode and a graphite anode as an example.¹⁹ In the charge process, the LiCoO_2 cathode loses Li^+ and e^- to produce $\text{Li}_{0.5}\text{CoO}_2$ ($\text{LiCoO}_2 \rightarrow \text{Li}_{0.5}\text{CoO}_2 + \frac{1}{2}\text{Li}^+ + \frac{1}{2}e^-$), and the C_6 anode accepts Li^+ and e^- to produce LiC_6 ($\text{C}_6 + \text{Li}^+ + e^- \rightarrow \text{LiC}_6$). The overall charge reaction in Li-ion battery is $2\text{LiCoO}_2 + \text{C}_6 \rightarrow 2\text{Li}_{0.5}\text{CoO}_2 + \text{LiC}_6$.²⁰⁻²⁵ The opposite reaction occurs in the discharge process.

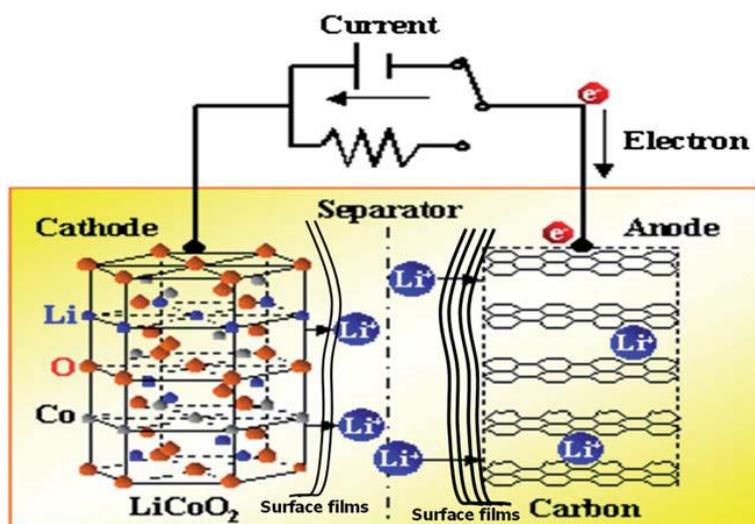


Figure 1-1 Schematic of lithium-ion battery based on LiCoO_2 cathode and graphite anode. Reproduced from Ref. ¹⁹ with permission from the Royal Society of Chemistry 2011.

1.2.2 Cathodes in lithium-ion batteries

The cathode material is critical in determine the energy density, safety, life cycle and cost in LIBs.^{4, 26, 27} Three types of cathode materials have been intensively investigated, i.e. layered transition metal oxides, Mn-based spinels and polyanion-type materials.²⁸⁻³³ The structure, properties and electrochemical performance of the promising cathode materials are discussed below.

(1) Layered transition metal oxide cathode materials. LiCoO_2 is the most commonly used cathode material in LIBs.³⁰ LiCoO_2 with $\alpha\text{-NaFeO}_2$ structure has a distorted rock-salt structure (Figure 1-2). The cations order in alternating (111) planes for lithium transport, which results in a trigonal structure ($R\bar{3}m$).³⁴ LiCoO_2 has been successfully applied in commercial use, but it has been limited in large scale industrial application due to the high cost and limited availability of cobalt and unstable cycle stability during charge/discharge in Li-ion batteries.^{35, 36}

LiNiO_2 with the $\alpha\text{-NaFeO}_2$ structure has lower cost and higher energy density than LiCoO_2 . However the structure of LiNiO_2 is less ordered and less stable, which causes Ni occupying sites in the lithium plane to impede lithium transport during charge/discharge.^{37, 38} The substitution of Co in LiNiO_2 to

form $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ improves the degree of ordering to obtain higher specific capacity and cycle performance in Li-ion batteries.³⁹

LiMnO_2 with a monoclinic structure can transform to a layered hexagonal structure during cycling.^{40, 41} The substitution of Ni or Co in LiMnO_2 to form $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ leads to an $\alpha\text{-NaFeO}_2$ structure, which exhibited high specific capacity and good cycle stability and rate capability.⁴² The Co substitution can improve the conductivity and structural stability of LiMnO_2 ,⁴³ and Ni substitution can stabilize the structure during charge/discharge.⁴⁴

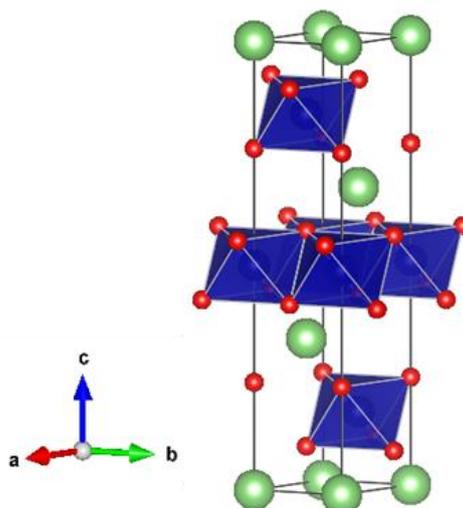


Figure 1-2 Crystal structure of layered LiCoO_2 (green: Li atoms, blue: CoO_6 octahedra, red: O atoms).

(2) Mn-based spinels cathode materials. Mn-based spinel cathode materials like LiMn_2O_4 exhibit a spinel structure ($Fd\bar{3}m$ space group), in which Li and Mn mainly occupy the tetrahedral and octahedral sites, respectively (Figure 1-3).⁴⁵ The lithium transport paths are three dimensional networks instead of planes. Compared with the layered transition metal oxide cathode materials such as LiCoO_2 , LiMn_2O_4 exhibited lower cost and higher safety, but with lower theoretical capacity of 148 mA h g^{-1} .⁴⁶⁻⁴⁸ The LiMn_2O_4 suffers from capacity fading caused by the dissolution of Mn^{2+} into the electrolyte and phase change during charge/discharge.⁴⁹ The substitution of other transition metals such as Fe, Co and Ni in LiMn_2O_4 has been investigated. It was found that the substitution of Fe leads to higher discharge capacity, Co substitution enhances the structural stability and cycle performance in charge/discharge, and Ni addition on the surface of LiMn_2O_4 improves cycle stability.^{30, 50-52}

The Ni Substituted spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a promising high-voltage cathode material for LIBs due to its high redox potential of $\sim 4.7 \text{ V vs. Li/Li}^+$ and improved energy density.^{28, 53} $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with Ni and Mn occupying the octahedral sites randomly, forms three-dimensional Li^+ transport channels.⁵⁴ However, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ suffers from capacity fading during cycling, especially at elevated

temperature, which is ascribed to the dissolution of Mn^{2+} and the decomposition of electrolyte at high working voltage.^{28, 29, 48} Element doping with metallic cations such as Mg, Fe, Al, Co have been proved to be effective in improving the electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.⁵⁵⁻⁵⁷

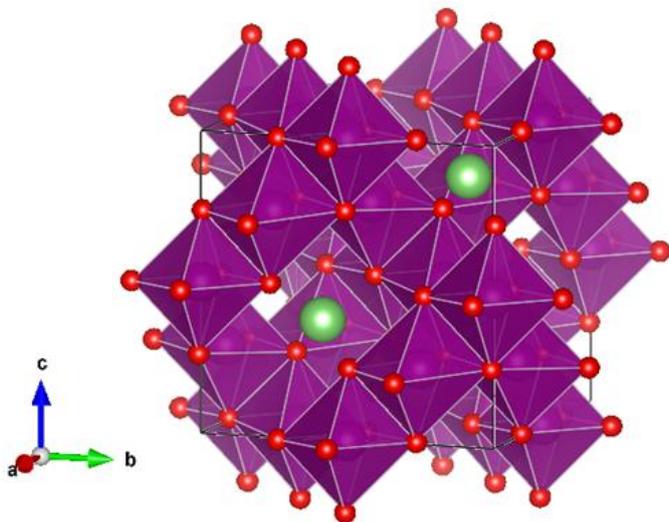


Figure 1-3 Crystal structure of spinel LiMn_2O_4 (green: Li atoms, purple: MnO_6 octahedra, red: O atoms).

(3) Polyanion-type cathode materials. Polyanion-type cathode materials like phosphates (LiMPO_4 , $\text{M} = \text{Fe, Mn, Co, Ni}$) have attracted considerable attention as cathode materials for LIBs due to their high theoretical specific capacities, good thermal stability and high redox potentials vs Li/Li^+ .^{4, 6, 58} The phosphates exhibited the olivine structure ($Pnma$ space group), in which the Li and transition metal (M) occupy octahedral sites, P occupies tetrahedral sites, and Li forms one-dimensional channels along the $[010]$ direction (Figure 1-4).⁵⁹ The most commonly used phosphate is LiFePO_4 with a redox potential of 3.45 V vs Li/Li^+ and theoretical specific capacity of 170 mA h g^{-1} , which has the best electrochemical performance and has been successfully commercialised.⁶⁰⁻⁶⁵

Other members of the olivine family such as LiMnPO_4 and LiCoPO_4 are also being researched intensively.^{4, 66-68} LiMnPO_4 exhibits a redox potential of 4.1 V vs. Li/Li^+ and a theoretical specific capacity of 170 mA h g^{-1} .⁶⁹ However, it suffers from very low electrical conductivity, which resulting in poor rate capability when performed in LIBs.^{70, 71} LiCoPO_4 was firstly reported by Amine *et al* in 2000,⁷² and has received particular attention due to the high redox potential of 4.8 V vs Li/Li^+ and a theoretical capacity of 167 mA h g^{-1} comparable to LiFePO_4 of 170 mA h g^{-1} .⁷³⁻⁷⁵ However, the use of LiCoPO_4 as a cathode has been hindered by the unsatisfactory cycle stability and rate performance due to its low electronic conductivity and Li^+ ion conductivity, as well as the decomposition of electrolytes under high potentials.⁷⁶⁻⁸³

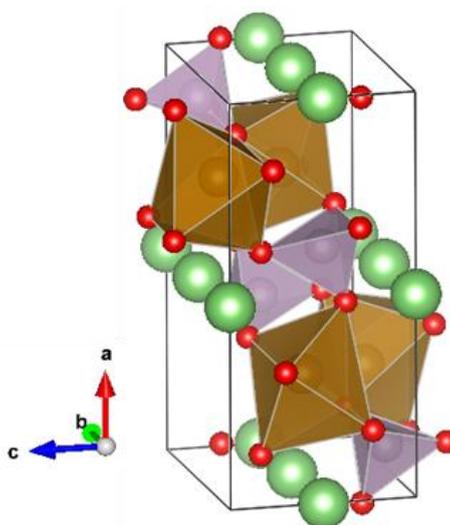


Figure 1-4 Crystal structure of olivine structured LiFePO_4 (green: Li atoms, brown: FeO_6 octahedra, purple: PO_4 tetrahedra, red: O atoms).

1.2.3 Anodes in lithium-ion batteries

The anode is also a crucial component affecting the electrochemical performance of LIBs. The most intensively investigated anode materials could be mainly classified as carbon-based materials, alloys-based materials, spinel structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and metal oxide-based anodes.^{22, 23}

(1) Carbon-based anodes. Carbon-based materials were the most successfully commercialised anode materials in LIBs, with high specific charges and redox potentials close to 0 V vs Li/Li^+ .^{22, 25} The carbon-based materials could be classified into graphite/graphitized material, non-graphitized soft carbon and hard carbon.²⁴ Graphitized carbon materials exhibited a high theoretical capacity of 372 mA g^{-1} , but the formation of solid electrolyte interface (SEI) in charge/discharge process can reduce the reversibility of the lithium intercalation reaction and increase battery resistance, thus reducing the power density during cycling.^{24, 84} Hard carbon exhibited a high Li-storage capacity and good power capability,^{85, 86} while the poor capacity reversibility and low electrical conductivity of non-graphitized soft carbon limits their industrial application as anode materials in LIBs.²⁴

(2) Spinel structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a superior cycling stability owing to its negligible volume change during charge/discharge process, high potential of $\sim 1.55 \text{ V}$ vs. Li/Li^+ , high thermal stability and good safety.^{87, 88} This makes it a promising anode material for high power LIBs used for large-scale applications such as electric vehicles (EVs) or hybrid electric vehicles (HEVs).⁸⁹⁻⁹¹ However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ suffers from a low electrical conductivity ($\sim 10^{-13}$ to $10^{-8} \text{ S cm}^{-1}$)⁹²⁻⁹⁴ and lithium diffusion coefficient ($\sim 10^{-13} \text{ cm}^2 \text{ s}^{-1}$),⁹⁵⁻⁹⁹ which results in poor rate capability in LIBs. Tremendous efforts such as surface modification and ion doping have been made to tackle these issues, thus resulting in improved electrochemical performance for Li-ion batteries.⁸⁷⁻⁸⁹

(3) Alloy-based anodes. Alloy-based anodes were formed by Li alloyed with metallic and semi-metallic elements in groups IV (Si, Ge, Sn and Pb) and group V (P, As, Sb and Bi), as well as other elements such as Al, Ga, In, Mg, Ag, Au, Zn and Cd.^{23, 100-102} These Alloy-based anodes exhibited high specific capacity, high safety and moderate working potential vs. Li/Li⁺. However, the large volume change in the process of Li alloying/dealloying causes electrode cracking and poor electrical contact, thus resulting in rapid capacity fading during cycling.²³⁻²⁵ Strategies such as morphology control and carbon coating have been applied to overcome the large volume change to improve the cycle stability of LIBs, with partial success.¹⁰⁰⁻¹⁰²

(4) Metal oxide-based anodes. Metal oxide-based anodes have high specific capacities of 500-1000 mA h g⁻¹.²²⁻²⁵ For example, SnO₂ anodes showed a high theoretical capacity of 790 mA h g⁻¹ but it suffers from large capacity loss due to the irreversible Li intercalation reaction.¹⁰³ Anatase TiO₂ with advantages of low-cost, non-toxicity and abundant availability is a promising anode material for LIBs.^{104, 105} Iron oxides, such as hematite (Fe₂O₃) and magnetite (Fe₃O₄), showed a theoretical capacity of 1007 and 926 mA h g⁻¹, respectively.^{106, 107} But these iron oxide anodes exhibit poor cycle stability caused by their low electrical and ionic conductivity, and large volume change in the charge/discharge process.^{108, 109} Cobalt oxides, such as Co₃O₄ and CoO, showed a theoretical capacity of 890 and 715 mA h g⁻¹, respectively.^{107, 110} Strategies like morphology control to form nanostructured metal oxide materials have been employed to obtain anodes with high specific capacity and good cycle stability.^{22, 23}

1.3 Lithium-sulfur batteries

Lithium-sulfur (Li-S) batteries have a theoretical energy density of ~2500 W h kg⁻¹, which is much higher than that of Li-ion batteries.^{111, 112} Moreover, the sulfur cathode is cheap, abundant and environmentally benign.^{113, 114} Therefore, Li-S batteries are regarded as a promising energy storage system for large scale industrial application such as electric vehicles.⁹⁻¹¹

1.3.1 Principles of lithium-sulfur batteries

The schematic of Li-S batteries is shown in Figure 1-5.¹¹⁵ In the discharge process, the lithium anode is oxidized to produce Li⁺ and e⁻ (Li → Li⁺ + e⁻), and the sulfur cathode is reduced by reacting with Li⁺ and e⁻ to produce lithium sulfide (S₈ + 16Li⁺ + 16e⁻ → 8Li₂S). The overall discharge reaction in a Li-S battery is 16Li + S₈ → 8Li₂S. The opposite reaction occurs in the charge process.¹¹⁵⁻¹¹⁷

The actual charge/discharge process is more complicated than the reactions above (Figure 1-5 b).¹¹⁵ During discharge, sulfur is first lithiated to produce long-chain lithium polysulfides (S₈ → Li₂S₈ → Li₂S₆ → Li₂S₄), which correspond to the upper plateau at ~2.3 V in the discharge voltage

profile. Then, the long-chain lithium polysulfides are further lithiated to produce short-chain lithium sulfides ($\text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_2 \rightarrow \text{Li}_2\text{S}$), represented by the lower discharge plateau at ~ 2.1 V. The backward reaction occurs in the charge process.¹¹⁵⁻¹¹⁷

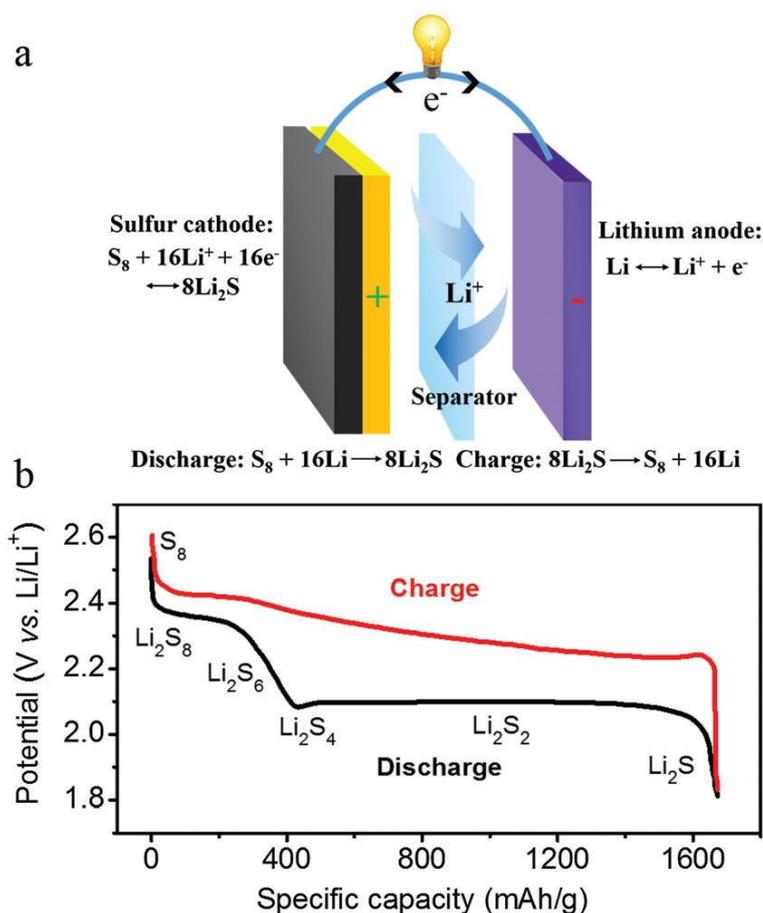


Figure 1-5 (a) Schematic of Li-S batteries and (b) charge/discharge voltage profile of Li-S batteries in ether-based electrolytes. Reproduced from Ref. ¹¹⁵ with permission from the Royal Society of Chemistry 2016.

1.3.2 Challenges and solutions of lithium-sulfur batteries

The practical use of Li-S batteries has been inhibited by the poor conductivity of sulfur and lithium sulfide, the large volume expansion of the sulfur cathode in discharge ($\sim 80\%$), the shuttle effect caused by the dissolution and diffusion of intermediate long-chain lithium polysulfides in electrolytes, as well as safety issues of lithium metal anodes.¹¹⁸ Tremendous efforts have been applied to tackle these issues, such as encapsulating sulfur cathodes with conductive host materials like carbon, polymeric and inorganic materials. The host materials can improve the conductivity of the sulfur cathode, confine lithium polysulfides within the host and buffer the volume change of sulfur cathode during the charge/discharge process.¹¹⁵

1.3.3 Cathodes in lithium-sulfur batteries

Conductive host materials have been combined with sulfur cathodes to improve the specific charge/discharge capacity, cycle stability and rate capability of Li-S batteries. These cathodes can be divided into sulfur-carbon composite cathodes, sulfur-polymer composite cathodes, sulfur-inorganic materials composite cathodes, as well as lithiated sulfur cathodes.

(1) Carbon host materials for sulfur cathodes. Various carbon host materials combined with sulfur to form sulfur-carbon composite cathodes have been reported to improve the specific capacity and cycle stability of Li-S batteries. These carbon based host materials can be divided into porous carbons, carbon nanotubes/nanofibers and graphene or graphene oxides.

Porous carbon-sulfur composites have been prepared by Gao et al. via thermal treatment of sublimed sulfur and microporous carbon spheres.¹¹⁹ A sulfur-carbon composite with 42 wt% sulfur loading exhibited a reversible capacity of $\sim 650 \text{ mA h g}^{-1}$ after 500 cycles at a current density of 400 mA g^{-1} . The micropores confined sulfur and lithium polysulfides to prevent them from releasing into the electrolyte, thus the electrochemical reaction of the sulfur cathode was constrained within the narrow micropores, resulting in an improved cycle stability of Li-S batteries.¹¹⁹ Li et al. prepared mesoporous carbon-sulfur composite cathodes for Li-S batteries with tunable pore sizes ranging from 3 nm to 22 nm. It was found that the partial sulfur-filling composites exhibited higher initial discharge capacity and better cycle stability as full sulfur-filling in mesopores hinders the access of electrolyte and ion transport. An initial specific capacity of $\sim 1390 \text{ mA h g}^{-1}$ at 0.1 C rate and good cycle stability of $\sim 840 \text{ mA h g}^{-1}$ over 100 cycles were achieved via optimising the pore size of mesoporous carbon (22 nm) and sulfur loading (50 wt%).¹²⁰

A hollow carbon nanofiber encapsulated sulfur cathode was prepared by Cui et al. using anodic aluminium oxide as a template. The small dimension of these hollow carbon nanofibers can trap polysulfides, and the thin carbon wall enables quick Li^+ ion transport. The sulfur-carbon nanofiber composite cathodes showed a reversible capacity of $\sim 730 \text{ mA h g}^{-1}$ at 0.2 C rate after 150 cycles.¹²¹ Wang et al. prepared a binder-free sulfur-carbon nanotube composite cathode via a solution-based method. The conductive carbon nanotubes confine the sulfur and polysulfides, buffer the volume change of the sulfur cathode during the charge/discharge process, and offer the three-dimensional electron pathway. The sulfur-carbon nanotube composite cathode in Li-S batteries exhibited an initial discharge capacity of 1071 mA h g^{-1} at 1 C rate and a capacity retention of 85% over 100 cycles, with good rate capabilities of 1006 mA h g^{-1} at 2 C, 960 mA h g^{-1} at 5 C, and 879 mA h g^{-1} at 10 C.¹²²

Due to its high electronic conductivities and large surface areas, graphene or graphene oxides have been used as host materials for sulfur to improve the conductivity of the sulfur cathode and trap the intermediate lithium polysulfides. A graphene-sulfur-graphene sandwich structured cathode has been fabricated by Li et al. As shown in Figure 1-6, one graphene membrane for use as a current collector (GCC) was coated with sulfur, and the other graphene membrane was coated onto a separator (G-separator) (denoted as GCC/S+G-separator). Comparing to Al foil current collector and uncoated separator, the graphene current collector and graphene coated separator have advantages of enabling quick electronic and ionic transport, reducing the contact impedance between current collector, sulfur and electrolyte (Figure 1-6 c), buffering the volume change of sulfur cathode, and trapping the intermediate lithium polysulfides to alleviate the shuttle effect during charge/discharge. The Li-S battery with GCC/S+G-separator showed a stable long-term cycle performance with a Coulombic efficiency above 97% at 1.5 A g⁻¹ over 300 cycles (Figure 1-6 b). An initial specific capacity of 1345 mA h g⁻¹ with a capacity retention of higher than 1000 mA h g⁻¹ was obtained at a current density of 0.3 A g⁻¹ (Figure 1-6 d).¹²³ Chen et al. deposited monodispersed sulfur nanoparticles with diameter of 5 nm on the surface of reduced graphene oxide via the sulfur-amine chemistry. These Li-S batteries showed high specific capacities of 1672 and 1089 mA h g⁻¹ at 0.1 C and 4 C, respectively, and good cycle stability of 1017 and 965 mA h g⁻¹ after 500 cycles at 0.5 C and 1 C, respectively.¹²⁴

(2) Inorganic host materials for sulfur cathodes. Inorganic materials have been considered as promising host materials for sulfur cathodes as some inorganic materials such as metal oxides exhibited strong affinity with lithium polysulfides.

A sulfur-TiO₂ yolk-shell nanostructure with internal void space to accommodate the volume expansion of sulfur was reported by Seh et al. The sulfur-TiO₂ nanocomposites showed an initial specific capacity of 1030 mA h g⁻¹ at 0.5 C, with capacity retention of 67% and Coulombic efficiency of 98% after 1000 cycles.¹²⁵ Zhang et al. discovered a strong sulfur binding with conductive Magnéli phase Ti₄O₇. Due to the strong adsorption of sulfur on the low-coordinated Ti sites of Ti₄O₇, the Ti₄O₇-sulfur cathodes showed specific capacities of 1342, 1044, and 623 mA h g⁻¹ at 0.02, 0.1, and 0.5 C, respectively, and a good cycle stability of 99% capacity retention at 0.1 C for 100 cycles.¹²⁶ Ti₂C conductive MXene nanosheets have been reported to be promising host materials for sulfur cathodes in Li-S batteries due to the strong interaction between surface Ti atoms and lithium polysulfides. This Ti₂C-sulfur cathode exhibited a specific capacity of 1200 mA h g⁻¹ at 0.2 C, and a capacity retention of 80% at 0.5 C over 400 cycles.¹²⁷

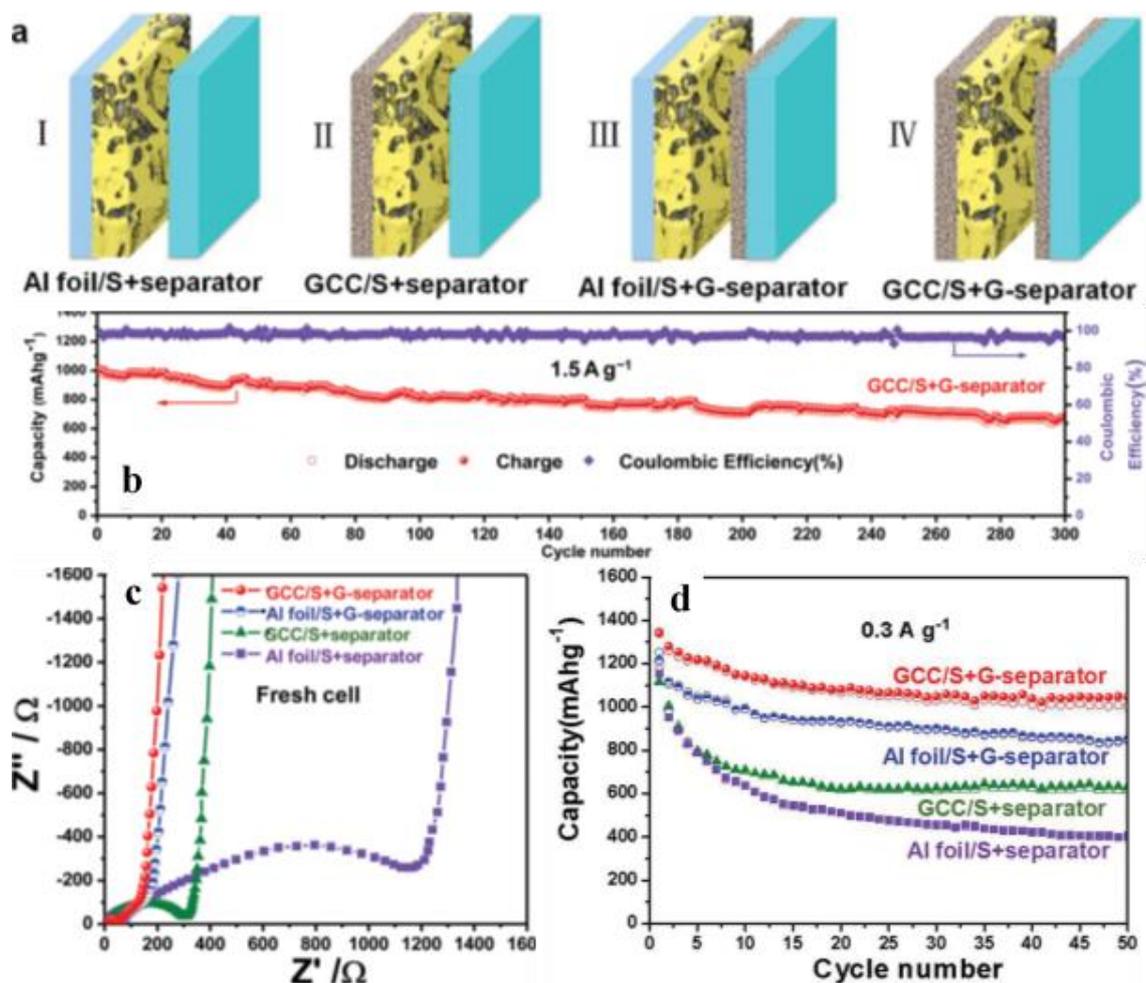


Figure 1-6 (a) Schematic of electrode configurations of: (I) an Al foil current collector, sulfur cathode, and separator (Al foil/S+separator), (II) a graphene current collector, sulfur cathode, and separator (GCC/S+separator), (III) an Al foil current collector, sulfur cathode, and graphene coated separator (Al foil/S+G-separator), (IV) a graphene current collector, sulfur cathode, and graphene coated separator (GCC/S+G-separator). (b) Cycle stability and Coulombic efficiency of Li-S batteries with GCC/S+G-separator at a current density of 1.5 A g⁻¹ for 300 cycles. (c) Nyquist plots of electrodes in different configurations. (d) Cycle performance of Li-S batteries with different configurations at 0.3 A g⁻¹ for 50 cycles. Reproduced from Ref. ¹²³ with permission from John Wiley and Sons 2014.

(3) Polymer host materials for sulfur cathodes. Conductive polymers with flexible structure have been developed as host materials for sulfur cathodes to facilitate electronic conduction, accommodate the volume expansion of sulfur and trap lithium polysulfides produced during charge/discharge process.

Core-shell structured sulfur-polythiophene composites were obtained by Chen et al. via an in situ chemical oxidative polymerization process. The core-shell composites showed an initial specific capacity of 1119 mA h g⁻¹, with a capacity retention of 830 mA h g⁻¹ after 80 cycles.¹²⁸ A polyaniline-

sulfur yolk-shell nanocomposite was synthesized by Zhou et al. via a heating vulcanization of a polyaniline-sulfur core-shell structure. Due to the internal void space inside the polymer shell to accommodate the volume expansion of sulfur in the discharge process, the yolk-shell nanocomposites delivered an improved cycle stability of 765 mA h g^{-1} at 0.2 C over 200 cycles.¹²⁹ Cui et al. investigated the effects of three typical conductive polymers such as polyaniline (PANI), polypyrrole (PPY) and poly(3,4-ethylenedioxythiophene) (PEDOT) on the sulfur cathode. The conductive polymers were uniformly coated onto monodisperse hollow sulfur nanospheres via a polymerization process. It was found that the functional groups in these conductive polymers exhibited strong chemical interactions with lithium polysulfides, thus improving the long-term cycle stability and rate capability of sulfur cathodes in Li-S batteries.¹³⁰ The PEDOT coated sulfur nanospheres showed the highest specific capacity of 1165 mA h g^{-1} at 0.5 C , with a capacity retention of 67% over 500 cycles, and good rate capability of 858 and 624 mA h g^{-1} at 2 C and 4 C , respectively.¹³¹

1.3.4 Anodes in lithium-sulfur batteries

Lithium metal is the typical anode material for Li-S batteries, which exhibits high gravimetric energy density and cell voltage when coupled with the sulfur cathode. However, the lithium anodes are likely to be attacked by dissolved lithium polysulfides in ether-based electrolytes, thus resulting in the shuttle effect and low Coulombic efficiency during cycling in Li-S batteries. Tremendous efforts have been applied to protect lithium metal anodes from dissolved polysulfides to alleviate the shuttle effect in Li-S batteries.

Liu et al. designed a hybrid anode structure using an electrically connected graphite and lithium metal to control undesirable surface reactions on lithium. This lithiated graphite acts as a solid electrolyte interface layer to protect lithium metal from side reactions, thus resulting in a reversible specific capacity of higher than 800 mA h g^{-1} after 400 cycles at 1737 mA g^{-1} , with a Coulombic efficiency of higher than 99%.¹³² Also, a Li_3N layer is coated on the surface of lithium anode via an in situ method by Wen et al. It was found that the Li_3N layer with high Li^+ conductivity on the surface of lithium anode acts as a solid electrolyte interface layer to suppress the undesirable side reactions between the lithium anode and electrolyte, and inhibit the growth of lithium dendrites to enhance the safety of Li-S batteries. This Li_3N coated lithium anode showed a discharge capacity of 1087 mA h g^{-1} at 0.5 C and a reversible capacity of 773 mA h g^{-1} after 500 cycles, with a Coulombic efficiency of 92%.¹³³

1.4 Applications of TiN in batteries

TiN has been applied in battery systems due to its good electrical conductivity, low cost, and good chemical and thermal stability.^{17, 18} In this regard, TiN modified electrodes are expected to be promising electrode materials with high reversible capacity, good cycle stability and high rate capability.¹³⁴

1.4.1 TiN in lithium-ion batteries

TiN could be used as a conductivity additive for electrode materials in lithium-ion batteries, i.e. $\text{Li}_4\text{Ti}_5\text{O}_{12}$, silicon nanowires, etc. Kumta et al. synthesized Si/TiN nanocomposites as anode materials for LIBs via high-energy mechanical milling. It was found that TiN acts as an inactive material to provide structural stability of the nanocomposites.¹⁵ Also, Wu et al. prepared carbon coated Si/graphite composites with inactive TiN additives, which act as a buffer to prevent Si from cracking during cycling, thus improves the cycle stability and Coulombic efficiency of anodes in LIBs.¹³⁵ After that, Kalisvaart et al. produced a TiN conductive layer between the Si nanowires anode and the current collector, which showed improved specific capacity of 3581 mA h g^{-1} and high Coulombic efficiency in charge/discharge process.¹⁸ Furthermore, they deposited a 5 nm thick TiN conductive coating onto Si nanowire via atomic layer deposition, which exhibited a capacity retention of 55% over 100 cycles and Coulombic efficiency of 98% at 50th cycles.¹³⁶ Wang et al. prepared TiN coated Si nanoparticles with enhanced specific capacity and rate capability due to the improved conductivity after TiN coating.¹³⁷ A novel TiN nanowire supported Si nanorods anode has been developed by Zhang et al., which delivered a reversible capacity of 3259 mA h g^{-1} over 200 cycles at 1 A g^{-1} and good rate capability of 2257 mA h g^{-1} at 10 A g^{-1} . This could be attributed to the good electrical conductivity and mechanical stability of TiN, which not only provides conductive pathways for Si, but also acts as a stable support to buffer volume changes in charge/discharge process.¹³⁸

DeSisto *et al.* showed that atomic layer deposition of TiN coatings onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder improved the electronic conductivity to deliver a higher capacity (162 mA h g^{-1}) and cycling stability compared with that of uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (133 mA h g^{-1}).¹⁶ Also, Park et al. produced TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanocomposites by thermal nitridation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in NH_3 . The TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode showed a reversible capacity of 120 mA h g^{-1} at 10 C over 70 cycles, which could be attributed to the amorphous TiN formed on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ improved the conductivity of composites.¹³⁹ TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanocomposites has been prepared by Zhang et al. via high-energy ball-milling. The TiN coating can improve the electronic conductivity of the composites, this results in good rate capability of 130 mA h g^{-1} at 20 C, and capacity retention of 85% after 1000 cycles at 20 C.¹⁴⁰ After that, Zheng et al. produced well-dispersed TiN on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via thermal nitridation of

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ with urea as the nitrogen source. The conductivity of anodes was enhanced after TiN coating, this results in an improved specific capacity and cycle stability.¹⁴¹ Well-distributed N-doped carbon and TiN conductive structure on the surface and in the bulk of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been synthesized by Zhang et al. via chemical vapour deposition assisted solid-state reaction. This anode showed a good rate capability of 162 mA h g^{-1} at 20 C, and a capacity retention of 75% after 2500 cycles at 10 C.¹⁴² Also, Wang et al. prepared micron-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with both TiN coating and Ta^{5+} doping via solid-state reaction combined with surface thermal nitridation. The TiN coating improves the electrical contact between particles, and Ta^{5+} doping enhances the intrinsic electronic and ionic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This anode delivered a reversible capacity of 145 mA h g^{-1} at 5 C after 500 cycles with a capacity retention of 92%.¹⁴³ TiN-TiC-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials were prepared by Yan et al. via solid-phase sintering in N_2 with C and Ti as reducing agents. This anode showed specific capacity of 168 and 123 mA h g^{-1} at 0.5 C and 5 C, respectively, with capacity retention of 94% after 200 cycles at 5 C.¹⁴⁴

A novel graphene/TiN hybrid anode with TiN nanoparticles ($\sim 5 \text{ nm}$) uniformly anchored on graphene (Figure 1-7) were produced by Gu et al. via a combination of in situ hydrolysis method and ammonia annealing. The anchoring of TiN nanoparticles on graphene forms highly electronic and ionic conductive network. This graphene/TiN hybrid anode exhibited a reversible capacity of 646 mA h g^{-1} at 20 mA g^{-1} with capacity retention of 86% after 200 cycles, and rate capability of 325 mA h g^{-1} at 2000 mA g^{-1} (Figure 1-7).¹⁴⁵ Flexible TiN nanowires were firstly studied as anodes for LIBs by Lu et al. prepared via a hydrothermal method and annealing on a carbon fabric. TiN nanowires anode exhibited an initial capacity of 567 mA h g^{-1} with a capacity retention of 80% at 335 mA g^{-1} over 100 cycles, and a rate capability of 288 mA h g^{-1} at 1675 mA g^{-1} .¹⁴⁶

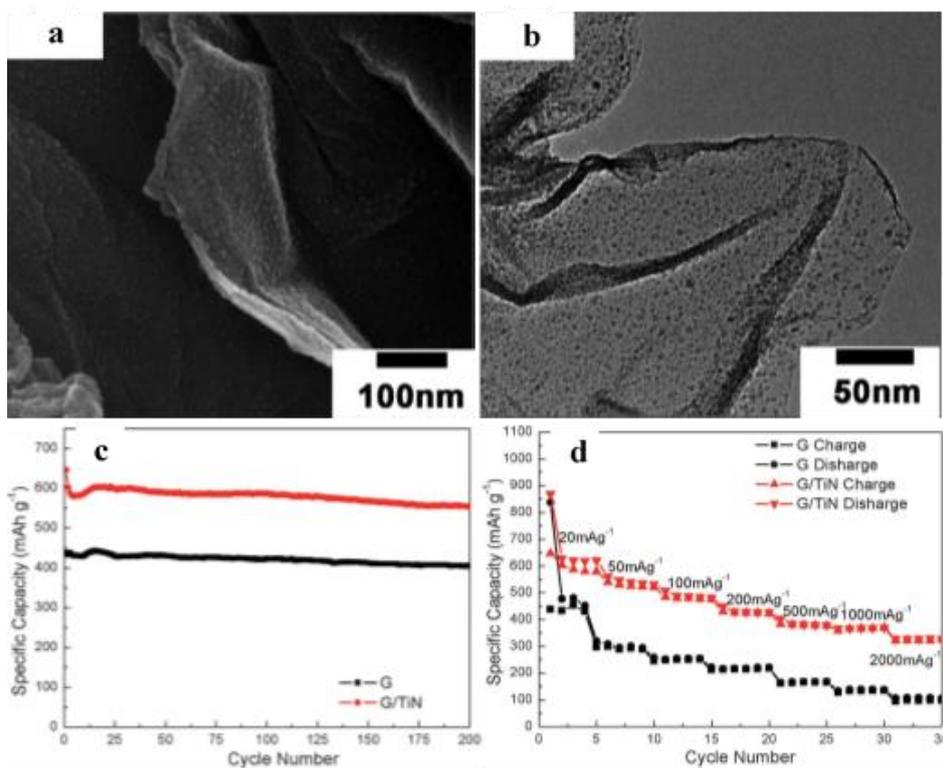


Figure 1-7 (a) SEM and (b) TEM images of graphene/TiN hybrids; (c) cycle stability at 20 mA g⁻¹ and (d) rate capability of graphene/TiN hybrids and graphene at various rates from 20 mA g⁻¹ to 2000 mA g⁻¹. Reproduced from Ref. ¹⁴⁵ with permission from the Royal Society of Chemistry 2012.

1.4.2 TiN in lithium-air batteries

There are opportunities to use TiN in lithium-air batteries to provide electrocatalytic activity or act as an electrode with a stable surface and high surface area. Zhou et al. reported that TiN acts as an oxygen reduction reaction (ORR) catalyst for Li-air fuel cell in a weak acidic aqueous electrolyte.¹⁴⁷ Later, they found that nano- and micro-sized TiN exhibited electrocatalytic activities toward ORR in alkaline media and for Li-air fuel cell, and the nano-sized TiN showing much better catalytic activity.¹⁴⁸ Furthermore, an 1D coaxial Pt/TiN nanotube arrays with enhanced electrocatalytic activity towards ORR for Li-air batteries was designed by Cui et al. via electrodeposition of Pt into a TiN nanotube array (Figure 1-8).¹⁴⁹ Later, they developed a carbon- and binder-free RuO_x/TiN nanotube arrays as the cathode for nonaqueous Li-O₂ batteries by electrodepositing RuO_x into TiN nanotubes. This RuO_x/TiN nanotube cathode exhibited improved electronic conductivity, as well as higher stability due to the coaxial nanostructure, thus resulting in an excellent cycle stability without capacity fading for over 300 cycles.¹⁵⁰

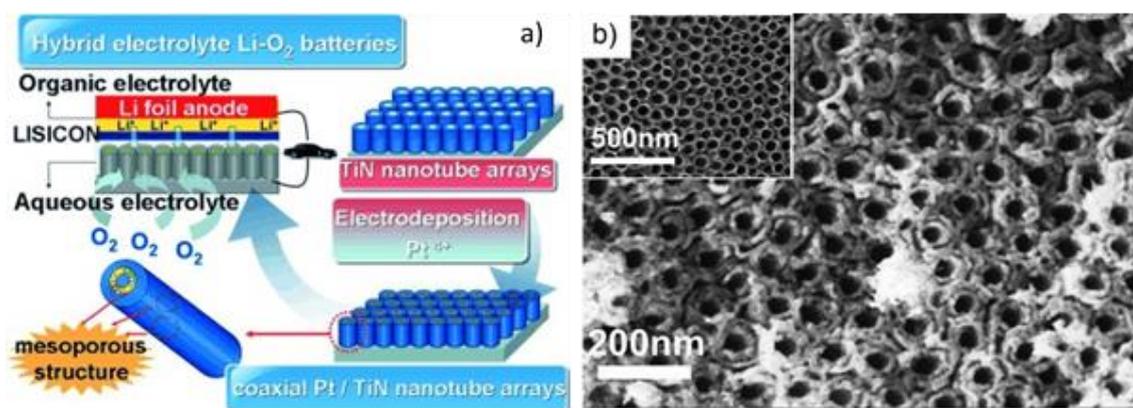


Figure 1-8 (a) Schematic of the preparation of Pt/TiN nanotube arrays and the structure of the Li-air batteries. (b) Top-view SEM images of Pt/TiN nanotube arrays and TiN nanotube arrays (inset). Reproduced from Ref. ¹⁴⁹ with permission from John Wiley and Sons 2012.

Bimodal mesoporous TiN/C microfibers were prepared by Jun et al. as electrocatalysts for Li-O₂ batteries. The bimodal mesoporous TiN/C forms a catalyst-membrane to accommodate Li₂O₂ and transfer the electrolyte and oxygen. The catalyst is stable against Li₂O₂ and efficient for both ORR and oxygen evolution reaction (OER) in Li-O₂ batteries.¹⁵¹ Lee et al. prepared ordered mesoporous TiN as a carbon-free cathode for aprotic Li-O₂ batteries, which showed a robust cycle stability for over 100 cycles. This could be attributed to the well-aligned mesoporous structure and good electric conductivity of TiN.¹⁵² Recently, Cui et al. designed novel cathodes of Ir or MnO₂ supported on well-defined TiN nanorod arrays, which delivered discharge capacity of 2637 and 2530 mA h g⁻¹ at 100 mA g⁻¹, respectively, without obvious capacity fading over 200 cycles. This can be attributed to the 3D array structure with high surface area to promote the dispersion of active materials and inhibit Li₂O₂ formation.¹⁵³

1.4.3 TiN in lithium-sulfur batteries

TiN with high conductivity and unique morphology such as porous structure or hollow sphere are promising host materials for sulfur cathodes in Li-S batteries. For example, Zheng et al. prepared hollow porous TiN tubes with high conductivity as a sulfur host cathode material for Li-S batteries. The TiN not only reduces the shuttle effect in charge/discharge process due to the strong interaction between TiN and lithium polysulfides, but also acts as a catalyst to facilitate the oxidation process in Li-S batteries. The TiN-S cathodes delivered a reversible capacity of 840 mA h g⁻¹ at 0.5 C after 450 cycles, and a rate capability of 1026 mA h g⁻¹ at 5 C.¹⁵⁴ Later, Goodenough et al. reported the mesoporous TiN-enabled highly stable Li-S batteries, which showed a discharge capacity of 988 mA h g⁻¹ at 0.5 C, with capacity retention of 644 mA h g⁻¹ after 500 cycles. This can be ascribed to the high electrical conductivity, robust porous framework and favourable adsorption properties of TiN.¹⁵⁵ Conductive TiN hollow nanospheres with strong lithium polysulfide

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chemisorption were produced by Lu et al. as sulfur hosts for Li-S batteries. This cathode exhibited a reversible capacity of 710 mA h g^{-1} at 0.2 C after 100 cycles.¹⁵⁶ Lu et al. designed uniform honeycomb-like microspheres constructed with TiN to confine polysulfides for Li-S batteries, which delivered a reversible capacity of 650 mA h g^{-1} at 100 mA g^{-1} after 500 cycles.¹⁵⁷

TiN with high electronic conductivity was used as a polysulfide immobilizer for Li-S batteries due to the strong chemisorption effect between TiN and polysulfides. The TiN-S cathodes exhibited a specific capacity of 1012 mA h g^{-1} at 0.5 C, and rate capability of 550 mA h g^{-1} at 5 C.¹⁵⁸ Later, Ng et al. developed nanostructured TiN as cathode materials for lithium/dissolved polysulfide batteries, which delivered a specific capacity of 1524 mA h g^{-1} at 0.1 C, and capacity retention of 1040 mA h g^{-1} for 100 cycles.¹⁵⁹ They also investigated a series of nanostructured transition metal nitrides such as WN, Mo₂N and VN as cathode materials for Li-S batteries.¹⁶⁰ Further investigation were performed on TiN nanotube arrays as sulfur host cathode materials for Li-S batteries, which showed a reversible capacity of 1338 mA h g^{-1} at 0.1 C after 180 cycles.¹⁶¹

TiN can be combined with carbon to form nanostructured host materials for sulfur cathodes in Li-S batteries. As shown in Figure 1-9, Yuan et al. designed a biomimetic root-like TiN/C nanofiber as a freestanding cathode with high sulfur loading for Li-S batteries. The root-like TiN/C matrix with porous interconnected structure transfers polysulfide, electron and electrolyte effectively for the redox reactions. TiN with high catalytic effect further promotes the redox reaction and it can also confine the polysulfides due to the polar Ti-S and N-S bond. The TiN/C cathode exhibited a specific capacity of 737 mA h g^{-1} at 1 C, and a discharge capacity of 983 mA h g^{-1} at 0.2 C with capacity retention of 685 mA h g^{-1} at 0.2 C after 300 cycles (Figure 1-9).¹⁶² You et al. reported a conductive TiN bridged carbon nanotube/sulfur composite cathode, which showed a specific capacity of 1269 and 586 mA h g^{-1} at 0.05 C and 2 C, respectively. This result could be attributed to the TiN bridged multi-porous highly-conductive architecture and the strong chemical interaction of S-N-Ti bond to confine polysulfides.¹⁶³ Recessed deposition of TiN nanoparticles into N-doped porous carbon as a cathode host for Li-S batteries were reported by Chen et al. This cathode delivered a specific capacity of 1338 and 690 mA h g^{-1} at 0.2 C and 5 C, respectively, and capacity retention of 700 mA h g^{-1} at 1 C after 800 cycles.¹⁶⁴ Recently, Xi et al. prepared C/TiN dual shell hollow nanospheres as multi-functional polysulfide hosts for Li-S batteries. It was found that TiN can promote the reduction of polysulfide in discharge and the oxidation of Li₂S in charge process. This C/TiN cathode exhibited a reversible capacity of 453 mA h g^{-1} at 3 C over 300 cycles, with average Coulombic efficiency of 99%.¹⁶⁵

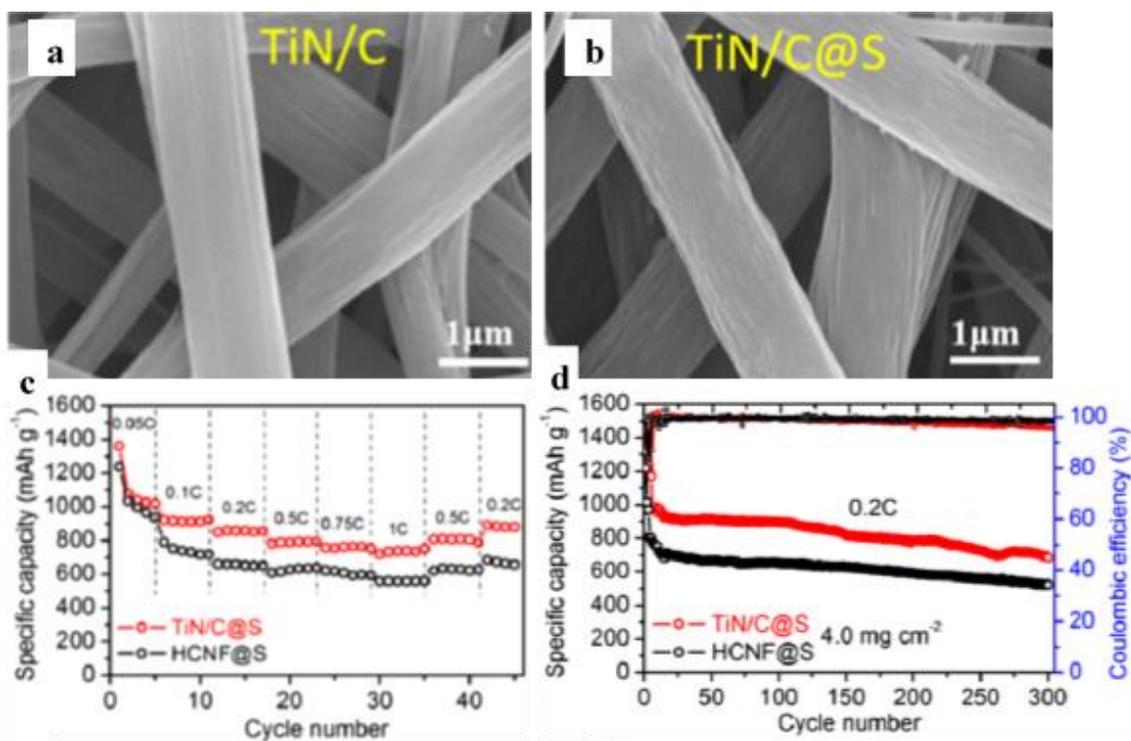


Figure 1-9 SEM images of (a) TiN/C nanofibers and (b) TiN/C with sulfur (TiN/C@S) composites; (c) rate capability and (d) cycle stability and Coulombic efficiency at 0.2 C for TiN/C@S and hollow carbon nanofibers with sulfur (HCNF@S) cathodes. Reproduced from Ref. ¹⁶² with permission from American Chemical Society 2018.

Apart from carbon, graphene and TiO₂ can also be combined with TiN to enhance the performance of Li-S batteries. A 3D nitrogen-doped graphene/TiN nanowires composite was designed by Xu et al. as a cathode for Li-S battery. Due to the high electronic and ionic conductivity of porous graphene and the TiN as a strong polysulfide anchor, this graphene/TiN cathode showed a specific capacity of 1510 mA h g⁻¹ at 0.5 C with capacity retention of 1267 mA h g⁻¹ after 100 cycles, and rate capability of 676 mA h g⁻¹ at 5 C.¹⁶⁶ Lv et al. developed twinborn TiO₂-TiN heterostructures enabling smooth trapping-diffusion-conversion of polysulfides towards Li-S batteries. TiO₂ exhibits high adsorption towards soluble lithium polysulfides, and conducting TiN facilitates their conversion into insoluble Li₂S, thus effectively reducing the shuttle effect during charge/discharge process. This electrode delivered a reversible capacity of 927 mA h g⁻¹ at 0.3 C after 300 cycles, and capacity retention of 73% at 1 C after 2000 cycles.¹⁶⁷

TiN modified separator has been employed to improve the electrochemical performance of Li-S batteries. Chen et al. developed a TiN modified separator to reduce the shuttle effect during charge/discharge process through the strong interaction between the conductive TiN and polysulfides. With this TiN modified separator, the Li-S battery presented a discharge capacity of 1296 mA h g⁻¹ at 0.5 C.¹⁶⁸ Zhang et al. introduced conductive mesoporous TiN microspheres to

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modify separator and as an efficient polysulfide barrier for Li-S batteries. With this TiN modified separator, the Li-S battery showed a capacity retention of 76 % at 0.5 C after 200 cycles, and rate capability of 672 mA h g⁻¹ at 3 C.¹⁶⁹ Li et al. designed TiN synergetic with micro/mesoporous carbon coated onto Celgard separator as a polysulfide interceptor in Li-S batteries to obtain specific capacity of 1130 mA h g⁻¹ at 1 C, and capacity retention of 500 mA h g⁻¹ after 400 cycles.¹⁷⁰

In conclusion, TiN has been applied in battery systems due to its good electrical conductivity, low cost, and good chemical and thermal stability.^{17, 18} Therefore, it is necessary and interesting to investigate the applications of TiN nanostructures in electrode materials for lithium-ion batteries and lithium-sulfur batteries.

Chapter 2: Experimental Techniques

2.1 Introduction

In this work, X-ray diffraction (XRD) with Rietveld refinement was used to characterise the phase compositions with lattice parameters and crystallite size. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with energy-dispersive X-ray (EDX) were used to characterise the phase morphology and compositions. Thermogravimetric analysis (TGA) was used to detect materials purity and thermal stability. Combustion (C, H, N) analysis was used to determine the elements ratio of the materials. N₂ physisorption analysis was used to characterise the specific surface area and particle size distribution of powders. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemistry of samples. Cyclic voltammetry (CV) was used to measure the solid-state conductivity. Galvanostatic testing and electrochemical impedance spectroscopy (EIS) were used to detect the electrochemical performance of materials used as electrodes in batteries.

2.2 X-ray diffraction (XRD)

2.2.1 Principles of XRD and Bragg's law

X-ray diffraction measures the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle and wavelength.¹⁷¹ Waves scattered at atoms at different positions arrive at the detector with a relative phase shift.¹⁷² The measured intensities provide information about the crystal structure and chemical composition of the sample (Figure 2-1).¹⁷²

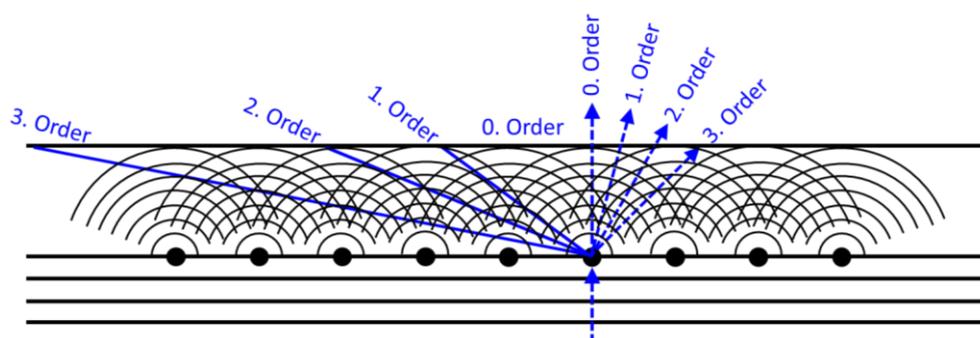


Figure 2-1 A plane wave was scattered by a one dimensional chain of atoms. The diffraction orders refer to the directions in which intensity maxima occur due to constructive interference of the scattered waves.¹⁷²

The method to obtain the structural information in X-ray diffraction is via the Bragg's law (illustrated in Figure 2-2) and Bragg equation (Equation 2-1) developed by W. L. Bragg in 1912.¹⁷³ It describes the principle of X-ray diffraction, which is a reflection of X-rays by sets of lattice planes.

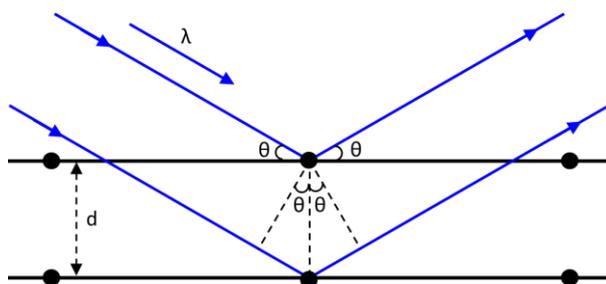


Figure 2-2 Illustration of Bragg's law.¹⁷⁴

$$n\lambda = 2d \sin \theta \quad \text{Equation 2-1}$$

Equation 2-1 Bragg equation, where n is an integer (constructive interference), λ is the X-ray wavelength, d is the interplanar spacing of parallel lattice planes and 2θ is the diffraction angle between the incoming and outgoing X-ray beams.

In this work, the XRD patterns of the samples were collected using a Bruker D2 Phaser X-ray diffractometer with $\text{CuK}\alpha$ radiation. The collection data was generally selected in the 2θ range between 10-80 degrees.

2.2.2 Rietveld refinement

Rietveld refinement was developed by H. M. Rietveld in 1969 to analyse X-ray diffraction data.¹⁷⁵ Rietveld refinement is a pattern fitting process to refine an experimentally collected diffraction pattern against a literature proposed structural model via a least squares method.¹⁷⁴ This least squares method minimises the difference between the experimental data and the fitted data by adjusting the lattice parameters in the proposed structure.^{176, 177} In this work, Rietveld refinement was carried out using the General Structure Analysis System (GSAS). It is capable of handling X-ray diffraction data from multiphase sample and refine structural parameters for each phase.¹⁷⁸

Crystallite size of samples can be achieved by Rietveld refinement of X-ray diffraction patterns. Equation 2-2 for calculating the crystallite size can be obtained by rearranging the expressions applied to model the peak shape (mostly instrumental broadening), in which the Lorentzian component mainly consists of mostly sample broadening.¹⁷⁹

$$p = \frac{18000K\lambda}{\pi X} \quad \text{Equation 2-2}$$

Equation 2-2 p is the crystallite size, K is the Scherrer constant. λ is the X-ray wavelength, X is the the Lorentzian component value extracted from GSAS refinement.

2.3 Scanning electron microscopy (SEM)

SEM images are formed by collecting and amplifying electrons backscattered or emitted from the sample surface when an electron beam is scanned across its surface.¹⁸⁰

A schematic of a typical SEM is illustrated in Figure 2-3. An electron beam is thermionically emitted from an electron gun fitted with a tungsten filament. The electron beam is focused by two electromagnetic condenser lenses to form into a thin, coherent electron beam. It then passes through pairs of deflection coils in the final lens, deflecting the beam in the x and y axes, and rasterising it over a rectangular area of the sample surface.^{181, 182}

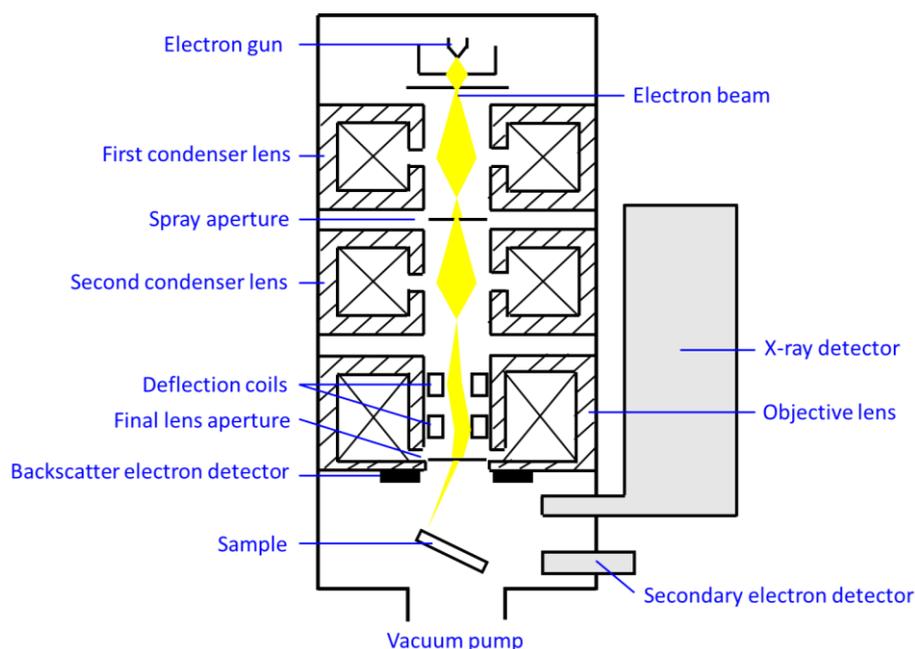


Figure 2-3 Schematic of scanning electron microscopy.¹⁸³

In this work, a Philips XL-30 ESEM (20 kV) with an attached EDS Thermofisher Ultradry detector with Noran System 7 processing was used to do the sample characterisation. The accelerating voltage and probe current were adjusted to achieve clear SEM images.

2.4 Transmission electron microscopy (TEM)

TEM is equipped with a field emission gun as an electron source, which produces an electron beam of higher brightness and spatial coherence compared to thermionic sources.¹⁸⁴ TEM images are formed from the interaction of the electrons transmitted through the specimen.

As shown in Figure 2-4, TEM can be divided into the illumination and imaging system.¹⁸⁴ The illumination system includes electron gun, condenser lenses and specimen, which controls the intensity and coherency of the electron beam.¹⁸⁴ The imaging system includes objective lens, objective aperture, selected area (SA) aperture, intermediate lens and projector lens. The objective lens collects the electrons emerging from the specimen and disperses them to form a diffraction pattern in the back-focal plane (BFP), then recombines them to produce an image in the image plane (IP).¹⁸⁴ The diffraction pattern or image is projected onto the viewing screen by adjusting the intermediate lens to ensure object plane coincides with the BFP or IP of the objective lens.¹⁸⁵

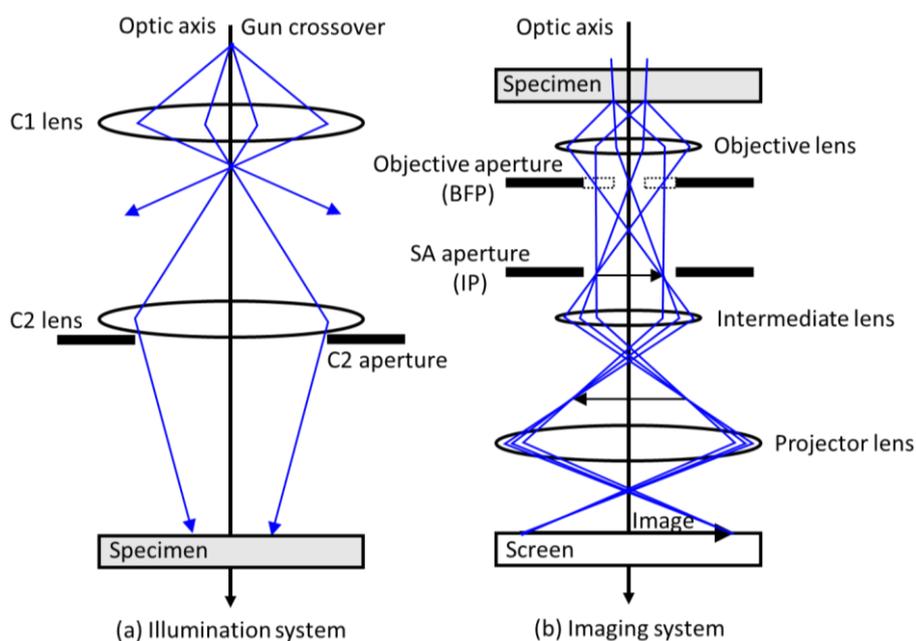


Figure 2-4 Simplified outline of a TEM consisting of the (a) illumination and (b) imaging system.¹⁸⁴

In this work, TEM was carried out on a FEI Tecnai T12 instrument with an accelerating voltage of 120 V. Sample powders were prepared by ultrasound dispersal using propan-2-ol as the solvent then deposited onto carbon coated Cu grids. This technique was used to characterise the morphology and particle sizes of the nanostructured composites.

2.5 Energy-dispersive X-ray (EDX) analysis

EDX is used for the elemental analysis or chemical characterization of a specimen. The measurements are based on the identification of the energy distribution of the X-rays produced under electron excitation.¹⁸²

As shown in Figure 2-5, an incident electron beam focused on the specimen ejects an electron and creates a vacancy in an inner shell (lower energy). Then the vacancy is filled by an electron from an outer shell (higher energy). The energy difference between the higher and lower energy shells results in the emission of an X-ray photon, which can be measured by the EDX spectrometer (a solid state semiconductor detector that can detect the energies of X-ray photons incident on it). The elemental composition of the specimen can then be examined since the energies of the X-rays are characteristic of the atomic structure of the emitting element.^{186, 187}

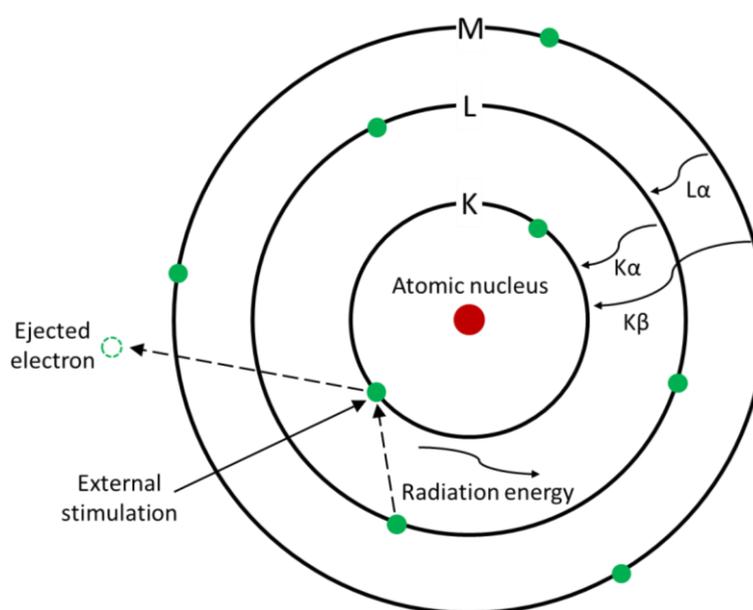


Figure 2-5 Principle of energy-dispersive X-ray analysis.¹⁸⁸

In this work, the EDX spectra were collected using a Thermofisher Ultradry detector with Noran System 7 analysis platform on a Philips XL30 ESEM. The spot size was raised from SEM for high magnifications of about 1000x, and the detector counts on the EDX showed a value higher than 10000, and the live time was 100 seconds.

2.6 Thermogravimetric analysis (TGA)

TGA is a method of thermal analysis in which mass changes of materials are measured as a function of increasing temperature with constant heating rate, or as a function of time with constant temperature.¹⁸⁹ This can be carried out under various gas environments to oxidise or reduce the materials or simply study decomposition under inert conditions.

In this work, TGA was carried out in NETZSCH TG 209 F1 Libra instrument. The sample powders (10-20 mg) were put in a dry alumina crucible (vol: 150 μ l), then moved onto the TGA balance. It was heated at 10 °C/min to 700 °C in O₂ (50 ml/min) as a reactant gas and Ar (20 ml/min) as a protecting gas, then cooled to 25 °C. The TGA instrument measures the mass change of material as a function of temperature and time in the whole process.

2.7 Combustion (C, H, N) analysis

Combustion analysis is a method to determine the elemental composition of a compound by combusting the specimen and measuring the concentration of CO₂, H₂O and NO₂ (or NO) using a gas chromatograph.¹⁹⁰ Once the amount of each combustion product has been measured, the empirical formula of the specimen can be determined.^{191, 192}

In this work, the sample (5-15 mg) was sealed and sent to MEDAC Ltd for carbon, hydrogen and nitrogen (C, H, N) combustion analysis. Samples were burned at high temperature in O₂ using tungstic oxide as a combustion aid. The original contents of C, H, N elements in the specimen were then calculated.

2.8 N₂ physisorption analysis

N₂ gas adsorption is an important tool to characterise the specific surface area and pore size distribution of porous solids and fine powders.^{193, 194} As shown in Figure 2-6, physisorption isotherms are displayed with the specific amount of gas adsorbed versus the equilibrium relative pressure (p/p^0), where p^0 is the saturation pressure.¹⁹⁵ The gas adsorption isotherms are classified into six types by International Union of Pure and Applied Chemistry (IUPAC).¹⁹⁶

Type I isotherms are commonly observed in the physisorption of N₂ on microporous materials with relatively small external surfaces. The steep increase of the adsorbed amount at low relative pressure is due to enhanced adsorbent-adsorbate interactions in narrow micropores.¹⁹⁷ Type II isotherms are produced by nonporous or macroporous adsorbents. This shape is due to the unrestricted monolayer-multilayer adsorption up to high relative pressure. Point B corresponds to

the completion of monolayer coverage.¹⁹⁷ Type III isotherms indicate weak adsorbent-adsorbate interactions and the adsorbed molecules are clustered on the surface of nonporous or macroporous solids.¹⁹⁷ Type IV isotherms are observed in the physisorption of N₂ on mesoporous or macroporous adsorbents with a similar shape to type II isotherms in the low relative pressure range. The presence of a hysteresis loop in type IV implies the occurrence of capillary condensation within mesopores, due to the strength of adsorbate-adsorbent and adsorbate-adsorbate interactions.¹⁹⁸ The type V isotherm shape is similar to that of Type III, which can be attributed to relatively weak adsorbent-adsorbate interactions.¹⁹⁷ The molecular clustering is followed by pore filling at higher relative pressure. The type VI isotherm indicates layer-by-layer adsorption on a uniform surface. The height of the step represents the capacity for each adsorbed layer.¹⁹³

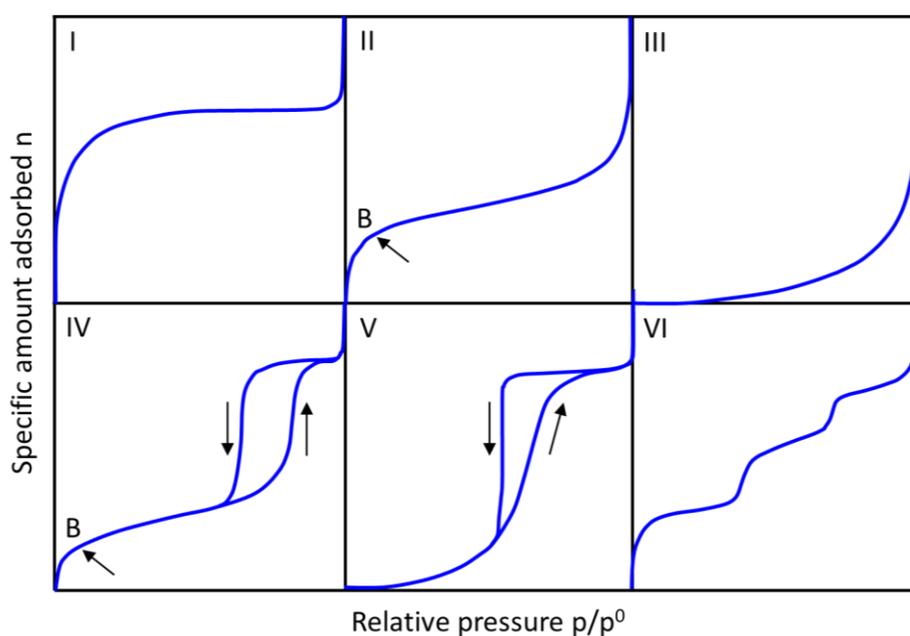


Figure 2-6 Six types of gas physisorption isotherms displayed with the specific amount of gas adsorbed versus the relative pressure.¹⁹⁷

2.8.1 Brunauer-Emmett-Teller (BET) method

The BET method is widely used with N₂ physisorption analysis for measuring the specific surface area of porous and finely-divided materials.¹⁹⁹ It is common to apply the BET equation (Equation 2-3) in a linear form.

$$\frac{p/p^0}{n(1 - p/p^0)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} (p/p^0) \quad \text{Equation 2-3}$$

Equation 2-3 The BET equation in a linear form, where n is the specific amount of adsorbed gas at the relative pressure p/p^0 , n_m is the monolayer adsorbed gas amount, C is a constant exponentially related to the energy of monolayer adsorption.¹⁹³

The BET specific surface area of the adsorbent S_{BET} is determined by Equation 2-4.

$$S_{BET} = \frac{n_m L \sigma_m}{m} \quad \text{Equation 2-4}$$

Equation 2-4 The specific surface of the adsorbent determined by BET method, where n_m is the monolayer adsorbed gas amount, L is Avogadro's number, σ_m is the molecular cross-sectional area, m is the mass of the adsorbent.¹⁹³

In this work, BET surface area and pore size distribution measurements were carried out with a Micromeritics TriStar II analyser. The samples were degassed at 120 °C under vacuum overnight prior to the measurement.

2.9 X-ray photoelectron spectroscopy (XPS)

XPS is a spectroscopic technique to characterise the elemental composition, empirical formula, chemical state and electronic state of the elements in the surface of a sample.²⁰⁰ As shown in Figure 2-7, XPS spectra are obtained by applying X-ray irradiation on a sample, and measuring the kinetic energy of electrons that escape from the surface of the sample (top 0-10 nm usually).^{201, 202} The binding energy of the electron can be calculated according to Equation 2-5.

$$BE = hv - (KE + \phi) \quad \text{Equation 2-5}$$

Equation 2-5 Binding energy of a photoelectron. BE is the binding energy of the electron, hv is the energy of the X-ray photons being used for excitation, KE is the measured kinetic energy of the electron, and the instrumental work function ϕ is dependent on both the spectrometer and the sample, to account for the energy difference between the Fermi level and the vacuum level of the sample (Figure 2-7).²⁰³

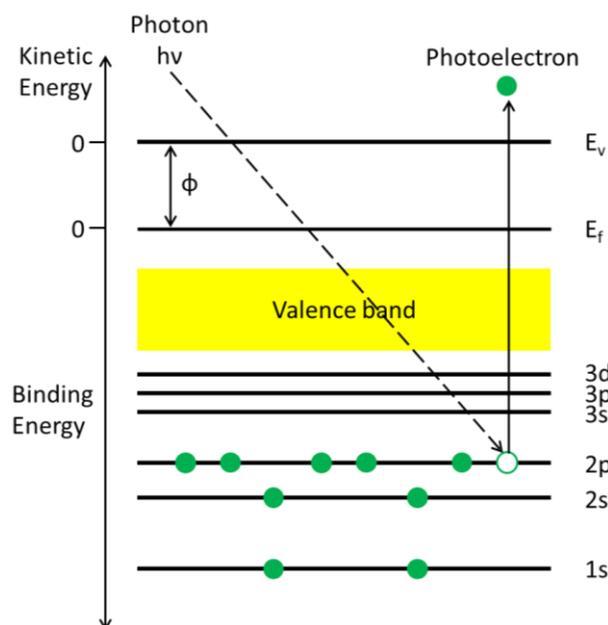


Figure 2-7 Schematic of the photoemission process in XPS measurement.²⁰⁴

In this work, XPS was collected with a two chamber Thermo K-alpha spectrometer with a monochromated Al K-alpha X-ray source (1486.6 eV) in constant analyser energy mode. Sample charging was prevented by use of a dual beam flood gun. X-rays were focused to a 400 μm spot at the sample surface. High resolution core peak spectra were recorded at 50 eV pass energy. Spectra were analysed using Casa XPS software. The binding energy scale was calibrated from the carbon at 285.0 eV. Core peaks were analysed with a nonlinear Shirley-type background.²⁰⁵ The peak positions and areas were optimized using a weighted least-squares fitting method with 70% Gaussian and 30% Lorentzian line shapes. Several spectral analyses were applied at different positions for each sample to ensure the results were statistically reliable.

2.10 Electrode preparation and battery assembly

The sample powders were made into electrodes and assembled in Swagelok cells before electrochemical testing.

The ink type electrodes were prepared by mixing the active materials (80 wt%) with acetylene black (Shawinigan Black, 10 wt%) and poly(vinylidene fluoride) (PVDF, 10 wt%) in N-methyl-pyrrolidone (NMP, Sigma Aldrich). The slurry was cast onto Al foil (125 μm thick, Temper annealed, 99.0 % purity, Advent Research Materials) and dried at 120 $^{\circ}\text{C}$ in vacuum for 12 h. The foil was cut into circular discs with a diameter of 11 mm and pressed at 10 tons to obtain the electrode with a typical mass of ~ 0.037 g.

Chapter 2

The pellet type electrodes were prepared by manually mixing the active materials (75 wt%) with acetylene black (20 wt%) and polytetrafluoroethylene (PTFE, 6C-N, DuPont, 5 wt%) in a pestle and mortar. The resulting solid paste was hand rolled (Durstion Rolling Mill) into a film of $\sim 90 \mu\text{m}$ thickness and cut into circular disks with diameter of 11 mm. The pellet was then dried at $120 \text{ }^\circ\text{C}$ in vacuum for 12 h to obtain the electrode with a typical mass of $\sim 0.022 \text{ g}$.

Swagelok cells were assembled in an argon-filled glove box with lithium foil anodes (Rockwood Lithium GmbH, 11 mm circular disk) and glass microfiber filter (Whatman, GF/F grade) separators soaked in 8 drops ($\sim 0.4 \text{ ml}$) of electrolyte. Electrolytes were made with $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ in ethylene carbonate/dimethyl carbonate (EC: DMC = 1:1 in volume) electrolyte (BASF, LP30), or with $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ in ethylene carbonate/ ethylmethyl carbonate (EC: EMC = 3:7 in weight) electrolyte (BASF, LP57). Galvanostatic testing was carried out at $25 \text{ }^\circ\text{C}$ at different rates of charge/discharge to characterise the electrochemical performance of batteries with various cathode or anode materials.

2.11 Galvanostatic testing

Galvanostatic testing simulates the charge/discharge process by measuring the electrode potential vs. a reference potential when a constant current is applied to an electrode to oxidise or reduce the active material.²⁰⁶ After either a specified period of time or charge has passed or a voltage limit is reached, the current is then reversed and the reverse reaction occurs.²⁰⁷

In this work, a Biologics VMP-2 multichannel potentiostat was used to investigate the electrochemical performance of materials used as electrodes in batteries. The galvanostatic testing was carried out at $25 \text{ }^\circ\text{C}$ at various rates of charge/discharge (e.g. 0.1C is a current calculated for 0.1X the theoretical capacity per hour) within a specific voltage range.

2.12 Cyclic voltammetry (CV)

The CV technique consists of varying the electrode potential in a linear fashion to probe the reactivity of the electrochemical system. It can also probe the kinetics of the reactions and the mass transfer process by varying the scan rate.²⁰⁸⁻²¹⁰

For an oxidation process, the voltage scans from an initial electrode potential value (where no oxidation takes place) to more positive values.

$$E(t) = E_i + vt \quad \text{Equation 2-6}$$

Equation 2-6 The electrode potential value when scanning to more positive value. E_i is the initial electrode potential, v is the scan rate, t is the time.

After reaching the final potential value, the electrode potential is scanned back to the initial value. In this process, part of the species oxidised on the forward scan is reduced.

$$E(t) = E_f - vt \quad \text{Equation 2-7}$$

Equation 2-7 The electrode potential value when scanning back to the initial value after reaching the final value. E_f is the final electrode potential, v is the scan rate, t is the time.

The current at the electrode is plotted versus the applied electrode potential to give the CV trace.

In this work, the CV was carried out using a Biologics VMP-2 multichannel potentiostat with built in CV analyser, and collected data at room temperature with special scan rates and voltage ranges for different electrodes. Electronic conductivity was determined from the current-voltage response on gold-coated sintered disks (11 mm in diameter and ~0.5 mm in thickness).²¹¹⁻²¹³ The conductivity of disk was calculated based on $C = S A / l$, where C (mA V^{-1}) is the conductance of the disk, S (S m^{-1}) is the conductivity, A (mm^2) is the cross-sectional area of the disk, and l (mm) is the thickness.

2.13 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy is a technique to investigate the electrochemical processes by analysing the current response when a sinusoidal voltage perturbation is applied to the circuit over a range of frequencies.^{214, 215}

Based on Equation 2-8, impedance spectra can be displayed using Nyquist plot (imaginary impedance part Z'' vs. real impedance part Z') and Bode plots (impedance Z vs. frequency and phase ϕ vs. frequency). These plots are modelled using simplified equivalent circuits.²¹⁵

$$Z = Z_0 (\cos \phi + j \sin \phi) = Z' + j Z'' \quad \text{Equation 2-8}$$

Equation 2-8 Z is the impedance, Z_0 is the magnitude of impedance, j equals to $\sqrt{-1}$, ϕ represents phase, Z' is the real component of impedance, Z'' is the imaginary component of impedance.

In this work, the EIS was obtained using a Biologics VMP-2 multichannel potentiostat with built in EIS analyser. A sinusoidal voltage perturbation with a frequency range of 200 kHz to 2 MHz and an amplitude of 10 mV was used.

Chapter 3: A sol-gel route to titanium nitride conductive coatings on battery materials and performance of TiN-coated LiFePO₄

3.1 Introduction

The ordered olivine structured LiFePO₄ has been intensively investigated as a cathode material in lithium-ion batteries due to its flat voltage profile, high theoretical capacity of 170 mA h g⁻¹, safety, low cost and environment benignity.²¹⁶⁻²¹⁹ However, the low intrinsic electronic conductivity ($\sim 10^{-8}$ - 10^{-10} S cm⁻¹) and lithium-ion diffusivity ($\sim 10^{-18}$ cm² s⁻¹) of LiFePO₄ are major obstacles which originally limited its practical applications.^{1, 7, 220} Approaches to ameliorate these drawbacks have included cation doping,²²¹⁻²²⁴ particle size reduction,^{225, 226} carbon coating²²⁷⁻²²⁹ and non-carbon second phase modification.^{230, 231} Carbon coating has become the standard method to enhance the electronic conductivity of LiFePO₄ particles. However, carbon layers have low density (2.2 g cm⁻³) and this may reduce the tap density of LiFePO₄ (3.6 g cm⁻³), leading to reduced volumetric energy density of the lithium ion battery electrodes.^{63, 232} New processes to produce conductive coatings could improve battery performance by providing alternatives to carbon, i.e. non-carbon second phase (such as metal, metal oxide, conductive polymer, etc.) modification, which has been widely used to improve the electrochemical performance of LiFePO₄.

3.2 Conductive coatings to improve the performance of LiFePO₄

3.2.1 Metal coating

Highly conductive metal (such as Ag, Au and Cu) coating on the surface of LiFePO₄ can improve the conductivity of the electrode effectively. Croce et al. enhanced the electronic conductivity of LiFePO₄ by dispersion with a low amount (~ 1 wt%) of metal (Cu or Ag) to improve the specific capacity and cycle stability of cathode.²³³ Also, Park et al. improved the discharge capacity of LiFePO₄ by surface modification of Ag via co-precipitation, which could be attributed to the increased electronic conductivity of cathode after Ag coating.²³⁴ Eftekhari et al. fabricated LiFePO₄/Au mixed film by depositing LiFePO₄ onto the substrate surface during Au electrodeposition. This cathode exhibited improved discharge capacity and cycle stability due to the increased electrical conductivity after Au modification.²³⁵ Later, Chung et al. improved the electrical conductivity of LiFePO₄ by coating highly conductive Ag nanoparticles onto the surface of

LiFePO₄ thin films. This Ag coated LiFePO₄ composite thin film showed a stable cycle performance and good rate capability up to 14 C.²³⁶

3.2.2 Metal oxide coating

Metal oxides have been used as coatings to improve the electrochemical performance of LiFePO₄. Wang et al. produced ZrO₂ nanolayer coated LiFePO₄ particles via a chemical precipitation strategy. The ZrO₂ nanocoating decreased the electrode/electrolyte interface charge transfer resistance, thus improved the discharge capacity of LiFePO₄ cathode.²³⁷ Tirado et al. obtained ZnO coated LiFePO₄ composite materials with improved capacity retention at different rates.²³⁸ Meanwhile, TiO₂ coated LiFePO₄ was prepared by Wu et al. via a sol-gel process. The TiO₂ coating as a protection layer inhibited Fe dissolution into electrolyte, thus reduced capacity fading of the LiFePO₄/Li cell, but it imposed a deteriorating effect in the LiFePO₄/C cell due to the erosion of TiO₂ upon cycling at 55 °C.²³⁹ CeO₂ modified LiFePO₄ cathode was prepared by Zhang et al. using the triblock copolymer poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethane oxide) (P123) as a template. The CeO₂ modification was found to produce a good electrical contact between LiFePO₄ particles, which resulted in an improved electrochemical properties at elevated temperature.²⁴⁰ Later, Zhao et al. prepared SiO₂ coated LiFePO₄ composites via a sol-gel process, which showed improved discharge capacity and cycle stability at elevated temperature. The SiO₂ coating not only prevented the LiFePO₄ from direct contact with the electrolyte to enhance the structural stability, but also increased the order of Li⁺ intercalating the outer lattice of LiFePO₄.²⁴¹

3.2.3 Other conductive additive coatings

Other conductive additive coatings such as polymers and phosphides have been investigated. Park et al. prepared LiFePO₄/Fe₂P composites via the reduction reaction of phosphate in excess of carbon. The electronic conductivity of the LiFePO₄/Fe₂P composite increased with the increasing amount of Fe₂P.²⁴² Later, Fedorková et al. developed polypyrrole and polyethylene glycol coated LiFePO₄ (PPy/PEG-LiFePO₄) hybrid films which delivered a stable discharge capacity of 156 mA h g⁻¹ at 0.1 C. Due to its favourable mixed ionic and electronic conductivity, the PPy/PEG coating reduced the charge transfer resistance of the cathode effectively.²⁴³ Song et al. deposited NiP on the surface of LiFePO₄ particles via electroless plating. The conductive metallic NiP nano-coating not only enhanced the electronic conductivity of LiFePO₄, but also acted as a protective layer to prevent the dissolution of Fe from LiFePO₄, which improved the battery cycle stability remarkably.²⁴⁴

3.2.4 Additive and carbon co-coating

Additives such as metals and metal oxides have been combined with carbon to obtain co-coating layers on the surface of LiFePO_4 cathodes. For example, Mi et al. produced Ag and C co-coated LiFePO_4 composite cathodes by an aqueous co-precipitation and a sol-gel process, which showed improved discharge capacities of higher than 160 mA h g^{-1} .²⁴⁵ Nano-sized Sn was deposited onto carbon coated LiFePO_4 by Lin et al. via an electroless deposition process, which delivered improved specific capacity, better cycle stability and rate capability. The Sn and C co-coated LiFePO_4 showed good electric contact among particles and lower charge transfer resistances. The Sn and C co-coating can protect the LiFePO_4 from chemical attack by HF to suppress the dissolution of Fe from LiFePO_4 in the LiPF_6 based electrolyte.²³¹

Metal oxide is the most commonly used additive to form co-coating layers with carbon on the surface of LiFePO_4 . As shown in Figure 3-1, Guo et al. found that C coated porous LiFePO_4 cannot provide fast kinetics for Li^+ insertion at high charge/discharge rates due to the insufficient electronic conductivity. While the RuO_2 and C co-coated LiFePO_4 with nano-sized RuO_2 as an oxidic nanoscale interconnect showed remarkably improved rate capability, which can be attributed to the enhanced electrical conductivity.²⁴⁶ Wu et al. prepared CeO_2 and C co-coated LiFePO_4 cathode, which showed improved specific capacity, especially at high rates and low temperature.²⁴⁷ V_2O_3 and C modified LiFePO_4 was synthesized by Chen et al. via a solid-state reaction, which exhibited improved rate capability and low-temperature performance due to the presence of highly conductive V_2O_3 and C co-coating layer.²³⁰ Later, Liu et al. produced WO_2 modified LiFePO_4/C composites via a sol-gel process. This cathode showed enhanced specific capacity and low-temperature performance due to the improved electrochemical kinetics.²⁴⁸

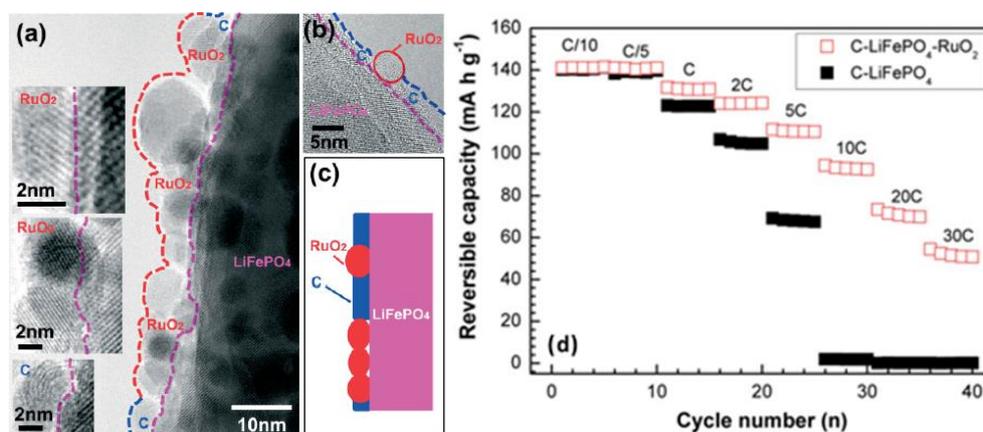


Figure 3-1 (a) and (b) HRTEM images of RuO_2 and C co-coated LiFePO_4 . (c) Schematic illustration of repairing the conductive carbon network on the surface of LiFePO_4 via RuO_2 co-coating. (d) Rate capabilities of RuO_2 and C co-coated LiFePO_4 and C coated LiFePO_4 samples. Reproduced from Ref. ²⁴⁶ with permission from John Wiley and Sons 2007.

Various kinds of metal oxides have been used by Guo et al. as co-coating additives in LiFePO_4 . For example, CuO (or ZnO) and C co-coated LiFePO_4 composites were prepared via a chemical precipitation method. As shown in Figure 3-2, the incomplete carbon network was repaired by the nano-sized CuO (or ZnO). These co-coatings improved the electrochemical kinetics and reduced the interfacial resistances of cathodes, thus resulting in enhanced rate capabilities.^{249, 250} They also modified LiFePO_4/C with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, $\text{Sr}_{0.85}\text{Ce}_{0.15}\text{CoO}_{3-\delta}$ or $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ via a suspension mixing process. These cathodes showed enhanced discharge capacity and rate capability, which could be attributed to the higher electronic conductivity and lower charge transfer resistance resulting from the nanolayer co-coatings.^{232, 251, 252} Later, they modified LiFePO_4/C with highly conductive nanolaminated Ti_3SiC_2 , which was characterized by a plane-to-point conducting mode. This cathode presented discharge capacities of 140 and 101 mA h g^{-1} at 1 C and 5 C, respectively.²⁵³

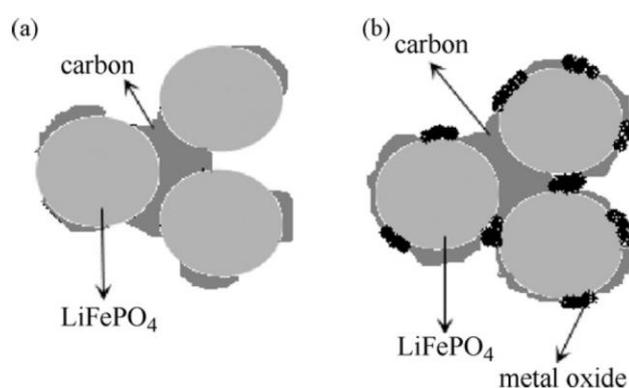


Figure 3-2 (a) Illustration of LiFePO_4 particles partially coated with carbon. (b) Illustration of LiFePO_4 particles fully coated with an integrate nanolayer. Reproduced from Ref. ²⁴⁹ with permission from Elsevier 2010.

In conclusion, second phase modification on the surface of LiFePO_4 is a good way to meet the performance and cost targets for industrial applications when comparing to pure carbon coating. Surface additives with good conductivity, higher density than carbon, or distinctive properties can produce good electrochemical performance in LiFePO_4 .

3.3 Research motivation

Metal nitrides have been studied as electrode materials for batteries and supercapacitors in their own right for some years.¹² However, they have also been combined with other electrode materials to form structured composites with improved conductivity and stability relative to the active electrode material itself.¹³⁻¹⁶ TiN is suitable for these purposes as it possesses good electrical conductivity, low cost, and good chemical and thermal stability.^{17, 18} For example, Kim and co-workers reported good electrochemical performance in Si/TiN nanocomposites in which the

electrochemically inactive TiN acts to maintain the stability of the nanocomposite during cycling as silicon undergoes volumetric change.¹⁵ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ suffers from poor electronic conductivity, but DeSisto *et al* showed that atomic layer deposition of TiN coatings onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder improved the electronic conductivity to deliver a higher capacity (162 mA h g^{-1}) and cycling stability compared with that of uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (133 mA h g^{-1}).¹⁶

Many methods have been developed to synthesise metal nitrides, from elemental combination, including at high pressure,²⁵⁴ to ammonolysis of oxides and other binary compounds,¹³⁴ vapour deposition of films,²⁵⁵ solid state metathesis and solvothermal reactions,^{256, 257} reactions of molecular precursors and sol-gel processing.^{258, 259} Sol-gel methods have been shown to be highly effective, low cost routes to nitride materials and are versatile in the preparation of high surface area materials or porous structures.^{260, 261} Ammonia can be used to cross-link precursor molecules *via* transamination reactions to produce materials such as nanocrystalline TiN,^{262, 263} but it has been shown that to process films²⁵⁸ and for controlled morphologies such as polymer sphere templated inverse opals^{264, 265} the use of a primary amine as the crosslinking agent can be particularly effective. The advantage for battery material coatings is that the use of a sol-gel route could be scalable with efficient material usage compared with vapour phase coating methods.

The ordered olivine structured LiFePO_4 has been intensively investigated as a cathode material in lithium-ion batteries due to its flat voltage profile, high theoretical capacity of 170 mA h g^{-1} , safety, low cost and environmental benignity.²¹⁶⁻²¹⁹ However, the low intrinsic electronic conductivity ($\sim 10^{-8}$ - $10^{-10} \text{ S cm}^{-1}$) and lithium-ion diffusivity ($\sim 10^{-18} \text{ cm}^2 \text{ s}^{-1}$) of LiFePO_4 are major obstacles which originally limited its practical applications.^{1, 7, 220} Approaches to ameliorate these drawbacks have included cation doping,²²¹⁻²²⁴ particle size reduction,^{225, 226} carbon coating²²⁷⁻²²⁹ and non-carbon second phase modification.^{230, 231} Carbon coating has become the standard method to enhance the electronic conductivity of LiFePO_4 particles. However, carbon layers have low density (2.2 g cm^{-3}) and this may reduce the tap density of LiFePO_4 (3.6 g cm^{-3}), leading to reduced volumetric energy density of the lithium ion battery electrodes.^{63, 232} Other electrode materials such as LiMnPO_4 , LiCoPO_4 , LiNiPO_4 , LiMn_2O_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ also suffer from poor electrical conductivity and can benefit from coating to enhance electron transport.²⁶⁶

New processes to produce conductive coatings could improve battery performance by providing alternatives to carbon. Whilst carbon-coated LiFePO_4 is highly optimised and is in commercial use,^{3, 267} other materials such as TiN could provide better stability with high voltage materials or in cells that are more stable at elevated temperature.^{12, 268} TiN could provide more effective protection from chemical attack by HF produced by electrolyte decomposition and thus suppress the dissolution of Fe from LiFePO_4 in LiPF_6 based electrolytes.^{231, 232} Since LiFePO_4 is well understood but

dependent on conductive coatings it provides an effective test bed for new coating materials. Hence in this work the possible sol-gel approaches to TiN coatings on battery materials, the feasibility of transferring these methods to LiFePO₄ particles and the electrochemical performance of TiN coated LiFePO₄ have been investigated.

3.4 Experimental

3.4.1 Synthesis

Titanium amides and the sol-gel intermediates were handled under nitrogen using glove box or Schlenk line methods. Two main methods were used to produce TiN based on literature routes using ammonia²⁶³ or propylamine²⁶⁵ cross-linking agents:

(1) Ti(NMe₂)₄ (2.65 cm³, 11.2 mmol, Epichem) was dissolved in dry THF (20 cm³, distilled from sodium/benzophenone). Liquid NH₃ (~20 cm³) was distilled from a sodium/ammonia solution into the stirred amide solution cooled to -78 °C. A bright yellow precipitate appeared on first exposure of the solution to ammonia, which turned brown and then black as the ammonia was allowed to evaporate and the temperature approached ambient.

(2) Ti(NMe₂)₄ (2.65 cm³, 11.2 mmol) was dissolved in dry THF (7.5 cm³). ⁿPrNH₂ (1.84 cm³, 22.4 mmol, distilled from BaO) was slowly added. The solution gradually changed colour from yellow to red-orange.

Both sol types were stirred at room temperature overnight and then pumped off to form viscous gels. These were then heated under a flow of NH₃ (dried with a column of molecular sieves) or 5% H₂ in N₂ at 3 °C min⁻¹ to 650°C and maintained for 6 h before cooling. The products were black powders, or a metallic red monolith from the propylamine crosslinked gel heated in ammonia. Both types were ground before further characterisation.

LiFePO₄ was prepared by a literature hydrothermal method.²⁶⁹ LiOH·H₂O (6.29 g, 0.15 mol, 98% purity, Fisher Scientific) was dissolved in deionised water (45 cm³), and H₃PO₄ aqueous solution (3.77 cm³, 0.05 mol, 85.3 wt% assay, Fisher Scientific) was added. FeSO₄·7H₂O (13.90 g, 0.05 mol, > 99% purity, ACROS Organics) was dissolved in water (45 cm³) and added slowly to the LiOH solution with constant stirring, during which time a light green suspension formed. The precursor solution was heated in a Parr 4748 Teflon-lined autoclave (125 cm³) at 180 °C for 6 h. The precipitate was then washed with deionized water and ethanol, and dried at 80 °C for 5 h under vacuum. The resulting material, which has been designated LFP(HT), was heated at 3 °C min⁻¹ to 650 °C and maintained for 6 h under ammonia or 5% H₂/N₂ to crystallise LiFePO₄.

TiN modified LiFePO₄ powders were prepared using a variation of the propylamine cross-linking sol-gel method described above, with the sol prepared from 0.21 cm³ Ti(NMe₂)₄, 7.5 cm³ THF and 0.15 cm³ propylamine. 0.5 g dry LFP(HT) or fired LiFePO₄ was added just before the propylamine. The suspension was stirred at room temperature for ~16 h and dried *in vacuo* to form a sticky powder. This was heated under ammonia or 5% H₂/N₂ as described above for TiN samples.

To obtain carbon coated LiFePO₄ as comparison, the uncrystallised LiFePO₄ (0.5 g) and sucrose (C₆H₁₂O₆, 0.13 g, Fisher Scientific) were separately dispersed in ethanol by sonication for 15 min followed by 4 h vigorous stirring. The dispersed sucrose suspension was added dropwise to the LiFePO₄. The mixed suspension was subjected to sonication for 30 min, and then continuously stirred at 60 °C to remove excess ethanol until thick slurry was formed. This was heated under 5% H₂/N₂ as described above for TiN samples.²³²

3.4.2 Characterisation and electrochemistry

Powder X-ray diffraction used a Bruker D2 Phaser with CuK_α radiation, and data was fitted using the GSAS package.²⁷⁰ Scanning electron microscopy was carried out with a Philips XL-30 ESEM (20 kV) and energy-dispersive X-ray (EDX) analysis with a Thermofisher Ultradry detector with Noran System 7 processing. Transmission electron microscopy used a FEI Tecnai T12 (120 kV). Combustion (C, H, N) analysis was outsourced to Medac Ltd. Thermogravimetric analysis (TGA) was carried out with NETZSCH TG 209 F1 Libra. Electrochemical testing used a Biologics VMP-2 multichannel potentiostat.

Conductivity measurements were carried out on TiN pellets made by manually mixing 0.2 g TiN powder with PTFE (0.02 g) in a pestle and mortar. The resulting solid lump was hand rolled (Durston Rolling Mill) into a film and cut into disks with diameter of 10 mm, and then the pellet was assembled into a Swagelok cell without any electrolyte. Cyclic voltammograms (CV) were collected at 20 mV s⁻¹ over the range of -0.3 to +0.3 V (-0.1 to +0.1 V for more conductive samples) at room temperature.

Electrodes for use in lithium half cells were prepared by mixing the LiFePO₄, TiN coated LiFePO₄ or C coated LiFePO₄ powder (80 wt%) with acetylene black (10 wt%) and poly(vinylidene fluoride) (10 wt%) dissolved in N-methyl-pyrrolidone. The slurry was cast onto Al foil (125 μm thick, Temper annealed, 99.0 % purity, Advent Research Materials) and dried at 120 °C in vacuum for 12 h. The foil was cut into circular discs with a diameter of 1 cm and pressed at 10 tons to obtain the cathode with a typical mass of ~0.037 g. Swagelok cells were assembled in an argon-filled glove box with lithium foil (Rockwood Lithium GmbH) anodes and glass microfiber filter (Whatman, GF/F grade) separators soaked in 8 drops of 1 mol dm⁻³ LiPF₆ in ethylene carbonate/dimethyl carbonate (EC:

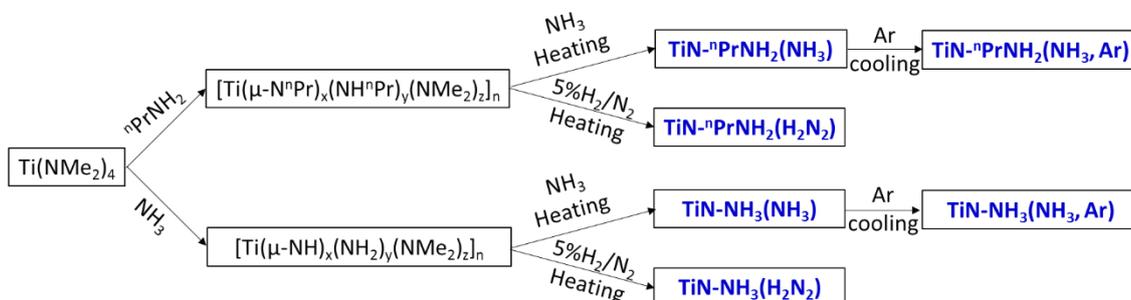
DMC = 1:1 in volume) electrolyte (BASF, LP30). Galvanostatic testing was carried out (at least in duplicate) at 25 °C at various rates of charge/discharge (e.g. 0.1 C is a current calculated for 0.1× the theoretical capacity per hour) within the voltage range of 2.5-4.5 V (vs. Li⁺/Li).

3.5 Results and discussion

Titanium nitride was initially made by two different sol-gel routes, then the route that led to the more conductive nanocrystalline material was used to coat LiFePO₄ with a variety of processing conditions and thicknesses.

3.5.1 Synthesis, microstructure and electrochemistry of TiN

The sol-gel routes to TiN employed Ti(NMe₂)₄ with either propylamine or ammonia as the cross-linking agent (Scheme 3-1). Research within Hector's group have previously used these routes to produce TiN in nanocrystalline form and shown that it can be produced at a range of temperatures,^{258, 263, 271} but here samples have been fired under a range of conditions relevant to the production of coated LiFePO₄. The crystallisation temperature affects purity, crystallite/particle size distribution and discharge capacity of LiFePO₄,^{26, 272, 273} but most successful studies produce LiFePO₄ samples at 600-700 °C.^{63, 274, 275} In this study, samples were fired at 650 °C. Heating in ammonia minimises the amount of carbon incorporated into the samples but may result in residual surface amide groups that could reduce the stability of the material and the conductivity. These may be removed by cooling in argon. LiFePO₄ is typically made in a dilute hydrogen stream,^{276, 277} but when used to fire TiN is likely to result in more ligand pyrolysis and carbon incorporation either as carbonitride or a separate phase. All three approaches were used. The samples were characterized by X-ray diffraction, electrochemical measurements of the effective conductivity, TEM and elemental analysis, and the main results are summarized in Table 3-1.



Scheme 3-1 ⁿPrNH₂- or NH₃-based sol-gel routes to TiN and sample labels

All the X-ray diffraction peaks of the resulting TiN samples (Figure 3-3) can be indexed to the standard cubic TiN structure (JCPDS Card No. 65-0414). Table 3-1 shows the crystallographic data

of TiN series samples. The Rietveld fits (Figure 3-4) to this XRD data resulted in similar lattice parameters (Table 3-1) to those in the literature for TiN.²⁷⁸ The peak broadening in the Rietveld fit indicated average TiN crystallite sizes of 5-10 nm. These were consistent with TEM images (Figure 3-5), which showed aggregates of particles within the same size range. These small sizes are important for coating of battery materials and are probably necessary to evenly coat particles that may only be 10s or 100s of nm in size.

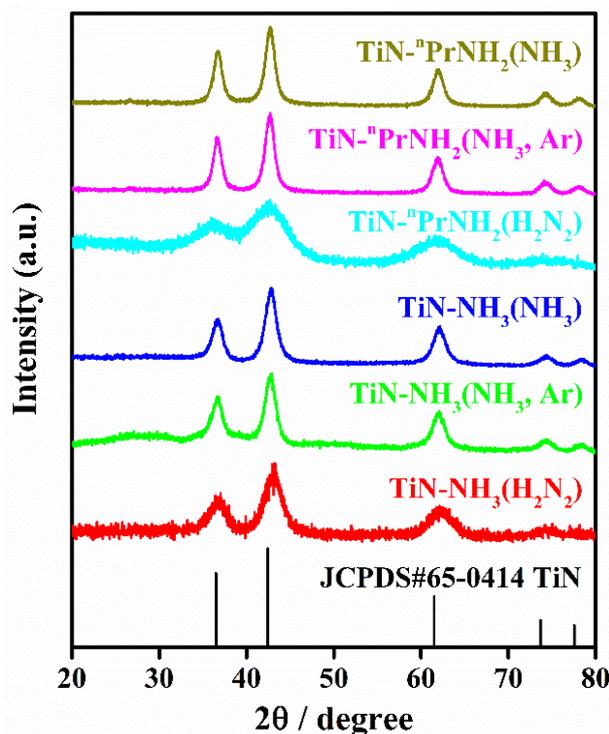


Figure 3-3 XRD patterns of TiN series samples prepared using the propylamine or NH_3 based sol-gel routes and heated to 650 °C under different atmospheres (labels explained in Scheme 3-1). The black stick pattern denotes the literature TiN reflection positions and intensities.

Table 3-1 Lattice parameters and crystallite sizes obtained from the Rietveld fits to the XRD patterns, combustion analysis (C, H, N) results and conductivities of the TiN samples (labels explained in Scheme 3-1).

Sample	$a / \text{Å}$	Crystallite size / nm	%C	%H	%N	Conductivity / S m^{-1}
$\text{TiN-}^n\text{PrNH}_2(\text{NH}_3)$	4.2349(2)	9.57(6)	1.55	< 0.10	21.26	5.5
$\text{TiN-}^n\text{PrNH}_2(\text{NH}_3, \text{Ar})$	4.2336(2)	9.89(6)	1.29	< 0.10	21.31	7.9
$\text{TiN-}^n\text{PrNH}_2(\text{H}_2\text{N}_2)$	4.2359(11)	5.02(16)	20.70	1.18	16.15	1.1×10^{-4}
$\text{TiN-NH}_3(\text{NH}_3)$	4.2237(2)	8.47(7)	2.53	1.49	16.43	7.7×10^{-3}
$\text{TiN-NH}_3(\text{NH}_3, \text{Ar})$	4.2220(3)	7.00(7)	0.55	1.25	18.65	1.3×10^{-1}
$\text{TiN-NH}_3(\text{H}_2\text{N}_2)$	4.2350(11)	7.61(23)	5.36	1.25	15.65	1.7×10^{-2}

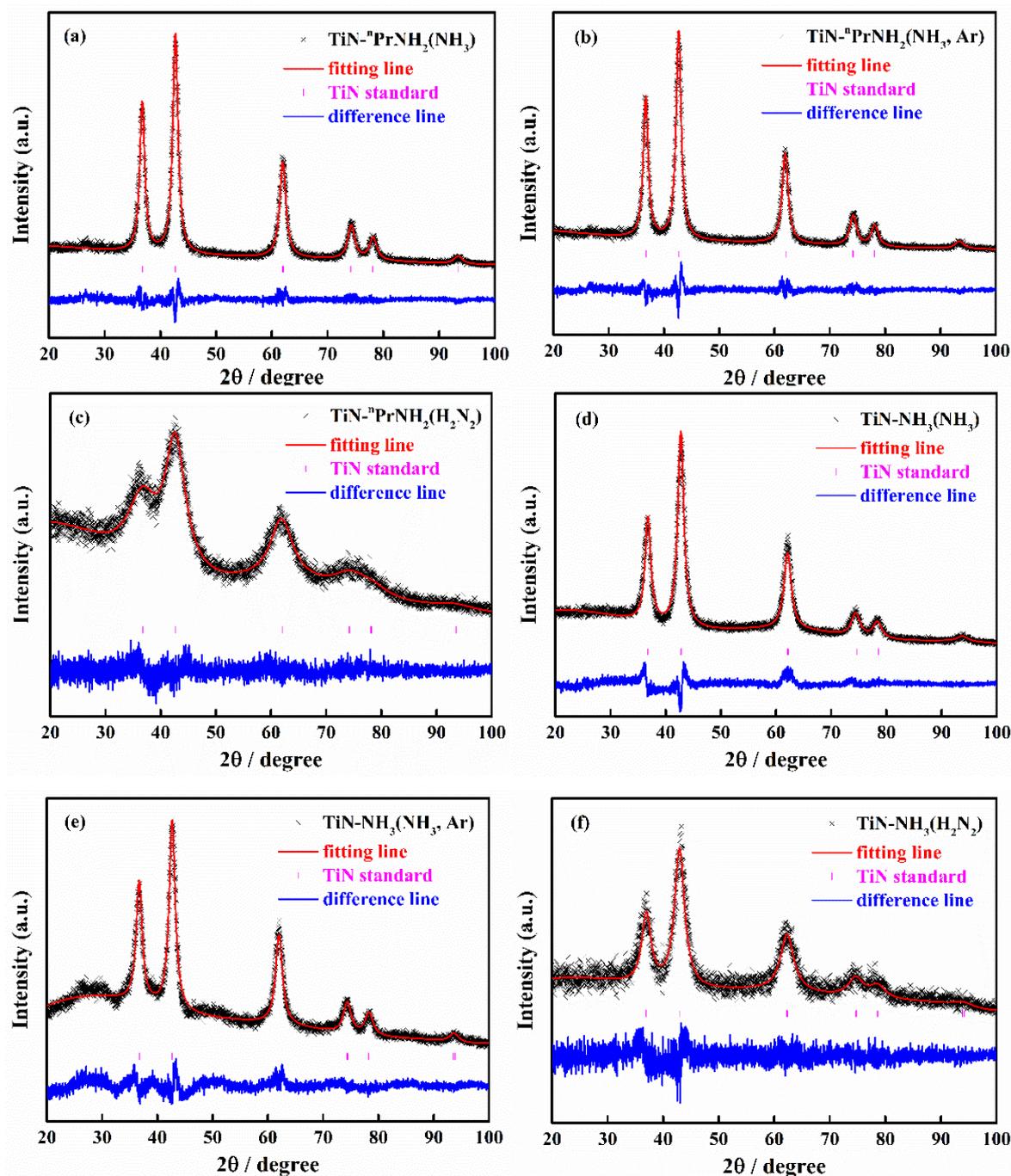


Figure 3-4 Rietveld fits to the XRD patterns of (a) $\text{TiN-}^n\text{PrNH}_2(\text{NH}_3)$ ($R_{\text{WP}} = 9.44\%$ and $R_{\text{p}} = 7.29\%$), (b) $\text{TiN-}^n\text{PrNH}_2(\text{NH}_3, \text{Ar})$ ($R_{\text{WP}} = 9.92\%$ and $R_{\text{p}} = 7.77\%$), (c) $\text{TiN-}^n\text{PrNH}_2(\text{H}_2\text{N}_2)$ ($R_{\text{WP}} = 8.44\%$ and $R_{\text{p}} = 6.37\%$), (d) $\text{TiN-NH}_3(\text{NH}_3)$ ($R_{\text{WP}} = 9.65\%$ and $R_{\text{p}} = 7.71\%$), (e) $\text{TiN-NH}_3(\text{NH}_3, \text{Ar})$ ($R_{\text{WP}} = 9.93\%$ and $R_{\text{p}} = 7.90\%$) and (f) $\text{TiN-NH}_3(\text{H}_2\text{N}_2)$ ($R_{\text{WP}} = 18.88\%$ and $R_{\text{p}} = 14.47\%$) samples. The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for TiN with space group $Fm\bar{3}m$.

The propylamine-derived sample heated in 5% H_2/N_2 ($\text{TiN-}^n\text{PrNH}_2(\text{H}_2\text{N}_2)$) contained more carbon (20.7 wt%) than those heated in ammonia. This sample had the smallest crystallite size of 5.02(16) nm. The TEM image in Figure 3-5 shows an amorphous layer on its surface which is likely to be

carbon, but since no carbon diffraction peaks are observed the carbon must be amorphous. All samples heated in NH_3 have C contents of 2.5% or less. Incorporation of carbon into the rocksalt lattice to make $\text{Ti}(\text{C},\text{N})$ compositions occurs readily and where small amounts of carbon are in the sample it is likely to be in the lattice. The carbonitrides are also good conductors and this is unlikely to reduce functionality. $\text{TiN}-^n\text{PrNH}_2(\text{H}_2\text{N}_2)$ and all the ammonia crosslinked samples also had high hydrogen contents. This suggests the presence of alkyl or amide/imide groups, which may reduce the conductivity of the materials.

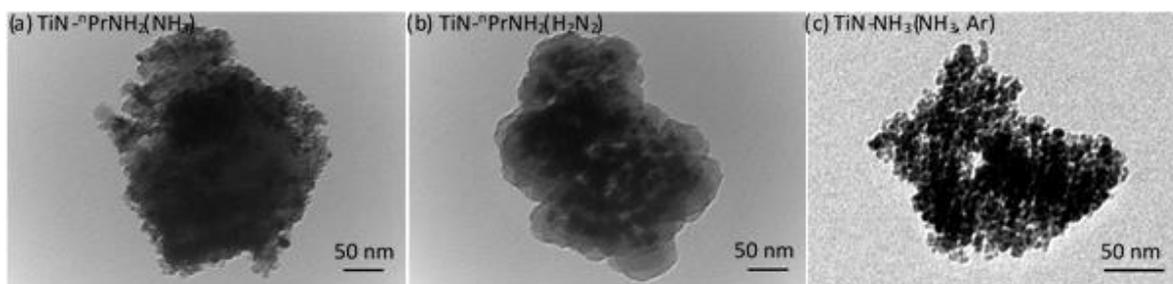


Figure 3-5 TEM images (scale bar = 50 nm) of (a) $\text{TiN}-^n\text{PrNH}_2(\text{NH}_3)$, (b) $\text{TiN}-^n\text{PrNH}_2(\text{H}_2\text{N}_2)$ and (c) $\text{TiN}-\text{NH}_3(\text{NH}_3, \text{Ar})$ samples.

In order to evaluate the conductivity that TiN samples would produce in a composite electrode, TiN samples were mixed with PTFE binder and calendared to produce self-standing TiN disks, which were dry contacted with two cylindrical pistons in a Swagelok cell and cyclic voltammograms measured to observe the current-voltage profile. The conductivity of TiN was calculated based on $C = S A / l$, where C (mA V^{-1}) is the conductance of the pellet, S (S m^{-1}) is the conductivity of the TiN, A (mm^2) is the cross-sectional area of the TiN pellet, and l (mm) is the thickness of the TiN pellet. The measured conductivities in Table 3-1 were calculated from the current-potential plots shown in Figure 3-6 and Figure 3-7. As expected the propylamine crosslinked samples heated in ammonia, where hydrogen contents were low, had significantly higher conductivities. Replacing the gas flow with Ar after heating improved the conductivity a little, but it was a small effect. The clearest outcome was that coating of LiFePO_4 should be attempted using the propylamine crosslinker.

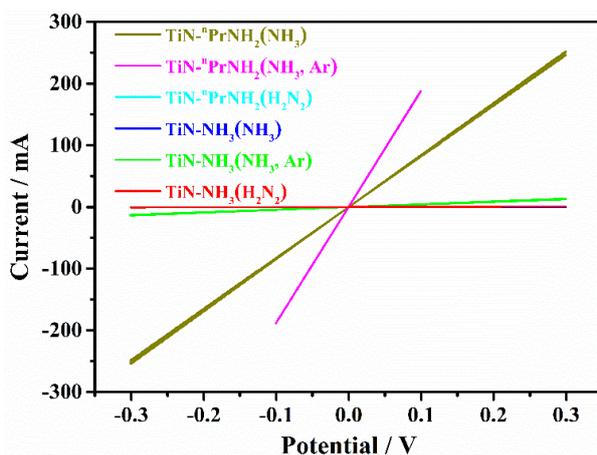


Figure 3-6 Current-potential plots (3 cycles each) for dry TiN samples at scanning rate of 20 mV s^{-1} , showing the Ohmic behaviour of the samples (labels explained in Scheme 3-1). Note that the cyan and blue lines are coincident with the red line, which has been plotted separately as below.

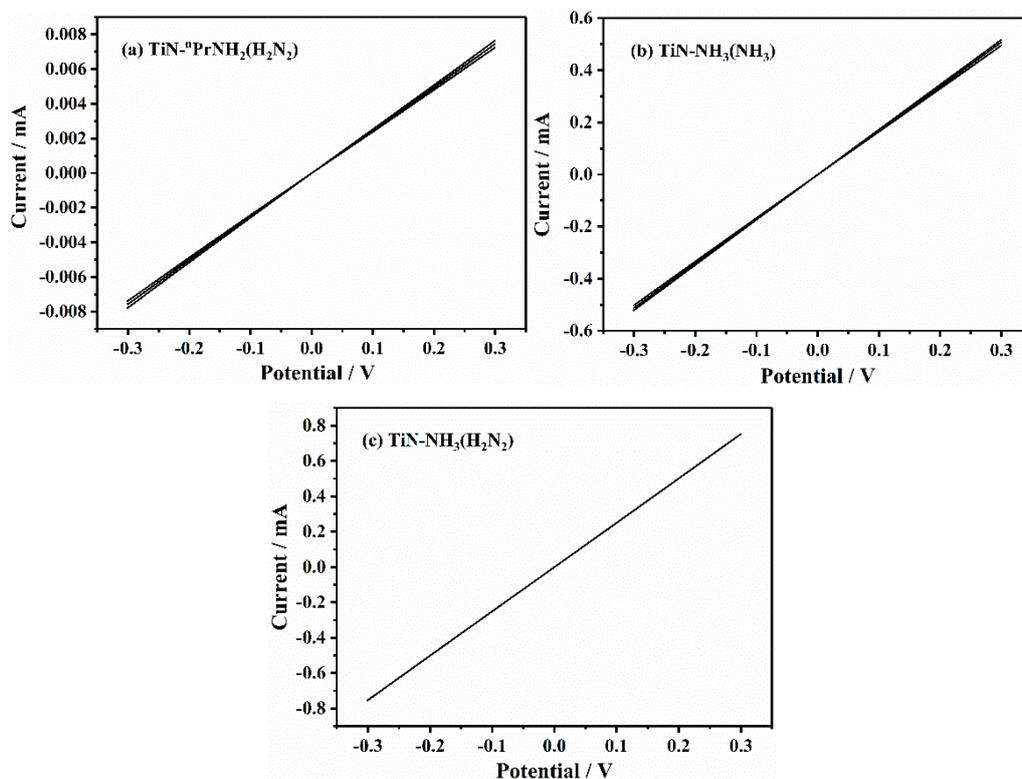
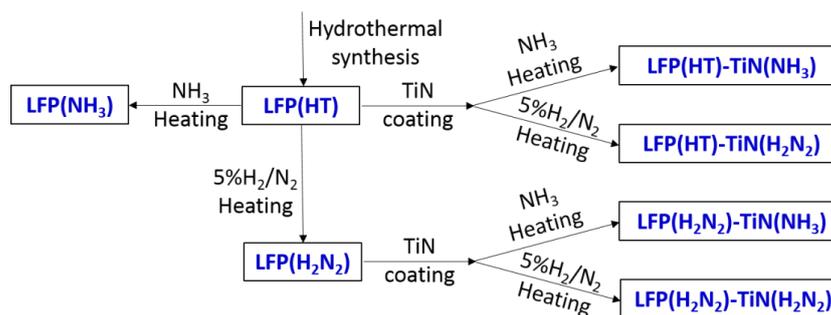


Figure 3-7 Cyclic voltammetry plots for (a) $\text{TiN-}^n\text{PrNH}_2(\text{H}_2\text{N}_2)$, (b) $\text{TiN-NH}_3(\text{NH}_3)$ and (c) $\text{TiN-NH}_3(\text{H}_2\text{N}_2)$ samples at scanning rate of 20 mV s^{-1} .

3.5.2 Effect of heating environment on LiFePO_4

TiN from the chosen propylamine crosslinking route was found to be more conductive when fired in ammonia (Table 3-1). Uncoated LiFePO_4 was produced with firing in ammonia or in the more

typical dilute hydrogen,^{276, 277} to check whether heating in ammonia caused a deterioration in the LiFePO_4 properties. Scheme 3-2 shows the sample labels used for different sample types.



Scheme 3-2 Preparation conditions and sample labels for TiN-coated LiFePO_4 materials

All the X-ray diffraction peaks of LiFePO_4 produced by heating the hydrothermal product (LFP(HT)) at $650\text{ }^\circ\text{C}$ under $5\% \text{H}_2/\text{N}_2$ (Figure 3-8) were consistent with the standard olivine LiFePO_4 structure (JCPDS Card No. 40-1499, space group $Pnma$) as expected. The lattice parameters obtained from Rietveld fitting (Figure 3-9 and Table 3-2) are very close to the literature value.²⁷⁹ LFP(HT) was also heated at temperatures between 450 and $750\text{ }^\circ\text{C}$ under NH_3 to investigate any effects on the microstructure of LiFePO_4 . The XRD patterns of these samples are shown in Figure 3-8 and Figure 3-10. Very little change is observed, with no secondary phases and very little variation in the lattice parameters from the Rietveld fits (Table 3-2). Hence heating in NH_3 at temperatures up to $750\text{ }^\circ\text{C}$ does not affect the crystal structure of LiFePO_4 .

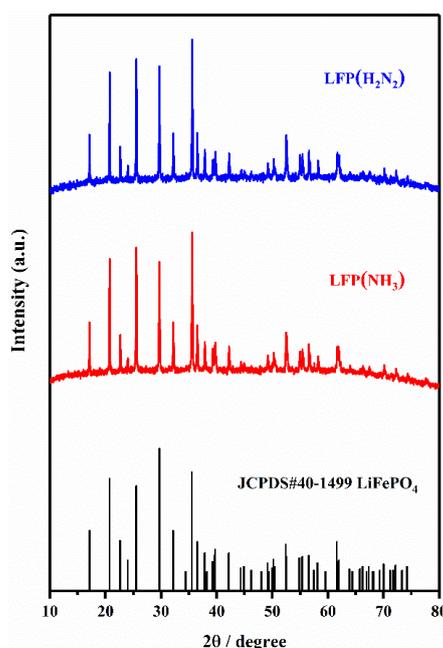


Figure 3-8 XRD patterns of LiFePO_4 samples heated under $5\% \text{H}_2/\text{N}_2$ and NH_3 , respectively, at $650\text{ }^\circ\text{C}$ (labels explained in Scheme 3-2). The black stick pattern denotes the literature positions and intensities of LiFePO_4 reflections.

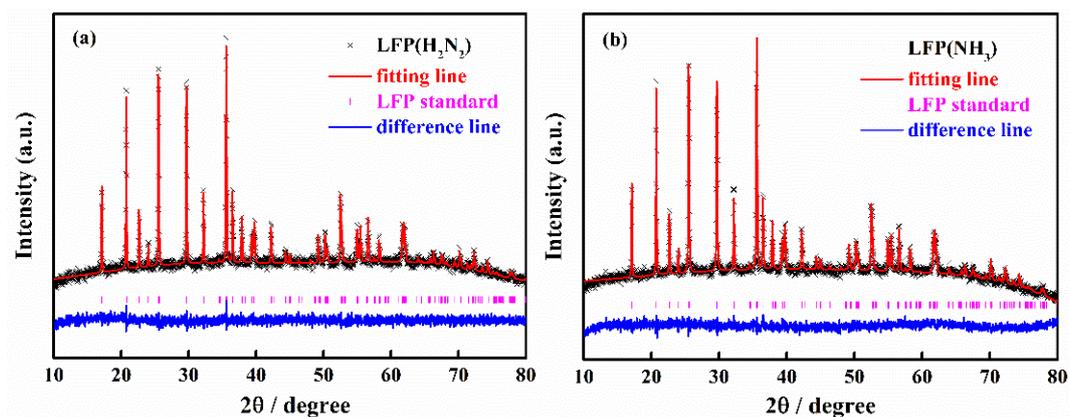


Figure 3-9 Rietveld fits to the XRD patterns of (a) LFP(H₂N₂) ($R_{WP} = 2.29\%$ and $R_p = 1.82\%$) and (b) LFP(NH₃) ($R_{WP} = 1.96\%$ and $R_p = 1.55\%$) samples. The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for LiFePO₄ with space group *Pnma*.

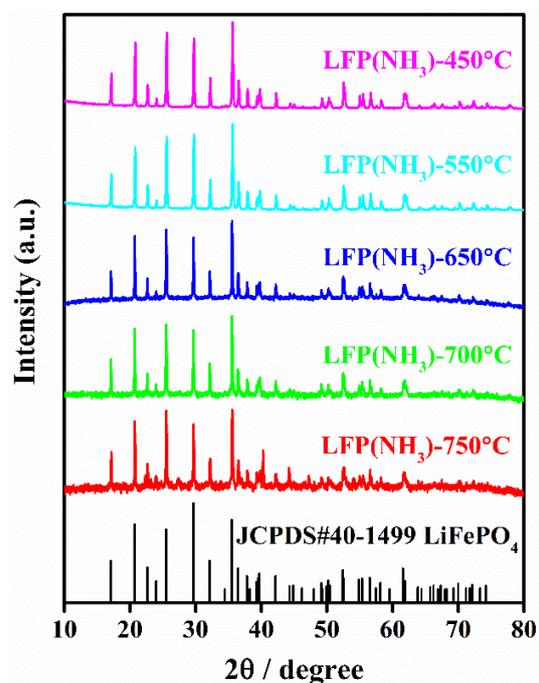


Figure 3-10 XRD patterns of LFP(NH₃)-450°C, LFP(NH₃)-550°C, LFP(NH₃)-650°C, LFP(NH₃)-700°C and LFP(NH₃)-750°C samples prepared by hydrothermal method and heated under NH₃ at the temperature of 450 °C to 750 °C. The black stick pattern denotes the literature positions and intensities of LiFePO₄ reflections.

Table 3-2 Lattice parameters obtained from the Rietveld fits of XRD patterns for LFP(NH₃)-450°C, LFP(NH₃)-550°C, LFP(NH₃)-650°C, LFP(NH₃)-700°C, LFP(NH₃)-750°C and LFP(H₂N₂) samples.

Sample	a (Å)	b (Å)	c (Å)
LFP(NH ₃)-450°C	10.3232(2)	6.0015(1)	4.6890(8)
LFP(NH ₃)-550°C	10.3216(1)	6.0022(9)	4.6904(8)
LFP(NH ₃)-650°C	10.3254(2)	6.0057(1)	4.6938(1)
LFP(NH ₃)-700°C	10.3233(3)	6.0061(2)	4.6930(2)
LFP(NH ₃)-750°C	10.3246(6)	6.0082(3)	4.6958(3)
LFP(H ₂ N ₂)	10.3274(2)	6.0060(1)	4.6919(1)

The electrochemical performance of uncoated LiFePO₄ is expected to be poor because of its low electronic conductivity.^{220, 280} Cui et al.²⁵¹ reported similar LiFePO₄ samples to have a capacity of 96 mA h g⁻¹ at 0.1 C and that this capacity drops quickly with cycling, especially at high rates. Figure 3-11 shows the initial charge/discharge curves at 0.1 C and cycle stability of the samples produced at 650 °C. In addition to the expected plateau at ~3.5 V an additional plateau at ~4 V was observed in the initial charge curve of the material produced in 5% H₂/N₂. The amount of charge associated with the feature faded over subsequent cycles and may be due to the poor conductivity of the electrode or an initial incomplete dispersion of the electrolyte into the electrode.^{237, 250} The initial discharge capacities of LFP(H₂N₂) and LFP(NH₃) were 108.3 and 93.1 mA h g⁻¹, respectively, suggesting that ammonia heating results in a poorer material. However, the capacity of LFP(NH₃) increased slightly to 96.3 mA h g⁻¹ over 20 cycles, whereas the capacity of LFP(H₂N₂) faded to 80.8 mA h g⁻¹ over the same number of cycles. Overall this suggested that ammonia is a valid environment for the crystallisation of LiFePO₄, but since the results were somewhat similar both heating environments were carried forward to the TiN-coated LiFePO₄ samples.

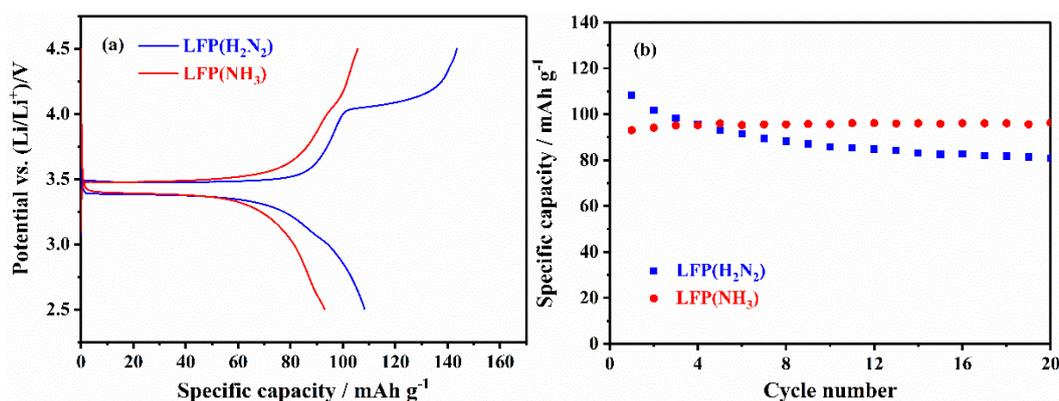


Figure 3-11 (a) The initial cycle voltage profile vs specific capacity and (b) specific capacity vs cycle number of the same materials in Li half cells, cycled between 2.5 and 4.5 V for 20 cycles at a current rate of 0.1 C.

3.5.3 Synthesis, microstructure and electrochemistry of TiN-coated LiFePO₄

Two forms of LiFePO₄ were selected for coating, the uncrystallised material directly after the hydrothermal synthesis, giving the possibility of just one heating step, and the material already crystallised under 5% H₂/N₂ (Scheme 3-2). These were coated using a propylamine-crosslinked sol and the solvent was removed *in vacuo*. The resulting samples were then fired at 650 °C for 6 h under 5% H₂/N₂ or ammonia, leading to black solids.

The diffraction patterns of all of the LiFePO₄ samples coated with 10% TiN (based on amount of Ti(NMe₂)₄ used in preparing the coating sol) were dominated by reflections due to LiFePO₄ (Figure 3-10). Rietveld fits to these data (Figure 3-12 and Figure 3-13) yielded typical LiFePO₄ lattice parameters (Table 3-3), suggesting that the TiN coating process did not cause any chemical change to the LiFePO₄. The average LiFePO₄ crystallite sizes were 123-175 nm. Broad reflections matching the expected peak positions for TiN could be observed by close inspection of the difference plots in Rietveld fits where only the LiFePO₄ intensity was modelled (Figure 3-12b, red line). However, these were only distinct enough to fit in the case of the sample produced from pre-fired LiFePO₄ and then fired under ammonia after coating (Figure 3-12). The two phase fit (including LiFePO₄ and TiN) resulted in a flatter difference line and an improvement in the fit statistics, with R_{wp} reducing from 0.79% to 0.72% (Figure 3-12b, blue line). The refined TiN lattice parameter was 4.217(5) Å, close to that of the TiN samples (Table 3-1). The TiN crystallite size was refined as 2.6(1) nm, significantly smaller than in the bulk TiN samples and potentially useful for producing an even coating on the small LiFePO₄ particles. The refined TiN phase fraction was 9.7(6)%, close to the 10% TiN content expected from the Ti(NMe₂)₄ content of the sol.

Table 3-3 Lattice parameters and crystallite sizes of LiFePO₄ obtained from the Rietveld fits of XRD patterns for LFP(HT)-TiN(NH₃), LFP(HT)-TiN(H₂N₂), LFP(H₂N₂)-TiN(NH₃) and LFP(H₂N₂)-TiN(H₂N₂) samples.

Sample	LiFePO ₄			Crystallite size (nm)
	a (Å)	b (Å)	c (Å)	
LFP(HT)-TiN(NH ₃)	10.3267(3)	6.0052(2)	4.6939(2)	123(2)
LFP(HT)-TiN(H ₂ N ₂)	10.3195(4)	6.0009(2)	4.6951(2)	173(5)
LFP(H ₂ N ₂)-TiN(NH ₃)	10.3249(1)	6.00473(4)	4.69113(3)	153(1)
LFP(H ₂ N ₂)-TiN(H ₂ N ₂)	10.3168(3)	6.0021(1)	4.6938(1)	175(3)

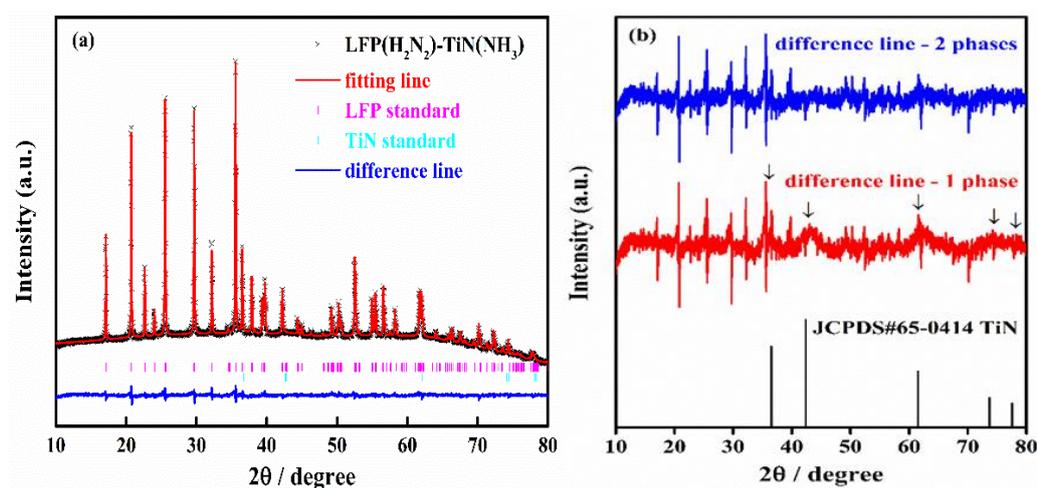


Figure 3-12 (a) Rietveld fit ($R_{wp} = 0.72\%$ and $R_p = 0.53\%$) to the XRD pattern of LFP(H_2N_2)-TiN(NH_3) (sample labels explained in Scheme 3-2, 10% TiN). The data points and Rietveld fit are overlaid in black crosses and a red line, respectively. The difference plot is shown in blue. The pink and cyan tick marks represent the allowed reflection positions for $LiFePO_4$ with space group $Pnma$ and for TiN with space group $Fm\bar{3}m$, respectively. (b) The difference lines in the 2-phase ($LiFePO_4$ and TiN) and 1-phase ($LiFePO_4$) Rietveld fits to the same XRD pattern.

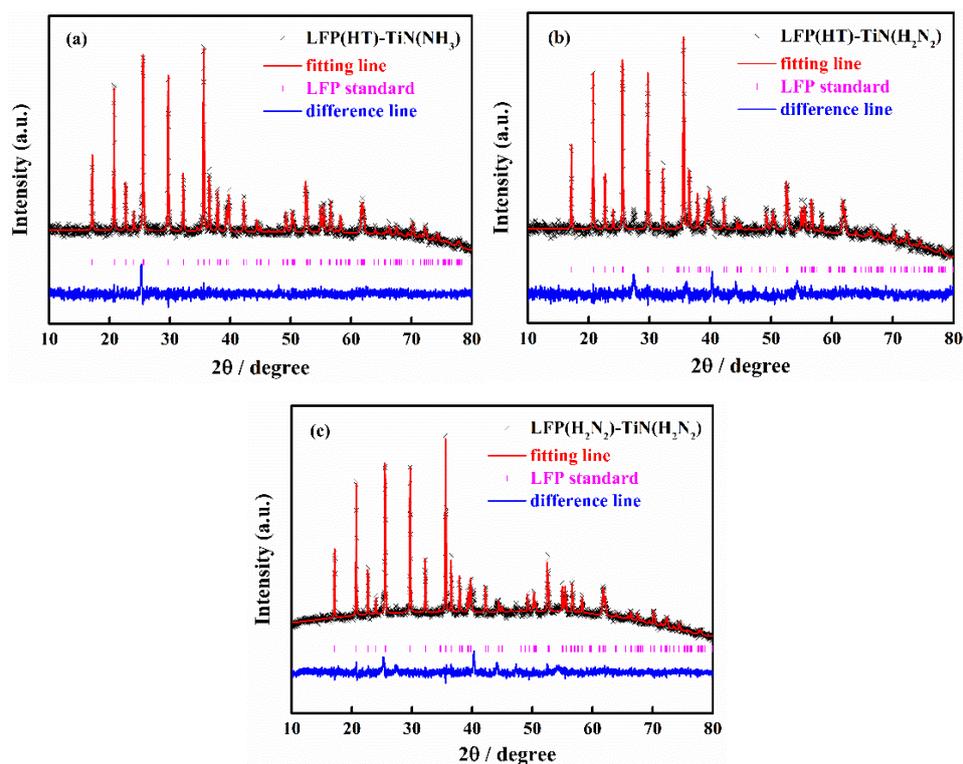


Figure 3-13 Rietveld fits to the XRD patterns of (a) LFP(HT)-TiN(NH_3) ($R_{wp} = 2.45\%$ and $R_p = 1.86\%$), (b) LFP(HT)-TiN(H_2N_2) ($R_{wp} = 2.69\%$ and $R_p = 2.03\%$) and (c) LFP(H_2N_2)-TiN(H_2N_2) ($R_{wp} = 2.36\%$ and $R_p = 1.73\%$) samples. The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for $LiFePO_4$ with space group $Pnma$.

The electrochemical performance of TiN-coated LiFePO₄ samples was assessed by galvanostatic cycling of Li half cells. The initial cycle charge/discharge curves and the variations in discharge capacity over the first 20 cycles are shown in Figure 3-14. LFP(HT)-TiN(H₂N₂) and LFP(H₂N₂)-TiN(NH₃) had the largest initial discharge capacities of 145 and 150 mA h g⁻¹, respectively. The TiN sample produced with ⁿPrNH₂ and fired in 5% H₂/N₂ contained 20.7 wt% carbon and the TiN-coated LiFePO₄ samples produced under these conditions can be expected to contain some carbon, which may play the role of a conductive additive. The capacity of LFP(HT)-TiN(H₂N₂) drops to 133 mA h g⁻¹ after 20 cycles whereas LFP(H₂N₂)-TiN(NH₃) retains 145 mA h g⁻¹ after 20 cycles. This material performed significantly better than the uncoated LiFePO₄, suggesting that the TiN is providing the required improvement in the electronic conductivity of the composite powders.

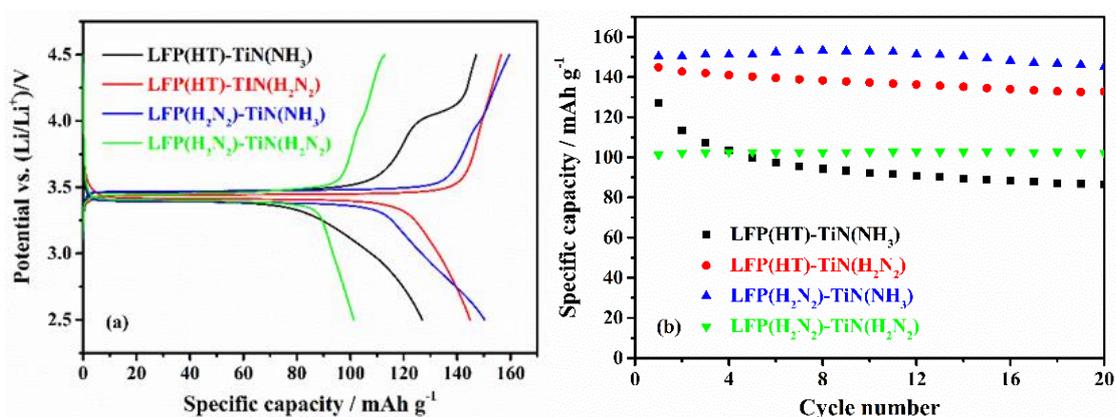


Figure 3-14 The initial cycle of voltage profile against specific capacity (a) and specific capacity versus cycle number (b) of TiN-coated LiFePO₄/Li half cells, under galvanostatic cycling between 2.5 and 4.5 V at 0.1 C (sample labels explained in Scheme 3-2, 10% TiN).

TEM images of LFP(H₂N₂)-TiN(NH₃) (Figure 3-15) showed TiN nanoparticles distributed across the LiFePO₄ surface. Where particles were aggregated the TiN particles acted to separate the LiFePO₄ particles. The presence of the TiN on the surface provides a conducting network between the particles and this is also reflected in the electrochemical performance discussed above. Coatings are also important to prevent Fe²⁺ dissolution from LiFePO₄, which limits degradation of the charge/discharge performance.^{231, 232} Figure 3-16 shows the EDS analysis of LFP(H₂N₂)-TiN(NH₃), which confirms the presence of Ti on the LiFePO₄, with a 9.5 wt% TiN content calculated from the Ti:Fe ratio. The combustion analysis of this sample showed it to contain 0.55% C, <0.10% H and 1.78% N. A sample containing 10% TiN would contain 2.26% N, a value that is close to the carbon and nitrogen content of this sample combined. Hence the coating is probably a carbonitride of approximate composition TiC_{0.25}N_{0.75}.

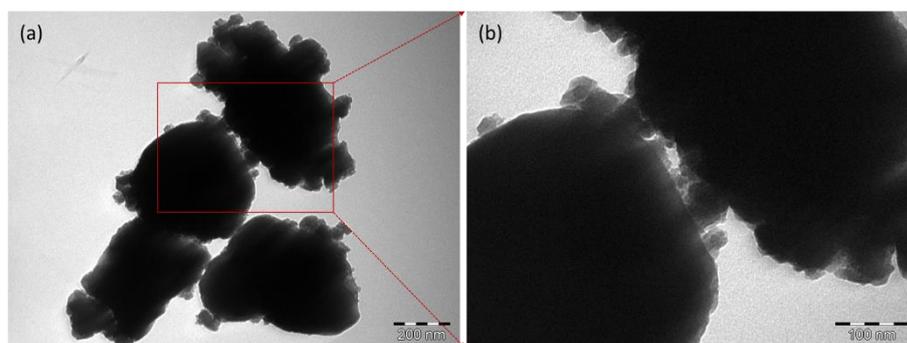


Figure 3-15 TEM images of LFP(H₂N₂)-TiN(NH₃) ((a), scale bar = 200 nm, 10% TiN) and enlarged view of the region marked by the red box ((b), scale bar = 100 nm). Sample labels are explained in Scheme 3-2.

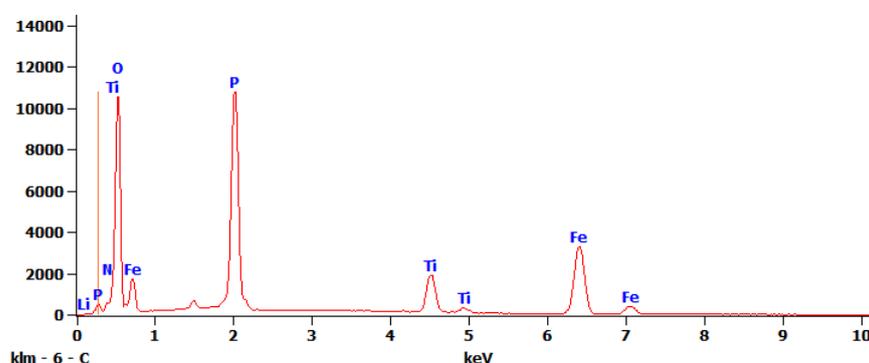


Figure 3-16 EDS spectrum of LFP(H₂N₂)-TiN(NH₃) sample.

The 10% TiN compositions described above were initially studied based on producing a coating of similar thickness to a typical carbon coating, which is typically 5-8% C, a lower content by mass because carbon is less dense.^{267, 281} For LFP(H₂N₂)-TiN(NH₃), which was the highest capacity material at 10% TiN, variations in the TiN content of the composites were examined. The initial charge/discharge curves of materials containing 0%, 2.5%, 5%, 7.5%, 10% and 12.5% TiN are shown in Figure 3-17, with initial discharge capacities of 108, 112, 129, 132, 150 and 142 mA h g⁻¹, respectively. These results support the original assumption that 10% TiN is optimal, probably because this amount is needed to make a fairly continuous conductive network. The drop in capacity at 12.5% suggests that the TiN may then be starting to hinder lithium diffusion.

Figure 3-17 also shows the variation in discharge capacity over 50 cycles of LFP(H₂N₂)-TiN(NH₃) samples with various TiN contents. The discharge capacity of LFP(H₂N₂)-10TiN(NH₃) decayed gradually with continuous cycling, retaining 123 mA h g⁻¹ after 50 cycles, 82% of its initial capacity. The discharge capacity of the uncoated material faded to 68 mA h g⁻¹ over 50 cycles, a 37% capacity loss. It is well-established that the dissolution of Fe from LiFePO₄ in LiPF₆ electrolyte causes capacity fade.²²⁰ The improvement in cycle performance of LFP(H₂N₂)-10TiN(NH₃) relative to the uncoated

material suggests that TiN modification on the surface of LiFePO_4 is impeding erosion of the active material by the electrolyte.^{231, 232} Figure 3-15 shows that the coatings are still not continuous, so it is possible that further refinement of the coating method could deliver further improvements.

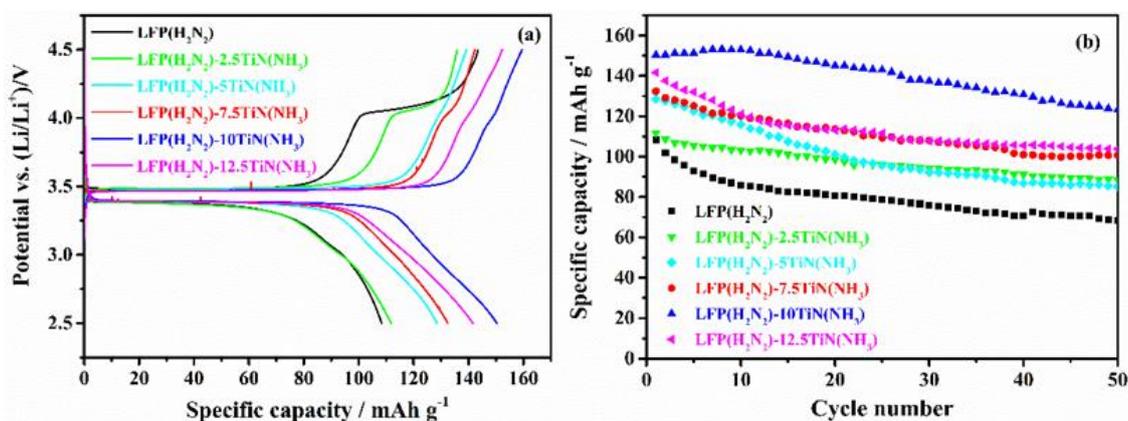


Figure 3-17 The initial cycle of voltage profile against specific capacity (a) and specific capacity versus cycle number (b) of TiN-coated $\text{LiFePO}_4/\text{Li}$ half cells under galvanostatic cycling between 2.5 and 4.5 V at 0.1 C (sample labels explained in Scheme 3-2, with the percentage of TiN in the composite written after the hyphen).

Coating LiFePO_4 was intended to improve its performance by improving conductivity and surface stability, but TiN itself can undergo conversion reactions at low potential¹² so it is worth to check whether it was contributing to the capacity. Hence $\text{TiN}-\text{PrNH}_2(\text{NH}_3)$ was treated as the active material to test this contribution. TiN electrodes were produced with acetylene black and a PVDF binder in exactly the same way as the TiN-coated LiFePO_4 samples and assembled into lithium half-cells. The cyclic voltammetry over the potential range in which the TiN- LiFePO_4 cells are operated (Figure 3-18) shows small currents and very little change over 100 cycles of CV testing. This result is confirmed by the voltage profile vs specific capacity during galvanostatic cycling (Figure 3-18). This experiment was carried out at a current rate of 170 mA g^{-1} of TiN, 10 \times that used in the 90% LiFePO_4 /10% TiN electrodes, in order to keep the specific current relative to the TiN content the same. $\text{TiN}-\text{PrNH}_2(\text{NH}_3)$ had a very low initial specific capacity of 0.46 mA h g^{-1} , and this remained lower than 0.5 mA h g^{-1} after 100 cycles. Hence the TiN was found to be electrochemically inert, confirming its action was mainly on the conductivity.

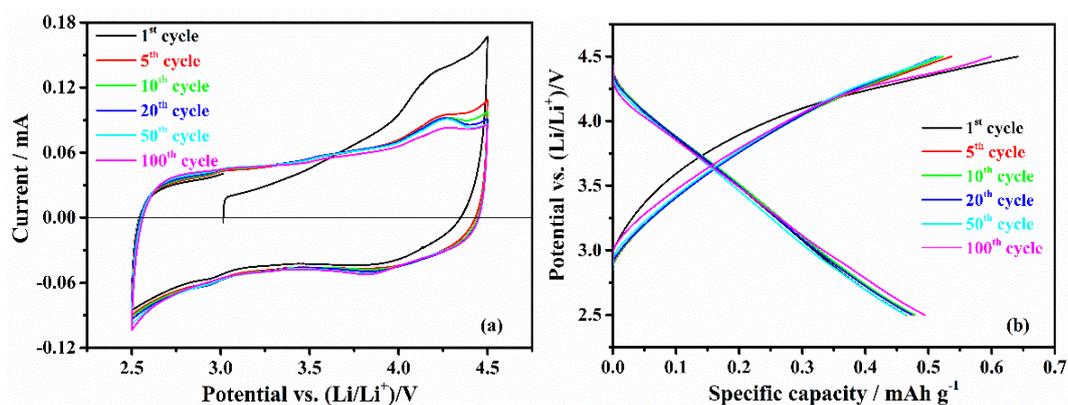


Figure 3-18 (a) Cyclic voltammograms plots of $\text{TiN-}^n\text{PrNH}_2(\text{NH}_3)/\text{Li}$ half cell at 20 mV s^{-1} over the range of 1 to 5 V at room temperature; (b) The voltage profile against specific capacity of $\text{TiN-}^n\text{PrNH}_2(\text{NH}_3)/\text{Li}$ half cell under galvanostatic cycling between 2.5 and 4.5 V for 100 cycles.

Figure 3-19 shows the discharge capacity of selected samples at faster charge/discharge rates. The higher discharge capacities in the sample containing 10% TiN were maintained at these higher rates, with average capacities (over 5 cycles each) of 159, 149, 130, 109 and 89 mA h g^{-1} found at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C, respectively. The capacity plot vs inverse scan rate does not plateau, showing that at still lower scan rates further capacity would be available. According to Huang,²⁸² the capacity is most affected by the supply of electrons at high rates and hence this is the regime in which a low charge transfer resistance is most critical. Hu *et al* found that carbon coating on porous LiFePO_4 works well for lithium insertion at low current rates but does not at high current rates because of the insufficient electronically conducting network.²⁴⁶ Using nanometer-sized RuO_2 as an oxidic interconnect, the kinetics and rate capability of the composite were significantly improved. Lu *et al* reported a simple approach to enhance the electrical conductivity of olivine-structured LiFePO_4 thin films by uniformly dispersing small fractions of highly conductive silver throughout the LiFePO_4 film.²³⁶ The as-obtained 200 nm-thick $\text{LiFePO}_4\text{-Ag}$ composite thin films provided a reversible discharge capacity of $46.3 \mu\text{A h } \mu\text{m}^{-1} \text{ cm}^{-2}$ ($>135 \text{ mA h g}^{-1}$) at a current density of $8 \mu\text{A cm}^{-2}$ (*ca* 0.7 C). The observation that the capacity of $\text{LFP}(\text{H}_2\text{N}_2)\text{-10TiN}(\text{NH}_3)$ drops quite significantly at higher rates suggests that the TiN coatings are not yet fully optimised to provide the fastest kinetics, but it is promising that the obtained capacities at similar rates (130 mA h g^{-1} at 0.5 C; 109 mA h g^{-1} at 1 C) are comparable.

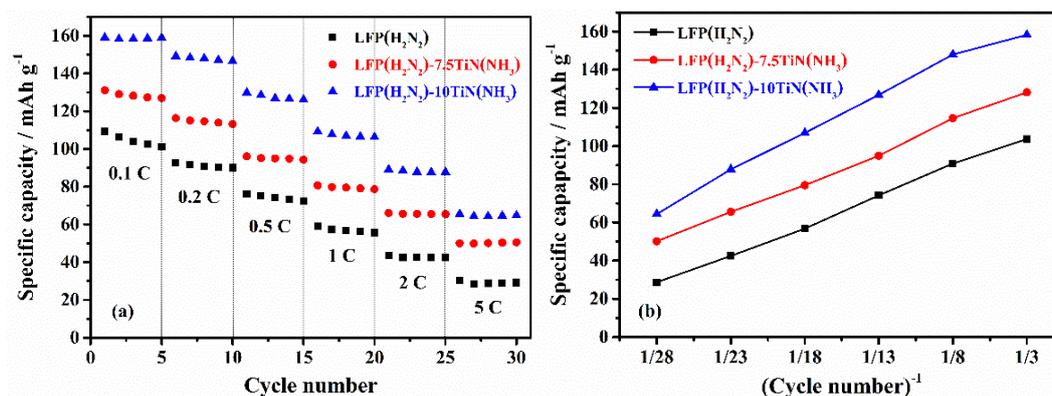


Figure 3-19 The discharge specific capacity vs cycle number (a) and plot of the average capacity in those groups vs inverse cycle number (b) of uncoated and TiN coated LiFePO₄ in Li half cells, cycled at various sequential rates from 0.1 C to 5 C, between 2.5 and 4.5 V over 30 cycles (sample codes are described in Scheme 3-2, with the % TiN noted after the hyphen).

3.5.4 Synthesis, microstructure and electrochemistry of carbon-coated LiFePO₄

The uncrystallised LiFePO₄ precursor directly after the hydrothermal synthesis was selected for carbon coating by suspension mixing method. The resulting materials were then fired at 650 °C for 6 h under 5% H₂/N₂, leading to black solids. The obtained 5 wt.% and 10 wt.% carbon coated LiFePO₄ were denoted as LFP(HT)-5C(H₂N₂) and LFP(HT)-10C(H₂N₂), respectively.

The XRD patterns of LFP(HT)-5C(H₂N₂) and LFP(HT)-10C(H₂N₂) samples were shown in Figure 3-20. All the X-ray diffraction peaks could be indexed to the standard olivine LiFePO₄ structure (JCPDS card No. 40-1499, space group *pnma*) which indicates that carbon coating does not affect the crystal structure of LiFePO₄. The TEM image of LFP(HT)-5C(H₂N₂) sample (Figure 3-21) showed the particle size of the oval-like LiFePO₄ is about 400 nm. A smooth and clean surface was observed on LiFePO₄ particles which is assumed to be carbon layer.

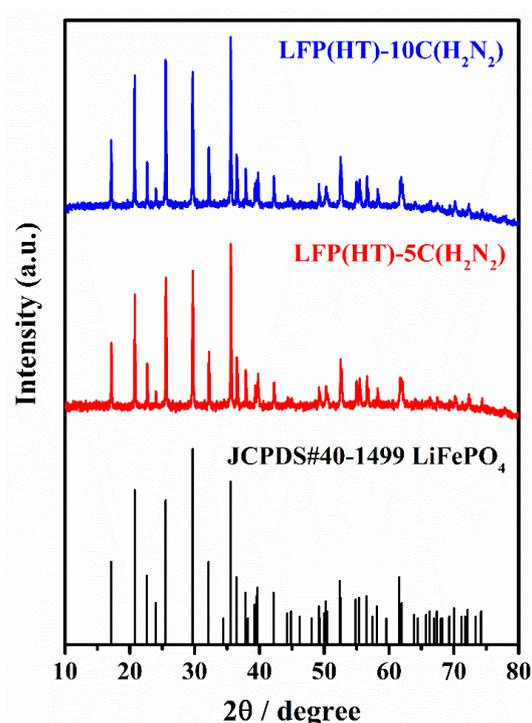


Figure 3-20 XRD patterns of LFP(HT)-5C(H₂N₂) and LFP(HT)-10C(H₂N₂) samples prepared by suspension mixing method and heated to 650 °C under 5% H₂/N₂. The black stick pattern denotes the literature positions and intensities of LiFePO₄ reflections.

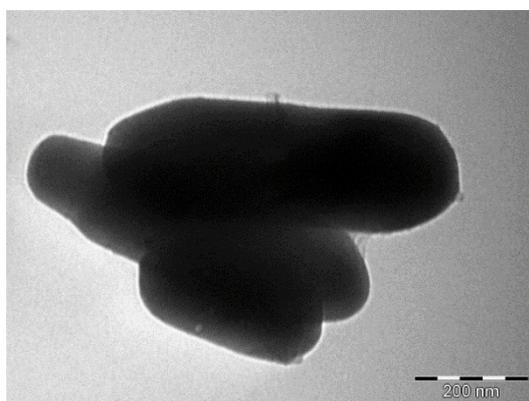
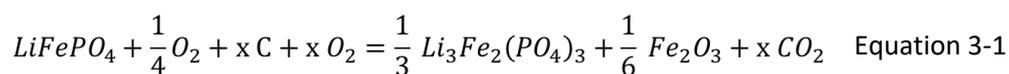


Figure 3-21 TEM image of LFP(HT)-5C(H₂N₂) sample (scale bar = 200 nm).

The carbon content in a LFP(HT)-10C(H₂N₂) sample was estimated by thermogravimetric analysis (TGA) and the curve is shown in Figure 3-22. In the temperature range of 250-500 °C, the olivine LiFePO₄ can be oxidized to Li₃Fe₂(PO₄)₃ and Fe₂O₃, corresponding to a theoretical weight gain of 5.07 %. The carbon in the composite starts to be oxidized to CO₂ gas above 350 °C, leading to a weight loss, and burns out completely above 500 °C, based on Equation 3-1:



Equation 3-1 The reaction equation of LiFePO_4 during TGA, where x denotes the carbon content in the composite.

The percentages of present carbon in LFP(HT)-10C(H_2N_2) sample can be calculated to 8.74 wt. %.

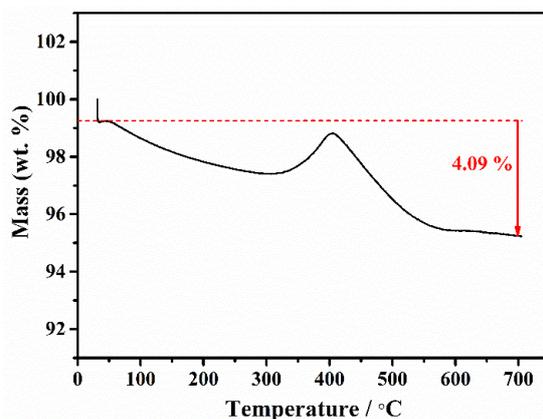


Figure 3-22 TGA curve of LFP(HT)-10C(H_2N_2) sample, examined by heating to 700 °C at 10 °C /min under O_2 as reactant gas and Ar as protecting gas.

The electrochemical performance of carbon-coated LiFePO_4 samples were assessed by galvanostatic cycling of Li half cells. The initial cycle charge/discharge curves and the variations in discharge capacity over the first 10 cycles are shown in Figure 3-23. The initial discharge capacities of LFP(HT)-5C(H_2N_2) and LFP(HT)-10C(H_2N_2) were 169.4 and 154.6 mA h g^{-1} , respectively, and their capacities increased slightly over 10 cycles. These materials performed significantly better than the uncoated LiFePO_4 , probably due to the improved electronic conductivity of the composite powders after carbon coating.

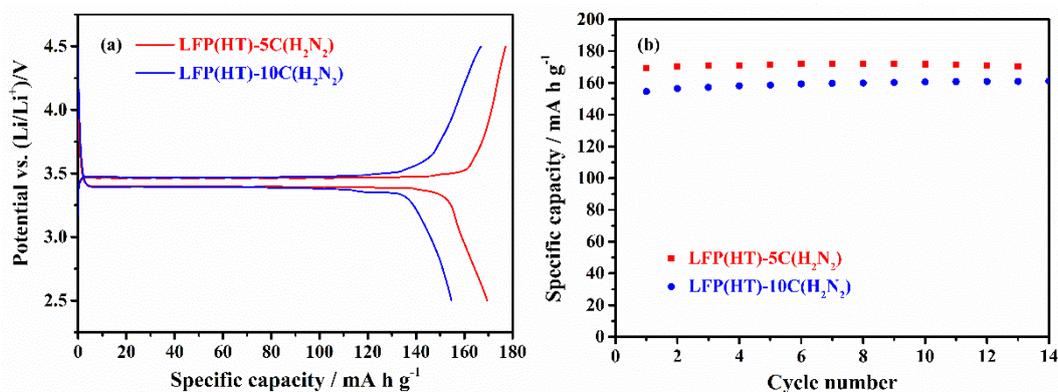


Figure 3-23 The initial cycle of voltage profile against specific capacity (a) and specific capacity versus cycle number (b) of carbon-coated LiFePO_4 / Li half cells under galvanostatic cycling between 2.5 and 4.5 V at 0.1C.

Figure 3-24 shows the discharge capacity of carbon coated LiFePO_4 samples at faster charge/discharge rates. Compared with $\text{LFP(HT)-5C(H}_2\text{N}_2)$, the capacity of $\text{LFP(HT)-10C(H}_2\text{N}_2)$ is slightly lower at low rates, but it exceeds at high rates, with average capacities (over 5 cycles each) of 163, 162, 158, 154, 148, 131, 104 mA h g^{-1} found at 0.1C, 0.2C, 0.5C, 1C, 2C, 5C and 10C, respectively. The specific capacity of $\text{LFP(HT)-10C(H}_2\text{N}_2)$ can return to 164 mA h g^{-1} (0.1C) after undergoing 35 cycles of high rate discharge, which indicated a favourable reversibility and cycling stability even under high-rate discharge. The capacity plot vs. inverse scan rate does not plateau, showing that at still lower scan rates further capacity would be available.

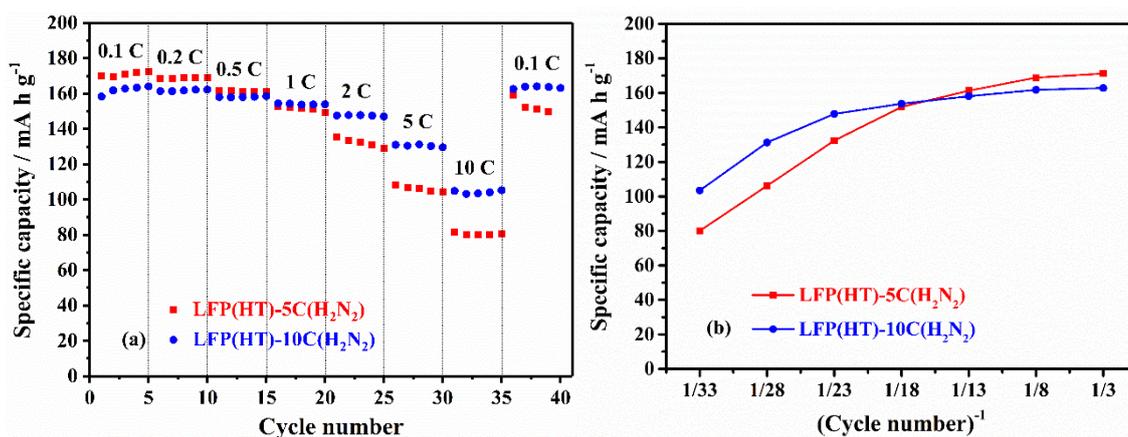


Figure 3-24 The discharge specific capacity vs. cycle number (a) and plot of the average capacity in those groups vs. inverse cycle number (b) of carbon coated LiFePO_4 in Li half cells, cycled at various sequential rates from 0.1C to 10C, 5 and 4.5 V over 40 cycles.

Since the olivine LiFePO_4 was reported by Goodenough and co-workers in 1997,²⁸³ many researchers have tried to improve the performance of LiFePO_4 by coating with carbon, metals or metal oxides to improve electronic conductivity.^{227, 228, 230, 231, 236, 246} Well optimised carbon coatings allow 90% of its theoretical capacity to be used with acceptable rate capabilities.^{217, 284} The novel propylamine cross-linking based sol-gel method to produce TiN coatings on LiFePO_4 described herein already delivers a significant fraction of the electrochemical performance that is currently achieved with carbon after several years of intense activity. It appears to both increase the electronic conductivity of the LiFePO_4 to deliver higher capacities than the uncoated material, and to reduce corrosion due to iron dissolution and hence retain a larger fraction of the initial capacity during continuous cycling. The sol-gel process transfers close to 100% (mechanical losses only) of the titanium precursor to the TiN/ LiFePO_4 composite so has a lower precursor cost than more wasteful CVD or ALD approaches. However, TiN will always be a more costly coating material than carbon and would not be expected to replace it in standard applications. It may have advantages for battery materials run under non-standard conditions where carbon coatings may be unstable,

e.g. with high voltage electrode materials or for cells that need to be able to operate at high temperature.

3.6 Conclusions

Sol-gel approaches to the coating of battery materials with titanium nitride have been explored. A propylamine cross-linking method gave higher electronic conductivity materials than ammonia cross-linking, and hence was used to produce the coatings. Firing in ammonia also resulted in lower carbon contents, so LiFePO_4 was examined after firing in ammonia and found to be comparable with the material fired more conventionally in a dilute hydrogen mix. TiN-coated LiFePO_4 performed well as an electrode material in lithium half cells, with capacities, cycling performance and rate capabilities in the best cases that were competitive with other coating materials. LiFePO_4 modified with 10 wt% TiN from the propylamine cross-linking method and fired in ammonia exhibits a maximum discharge capacity of 159 mA h g^{-1} , that is 93% of the theoretical capacity (170 mA h g^{-1}), at the rate of 0.1 C. There is room to further improve the performance of these coating materials, and they may provide good options for batteries used in non-standard conditions.

Chapter 4: Review of understanding and development of olivine LiCoPO_4 cathode materials for lithium-ion batteries

4.1 Introduction

Development of environmentally friendly, sustainable and renewable energy supplies is vital to meet the increasing energy demand of modern society and emerging ecological concerns.¹⁻³ As reversible energy storage devices, lithium-ion batteries (LIBs) exhibit high energy density, high power density, and light weight compared to conventional batteries.⁴⁻⁶ LIBs are not only widely used in portable electronic devices such as laptops, cameras and smart phones, but also to power emerging large-scale applications such electric vehicles and hybrid electric vehicles.⁵⁻⁸ The cathode material plays an important role in the energy density, safety, life cycle and cost in LIBs.^{4, 26, 27} Cost and safety concerns associated with the conventional cathode material, LiCoO_2 , have motivated the search for new high-performance materials that can be safely scaled up at reasonable cost.^{2, 285, 286}

Olivine-structured lithium transition-metal orthophosphates LiMPO_4 (M = Fe, Mn, Co, Ni) have attracted considerable attention as cathode materials for LIBs due to their high theoretical specific capacities, good thermal stability and high redox potentials vs Li/Li^+ .^{4, 6, 58} Although LiFePO_4 , with a redox potential of 3.45 V vs Li/Li^+ and capacity of 170 mA h g^{-1} , has so far exhibited the best electrochemical performance and has been successfully commercialised,⁶⁰⁻⁶⁵ other members of the olivine family are also being researched intensively.^{4, 66-68} LiCoPO_4 was firstly reported by Amine *et al* in 2000,⁷² and has received particular attention due to the high redox potential of 4.8 V vs Li/Li^+ and a theoretical capacity of 167 mA h g^{-1} comparable to LiFePO_4 of 170 mA h g^{-1} .⁷³⁻⁷⁵ Even though Co is more expensive than the other transition metals (e.g. Fe), the cost of LiCoPO_4 can be lower than other commercialized LIBs in some cases, when the higher energy density delivered by its high redox potential and specific capacity are taken into account.^{287, 288} Applying LiCoPO_4 in 18650 batteries, Howard *et al* estimated the cost of LiCoPO_4 to be $142 \text{ \$ kW}^{-1} \text{ h}^{-1}$, while LiCoO_2 and LiFePO_4 were 198 and $158 \text{ \$ kW}^{-1} \text{ h}^{-1}$, respectively.^{289, 290}

Although attractive for high energy and high power applications, use of LiCoPO_4 as a cathode has been hindered by the unsatisfactory cycle stability and rate performance, which is due, in part, to its low electronic conductivity and Li^+ ion conductivity relating to the one-dimensional ion transport channel.^{74, 211, 291-301} Also, the decomposition of electrolytes under high potentials results in poor cycle stability and coulombic efficiency.⁷⁶⁻⁸³ A variety of synthesis methods have been used to

produce LiCoPO_4 , including solid-state reaction,^{302, 303} hydrothermal/solvothermal methods,^{291, 304} sol-gel synthesis,^{305, 306} etc. Alternative approaches like surface modification,^{291, 307} ion doping,^{74, 308} size reduction and morphology control^{304, 309} have also been investigated to modify the electrochemical performance of LiCoPO_4 . Typically, the electrochemical performance is characterised by galvanostatic testing at various C rates of charge/discharge, where the C rate is the current normalised by capacity (e.g. 0.1 C for a capacity of 167 mA h g^{-1} corresponds to a current of 16.7 mA g^{-1}). In practical applications like portable electronic devices, the charge/discharge rates of LIBs are 0.2-1 C in general. The structure and properties of three different polymorphs of LiCoPO_4 (space groups: *Pnma*, *Cmcm*, and *Pna2₁*) have been summarised recently.³¹⁰ The olivine-type *Pnma*- LiCoPO_4 exhibits promising electrochemical properties as a high-voltage cathode in LIBs. This chapter reviews the strategies for performance improvement with various synthesis methods for olivine LiCoPO_4 cathode materials in LIBs.

4.2 Structure and properties

The olivine structured LiCoPO_4 belongs to space group *Pnma* with lattice parameters of $a = 10.20 \text{ \AA}$, $b = 5.92 \text{ \AA}$, and $c = 4.70 \text{ \AA}$.^{72, 82, 299, 311-317} The crystal structure consists of a polyoxyanionic framework including LiO_6 octahedra, CoO_6 octahedra and PO_4 tetrahedra,⁷⁶ as illustrated in Figure 4-1. Strong P-O covalent bonds in the $(\text{PO}_4)^{3-}$ polyanion network stabilize the oxygen when fully charged and hinder O_2 release at high states of charge.^{285, 301, 318-321} Moreover, as the fully charged state CoPO_4 phase has the same olivine structure as LiCoPO_4 , when Li^+ ions are removed from the structure during charging, Co^{2+} ions are oxidised to Co^{3+} and the lattice volume shrinks by only $\sim 7\%$.^{76, 82, 317, 319, 322-324} Thus major volume changes during charge-discharge are avoided, resulting in a stable olivine structured LiCoPO_4 cathode.

The skeleton of PO_4 polyanions in LiCoPO_4 is thermally stable, but the corner-shared CoO_6 octahedra of LiCoPO_4 are separated by the oxygen atoms of the PO_4^{3-} tetrahedra and cannot form a continuous CoO_6 network.^{76, 304, 321, 325, 326} This makes electron delocalization difficult and thus results in the poor electronic conductivity of LiCoPO_4 .^{211, 285, 292-296} Each PO_4 tetrahedron and CoO_6 octahedron shares edges with its neighbours, forming one dimensional tunnels parallel to the [010] direction down which Li-ion migration occurs preferentially (Figure 4-1).^{301, 325} The 1D channels are easily blocked by defects and impurities, which may hinder the Li^+ ion diffusion.^{327, 328} The conductivity of sintered pellets of LiCoPO_4 depends on the synthesis method, but for samples with composition close to stoichiometric LiCoPO_4 , values of conductivity lower than $10^{-9} \text{ S cm}^{-1}$ have been reported,²⁹⁶⁻³⁰¹ which are much lower than those of LiCoO_2 ($\sim 10^{-3} \text{ S cm}^{-1}$)³²⁹ and LiMn_2O_4 ($\sim 10^{-4} \text{ S cm}^{-1}$).³³⁰

Upon charge and discharge in LIBs, LiCoPO_4 undergoes two distinct two-phase reactions, both involving an intermediate $\text{Li}_{2/3}\text{CoPO}_4$ phase, coexisting with the fully lithiated phase at higher Li contents and with the delithiated phase at low Li contents.^{315-317, 322-324, 331-333} This process produces two oxidation peaks (close to 4.8 and 4.9 V vs Li/Li^+) and two reduction peaks (close to 4.7 and 4.8 V vs Li/Li^+) in cyclic voltammetry, with corresponding plateau (~ 4.8 and 4.9 V vs Li/Li^+ for charge, ~ 4.7 and 4.8 V vs Li/Li^+ for discharge) in charge-discharge curves.^{76, 334}

A number of studies on LiCoPO_4 examined the microstructure,³³⁵ structural stability,³³⁶ Li-ion intercalation³³⁷ and phase changes during charge-discharge^{76, 317} using first-principles methods based on density functional theory (DFT). Grey and coworkers identified the structure of the intermediate $\text{Li}_{2/3}\text{CoPO}_4$ formed during cycling of LiCoPO_4 using first-principles solid-state DFT calculations in combination with experimental NMR and XRD data.³¹⁷ It was found that both the Co^{3+} ions and Li vacancies order along the b-axis in the lowest energy configuration. Two other low energy Li^+ /vacancy ordering schemes have energy of only 5 meV per formula unit higher. All three configurations lie below the LiCoPO_4 - CoPO_4 convex hull, which can be easily converted to each other via Li^+ hops along the b-direction.

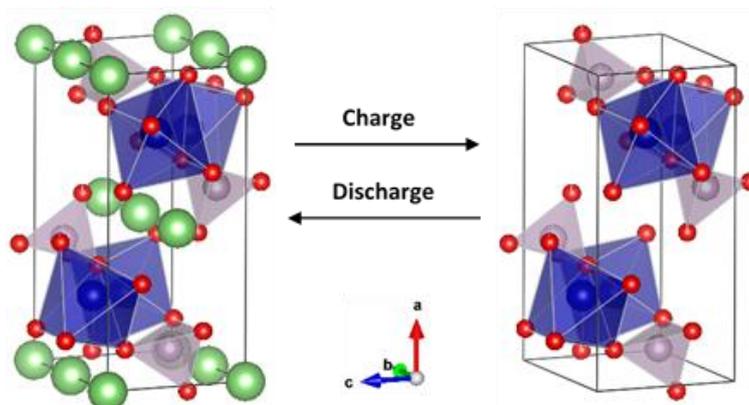


Figure 4-1 Unit cell of olivine-type LiCoPO_4 (space group: Pnma) showing Li (green) in 1D channels along $[010]$ between CoO_6 octahedra (blue) corner-linked to PO_4 tetrahedra (purple), and the olivine structure remains stable during Li-ion insertion and extraction.

4.3 Synthesis methods

To prepare LiCoPO_4 cathodes for LIBs with good cycle stability and rate capability and low cost, various synthetic routes such as solid-state reactions, hydrothermal/solvothermal synthesis and sol-gel processes have been proposed.

4.3.1 Solid-state reaction

Solid-state reaction is an economic, efficient, and scalable strategy to prepare LiCoPO₄ for LIBs.^{338, 339} In this process, the precursors are firstly mixed and ground or milled thoroughly, then heated to 300-400 °C to decompose the precursors and expel the gases.^{298, 340-342} After that, the mixture is ground again, then calcined at elevated temperatures of 600-800 °C for 10-36 h.^{303, 317, 343, 344} As shown in Table 4-1, the influence of the synthesis precursors and calcination conditions on the structure, particle size (particle growth) and electrochemical performance of LiCoPO₄ has been studied in detail.

Table 4-1 Solid-state methods: the influence of the synthesis precursors and calcination conditions on the particle size and electrochemical performance of LiCoPO₄.

Precursors	Sintering conditions (temperature, time, gas)	Particle size	Rate performance, mA h g ⁻¹ (rate, C)	Cycle stability	Ref.
Li ₂ CO ₃ , Co ₃ O ₄ , NH ₄ H ₂ PO ₄	300 °C, 6 h, air 780 °C, 36 h, air	3-10 μm	125 (0.1 C)	30 mA h g ⁻¹ at 0.1 C after 25 cycles	341
LiOH·H ₂ O, CoO, (NH ₄) ₂ HPO ₄	750 °C, 8 h, air 350 °C, 6 h, air 750 °C, 36 h, air	90-100 nm	110 (0.05 mA cm ⁻²) 89 (0.1 mA cm ⁻²) 83 (0.2 mA cm ⁻²) 62 (0.4 mA cm ⁻²) 56 (0.8 mA cm ⁻²)	40 mA h g ⁻¹ at 0.05 mA cm ⁻² after 30 cycles	356
LiOH·H ₂ O, Co ₃ O ₄ , (NH ₄) ₂ HPO ₄	400 °C, 10 h, air 800 °C, 10 h, air	100-150 nm	132 (0.1 C)	92 mA h g ⁻¹ at 0.1 C after 17 cycles	344
LiOH·H ₂ O, Co ₃ O ₄ , (NH ₄) ₂ PO ₄	400 °C, 10 h, air 800 °C, 10 h, Ar	-	128 (0.1 mA cm ⁻²)	70% capacity retention at 0.1 mA cm ⁻² after 20 cycles	303
Li ₂ CO ₃ , Co(CH ₃ COO) ₂ ·4H ₂ O, NH ₄ H ₂ PO ₄	350 °C, 6 h, air 750 °C, 12 h, Ar	1 μm	109 (0.1 C) 46 (5 C)	55 mA h g ⁻¹ at 0.1 C after 50 cycles	352
LiOH·H ₂ O, Co ₃ O ₄ , (NH ₄) ₂ PO ₄	400 °C, 10 h, air 800-900 °C, 10 h, Ar	-	130 (0.1 C)	117 mA h g ⁻¹ at 0.1 C after 15 cycles	350
LiOH·H ₂ O, CoO, NH ₄ H ₂ PO ₄	400 °C, 10 h, air 800 °C, 10 h, air	500-700 nm	112 (0.05 C)	83 mA h g ⁻¹ at 0.05 C after 25 cycles	353
Li ₂ CO ₃ , CoCO ₃ , NH ₄ H ₂ PO ₄	300 °C, 8 h, air/Ar 700 °C, 8 h, air/Ar	-	123 (0.1 C) 114 (0.2 C) 102 (1 C) 93 (2 C) 81 (5 C)	89% capacity retention at 0.1 C after 30 cycles	302
Li ₂ CO ₃ , (NH ₄)Co(PO ₄)·H ₂ O	600 °C, 16 h, air 600 °C, 8 h, air	350-700 nm	93 (0.05 C)	64 mA h g ⁻¹ at 0.05 C after 20 cycles	316
Li ₂ CO ₃ , Co(NO ₃) ₂ ·6H ₂ O, NH ₄ H ₂ PO ₄	350 °C, 2 h, Ar 500 °C, 8 h, Ar/5% H ₂	100-300 nm	146 (0.1 C) 93 (2 C)	92 mA h g ⁻¹ at 0.1 C after 40 cycles	359
Li ₂ CO ₃ , CoC ₂ O ₄ ·2H ₂ O, NH ₄ H ₂ PO ₄	375 °C, 8 h, air 750 °C, 12 h, Ar	50-400 nm	128 (0.05C)	115 mA h g ⁻¹ at 0.05 C after 5 cycles	360

The raw materials generally consist of a stoichiometric amount of lithium source (Li₂CO₃, LiOH·H₂O or CH₃COOLi),^{316, 345-347} cobalt source (Co(CH₃COO)₂·4H₂O, Co₃O₄ or CoO)^{313, 348-350} and phosphorus source (NH₄H₂PO₄ or (NH₄)₂HPO₄).^{293, 351-353} The long and complex procedures, requiring repeated grinding and calcination, led to undesirable particle growth and agglomeration.³⁵⁴⁻³⁵⁶ This can be prevented by adding growth inhibitors such as carbon or carbonate anions to obtain nanoparticles.³⁵⁷⁻³⁶⁰ After optimising the solid-state reaction conditions, a carbon coated LiCoPO₄ (LiCoPO₄/C) nanocomposite with growth controlled by carbonate anions CO₃²⁻ was reported by

Nallathamby *et al.*³⁰² This cathode delivered a capacity of 123 mA h g⁻¹ at 0.1 C, and capacity retention of 89% over 30 cycles, as well as reasonable rate capability up to 5 C.

4.3.2 Hydrothermal/solvothermal synthesis

Hydrothermal/solvothermal synthesis is a simple and easily scalable method to synthesize LiCoPO₄ at relatively low temperature with small crystallites (nanoscale to microns)^{309, 361, 362} and well controlled morphology (e.g., cubic, spherical, and plate-like).³⁶³⁻³⁶⁷ In this process, the precursors are dissolved and mixed in solvents, then sealed in an autoclave to react at temperature above the boiling point of the solvent.³⁶⁸⁻³⁷¹ As shown in Table 4-2, the particle size and morphology of LiCoPO₄ can be tuned by changing the stoichiometric ratio and concentrations of reactants,³⁷²⁻³⁷⁴ solvents,^{304, 309, 375, 376} pH values of solution,^{361, 377, 378} additives,^{291, 372, 379-381} reaction conditions^{316, 382-384} and sintering conditions.^{352, 368}

Hydrothermal/solvothermal reactions can be heated in a conventional or microwave oven.^{385, 386} Whereas conventional heating transfers heat by conduction through the autoclave, microwave heating can transfer energy selectively to the microwave absorbing materials, thus the reactant mixture can be heated evenly.^{66, 383, 387} This microwave assisted strategy promotes uniform nucleation conditions in hydrothermal/solvothermal reactions, thus the method results in highly crystalline LiCoPO₄ with narrow particle size distribution and homogeneous morphology.^{362, 374} Also, the reaction time can be decreased to less than 30 min due to the increased reaction rate, thus offers considerable energy and cost savings.^{372, 374, 378} For example, Nilges *et al* prepared LiCoPO₄ nano-platelets *via* microwave-assisted solvothermal synthesis using water/ethylene glycol co-solvent (1:1 in volume ratio) at 250 °C for 30 min, without post-annealing or carbon coating processes.³⁸⁸ The solvents were found to be critical in tailoring the particle size, morphology and crystal orientation of LiCoPO₄.³⁰⁴ The as-prepared LiCoPO₄ exhibited an initial capacity of 137 mA h g⁻¹ at 0.1 C, and a capacity retention of 68% over 100 cycles at 0.5 C.³⁸⁸

Since Li-ion transport in LiCoPO₄ occurs through one-dimensional channels that are easily blocked by defects or impurities, it is important to ensure complete ordering of lithium and cobalt ions, to eliminate stacking faults and avoid undesirable impurities.^{309, 389, 390} It was found that increasing the reaction temperature can minimize the unfavorable effects of Co-Li anti-site defects,^{64, 316, 362} and well crystallized LiCoPO₄ can be obtained if high-pressure reactors are used.^{316, 365, 374}

In hydrothermal/solvothermal synthesis, it is possible to obtain LiCoPO₄ directly from the heated solution without post heat treatment.^{366, 367, 387, 391} However if a carbon coating is desired, it is necessary to carry out the heat treatment step at higher temperatures, which could also help to eliminate the Co-Li anti-site defects.^{309, 374, 375} Carbon sources used include glucose,^{363, 378, 392}

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sucrose^{382, 393} and ascorbic acid,^{376, 391} and these can also act as reducing agents to prevent the oxidation of Co²⁺ in hydrothermal process.^{291, 372}

Table 4-2 Hydrothermal/solvothermal synthesis: the influence of stoichiometric ratio and concentrations of reactants, solvents, pH values of solution, additives, reaction conditions and sintering conditions on the morphology, particle size and electrochemical performance of LiCoPO₄.

Precursors	Li:Co:P molar	Concentration of Co (M)	Solvents (v/v)	Additive	Reaction conditions (temperature, time, pressure)	Sintering conditions (temperature, time, gas)	Morphology, particle size	Rate performance, mA h g ⁻¹ (rate, C)	Cycle stability	Ref.
LiOH, CoSO ₄ , H ₃ PO ₄	3:1:1	-	H ₂ O	Glucose as reducing agent and carbon source, NH ₄ OH to adjust pH=9.9	230 °C, 15 min, 80 bar, microwave assisted: 600 W, 2.45 GHz	700 °C, 1 h, Ar	Cubes, 1.2-1.5 μm x 250 nm	52 (0.1 C)	15 mA h g ⁻¹ at 0.1 C after 25 cycles	363
LiOH·H ₂ O, Co(CH ₃ COO) ₂ ·4H ₂ O, H ₃ PO ₄ or (NH ₄) ₂ HPO ₄	2:1:1	0.05	H ₂ O	PVP ^a as dispersant, NH ₄ OH to adjust pH=8.5	220 or 300 °C, 5 h, 2 or 6.5 MPa	-	Rod, 300-700 nm in diameter, 5 μm in length	65 (0.1 C)	50 mA h g ⁻¹ at 0.1 C after 10 cycles	361
LiOH, CoSO ₄ ·7H ₂ O, (NH ₄) ₂ PO ₄ ·3H ₂ O	3:1:1	0.1	H ₂ O:BA ^a =1:1	Glucose as carbon source	200 °C, 8 h	750 °C, 2 h, Ar	Hedgehog-like, 5-8 μm (compose of nanorods, 40 nm x 1 μm)	136 (0.1 C) 85 (5 C)	91% capacity retention at 0.1 C after 50 cycles	352
LiCl, Co(NO ₃) ₂ ·6H ₂ O, H ₃ PO ₄	2:2:1	0.325	EG ^a	Glucose as carbon source, NH ₃ ·H ₂ O as buffer, Mn doping	200 °C, 10 h	-	Nanoparticle agglomeration, 2-3 μm	105 (0.2 C)	90% capacity retention at 0.2 C after 30 cycles	392
LiOH·H ₂ O, CoSO ₄ ·7H ₂ O, LiH ₂ PO ₄	2.75:1:1	0.1	H ₂ O:EG ^a =1:2	Sucrose as reducing agent	220 °C, 15 h	-	Hexagonal/octagonal platelet, thickness of 50-100 nm	95 (0.1 C) 76 (0.5 C)	75 mA h g ⁻¹ at 0.1 C after 10 cycles	366, 367
CH ₃ COOLi·2H ₂ O, Co(CH ₃ COO) ₂ ·4H ₂ O, (NH ₄) ₂ HPO ₄	6:1:1	0.04, 0.125	H ₂ O	L-ascorbic, citric or polyacrylic acid as organic additive, NH ₄ OH to adjust pH=8.6-9	220 °C, 30 s, microwave assisted	650 °C, 30 min, Ar	Flower-like, 5-10 μm (compose of plate-like, 1-2 μm x 200 nm)	107 (0.05 C) 60 (2 C)	30 mA h g ⁻¹ at 0.05 C after 20 cycles	372
LiOH, Co(NO ₃) ₂ , CoSO ₄ , Co(CH ₃ COO) ₂ or CoCO ₃ , LiH ₂ PO ₄	1.75~2.2 5:1:1	0.1	H ₂ O:EG ^a =1:2	Sucrose as reducing agent	200-240 °C, 4-10 h	-	Hexagonal platelets, thickness < 200 nm	120 (0.1 C) 85 (0.5 C) 75 (1 C)	90 mA h g ⁻¹ at 0.1 C after 10 cycles	382
LiOH·H ₂ O, CoSO ₄ ·7H ₂ O, H ₃ PO ₄	3:1:1	0.25	H ₂ O:EG ^a =1:1	Ascorbic acid as reducing agent and buffer to adjust pH=5.5	250 °C, 30 min, microwave assisted: 600 W	-	Hexagonal platelets, 400-600 x 700-800 x 100-220 nm	137 (0.1 C) 114 (0.5 C) 97 (2 C)	68% capacity retention at 0.5 C after 100 cycles	388
Li ₃ PO ₄ , CoSO ₄ ·7H ₂ O	3:1:1	-	EG ^a :H ₂ O =0, 0.5, 1, 2, 4, 5, 10, 20	Sucrose as carbon source	180 °C, 24 h	650 °C, 5 h, Ar	Particles, 500 nm-10 μm	124 (0.1 C) 111 (0.5 C) 100 (1 C) 85 (2 C) 51 (5 C)	83% capacity retention at 0.1 C after 100 cycles	309
LiOH·H ₂ O, Co(CH ₃ COO) ₂ ·4H ₂ O, H ₃ PO ₄	1:1:1	0.238	TTEG ^a	NH ₄ OH as additive, V ³⁺ doping	240 °C, 30 min, 5 bar, microwave assisted: 850 W	525 °C, 12 h, 10%H ₂ /Ar	Particles, 100-500 nm	97 (0.1 C)	82 mA h g ⁻¹ at 0.1 C after 20 cycles	368
LiNO ₃ , Co(NO ₃) ₂ ·6H ₂ O, (NH ₄) ₂ HPO ₄	1:1:1	-	Isopropanol	Tannic acid as carbon source	140-220 °C, 30 min, 20 bar, microwave assisted: 2.45 GHz, 600 rpm	650 °C, 6 h, Ar	Irregular particles, 200 nm-1 μm	155 (0.1 C) 129 (1 C) 98 (5 C) 70 (10 C) 51 (20 C)	91% capacity retention at 0.1 C after 80 cycles	383
Li ₃ PO ₄ , CoSO ₄ ·7H ₂ O	3:1:1	3	H ₂ O	CMC ^a , glucose or ascorbic acid as organic additives and carbon source	200 °C, 24 h, 800 rpm	700 °C, 1 h, Ar/3% H ₂	Irregular particles, 0.39-2.8 μm	135 (0.1 C) 132 (0.5 C) 125 (1 C) 117 (2 C) 101 (5 C)	52% capacity retention 0.1 C after 30 cycles	291
LiOH·H ₂ O, Co(CH ₃ COO) ₂ ·4H ₂ O, H ₃ PO ₄	1:1:1	0.2	TTEG ^a	V doping, LiFePO ₄ coating	240 °C, 30 min, microwave assisted: 850 W	525 °C, 4 h, Ar	Spherical or oblong spheroid, 50 - 250 nm	145 (0.1 C)	51% capacity retention at 0.1 C after 20 cycles	364
LiOH·H ₂ O, CoSO ₄ ·7H ₂ O, H ₃ PO ₄	3:1:1	-	H ₂ O:(EG, DEG, TEG, TTEG, PEG, BA) ^a =1:1	Ascorbic acid as reducing agent, pH=5.0-5.5	250 °C, 30 min, microwave assisted: 600 W	-	Square, rhombic and hexagonal platelets, 600-800 x 400-600 x 100-150 nm to 9 x 7 x 3 μm	141 (0.1 C) 135 (0.2 C) 130 (0.5 C) 123 (1 C) 112 (2 C)	96% capacity retention at 0.5 C after 15 cycles	304
LiOH·H ₂ O, CoSO ₄ ·7H ₂ O, H ₃ PO ₄	3:1:1	0.25	EG ^a :(H ₂ O+E G ^a) =0-1	Ascorbic acid as reducing agent, pH = 5.0	250 °C, 30 min, microwave assisted: 600 W	-	Hexagonal platelets, 200 x 100 x 50 nm to 1.2 x 1.2 x 0.5 μm	136 (0.1 C) 125 (0.2 C) 115 (0.5 C) 105 (1 C) 95 (2 C)	94% capacity retention at 0.5 C after 15 cycles	376
LiNO ₃ , Co(NO ₃) ₂ ·6H ₂ O, (NH ₄) ₂ HPO ₄	-	-	H ₂ O	Alginate acid as carbon source	180 °C, 30 min, 20 bar, microwave assisted: 15-20 W, 2.45 GHz, 600 rpm	700 °C, 6 h, Ar	-	160 (0.1 C) 138 (1 C) 120 (2 C) 88 (5 C)	86% capacity retention at 0.1 C after 100 cycles	385

LiNO ₃ , Co(NO ₃) ₂ , (NH ₄) ₂ HPO ₄	-	-	EG ^a	-	200 °C, 60 min, 20 Bar, microwave assisted: 40-50 W, 2.45 GHz, 600 rpm	650 °C, 6 h, Ar/5%H ₂	-	78 (0.1 C) 68 (0.5 C) 57 (1 C) 44 (2 C) 32 (5 C)	53% capacity retention at 0.1 C after 50 cycles	386
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^a PVP: poly(vinylpyrrolidone); CMC: carboxymethylcellulose sodium salt; EG: ethylene glycol; DEG: diethylene glycol; TEG: tri-ethylene glycol; TTEG: tetra-ethylene glycol; PEG: polyethylene glycol 400; BA: benzyl alcohol.

4.3.3 Sol-gel process

The sol-gel process is a low temperature, wet-chemical technique, which can provide high purity, good homogeneity and small particle size due to the homogeneous mixing of the reactants in solution at atomic or molecular level.^{261, 394-397} In this process, the reactants are firstly dissolved in solvents, and the resulting sol evolves gradually into a gel-like network,^{66, 398-402} then the gel is calcined at 500-800 °C to obtain LiCoPO₄.⁴⁰³⁻⁴⁰⁶ As shown in Table 4-3, reaction parameters such as precursors,^{306, 407, 408} carbon sources,^{385, 389, 409} sintering temperature and time^{305, 410, 411} had significant effect on the electrochemical performance of LiCoPO₄.

Table 4-3 Sol-gel synthesis: the influence of precursors, carbon sources, reaction and sintering conditions on the electrochemical performance of LiCoPO₄.

Precursors	Additives	Reaction conditions	Sintering conditions (temperature, time, gas)	Particle size	Rate performance, mA h g ⁻¹ (rate, C)	Cycle stability	Ref.
LiNO ₃ , Co(NO ₃) ₂ ·6H ₂ O, (NH ₄) ₂ HPO ₄	Citric acid as chelating agent and carbon source	Stirring for 3.5 h, evaporation at 85 °C, dry at 100 °C, pyrolysis at 350 °C for 2 h in Ar	500 °C, 4 h, air	240-350 nm	137 (0.1 C)	68% capacity retention at 0.1 C after 30 cycles	403
LiNO ₃ , Co(NO ₃) ₂ , NH ₄ H ₂ PO ₄	Citric acid as chelating agent and carbon source	Stirring at 80 °C for 2 h, evaporation at 120 °C for 12 h, pyrolysis at 350 °C for 2 h in air	500 °C, 5 h, air	100-300 nm	117 (0.1 C) 93 (0.2 C) 80 (0.5 C) 67 (1 C)	57 mA h g ⁻¹ at 0.1 C after 20 cycles	389
CH ₃ COOLi·2H ₂ O, Co(CH ₃ COO) ₂ ·4H ₂ O, H ₃ PO ₄	Citric acid as chelating agent	Evaporative at 80 °C for 3 h in air	300 °C, 5 min, air, 730 °C, 12 h, N ₂	-	68 (0.1 C)	15 mA h g ⁻¹ at 0.1 C after 21 cycles	305
LiNO ₃ , Co(NO ₃) ₂ ·6H ₂ O, (NH ₄) ₂ HPO ₄	Citric acid as chelating agent, Y doping	Evaporation at 85 °C, dry at 100 °C for one day	600 °C, 8 h, air	500 nm	154 (0.1 C)	32 mA h g ⁻¹ at 0.1 C after 30 cycles	412
LiH ₂ PO ₄ , CH ₃ COOLi·2H ₂ O, Co(CH ₃ COO) ₂ ·4H ₂ O, NH ₄ H ₂ PO ₄	Citric acid as chelating agent, Fe doping	Evaporation at 70 °C for 1 h, decompose at 300 °C for 5 h in air	550 °C, 10 h, air	200-400 nm	128 (0.1 C) 120 (1 C) 95 (10 C)	95% capacity retention at 0.1 C after 50 cycles	407
CH ₃ COOLi·2H ₂ O, Co(C ₅ H ₇ O ₂) ₂ , H ₃ PO ₄	Ethylene glycol as solvent and carbon source	Aging for 2 days	700 °C, 12 h, Ar	300 nm	114 (2 C)	57 mA h g ⁻¹ at 2 C after 15 cycles	413
CH ₃ COOLi·2H ₂ O, Co(CH ₃ COO) ₂ ·4H ₂ O, H ₃ PO ₄	Citric acid as chelating agent, graphitic carbon foam modification	Evaporation at 80 °C for 2 h	300 °C, 0.1 h, air, 730 °C, 12 h, N ₂	-	100 (0.1 C)	33 mA h g ⁻¹ at 0.1 C after 11 cycles	408
LiNO ₃ , Co ₃ (PO ₄) ₂ , (NH ₄) ₂ HPO ₄	Citric acid as chelating agent, Mn doping, gallic acid as reducing agent and carbon source	Evaporation at 70 °C for 24 h, decompose at 350 °C for 3 h in air	650 °C, 6 h, Ar/15%H ₂	40-80 nm	140 (0.1 C) 108 (0.5 C) 96 (2 C) 77 (5 C)	92% capacity retention at 0.1 C after 60 cycles	414
Li ₂ CO ₃ , Co(CH ₃ CO ₂) ₂ ·4H ₂ O, NH ₄ H ₂ PO ₄	Citric acid as carbon source	Evaporation at 80 °C for 12h, dry at 80 °C for 12h in vacuum	300 °C, 3 h, N ₂ , 700 °C, 10 h, N ₂	-	83 (0.5 C)	59% capacity retention at 0.5 C after 30 cycles	415
LiNO ₃ , Co(NO ₃) ₂ ·6H ₂ O, (NH ₄) ₂ HPO ₄	Citric acid as chelating agent, alginate acid as carbon source	Dry at 80 °C	700 °C, 6 h, Ar	-	150 (0.1 C) 130 (1 C) 101 (2 C) 63 (5 C)	112 mA h g ⁻¹ at 0.1 C after 100 cycles	385

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Various precursors and solvents are used in sol-gel synthesis to produce LiCoPO₄ (Table 4-3).^{412, 413, 416, 417} The raw materials generally consist of a stoichiometric amount of lithium acetate or lithium nitrate as a lithium source, cobalt(II) acetate or cobalt(II) nitrate as a cobalt source, as well as a phosphorus source such as phosphoric acid, ammonium dihydrogen phosphate or diammonium phosphate.^{407, 408, 418, 419} Water is the most commonly used solvent to control the structure of LiCoPO₄,^{385, 389, 409, 412} but organic solvents including ethanol,⁴¹⁰ ethylene glycol,⁴¹³ diethylene glycol⁴¹⁷ and water/isopropanol co-solvent can also be used in sol-gel synthesis.⁴⁰⁵ Citric acid is widely used as a chelating agent.^{414, 415, 420} During gelation, it provides strong bonding with metal ions through its carboxylic groups leading to a homogeneous precursor gel with finer particle size and homogenous distribution.⁴¹⁴ In the sol-gel process, carbon precursors like citric acid can also decompose to produce a uniform carbon coating layer *in situ* during the post-annealing step.^{403, 414} Also, carbon deposition on the surface of LiCoPO₄ can effectively suppress the particle growth during calcination.^{389, 403, 414} Therefore, the sol-gel synthesis of LiCoPO₄ provides control and fine particle size to shorten Li-ion diffusion path lengths, as well as uniform carbon coating to improve its electrical conductivity.

4.3.4 Summary of synthesis methods

The comparison of solid-state reaction, hydrothermal/solvothermal synthesis and sol-gel process for preparation of LiCoPO₄ are summarised in Table 4-4. As the conventional method for mass production of most cathode materials for LIBs, the solid-state method is widely used for preparation of LiCoPO₄, in spite of the drawback of poor particle size control. In contrast, wet-chemical methods like hydrothermal/solvothermal synthesis and the sol-gel process provide better control of the morphology and particle size of LiCoPO₄, but suffer from process complexity and higher cost. Apart from these most commonly used preparation methods for obtaining LiCoPO₄, some other synthesis methods also appear in the literature,⁴²¹⁻⁴²³ such as spray pyrolysis,^{307, 424-428} co-precipitation,^{300, 358, 385, 429-431} polyol process,^{375, 432-436} supercritical fluid processes,^{390, 437-440} microwave heating^{335, 385, 441-444} and carbo-thermal reduction.^{414, 445, 446} Further improvements are still required to develop a simple, time and energy saving, easy to control and industrially compatible synthesis method to prepare LiCoPO₄ with high purity, small particle size and good cycle stability and rate capability.

Table 4-4 Comparison of solid-state reaction, hydrothermal/solvothermal synthesis and the sol-gel process for preparation of LiCoPO₄.

Synthesis methods	Advantages	Disadvantages	Size	C addition
Solid-state reaction	Low cost, process simplicity	Difficult to control particle growth	Sub-micro or micro-size	<i>In situ</i> coating or post-addition
Hydrothermal/solvothermal synthesis	Nanosize, morphology control	Strict reaction conditions (temperature, pH, time, etc.), waste liquid	Nano-size	<i>In situ</i> coating or post-addition
Sol-gel process	High purity and homogeneity, nanosize	Long process	Nano-size	<i>In situ</i> coating

4.4 Strategies for performance improvement

Olivine LiCoPO_4 cathodes exhibit some unsatisfactory features in LIBs including low specific capacity, poor cycle stability and poor rate performance. Tremendous efforts have been made to improve the electronic and ionic conductivity of LiCoPO_4 , using approaches such as surface modification (e.g. carbon coating), carbon network support structures, ion doping, size reduction and morphology control.^{211, 292-301} The poor capacity and cycle stability of LiCoPO_4 electrodes in conventional LiPF_6 -containing electrolyte solutions has been attributed to degradation of the olivine structure.⁷⁷⁻⁸¹ Bramnik *et al* investigated the thermal stability of LiCoPO_4 during delithiation via synchrotron diffraction and differential thermal analysis. It was found that CoPO_4 produced in the charge process of LiCoPO_4 is unstable during heating and easily decomposed at temperatures of 100-200 °C.³¹⁹ Similar observations were reported by Wohlfahrt-Mehrens *et al* who found that the fully charged cathode decomposes at 160-260 °C.³²⁰ Unlike other phosphates with Co^{3+} in octahedral coordination, Bramnik *et al* found that Co^{3+} is present in a high-spin configuration in delithiated (charged) CoPO_4 , which could explain the fact that CoPO_4 is unstable in contact with air or moisture and undergoes amorphisation.³¹⁵ Using *in situ* synchrotron diffraction, Bramnik *et al* also revealed that the LiCoPO_4 delithiation is accompanied by serious electrolyte decomposition, leading to capacity fading during cycling.⁸² This is in agreement with a first-principles investigation on LiCoPO_4 by Major *et al*, who found that fully delithiated CoPO_4 is energetically unstable.⁴⁴⁷ Markevich *et al* found this delithiated CoPO_4 phase to be prone to nucleophilic attack by F^- anions (produced by electrolyte decomposition at high voltages) on the P atoms to break the P-O bonds of the phosphate anions.⁷⁹ This process leads to the surface degradation of LiCoPO_4 (interfaced with the electrolyte solution),⁸³ accompanied by cobalt dissolution,⁴⁴⁸ olivine structure degradation,⁷⁷ formation of cracks in crystals after charging,^{449, 450} and Li depletion due to the reformation of the solid-electrolyte interface (SEI),⁸⁰ thus resulting in a fast capacity fading upon cycling. Brutti *et al* suggested that the self-discharge process in LiCoPO_4 materials is a self-feeding procedure with the spontaneous electrons transport from the electrolyte to the Co^{3+} in CoPO_4 , mediated by a porous and partially reactive SEI membrane that is unable to completely passivate the surface of the LiCoPO_4 electrode.⁴⁴⁹ Recently, Ikuhara *et al* investigated atomic level changes upon capacity loss in highly oriented LiCoPO_4 thin films.⁷⁶ It was found that many cation exchange (antisite) defects were formed in the surface of LiCoPO_4 after three cycles of charge/discharge. The concentration of these defects increases upon further cycling, with severe capacity loss. The formation of cation exchange defects is related to PO_4 tetrahedra deformation and oxygen loss, resulting in structural degradation harmful to the cycle stability of LiCoPO_4 electrodes.

Surface modification is an important strategy to improve the cycle stability of LiCoPO_4 electrodes by protecting LiCoPO_4 from direct contact with electrolyte thus avoiding surface degradation

caused by HF attack produced from electrolyte decomposition.^{307, 435, 448} Other strategies like ion doping to stabilise the olivine structure, and electrolyte optimisation to form a protective surface film with improved LiCoPO₄ surface stability will be discussed in the following sections.⁴⁵¹

4.4.1 Surface modification

Surface modification of LiCoPO₄ with a conductive agent is an effective way of improving the overall electronic conductivity of the composite electrodes and providing some protection against reaction with the electrolyte, water traces, etc.^{294, 303, 307, 435, 448, 452} The classical conductive agent introduced to modify electrode materials is carbon, which possesses high conductivity, low cost and good stability in batteries.^{60, 371} Relevant examples of the electrochemical performance of LiCoPO₄ after surface modification are shown in Table 4-5.

(1) Carbon coating. In general, the main role of carbon coating is to enhance the electronic conductivity of LiCoPO₄.^{307, 360, 403, 421, 427, 433, 448} For example, Wei *et al* prepared a core-shell LiCoPO₄/C nanocomposite by microwave heating. LiCoPO₄ with particle size of ~150 nm was coated with a uniform carbon layer of ~10 nm thickness.⁴⁴¹ Carbon with high conductivity distributed on the surface of LiCoPO₄ helps the transportation of electrons among particles. Also, the added carbon can reduce the LiCoPO₄ surface layers to the conductive Co₂P during heating under inert atmosphere.^{293, 294, 302, 316} Wolfenstine *et al* investigated the effect of added carbon on the electrical conductivity and specific capacity of LiCoPO₄ electrode. It was found that the added carbon was partly consumed to reduce the LiCoPO₄ surface layers to Co₂P during heating under Ar atmosphere. As the amount of the Co₂P phase increased to 4 wt.%, the electronic conductivity increased to ~10⁻⁴ S cm⁻¹ with the highest specific capacity of ~120 mA h g⁻¹ obtained.^{293, 294} Nallathamby *et al* confirmed that the formation of Co₂P in heat treatment enhanced the electronic conductivity and electrochemical performance of LiCoPO₄. It is found that the Co₂P formed only in an inert atmosphere.³⁰²

Meanwhile, carbon coating reduces the particle size and alleviates the aggregation of LiCoPO₄ particles by inhibiting undesirable particle growth.^{291, 309, 448} Thermal treatment is generally used in the preparation of LiCoPO₄ to achieve better crystallinity. LiCoPO₄ nanoparticles are easy to agglomerate, especially at high temperature. A perfect carbon coating limits agglomeration and restricts the further growth of the LiCoPO₄ crystals in the calcination process.^{60, 453}

In addition, carbon coating can protect LiCoPO₄ from direct contact with electrolyte thus avoiding surface degradation caused by HF attack produced from electrolyte decomposition.^{307, 435, 448} For batteries using LiPF₆ based electrolyte, LiCoPO₄ may suffer from partial dissolution due to the

presence of HF, which is produced by LiPF_6 hydrolysis with trace water impurities.^{60, 454, 455} This will lead to capacity decay upon long term cycling.

Due to the coating, Li-ions have to migrate through the surface layer before diffusing in and out of the LiCoPO_4 lattice.^{60, 340} Therefore, the coating on the surface of LiCoPO_4 should be thin, uniform and intact.^{404, 405, 444} Also, the addition of carbon reduces the tap density of LiCoPO_4 cathodes and thus decreases the volumetric energy density of LIBs. Taking these into consideration, the optimum carbon contents depends on various coating strategies.^{60, 80, 383, 448, 456}

Table 4-5 The effects of carbon and other surface coatings on the performance of LiCoPO_4 composites.

Synthesis methods	Carbon				Rate performance, mA h g^{-1} (rate, C)	Cycle stability	Ref.
	Precursors	Coating techniques	Content (wt.%)	Thickness (nm)			
Microwave heating	Acetylene black	<i>In situ</i>	3.3	10 nm	144 (0.1 C), 137 (1 C), 116 (5 C), 90 (10 C), 71 (20 C)	73 mA h g^{-1} at 0.1 C after 30 cycles	441
Spray pyrolysis	Citric acid	<i>In situ</i>	2.4	3-5 nm	123 (0.1 C), 82 (5 C)	95% capacity retention at 0.1 C after 20 cycles	424
Solvothermal synthesis	Glucose	<i>In situ</i>	3.4, 5.1	8 nm	136 (0.1 C), 85 (5 C)	91% capacity retention at 0.1 C after 50 cycles	352
Spray pyrolysis	Acetylene black	Wet ball mill	-	-	142 (0.05 C), 141 (0.1 C), 137 (1 C), 128 (5 C), 109 (20 C)	87% capacity retention at 0.1 C after 40 cycles	425
Sol-gel process	Citric acid	<i>In situ</i>	0.52	-	137 (0.1 C)	68% capacity retention at 0.1 C after 30 cycles	403
Planetary ball mill	Acetylene black	<i>In situ</i>	3, 5, 10	-	145 (0.1 C), 72 (5 C)	70% capacity retention at 0.1 C after 50 cycles	448
Spray pyrolysis	Acetylene black	Wet ball mill	10, 11.3, 11.7, 11.9	-	134 (0.05 C), 133 (0.1 C), 131 (0.5 C), 128 (1 C), 88 (10 C), 52 (20 C)	89%, 77%, 63% capacity retentions at 0.1 C, 0.5 C, 1 C after 30 cycles	427
Solvothermal synthesis	Glucose, Mn doping	<i>In situ</i>	12	-	105 (0.2 C)	90% capacity retention at 0.2 C after 30 cycles	392
Sol-gel process	Citric acid, acetylene black	<i>In situ, ex situ</i>	4.6, 5.8	15-20 nm	131 (0.1 C), 107 (0.5 C), 95 (1 C)	78% capacity retention at 0.1 C after 40 cycles	456
Aqueous precipitation	Sucrose, acetylene black, propane	Pyrolysis, spray, vapour deposition	5	4 nm	130 (0.06 C), 109 (0.3 C), 89 (0.9 C), 76 (1.8 C)	80% capacity retention at 0.06 C after 30 cycles	429
Sol-gel process	Citric acid	<i>In situ</i>	< 1	-	92 (0.05 C), 67 (0.2 C), 52 (0.5 C), 22 (1 C)	85% capacity retention at 0.05 C after 35 cycles	457
Solid-state fusion method	Super P [®] carbon	Ball mill	10	-	123 (0.1 C), 114 (0.2 C), 102 (1 C), 93 (2 C), 81 (5 C)	89% capacity retention at 0.1 C after 30 cycles	302
Emulsion drip combustion, ball mill	Kerosene, heptane	<i>In situ</i>	3, 8, 35, 37, 66,	10 nm	128 (0.1 C)	87% capacity retention at 0.1 C after 25 cycles	421
Microwave-assisted ball mill	Acetylene black	<i>In situ</i>	3.1	-	161 (1 C)	83% capacity retention at 1 C after 1700 cycles	444
Solvothermal synthesis	Sucrose	<i>In situ</i>	0.13-0.23	-	120 (0.1C)	78% capacity retention at 0.1 C after 20 cycles	458
Flame spray pyrolysis	Sucrose, polyacrylic acid, Tween 80 [®]	Planetary ball mill	1.8, 2, 2.6, 3.2	3 nm	120 (0.1 C), 80 (1 C)	58% capacity retention at 0.1 C after 112 cycles	307
Solvothermal synthesis	Sucrose	Ground	4	3 nm	124 (0.1 C), 111 (0.5 C), 100 (1 C), 85 (2C), 51 (5 C)	83% capacity retention at 0.1 C after 100 cycles	309
Solid-state ball mill	Sucrose, graphene oxide	Ball mill, suspension mixing	2, 2.8	3 nm	146 (0.1 C), 93 (2 C)	63% capacity retention at 0.1 C after 40 cycles	359
Sol-gel assisted carbothermal reduction	Citric acid	<i>In situ</i>	2.87, 2.97	5-10 nm	140 (0.1 C), 108 (0.5 C), 96 (2 C), 77 (5 C)	92% capacity retentions at 0.1 C after 60 cycles	414
PVP ^a assisted polyol process	Acrylic acid, ethylene glycol	Resin coating process	2	-	180 (0.1 C)	90% capacity retention at 0.1 C after 20 cycles	435
Microwave-solvothermal synthesis	Tannic acid	<i>In situ</i>	2.61-2.81	5-7 nm	155 (0.1 C), 129 (1 C), 98 (5 C), 70 (10 C), 51 (20 C)	91% capacity retention at 0.1 C after 80 cycles	383
One-pot hydrothermal synthesis	CMC ^a , glucose, ascorbic acid	<i>In situ</i>	3.1, 1.5, 0.9	6 nm	135 (0.1 C), 132 (0.5 C), 125 (1 C), 117 (2 C), 101 (5 C)	52% capacity retention at 0.1 C after 30 cycles	291

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Microwave-hydrothermal synthesis	Alginate acid	<i>Ex situ</i>	2.5-2.67	3-4 nm	160 (0.1 C), 138 (1 C), 120 (2 C), 88 (5 C)	86% capacity retention at 0.1 C after 100 cycles	385
Sol-gel process	Citric acid	<i>In situ</i>	1.45-1.52	8 nm	144 (0.1 C), 122 (0.2 C), 107 (0.5 C), 91 (1 C)	71% capacity retention at 0.1 C after 100 cycles	459
Solid-state reaction	LiFePO ₄ coating	Sol-gel route	10	2-3 nm	132 (0.1 C)	92 mA h g ⁻¹ at 0.1 C after 17 cycles	344
Solid-state reaction	LiFePO ₄ coating, Fe doping	Dry coating procedure	1.5	20 nm	128 (0.1 mA cm ⁻²)	70% capacity retention at 0.1 mA cm ⁻² after 20 cycles	303
Microwave-assisted solvothermal synthesis	LiFePO ₄ coating, V doping	<i>Ex situ</i>	5, 10	3-5 nm	145 (0.1 C)	51% capacity retention at 0.1 C after 20 cycles	364
Microwave-assisted hydrothermal synthesis	NiO coating	Stöber, hydrothermal synthesis	2.5, 5	7-8 nm	159 (0.1), 98 (2 C), 70 (5 C)	85% capacity retention at 0.1 C after 80 cycles	75
Sol-gel process	AlF ₃ coating	<i>Ex situ</i>	2, 4, 6 mol%	4, 8, 12 nm	159 (0.1 C), 135 (0.2 C), 110 (0.5 C), 90 (1 C)	91% capacity retention at 0.1 C after 50 cycles	452

^a: PVP: polyvinylpyrrolidone; CMC: carboxymethylcellulose sodium salt.

(2) Carbon source. Choice of carbon source strongly affects the quality of the carbon coating for LiCoPO₄. Various carbon sources have been used, including organic sources (e.g. sucrose, glucose, ascorbic acid and tannic acid)^{291, 307, 383, 414, 424, 435} and inorganic sources (e.g. carbon nanofibres, carbon nanotubes, graphene and acetylene black).^{360, 410, 418, 444, 448, 460}

Organic carbon sources have advantages in forming a homogeneous carbon layer on LiCoPO₄ and in controlling the structure of carbon coating (homogeneity, thickness, coverage) during the high temperature pyrolysis process, but it is hard to control the quality of carbon (conductivity, graphitized degree).^{61, 385, 392} Passerini *et al* reported that the choice of carbon source, such as sucrose, polyacrylic acid and Tween 80[®] has major effect on the purity, particle size, morphology and electrochemical performance of LiCoPO₄. With 20wt. % sucrose as carbon source, TEM images showed a uniform carbon layer with ~3 nm thickness (Figure 4-2 a). When reducing the sucrose amount to 10 wt.%, an unevenly coating layer was formed on the surface of LiCoPO₄ (Figure 4-2 b). The LiCoPO₄/C composites showed partially uncoated areas with polyacrylic acid or Tween 80[®] as carbon sources (Figure 4-2 c and d). Although carbon coating enhances the electrical conductivity of LiCoPO₄ and prevents the LiCoPO₄ particles from direct contact with the electrolyte, a decrease in capacity upon cycling is still observed, probably due to the electrolyte decomposition at high operating voltages.³⁰⁷ As shown in Figure 4-2 e-h, Kanamura *et al* prepared LiCoPO₄/C via one-pot hydrothermal synthesis with three different carbon sources i.e. carboxymethylcellulose sodium salt (CMC), glucose and ascorbic acid. CMC is critical in reducing the particle size to 390 nm and forming a continuous carbon coating on the surface of LiCoPO₄. LiCoPO₄/C synthesized with CMC exhibited higher initial specific capacity of 135 mA h g⁻¹ at 0.1 C, with better cycle stability and rate capability than the other samples.²⁹¹

Inorganic carbons offer an alternative approach to increase the conductivity of LiCoPO₄ electrodes.⁴⁶¹ Using inorganic carbons such as carbon nanotubes or nanofibres,^{365, 460} graphene and acetylene black,^{357, 425, 427, 429, 441, 444, 448, 456} a 3D conductive network can be obtained in the LiCoPO₄ electrode. As shown in Figure 4-2 i-k, Jin *et al* fabricated LiCoPO₄-multiwall carbon nanotube

nanocomposites by dispersing carbon nanotubes during the gelation step of LiCoPO_4 synthesis. The uniform distributions of carbon nanotubes within LiCoPO_4 particles could enhance the electrical conductance between LiCoPO_4 particles, thus improving its specific capacity.⁴⁶⁰

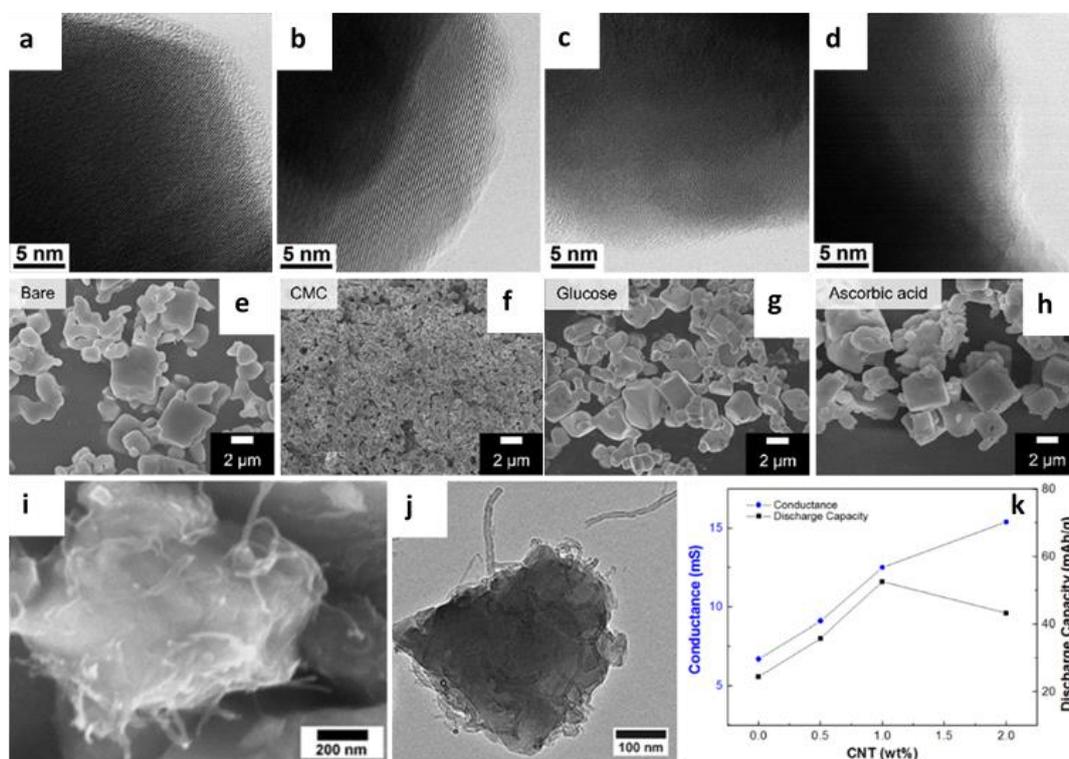


Figure 4-2 TEM images of LiCoPO_4/C particles prepared using (a) 20 wt.% sucrose, (b) 10 wt.% sucrose, (c) 20 wt.% polyacrylic acid and (d) 40 wt.% Tween 80[®] as carbon sources; Reproduced from Ref. ³⁰⁷ with permission from the Royal Society of Chemistry 2016. SEM images of (e) bare LiCoPO_4 and LiCoPO_4/C prepared using (f) CMC, (g) glucose and (h) ascorbic acid as carbon sources; Reproduced from Ref. ²⁹¹ with permission from Elsevier 2017. (i) SEM and (j) TEM images of LiCoPO_4 -multiwall carbon nanotube (LiCoPO_4 -MWCNT) nanocomposite, (k) MWCNT amounts vs conductance or discharge capacity of bare LiCoPO_4 and LiCoPO_4 -MWCNT cathodes for LIBs. Reproduced from Ref. ⁴⁶⁰ with permission from Springer Nature 2016.

(3) Carbon coating process. The carbon coating process includes mixing carbon sources with battery materials followed by heat treatment. Currently, it is still challenging in the formation of a uniform carbon nanolayer with full coverage on LiCoPO_4 . Too thin carbon coating cannot cover the LiCoPO_4 particle uniformly, but too thick carbon layer will limit Li-ion diffusion and decrease the volumetric energy density of the battery materials.⁶¹ In order to obtain battery materials with good performance, *ex situ* and *in situ* carbon coating technologies have been reported.

For *ex situ* carbon coating, the carbon is introduced onto previously prepared LiCoPO_4 .⁷⁸ Thus pure LiCoPO_4 can be obtained before carbon coating to improve the purity of the composite.^{285, 320, 358} Also, various kinds of carbon materials especially graphitic carbon can be chosen to improve the

quality of coating layer.^{408, 419, 462, 463} However, it is often a challenge to obtain a uniform carbon coating.⁴⁶¹ Gao *et al* compared three techniques, pyrolysis of sucrose, spray of acetylene black, and propane vapour deposition, to *ex situ* coat carbon on the LiCoPO₄ surface. Figure 4-3 a and b shows the vapour deposition technique helps forming a more uniform carbon coating on the surface of LiCoPO₄, to provide a discharge capacity of 130 mA h g⁻¹ at 0.06 C with capacity retention of 80% over 30 cycles (Figure 4-3 c).⁴²⁹

Some *in situ* carbon coating methods, such as the sol-gel^{414, 456, 457, 459} or solvothermal synthesis^{352, 379, 383, 458, 464} can generate uniform, compact, and intact carbon layers with appropriate thickness on LiCoPO₄.^{211, 424, 465} Gao *et al* synthesized a core-shell structured LiCoPO₄/C via sol-gel process with *in situ* carbon coating. The uniform carbon layer improves the LiCoPO₄ kinetics and hinders side reactions between electrode and electrolyte. The LiCoPO₄/C showed a discharge capacity of 131 mA h g⁻¹ at 0.1 C with capacity retention of 78% over 40 cycles, as well as rate capabilities of 107 and 95 mA h g⁻¹ at 0.5 and 1 C, respectively.⁴⁵⁶ Also, Örnek *et al* synthesized nanostructured LiCoPO₄/C by a sol-gel method. It was found that a carbon layer of 5-10 nm thickness was uniformly distributed on the surface of LiCoPO₄.⁴¹⁴ Meanwhile, a microwave assisted solvothermal method at temperatures from 140-220 °C was applied to synthesized LiCoPO₄ cathode with a thin (5-7 nm) and uniform carbon layer distributed on the surface (Figure 4-3 d).³⁸³ This nanostructured LiCoPO₄/C cathode exhibited a capacity of 155 mA h g⁻¹ at 0.1 C with a capacity retention of 91% over 80 cycles, and rate capability of 98 mA h g⁻¹ at 5 C (Figure 4-3 e and f).

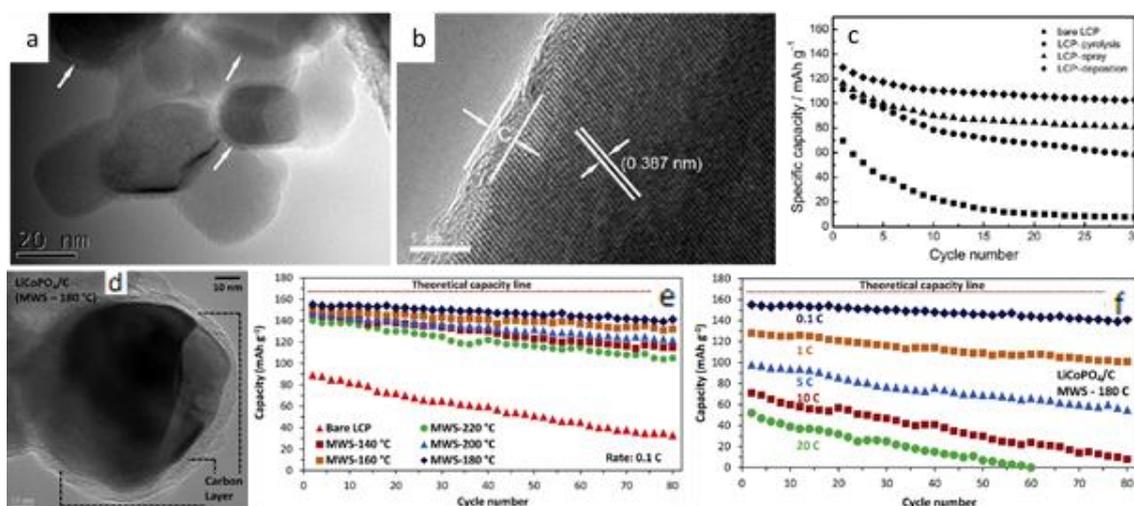


Figure 4-3 (a) and (b) TEM images of LiCoPO₄ showing the carbon coating via vapour deposition technique. The carbon layer is indicated by arrows in (a). (c) Discharge capacity of the bare and LiCoPO₄/C electrodes at 0.06 C versus cycle number. Reproduced from Ref. ⁴²⁹ with permission from Elsevier 2013. (d) High-resolution TEM image of LiCoPO₄/C. (e) and (f) Cycle stability and rate capability of bare and LiCoPO₄/C samples prepared by microwave assisted solvothermal synthesis at 140-220 °C. Reproduced from Ref. ³⁸³ with permission from Elsevier 2016.

(4) Surface modification with other materials. Surface modifications of LiCoPO_4 with non-carbon materials, such as LiFePO_4 ,^{303, 344, 364} NiO ,⁷⁵ AlF_3 ,⁴⁵² VO_x ,³⁰⁷ $\text{Li}_3\text{V}_2(\text{PO}_4)_3$,^{446, 466} Al_2O_3 ,⁴⁶⁷ have been reported to improve the cycle stability of LiCoPO_4 electrodes by producing a protective film on the LiCoPO_4 surface. Lee *et al* prepared LiFePO_4 coated LiCoPO_4 with a coating layer of ~ 20 nm in thickness. It was found that LiFePO_4 coating on the surface of LiCoPO_4 mitigated electrolyte degradation, which resulted in enhanced cycle stability of electrode.³⁰³ As shown in Figure 4-4, Örnek synthesized NiO-coated LiCoPO_4 nanocomposites via a three-step route, which includes advantages of Stöber method, hydrothermal and microwave syntheses. LiCoPO_4 particles are coated with a continuous NiO layer of 8-10 nm, which can alleviate the volumetric stresses and strains of LiCoPO_4 crystals in Li^+ insertion/extraction process. The 2.5 wt.% NiO-coated LiCoPO_4 had a specific capacity of 159 mA h g^{-1} at 0.1 C with capacity retention of 85% over 80 cycles.⁷⁵ Qiu *et al* prepared LiCoPO_4 cathode material with a nano-sized homogeneous AlF_3 layer distributed on the surface. 4 mol% AlF_3 coated LiCoPO_4 delivered an initial specific capacity of 159 mA h g^{-1} at 0.1 C with capacity retention of 91% over 50 cycles, and rate capability of 90 mA h g^{-1} at 1 C. The improved cycle stability and rate capability are ascribed to the fact that the AlF_3 layer can inhibit the decomposition of electrolyte at high voltages.⁴⁵²

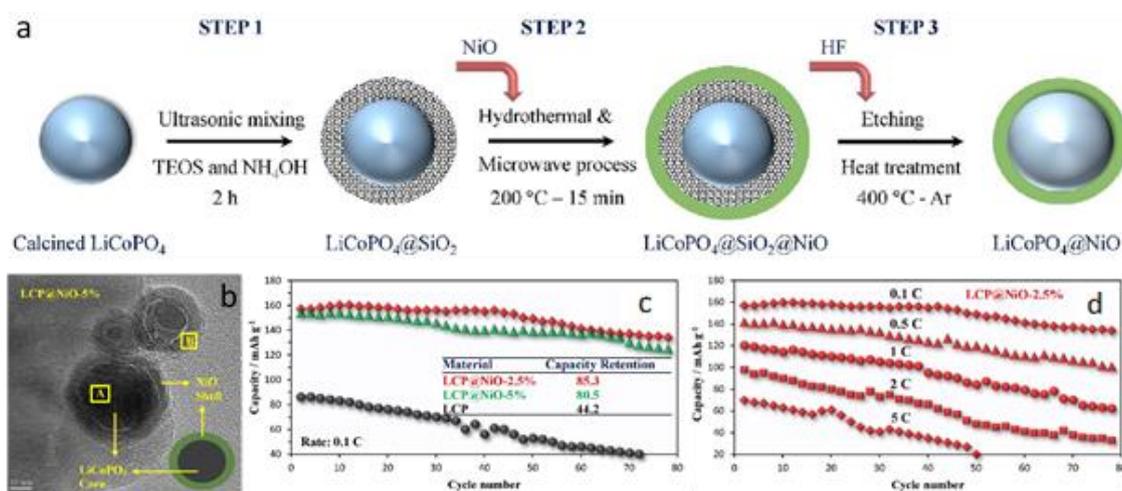


Figure 4-4 (a) Schematic illustration of NiO-coated LiCoPO_4 nanoparticles using stepwise synthesis methodology; (b) high-resolution TEM image of 2.5 wt.% NiO-coated LiCoPO_4 sample; (c) cycle stability of bare and NiO-coated LiCoPO_4 samples at 0.1 C; (d) rate capability of 2.5 wt.% NiO-coated LiCoPO_4 sample at various rates from 0.1 C to 5 C. Reproduced from Ref. ⁷⁵ with permission from Elsevier 2017.

4.4.2 Carbon network support structures

The use of carbon and other materials to coat LiCoPO_4 particles has been discussed in section 4.1. In this section, the use of carbon materials to support and disperse LiCoPO_4 particles will be

described. Carbon nanofibres,^{410, 418} carbon nanotubes,⁴⁶⁸ graphene sheets^{359, 469} and carbon foams^{397, 408, 419, 462, 463, 470} have been applied to form carbon network support 3D architectures on to which LiCoPO₄ particles have been deposited. Relevant examples of the electrochemical performance of LiCoPO₄ supported on these carbon network structures are shown in Table 4-6. The structural, morphological and electrochemical properties of composites are found to depend on the annealing atmosphere and time.^{397, 408, 419, 462, 463, 470-473}

Carbon nanofibers and carbon nanotubes with high electronic conductivity are considered to be promising materials to enhance the LiCoPO₄ performance, because these materials can easily connect the LiCoPO₄ particles to fabricate a continuous conductive network. Also, the good mechanical properties of the 3D carbon structures can effectively eliminate the residual stresses caused by volume changes in LiCoPO₄ during charge-discharge processes.^{1, 474, 475} In spite of these unique features, these carbon networks face some challenges in practical application that significantly decrease their advantages, such as easy aggregation, poor dispersion in common solvents, and complex and time-consuming synthesis processes. Dimesso *et al* introduced a novel and cheap Pechini-assisted sol-gel process to prepare LiCoPO₄-3D carbon nanofiber composites using electrospun and carbonized nanofibers dipped into a solution including Li⁺, Co²⁺ and PO₄³⁻. The LiCoPO₄ particles were homogeneously distributed on the surface of carbon nanofibers. With a specific capacity of 46 mA h g⁻¹ at 0.1 C, the composites required further optimization.⁴¹⁸ Sarapulova *et al* also prepared disordered carbon nanofiber/LiCoPO₄ composites (Figure 4-5 a and b) by a sol-gel method with a discharge capacity of 105 mA h g⁻¹.⁴¹⁰

The high thermal conductivity of individual multi-walled carbon nanotubes (MWCNTs) (3000 W m⁻¹ K⁻¹) reduces the risk of thermal runaway caused by local over-charge or high current charge/discharge.⁴⁷⁶ As shown in Figure 4-5 c and d, hybrid architectures composed of 3D aligned arrays of MWCNTs and LiCoPO₄ nanoparticles have been synthesized by Schneider *et al*.⁴⁶⁸

Some other carbon structures like carbon foams have also been employed in LiCoPO₄ composites. Dimesso *et al* prepared LiCoPO₄-carbon foams *via* a Pechini-assisted sol-gel process and heated under N₂ and air. Morphological investigation of the composites (Figure 4-5 e) showed the formation of crystalline “island-like” structures (typically 5-50 μm) supported on carbon.³⁹⁷

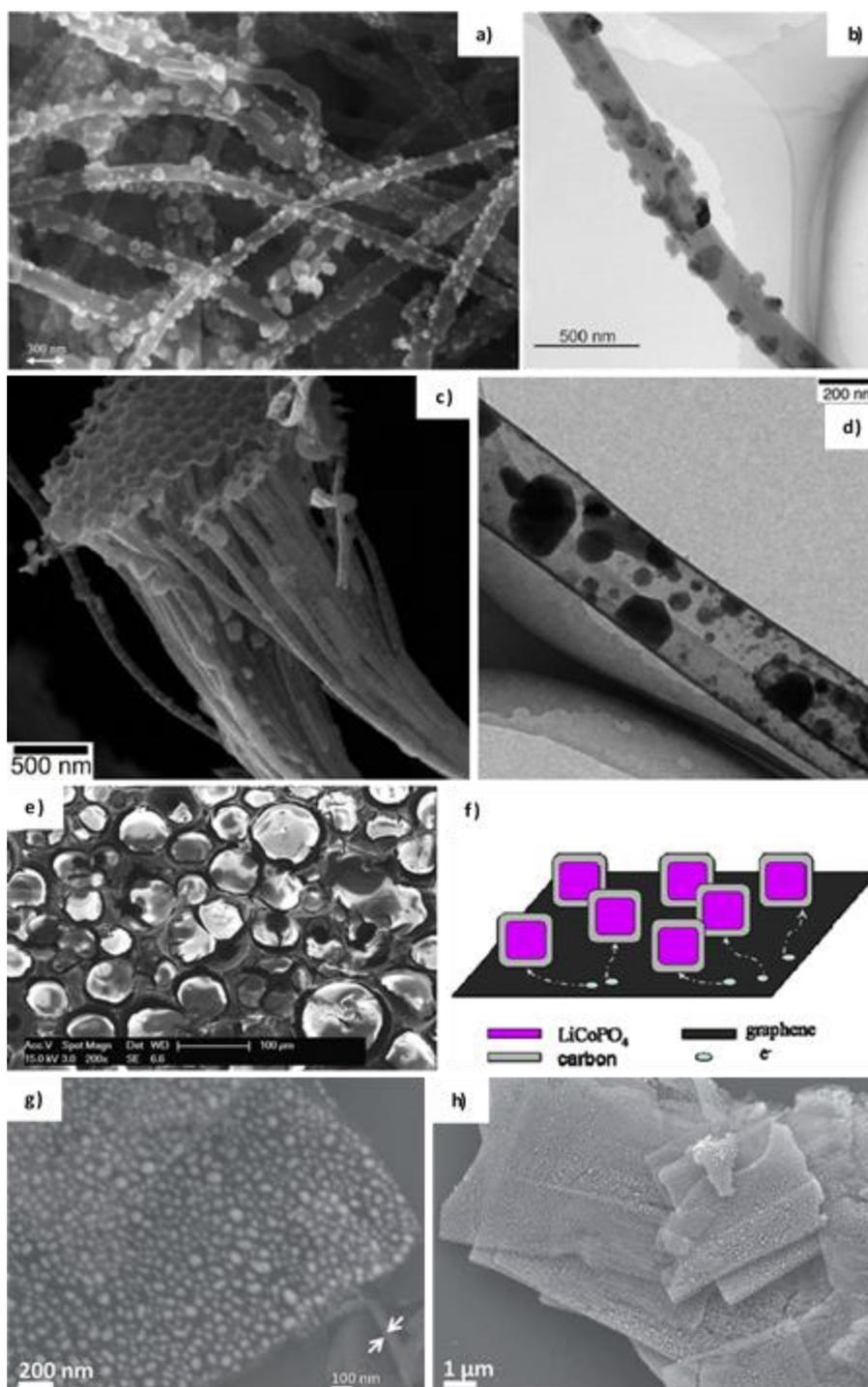


Figure 4-5 (a) SEM and (b) TEM images of carbon nanofibre/LiCoPO₄ composites; Reproduced from Ref. ⁴¹⁰ with permission from Springer Nature 2012. (c) SEM and (d) TEM images of ordered 3D carbon nanotube/LiCoPO₄ composites; Reproduced from Ref. ⁴⁶⁸ with permission from John Wiley and Sons 2011. (e) HREM image of carbon foam/LiCoPO₄ composites; Reproduced from Ref. ³⁹⁷ with permission from Elsevier 2012. (f) Schematic illustration of hierarchical LiCoPO₄/carbon/graphene composite; Reproduced from Ref. ³⁵⁹ with permission from Elsevier 2016. (g) SEM and (h) HRSEM images of 3D sandwiched graphene/LiCoPO₄ composites. Reproduced from Ref. ⁴⁶⁹ with permission from the Royal Society of Chemistry 2015.

Chapter 4

In recent years, graphene has become an intensively studied material in many fields.⁴⁷⁷⁻⁴⁸⁴ Graphene could be a suitable candidate as an electron conducting additive in the cathodes of LIBs^{478, 485} due to its extraordinary electronic conductivity higher than 10^2 S cm^{-1} .⁴⁸⁶⁻⁴⁹⁰ It can build a 3D conductive network for LiCoPO_4 , which can increase the inter-particle electrical contact and improve the cycle stability and rate capability.⁴⁶⁹ As shown in Figure 4-5 g and h, Wang *et al* prepared two-layer sandwiched graphene/ LiCoPO_4 nanocomposites via a newly designed method, with $(\text{NH}_4)_2\text{Co}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ nanosheets as template and glucose as carbon source. The LiCoPO_4 nanoparticles were tightly enveloped with two layers graphene sheets on the top and bottom to form a sandwiched structure. This 3D graphene/ LiCoPO_4 composite delivered rate capability of 85 mA h g^{-1} at 20 C, and cycle stability of 94.6% capacity retention over 100 cycles.⁴⁶⁹ However, a large amount of graphene can decrease the tap density, thus reducing the volumetric energy density of graphene/ LiCoPO_4 composites.¹

Carbon network supported LiCoPO_4 3D structures can be combined with methods of carbon coating to further improve the conductivity of LiCoPO_4 composites.³⁵⁹ Chen *et al* developed a solid-state reaction for synthesizing a novel hierarchical LiCoPO_4 /carbon/graphene composite, consisting of ~ 3 nm thickness carbon coated LiCoPO_4 nanoparticles crosslinked by wrinkled graphene (Figure 4-5 f). The LiCoPO_4 /carbon/graphene cathode exhibited specific capacities of 146 and 93 mA h g^{-1} at 0.1 and 2 C, respectively. This could be attributed to the high electronic conductivity due to the synergistic carbon coating and graphene crosslinking.³⁵⁹

Table 4-6 The electrochemical performance of carbon network support LiCoPO_4 3D structures.

Synthesis methods	Carbon network	Techniques	Rate performance, mA h g^{-1} (rate, C)	Cycle stability	Ref.
Sol-gel process	Multiwall carbon nanotubes	<i>Ex situ</i>	-	35% capacity retention at 0.1 C after 30 cycles	468
Pechini-assisted sol-gel process	3D nonwoven nanofibres	<i>In situ</i>	46 (0.1 C)	26% capacity retention at 0.1 C after 16 cycles	418
Pechini-assisted sol-gel process	Graphitic carbon foam	<i>In situ</i>	100 (0.1 C)	36% capacity retention at 0.1 C after 10 cycles	463
Hydrothermal synthesis	Graphene sheets	<i>In situ</i>	150 (0.1 C), 145 (1 C), 129 (5 C), 104 (10 C), 85 (20 C)	95% capacity retention at 0.1 C after 100 cycles	469
Solid-state ball mill reaction	Wrinkled graphene	<i>Ex situ</i>	146 (0.1 C), 93 (2 C)	63% capacity retention at 0.1 C after 40 cycles	359

4.4.3 Size reduction and morphology control

Conductive agents improve the electronic conductivity of LiCoPO_4 composites, whereas particle size reduction and morphology control could reduce the time required for Li-ion diffusion within LiCoPO_4 , thus improving its specific capacity and rate capability. Relevant examples of the electrochemical performance of LiCoPO_4 after size reduction or morphology control are shown in Table 4-7.

(1) Nanosized LiCoPO₄ particles. Reducing the LiCoPO₄ particle sizes to nanoscale can improve the rate capability in LIBs due to shortened 1D Li-ion diffusion channels.^{309, 362, 425} Smaller structures mean shorter diffusion paths for lithium ions, thus better utilization of the LiCoPO₄ active materials. Therefore, nanosized LiCoPO₄ cathode materials are more likely to obtain high discharge capacity and rate capability.^{425, 433} The effect of carbon coating to improve the electronic conductivity of LiCoPO₄ has been discussed in section 4.1. Here, this approach will be described further, as well as other approaches, in relation to the effect of reducing the particle size of LiCoPO₄. Taniguchi *et al* synthesized LiCoPO₄/C materials, which were agglomerates of LiCoPO₄ primary particles with ~87 nm size, *via* a combination of spray pyrolysis and wet ball-milling. Carbon coating reduced the particle sizes of LiCoPO₄ by inhibiting undesirable particle growth during calcination. Due to the uniform carbon coating and shortened Li-ion diffusion path in LiCoPO₄, it exhibited specific capacity of 142 mA h g⁻¹ at 0.05 C, and rate capability of 109 mA h g⁻¹ at 20 C.^{425, 441}

Controlled synthesis of LiCoPO₄ is an effective strategy for particle size reduction and morphology tailoring to enhance its rate capability. Solvothermal synthesis allows a well-controlled morphology and particle size for LiCoPO₄. Recently, it was found that the solvent plays an important role in tailoring the particle size. Some solvents with high viscosity such as ethylene glycol can control the crystal growth of LiCoPO₄. As shown in Figure 4-6, Mu *et al* found that the particle size of LiCoPO₄ could be effectively controlled by changing the water/ethylene glycol ratio in solvothermal synthesis.³⁰⁹ Figure 4-6 g and h show a LiCoPO₄/C sample with 500 nm particle size that provides an initial specific capacity of 124 mA h g⁻¹ at 0.1 C with capacity retention of 83% over 100 cycles, and rate capability of 85 mA h g⁻¹ at 2 C. Nilges *et al* prepared particle size-controllable LiCoPO₄ platelets *via* a microwave-assisted solvothermal synthesis using various ratios of water/ethylene glycol co-solvents. The particle size of LiCoPO₄ was decreased with increasing ethylene glycol concentration, which could be ascribed to the increased viscosities of the solvent mixtures.^{362, 376}

Furthermore, the particle size and morphology could be controlled by some other experimental conditions.^{433, 491, 492} For example, Brutti *et al* produced LiCoPO₄ *via* a solvothermal synthesis, and investigated the effects of solution acidity, cobalt counter-anions, synthesis temperature and time on the crystal growth of LiCoPO₄. It was found that a solution with moderate acidity or neutral pH is more likely to form phase pure LiCoPO₄; different cobalt counter-anions in the reactants can alter the crystal growth; lower synthesis temperatures result in less and bigger crystallites; and longer synthesis time increases the LiCoPO₄ crystal size.³⁸² Nallathamby *et al* prepared LiCoPO₄/C nanorods with morphologically controlled growth *via* a solid state fusion method using H₂CO₃ + (NH₄)₂CO₃ growth modifiers and heated under Ar. A discharge capacity of 123 mA h g⁻¹ at 0.1 C with capacity retention of 89% over 30 cycles, and rate capability of 81 mA h g⁻¹ at 5 C were achieved, due to the

synergistic effect of controlled growth, formation of conductive Co_2P phase in Ar atmosphere and carbon coating on LiCoPO_4 .³⁰²

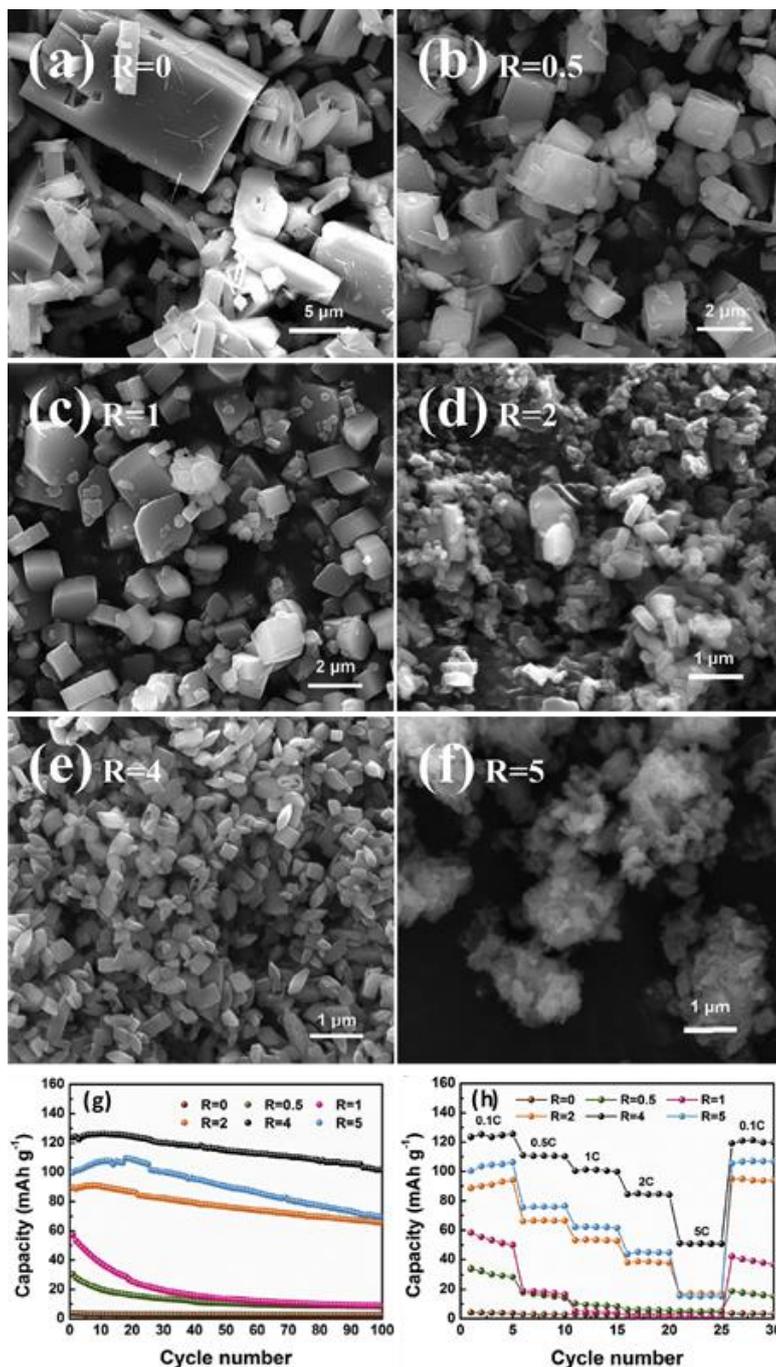


Figure 4-6 (a-f) SEM images of LiCoPO_4 samples prepared via solvothermal synthesis with different water/ethylene glycol ratio R (R = 0, 0.5, 1, 2, 4, and 5); (g) cycle stability at 0.1 C and (h) rate capability at various rates from 0.1 C to 5 C for LiCoPO_4 cathodes in LIBs. Reproduced from Ref. ³⁰⁹ with permission from Elsevier 2016.

As discussed above, reducing the LiCoPO_4 particle sizes to nanoscale can improve the rate capability in LIBs due to the shortened 1D Li-ion diffusion channels in LiCoPO_4 . However, the size reduction decreases the tap density and volumetric energy density. High surface area of nanosized LiCoPO_4

particles also increases the electrode/electrolyte interface area, so undesirable electrode/electrolyte by-reactions become more significant,⁶¹ thus resulting in a poor cycle stability. Therefore, it is important to optimize the synthesis conditions to prepare LiCoPO₄ with a suitable particle size, high tap density and high stability.

Table 4-7 The electrochemical performance of LiCoPO₄ after size reduction or morphology control.

Morphology, particle size	Synthesis methods	Solvents (v/v)	Additive	Rate performance, mA h g ⁻¹ (rate, C)	Cycle stability	Ref.
Spherical nanoparticles, 150 nm	Microwave heating	-	Carbon coating	144 (0.1 C), 137 (1 C), 116 (5 C), 90 (10 C), 71 (20 C)	73 mA h g ⁻¹ at 0.1 C after 30 cycles	441
Spherical nanoporous microparticles (70 nm primary particles agglomerates) with 68 nm pore size	Spray pyrolysis	H ₂ O	Carbon coating	123 (0.1 C), 82 (5 C)	95% capacity retention at 0.1 C after 20 cycles	424
Hedgehog-like, 5-8 μm (compose of nanorods, 40 nm x 1 μm)	Solvothermal synthesis	H ₂ O:BA ^a =1:1	Carbon coating	136 (0.1 C), 85 (5 C)	91% capacity retention at 0.1 C after 50 cycles	352
Nanoparticles agglomerates, 87 nm	Spray pyrolysis and wet ball-milling	H ₂ O	Carbon coating	142 (0.05 C), 141 (0.1 C), 137 (1 C), 128 (5 C), 109 (20 C)	87% capacity retention at 0.1 C after 40 cycles	425
Plate like, 50-200 nm x 100-300 nm x 5-15 nm	Supercritical method	Ethanol	Oleylamine as surfactant and reducing agent	130 (0.05C), 58 (1C)	86 mA h g ⁻¹ at 0.05 C after 20 cycles	365
Nanosheets with 4.6 nm thickness	Liquid-phase exfoliation with solvothermal lithiation process	Ethanol	NH ₄ CoPO ₄ ·H ₂ O nanosheets as templates, PVP ^a as surfactant, carbon coating	153 (0.2 C), 113 (5 C), 91 (10 C), 53 (20 C)	88% capacity retention at 0.2 C after 50 cycles	437
Needle and rod-like nanosized and micron-sized particles	Solid-state fusion method	-	Carbonate anion CO ₃ ²⁻ as growth modifier, carbon coating	123 (0.1 C), 114 (0.2 C), 102 (1 C), 93 (2 C), 81 (5 C)	89% capacity retention at 0.1 C after 30 cycles	302
Nanoplates, 500 nm x 200 nm x 50 nm; Nanorods, 500-1000 nm length and 50 nm thickness	Supercritical fluid processing	Ethanol	HMD ^a or HMT ^a as structure directing agent	121 (0.1 C), 107 (0.2 C), 92 (0.5 C), 72 (1 C)	63 mA h g ⁻¹ at 0.1 C after 20 cycles	438
Nanoplates, 500-800 nm with 50 nm thickness	Supercritical fluid process	Ethanol	Benzylamine as structure directing agent	123.0 (0.1 C), 109 (0.2 C), 95 (0.5 C), 71 (1 C), 32 (2 C)	81% capacity retention at 0.1 C after 10 cycles	439
Hexagonal/octagonal platelet, sub-micron particles with 50-100 nm thickness	Solvothermal synthesis	H ₂ O:EG ^a =1:2	Sucrose as reducing agent	95 (0.1 C), 76 (0.5 C)	75 mA h g ⁻¹ at 0.1 C after 10 cycles	366, 367
Flower-like, 5-10 μm (compose of plate-like, 1-2 μm x 200 nm)	Hydrothermal synthesis	H ₂ O	L-ascorbic, citric or polyacrylic acid as surfactant	107 (0.05 C), 60 (2 C)	30 mA h g ⁻¹ at 0.05 C after 20 cycles	372
Hexagonal platelets, submicron size with thickness < 200 nm	Solvothermal synthesis	H ₂ O:EG ^a =1:2	Sucrose as reducing agent	120 (0.1 C), 85 (0.5 C), 75 (1 C)	90 mA h g ⁻¹ at 0.1 C after 10 cycles	382
Hexagonal platelets, 400-600 nm x 700-800 nm x 100-220 nm	Microwave-assisted solvothermal synthesis	H ₂ O:EG ^a =1:1	Ascorbic acid as reducing agent and buffer	137 (0.1 C), 114 (0.5 C), 97 (2 C)	68% capacity retention at 0.5 C after 100 cycle	388
Badminton-like (compose of nanorods with 200 nm diameters and 3 μm length)	Hydrothermal method	H ₂ O	PEG 200 ^a as structure directing agent	132 (0.1 C), 125 (0.2 C), 113 (0.5 C), 91 (1 C), 69 (2 C)	75% capacity retention at 0.1 C after 50 cycles	381
Particles, 500 nm-10 μm	Solvothermal synthesis	EG ^a :H ₂ O =0, 0.5, 1, 2, 4, 5, 10, 20	Carbon coating	124 (0.1 C), 111 (0.5 C), 100 (1 C), 85 (2 C), 51 (5 C)	83% capacity retention at 0.1 C after 100 cycles	309

Porous nanoplates with 2-6.6 nm pore size	Modified hydrothermal synthesis	H ₂ O	NH ₄ CoPO ₄ ·H ₂ O nanosheets as templates, Fe doping	147 (0.1 C), 137 (0.5 C), 131 (1 C), 123 (5 C), 115 (10 C)	94% capacity retention at 0.1 C after 300 cycles	74
Sponge-like, 200 nm-50 μm	Sol-gel process	H ₂ O	Carbon coating	83 (0.5 C)	59% capacity retention at 0.5 C after 30 cycles	415
Square, rhombic and hexagonal platelets, 600-800 x 400-600 x 100-150 nm to 9 x 7 x 3 μm	Microwave-assisted solvothermal synthesis	H ₂ O:(EG, DEG, TEG, TTEG, PEG, BA) ^a =1:1	Ascorbic acid as reducing agent	141 (0.1 C), 135 (0.2 C), 130 (0.5 C), 123 (1 C), 112 (2 C)	96% capacity retention at 0.5 C after 15 cycles	304
Hexagonal platelets, 200 x 100 x 50 nm to 1.2 x 1.2 x 0.5 μm	Microwave-assisted solvothermal synthesis	EG ^a :(H ₂ O+EG ^a) =0-1	Ascorbic acid as reducing agent	136 (0.1 C), 125 (0.2 C), 115 (0.5 C), 105 (1 C), 95 (2 C)	94% capacity retention at 0.5 C after 15 cycles	376
Nanoflakes (compose of nanoplates with 10-20 nm in diameter)	solution-phase strategy	H ₂ O:DMSO ^a =1:1	Glucose	155 (0.1 C), 146 (0.2 C), 136 (0.5 C), 130 (1 C), 108 (2 C)	93% capacity retention at 0.1 C after 100 cycles	493

^a EG: ethylene glycol; DEG: diethylene glycol; TEG: tri-ethylene glycol; TTEG: tetra-ethylene glycol; PEG: polyethylene glycol 400; BA: benzyl alcohol; HMD: hexamethylenediamine; HMT: hexamethylenetetramine; PVP: poly(vinylpyrrolidone); BA: benzyl alcohol; PEG 200: polyethylene glycol 200; DMSO: dimethyl sulfoxide.

(2) Crystal growth orientation along the a-c plane. Apart from reducing the particle size, the orientation of LiCoPO₄ particles tailored by morphology control also plays an important factor in improving the kinetics of the Li-ion extraction/insertion process. [010]-oriented LiCoPO₄ nanoplates/nanoflakes and [100]-oriented or [001]-oriented nanorod/nanowire structures minimize the crystallite size along b, which is the direction of Li-ion diffusion through the channels (Figure 4-1). This can overcome the poor Li⁺ ionic diffusivity caused by the one-dimensional lithium diffusion pathway along the [010] direction, thus enhance its rate performance.^{74, 304, 365-367, 376, 382,}

438

At the thermodynamic equilibrium state, the surface area of each facet in a crystal usually depends on its free surface energy.⁴⁹⁴ However, the preference of crystal facets in LiCoPO₄ is also affected by the solvent properties. The (010) crystal facets in LiCoPO₄ are mostly achieved by controlling the solvothermal conditions, typically with ethylene glycol as the solvent.^{304, 366, 367, 376, 382} Nilges *et al* prepared LiCoPO₄ nano-platelets via microwave-assisted solvothermal synthesis using water/ethylene glycol co-solvent (1:1 in volume ratio). The ethylene glycol co-solvent was found to be critical in tailoring the particle size, morphology and crystal orientation of LiCoPO₄. The LiCoPO₄ (with dimensions of 700-800 nm x 400-600 nm x 100-220 nm) shows a hexagonal platelet-like morphology with the smallest dimension in [010] direction, alongside with the Li-ion diffusion pathways in LiCoPO₄.³⁸⁸ The binding energy of a solvent is considered to be a decisive factor to control the crystal facets of LiCoPO₄. The use of diethylene glycol or triethylene glycol as a solvent is more likely to produce (010) facets compared with ethylene glycol, because of the more stable binding geometry.³⁰⁴ Due to the hydrogen bonds between diethylene glycol molecules, the directional alignment of diethylene glycol molecules may take place at the (010) facet and produce a long chain, thus making the formed (010) surfaces more stable.⁶¹ For example, Nilges *et al* prepared LiCoPO₄ via a microwave-assisted solvothermal synthesis, using various water/alcohol co-

solvents (1:1 in volume ratio), including ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol 400 and benzyl alcohol. Figure 4-7 a-f SEM images show that these co-solvents significantly affect the particle size and morphology of LiCoPO_4 , to form square, rhombic and hexagonal platelets. Among them, the samples obtained from the water/diethylene glycol and water/triethylene glycol co-solvents showed the smallest dimension along [010], which is the direction of the Li-ion diffusion pathways in LiCoPO_4 . The anisotropic crystal orientations with improved lithium diffusion properties lead to specific capacities of 141 mA h g^{-1} at 0.1 C, with rate capability of 112 mA h g^{-1} at 2 C (Figure 4-7 g and h).³⁰⁴

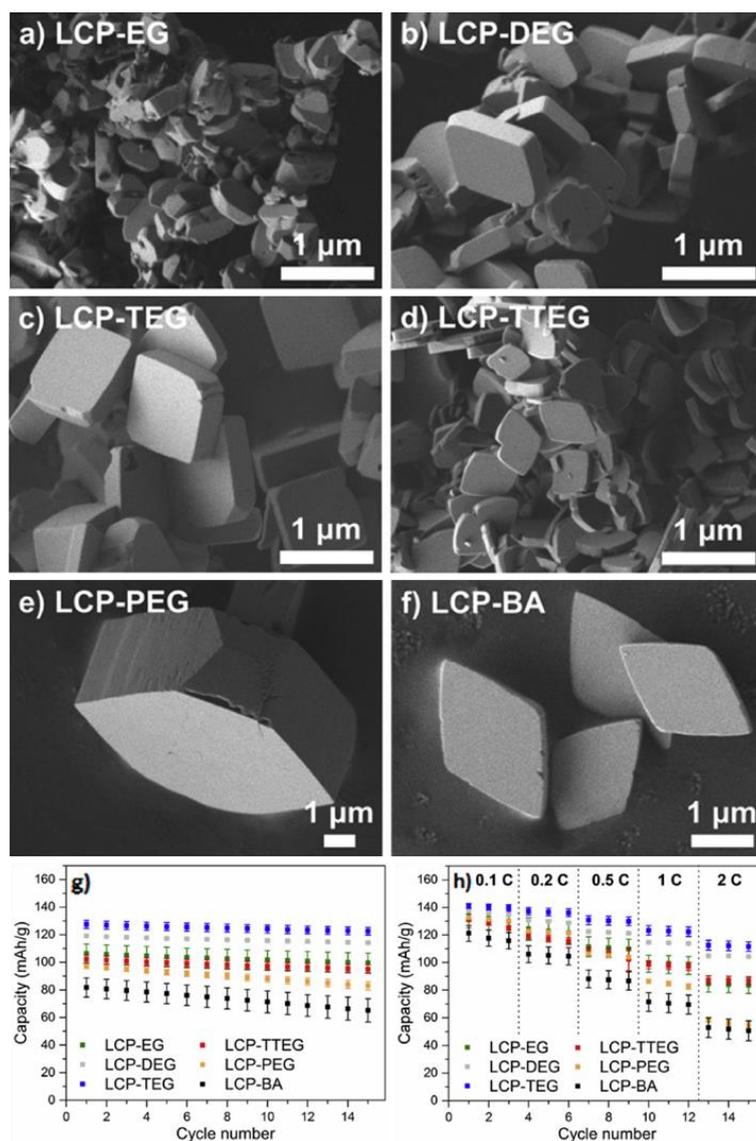


Figure 4-7 SEM images of the LiCoPO_4 samples prepared via microwave assisted solvothermal synthesis using various water/alcohol co-solvents (1:1 in volume ratio) including: (a) ethylene glycol, (b) diethylene glycol, (c) triethylene glycol, (d) tetraethylene glycol, (e) polyethylene glycol 400 and (f) benzyl alcohol, denoted as LCP-EG, LCP-DEG, LCP-TEG, LCP-TTEG, LCP-PEG and LCP-BA, respectively; (g) cycle stability at 0.5 C and (h) rate capability at various rates from 0.1 C to 2 C for LiCoPO_4 cathodes. Reproduced from Ref. ³⁰⁴ with permission from Elsevier 2017.

Chapter 4

In addition, the orientation of LiCoPO_4 crystals could be controlled by some other factors like surfactants, templates, etc.^{74, 365, 438} Devaraju *et al* reported a controlled synthesis of LiCoPO_4 nanoplates by supercritical solvothermal method in presence of oleylamine as a surfactant. The LiCoPO_4 nanoplates showed 100-300 nm in length, 50-200 nm in width and 5-15 nm in thickness.³⁶⁵ Truong *et al* prepared LiCoPO_4 nanoplates and nanorods with exposed (010) facets via a one-pot supercritical fluid process. The amines with long alkyl chains like hexamethylenediamine is critical in determining the morphology of LiCoPO_4 via selective adsorption on (010) facets. As shown in Figure 4-8 a-d, the SEM and TEM images show the LiCoPO_4 nanoplates with 500 nm in length, 200 nm in width and 50 nm in thickness. The high-resolution TEM image (Figure 4-8 d) presents the (200) and (020) atomic planes with a lattice spacing of 0.235 nm and 0.51 nm, and the LiCoPO_4 nanoplates are exposed (010) facets. It suggests that the thinnest direction of the LiCoPO_4 nanoplates is along the b-axis, which is a favorable direction for lithium diffusion in olivine crystals. Thus the LiCoPO_4 nanoplates exhibited better cycle stability and rate capability than nanoparticles.⁴³⁸ Truong *et al* also investigated the benzylamine-directed growth of LiCoPO_4 nanoplates with exposed (010) facets via a supercritical fluid process. The LiCoPO_4 nanoplates with a reduced lithium diffusion pathway, enables quick Li^+ extraction/insertion in crystals, thus resulting in an initial discharge capacity of 123 mA h g^{-1} and capacity retention of 81% after 10 cycles.⁴³⁹ Recently, Chang *et al* synthesized [010]-oriented LiCoPO_4/C nanoflakes *via* solution-phase strategies. The 5-hydroxymethylfurfural and levoglucosan produced in the dehydration of glucose is critical in controlling the morphology of LiCoPO_4 . The resulting LiCoPO_4/C nanoflakes as cathode materials exhibited a specific capacity of 155 mA h g^{-1} at 0.1 C and capacity retention of 93% over 100 cycles.⁴⁹³

Yan *et al* prepared ultrathin LiCoPO_4 nanosheets (thickness: 4.6 nm) with exposed (010) surface facets by using $\text{NH}_4\text{CoPO}_4 \cdot \text{H}_2\text{O}$ nanosheets as templates. The LiCoPO_4 nanosheets exhibit high contact area with the electrolyte and quick Li-ion transfer, thus resulting in an initial discharge capacity of 153 mA h g^{-1} at 0.2 C with capacity retention of 88% after 50 cycles, and rate capability of 91 mA h g^{-1} at 10 C.⁴³⁷ Also, with $\text{NH}_4\text{CoPO}_4 \cdot \text{H}_2\text{O}$ nanosheets as templates, Wang *et al* produced LiCoPO_4 nanoplates with porous structure (Figure 4-8 e and f), which exhibited an initial specific capacity of 147 mA h g^{-1} at 0.1 C with capacity retention of 94% after 300 cycles, and rate capability of 115 mA h g^{-1} at 10 C.^{74, 495}

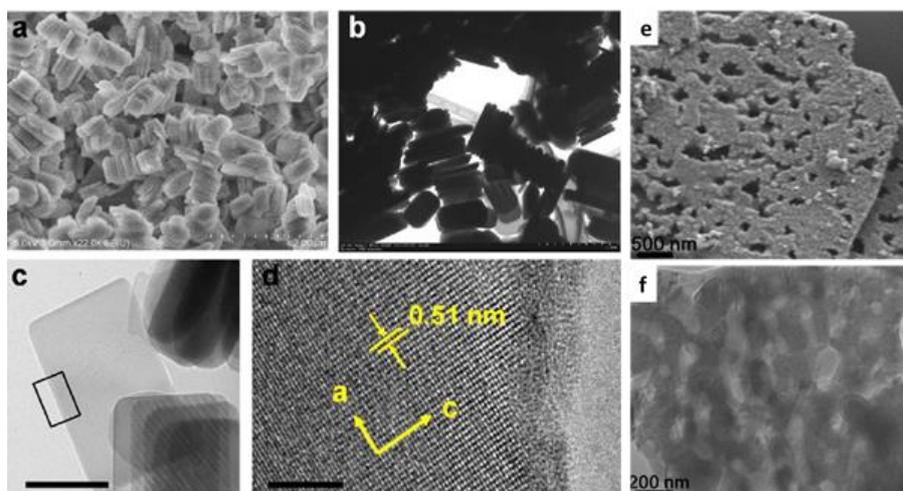


Figure 4-8 The LiCoPO_4 nanoplates prepared with hexamethylenediamine. (a) SEM image (scale bar = 2 μm); (b) low-magnification TEM image (scale bar = 1 μm); (c) high-magnification TEM image (scale bar = 200 nm); (d) HRTEM image of a portion of the LiCoPO_4 nanoplate shown in (c) (scale bar = 5 nm). Reproduced from Ref. ⁴³⁸ with permission from Nature Publishing Group 2014. (e) SEM and (f) TEM images for LiCoPO_4 nano-plates with porous structure prepared with $\text{NH}_4\text{CoPO}_4 \cdot \text{H}_2\text{O}$ nanosheets as templates. Reproduced from Ref. ⁷⁴ with permission from Elsevier 2016.

(3) 3D porous architectures with hierarchical structures. Hierarchical structures of LiCoPO_4 facilitate the fast transport of lithium ions through the LiCoPO_4 material, similarly to nanoparticles or planar structures. As shown in Figure 4-9 a-d, Richardson *et al* fabricated spherical nanoporous LiCoPO_4/C *via* spray pyrolysis. The porous micron-size particles consisted of an agglomeration of ~ 70 nm primary LiCoPO_4 particles with 3-5 nm thick conformal carbon coating. The LiCoPO_4/C cathode exhibited a specific capacity of 123 mA h g^{-1} at 0.1 C with capacity retention of 95% after 20 cycles.⁴²⁴

Hierarchical LiCoPO_4 with hedgehog-like (Figure 4-9 e),³⁵² flower-like,³⁷² dumbbell-like,³⁷⁵ straw-like (Figure 4-9 f),³⁷⁹ shuttlecock-like (consisting of many thin nanorods which are about 200 nm in diameters and 3 μm in length),³⁸¹ and spongy^{305, 406, 415, 462, 470} architectures have also been developed.^{297, 361} Yang *et al* prepared hedgehog-like LiCoPO_4/C by solvothermal synthesis using water/benzyl alcohol co-solvent. The LiCoPO_4/C hierarchical microstructures (size: 5-8 μm) consists of numerous LiCoPO_4 nanorods (40 nm in diameter and 1 μm in length) with carbon coating (8 nm in thickness). It exhibits an initial specific capacity of 136 mA h g^{-1} at 0.1 C with capacity retention of 91% over 50 cycles.³⁵²

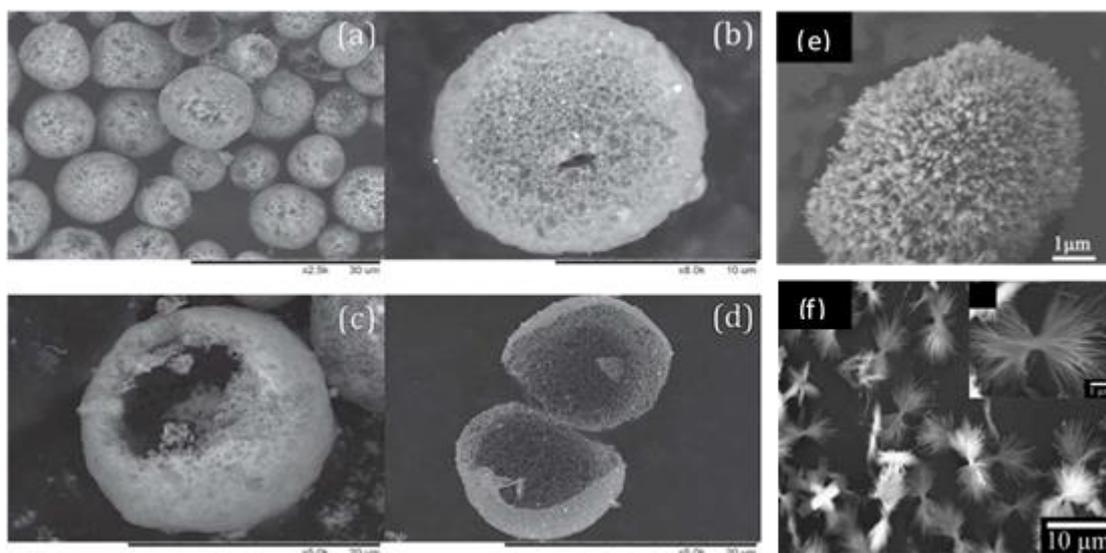


Figure 4-9 SEM images of (a) the spherical nanoporous LiCoPO_4/C composite microparticles synthesized by spray pyrolysis; (b) the surface of a single LiCoPO_4/C microparticle; (c) and (d) broken LiCoPO_4/C microparticles showing the 3D interconnected pores; Reproduced from Ref. ⁴²⁴ with permission from the Royal Society of Chemistry 2011. (e) hedgehog-like LiCoPO_4/C synthesized via a solvothermal process in water-benzyl alcohol mixed solvent at 200 °C; Reproduced from Ref. ³⁵² with permission from Elsevier 2011. (f) straw-like LiCoPO_4/C composite prepared by solvothermal process with poly(vinylpyrrolidone) as the carbon source and template; Reproduced from Ref. ³⁷⁹ with permission from Elsevier 2011.

4.4.4 Ion doping

Apart from carbon modification, size reduction and morphology control, ion doping is regarded as another important strategy to improve the intrinsic electronic and ionic conductivity of LiCoPO_4 .⁴⁹⁶ Ion doping is expected to improve the discharge capacity of LiCoPO_4 at high rates, since its poor rate capability is mainly due to the poor Li-ion diffusion. Many publications reported the improved cycle stability and rate capability of doped LiCoPO_4 , but the role of ion doping in LiCoPO_4 is still controversial. The metal ions could be doped on both Li sites and Co sites.^{293, 451, 497} The control of doping at chosen sites is important for the overall LiCoPO_4 performance improvement. Relevant examples of the electrochemical performance of LiCoPO_4 after ion doping are shown in Table 4-8.

Table 4-8 The effects of ion doping on the performance of LiCoPO₄ composites.

Doping site	Doping element	molecular formula of composites	Mechanism	Synthesis methods	Rate performance, mA h g ⁻¹ (rate, C)	Cycle stability	Ref.
Li site doping	Fe ²⁺	(Li _{0.893} Fe _{0.036})CoPO ₄	The lattice parameter a slightly increases and b tinily diminishes, resulting in a shorter and wider Li ⁺ diffusion pathway	Hydrothermal synthesis	150 (0.1 C), 145 (1 C), 129 (5 C), 104 (10 C), 85 (20 C)	95% capacity retention at 0.1 C after 100 cycles	469
Co site aliovalent doping	V ⁵⁺	Li _{1+0.5x} Co _{1-x} V _x (PO ₄) _{1+0.5x} /C (x = 0, 0.05, 0.10)	Form vacancies and structural defects, thus increases ionic and electronic conductivity	Solid-state reaction	135 (0.1 C)	85% capacity retention at 0.1 C after 25 cycles	446, 498, 499
	Y ³⁺	LiCo _{1-x} Y _x PO ₄ (x = 0, 0.005, 0.01, 0.02, 0.025)	Facilitate the Li-ion diffusion	Sol-gel process	154 (0.1 C)	32 mA h g ⁻¹ at 0.1 C after 30 cycles	412
	Fe ³⁺	Li _{1-x} Co _{1-x} Fe _x PO ₄ (x = 0, 0.05, 0.1)	Charge compensation by Li ⁺ deficiency, enhance antiferromagnetic ordering	Sol-gel process	128 (0.1 C), 120 (1 C), 95 (10 C)	95% capacity retention at 0.1 C after 50 cycles	407
	V ³⁺	LiCo _{1-3x/2} V _{x/2} PO ₄ (x = 0, 0.02, 0.04, 0.06, 0.08)	Decrease unit cell volume	Solvothermal synthesis	97 (0.1 C)	82 mA h g ⁻¹ at 0.1 C after 20 cycles	364, 368
	Cr ³⁺	LiCo _{1-1.5x} Cr _x PO ₄ /C (x = 0, 0.02, 0.04, 0.06)	Decrease antisite defect concentration, decrease unit cell volume	Sol-gel process	144 (0.1 C), 122 (0.2 C), 107 (0.5 C), 91 (1 C)	71% capacity retention at 0.1 C after 100 cycles	459
Co site isovalent doping	Fe ²⁺	LiCo _{0.95} Fe _{0.05} PO ₄	Preferential Fe occupation of 4c sites suppresses 4a-4c antisite mixing of Li and Co, thereby stabilizing the structure by compensating for the Co-encapsulating oxygen octahedron shrinkage due to Co ²⁺ oxidation during Li ⁺ extraction	Solid-state reaction	120 (0.05 C), 108 (0.1 C), 92 (0.2 C)	90 mA h g ⁻¹ at 0.05 C after 10 cycles	332, 335, 442, 500
		Li _{1+x} (Co _{1-y} Fe _y) _{1-x} PO ₄ (0 ≤ x ≤ 0.2, 0 ≤ y ≤ 0.2)	Improve the kinetics of the lithium insertion/extraction reaction	Solid-state reaction	130 (0.1 C)	117 mA h g ⁻¹ at 0.1 C after 15 cycles	303, 350, 417
		LiCo _{1-x} Fe _x PO ₄ (0 ≤ x ≤ 1)	Enlarge 1D diffusion channels and reduce cell volume change during the Li extraction/insertion process, resulting in the enhanced Li ⁺ diffusion	Carbothermal reduction	142 (0.1 C)	130 mA h g ⁻¹ at 0.1 C after 15 cycles	445
		LiCo _{0.8} Fe _{0.2} PO ₄	Improve interior conductivity and structural stabilization	Modified hydrothermal synthesis	147 (0.1 C), 137 (0.5 C), 131 (1 C), 123 (5 C), 115 (10 C)	94% capacity retention at 0.1 C after 300 cycles	74
	Mg ²⁺	LiCo _{1-x} Mg _x PO ₄ (x = 0, 0.025, 0.05, 0.1)	Decrease electrical resistance, improve Li-ion conductivity	Sol-gel process	88 (0.1 C)	13 mA h g ⁻¹ at 0.1 C after 21 cycles	305, 406, 419, 463
	Ca ²⁺	LiCo _{1-x} Ca _x PO ₄ (x = 0, 0.05, 0.1)	Decrease electrical resistance, improve Li-ion conductivity	Sol-gel process	104 (0.1 C)	13 mA h g ⁻¹ at 0.1 C after 11 cycles	305, 408, 463
	Ni ²⁺	LiCo _{1-x} Ni _x PO ₄ (0 = 0, 0.33, 0.66, 0.75, 1)	Enlarge cell volumes with longer atomic distances, thus weaken P-O and Co/Ni-O bonds	Sol-gel process	88 (2 C)	57 mA h g ⁻¹ at 2 C after 15 cycles	413
	Mn ²⁺	LiCo _{1-x} Mn _x PO ₄ /C (x = 0, 0.05)	Increase lattice parameters, increase unit-cell volume of 0.15%	Sol-gel and carbothermal reduction	140 (0.1 C), 108 (1 C), 96 (2 C), 77 (5 C)	92% capacity retentions at 0.1 C after 60 cycles	392, 414
Combination doping	Fe ³⁺ (Li site) and Fe ²⁺ /Fe ³⁺ (Co site)	Li _{0.92} Co _{0.8} Fe ²⁺ _{0.12} Fe ³⁺ _{0.08} PO ₄	Extra Li vacancies and more mobile hole polarons after Fe ²⁺ /Fe ³⁺ substitution, resulting in increased ionic conductivity and electronic conductivity, Fe ³⁺ substitution stabilize the structure	Citrate complexation route	121 (0.1 C), 86 (2 C)	80% capacity retention at 0.1 C after 500 cycles	295, 451, 501
	Fe ²⁺ /Fe ³⁺ (Co site)	Li _{0.973} (Fe _{0.1} Co _{0.9}) _{1.014} PO ₄	Changes of crystal structure and atomic coordination altering concentration of anti-site defects, natural concentration of Li ⁺ vacancies, size of Li ⁺ diffusion channels and local distortion, thus modulate Li ⁺ transport properties	Solvothermal synthesis	120 (0.1 C)	78% capacity retention at 0.1 C after 20 cycles	308, 458
	Fe ²⁺ , Cr ³⁺ and Si ⁴⁺ (Co site)	LiCo _{0.9-y-z/(1+0.5y)}} Fe _{0.1/(1+0.5y)}} Cr _{y/(1+0.5y)}} Si _z PO ₄ (y = 0.025, 0.05, 0.1, z = 0, 0.01, 0.02)	Charge compensation for Cr ³⁺ and Si ⁴⁺ substitution of Co ²⁺ is achieved through Li ⁺ site vacancies, thus increase the lattice volume	Solid-state reaction	140 (C/3)	100% capacity retention at C/3 after 250 cycles	287, 502, 503

(1) Li site doping. Through a first-principles investigation, Zhao *et al* found that the Li-site doping by Na⁺ and Cr³⁺ in LiCoPO₄ can reduce the volume change of the material during Li extraction/reinsertion process, but it could block the path of Li-ion diffusion.^{497, 504} Wang *et al* doped Fe into Li-site of LiCoPO₄ structure and found that the lattice parameter a increases and b diminishes slightly, leading to a shorter and wider Li-ion diffusion pathway in LiCoPO₄ crystals.⁴⁶⁹ Although the

rate performance of LiCoPO_4 has been improved by Li site doping in some reports,^{293, 451, 469, 501} the role of Li site doping in LiCoPO_4 is still unclear and under debate.

(2) Co site doping. Compared with Li site doping, Co site substitution (aliovalent and isovalent) is more intensively studied. Although the role of Co site doping, especially aliovalent doping remains controversial, LiCoPO_4 indeed has exhibited improved cycle stability and rate capability after aliovalent doping, using V^{3+} ,^{364, 368} V^{5+} ,^{446, 498, 499} Fe^{3+} ,^{295, 308, 407, 451, 458, 501, 505} Y^{3+} ,⁴¹² Cr^{3+} ,^{459, 502} Si^{4+} ⁵⁰² or Cu^+ .²⁹³ Yang *et al* improved the initial discharge capacity of LiCoPO_4/C cathode material from 112 to 135 mA h g^{-1} at 0.1 C after doping with V^{5+} . The $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ shows a narrower distribution of smaller particles (300-500 nm) when compared with the pristine LiCoPO_4/C with particle size of 400-800 nm.⁴⁹⁸ Similar phenomena were observed by Wang⁴¹² and Karthikeyan *et al*⁴⁹⁹ with Y^{3+} and V^{5+} doping at Co site in LiCoPO_4 , respectively. Manthiram *et al* reported a low-temperature microwave-assisted solvothermal synthesis of aliovalently substituted $\text{LiCo}_{1-3x/2}\text{V}_x\text{PO}_4$ ($x = 0-0.08$), and it was found that V^{3+} substitution produced a systematic decrease in the unit cell dimensions. The specific capacity and cycling stability were greatly improved compared to the unsubstituted LiCoPO_4 which was attributed to an improved conductivity of the vanadium doped sample.^{364, 368} Kosova *et al* achieved a better cycle stability of LiCoPO_4 by vanadium modification *via* mechanochemically assisted carbothermal reduction. Only a small amount of vanadium (with a mixed oxidation state of 3+, 4+ or 5+) substituted into the Co site of LiCoPO_4 crystal structure, and the other vanadium produced monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The compensation mechanism for the substitution of supervalent vanadium in LiCoPO_4 crystals includes the formation of Li vacancy. The $0.95\text{LiCoPO}_4 \cdot 0.05\text{Li}_3\text{V}_2(\text{PO}_4)_3$ delivers improved cycle stability due to the presence of structural defects enhancing the ionic and electronic conductivity, and to the formation of the Li-conductive $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ on LiCoPO_4 surface promoting the Li^+ transfer from electrolyte to electrode.⁴⁴⁶

In comparison to aliovalent doping, isovalent substitution has attracted more attention for LiCoPO_4 , and many divalent cations, such as Fe^{2+} ,^{74, 295, 303, 308, 332, 335, 350, 417, 428, 442, 445, 451, 458, 464, 500-502, 505, 506} Mn^{2+} ,^{341, 369, 380, 392, 414} Ca^{2+} ,^{305, 408, 463} Mg^{2+} ,^{305, 341, 406, 419, 463} Zn^{2+} ,³⁴⁹ and Ni^{2+} ^{300, 341, 413} were doped at the Co site, and showed improved cycle stability and rate capability. Among the isovalent cations, iron doping has been studied most intensively. Fe^{2+} doping at Co sites can enhance the discharge capacity and rate capability for LiCoPO_4 ,^{74, 502} which could be attributed to the improved Li^+ diffusivity induced by the enlargement of 1D Li^+ diffusion channel in LiCoPO_4 structure.^{350, 442} Furthermore, Kang *et al* used *ab initio* calculations with absorption spectroscopy and found that preferential Fe^{2+} occupation of the 4c sites suppresses 4a-4c antisite mixing of lithium and cobalt, to stabilize the LiCoPO_4 structure by compensating for the Co-encapsulating O octahedron shrinkage owing to the oxidation of Co^{2+} upon Li-ion extraction (Figure 4-10).³³⁵ This decreases the

cell volume change in LiCoPO_4 upon the Li-ion extraction/insertion process.⁴⁴⁵ Fe substituted LiCoPO_4 materials have also been shown to delithiate *via* a solid solution mechanism, which reduces the probability of particle cracking that can be produced during the formation of phase boundaries.^{317, 332, 500, 507} It has been reported that isovalent ion doping in Co site with Mn^{2+} ,^{369, 414} Fe^{2+} ,^{458, 508} Ni^{2+} ,⁴¹³ Ca^{2+} ^{305, 408} or Mg^{2+} ^{305, 406} can affect the size and morphology of products. For example, Örnek *et al* reduced the LiCoPO_4 particles size with homogenous particle distribution and well-defined grain boundaries after doping with Mn^{2+} .⁴¹⁴ Mn^{2+} can occupy the Co^{2+} site *via* doping, which induces the lattice distortion of LiCoPO_4 crystal. This lattice distortion could decrease the surface energy of LiCoPO_4 particles to impede the growth of LiCoPO_4 crystal.⁵⁰⁹ Similar observation was reported by Ni *et al* who found that Mn^{2+} doping can remarkably reduce the particles size of LiCoPO_4 from 1 μm to 100 nm as Mn^{2+} doping can promote the formation of the olivine structure in hydrothermal synthesis.³⁶⁹

The electrochemical performance of LiCoPO_4 could also be improved by a combination of Li site and Co site (aliovalent and isovalent) doping. Allen *et al* reported that Fe doped LiCoPO_4 showed enhanced cycle stability with 80% capacity retention after 500 cycles, while undoped LiCoPO_4 loses more than half capacity after 10 cycles. This is attributed to the partial substitution of Li^+ by Fe^{3+} and Co^{2+} by $\text{Fe}^{2+}/\text{Fe}^{3+}$ which could stabilize the olivine structure.^{451, 501} Further investigation showed that $\text{Fe}^{2+}/\text{Fe}^{3+}$ substituted LiCoPO_4 presents both higher ionic and electronic conductivity.²⁹⁵ This result is inconsistent with the first principles investigation on LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}$ and Ni) by Johannes *et al*, who found that the energy for a polaron to move from one transition metal site to the next is lowest for LiFePO_4 , thus Fe^{2+} substitution into LiCoPO_4 will improve the electronic conductivity.⁵¹⁰ Brutti *et al* also confirmed that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ doping into Co site of LiCoPO_4 significantly affects the crystal structure and atomic coordination of LiCoPO_4 . Thus changes the anti-site defects amount, the Li vacancies amount, and the size of Li-ion diffusion channels in [010] direction. These synergistically affect the Li-ion transfer properties in LiCoPO_4 crystals.^{308, 458} Besides, Fe, Cr and Si doped LiCoPO_4 ($\text{Cr}, \text{Si-LiCo}_{0.9}\text{Fe}_{0.1}\text{PO}_4$) was investigated by Allen *et al*. It was found that Fe doping significantly enhances the cycle life and energy density; Cr doping further improves the cycle life, energy density and rate capability; Si doping suppresses the reactivity of the cathode with electrolyte to improve the cycle life. Thus, the $\text{Cr}, \text{Si-LiCo}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ cathode exhibited a specific capacity of 140 mA h g^{-1} at C/3 rate without capacity fading after 250 cycles.⁵⁰² Further investigation reveals that doping ions to produce $\text{Li}_{1.025}\text{Co}_{0.84}\text{Fe}_{0.10}\text{Cr}_{0.05}\text{Si}_{0.01}(\text{PO}_4)_{1.025}$ can stabilize the electronic and crystal structure, to fully utilize the redox capacity of the cathode.^{287, 503}

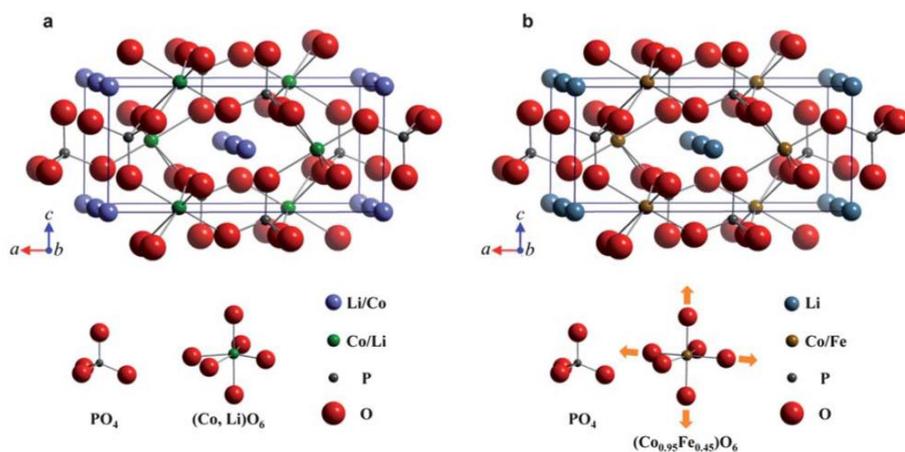


Figure 4-10 The atom configuration of (a) LiCoPO_4 with antisite-mixing and (b) $\text{LiCo}_{0.95}\text{Fe}_{0.05}\text{PO}_4$ without antisite-mixing, along the [010] projections. The atom configuration of $\text{LiCo}_{0.95}\text{Fe}_{0.05}\text{PO}_4$ shown in (b) exhibits larger Li-ion transfer channels owing to the enlarged oxygen octahedron (showed with arrows). Reproduced from Ref. ³³⁵ with permission from the Royal Society of Chemistry 2011.

4.4.5 Summary of strategies for performance improvement

The benefits of surface modification, carbon network support structures, ion doping, size reduction and morphology control to improve the electrochemical performance of LiCoPO_4 are summarised in Table 4-9. Surface modification (e.g. carbon coating) on LiCoPO_4 particles improves the electronic conductivity of composites. Furthermore, carbon coating not only reduces the particle size and alleviates the aggregation of LiCoPO_4 particles by inhibiting undesirable particle growth during heat treatment, but also protects LiCoPO_4 from direct contact with electrolyte thus avoiding surface degradation caused by HF attack produced from electrolyte decomposition. However, additional resistances with considerable values for Li-ion transfer may be added to the whole electrode processes if the carbon layers are too thick.⁶⁰ Also, it could reduce the tap density of LiCoPO_4 cathodes thus decrease the volumetric energy density of LIBs. Carbon network structures to support LiCoPO_4 particles provide good electrical conductivity, but it is hard to achieve uniform distribution. Decreasing the particle size of LiCoPO_4 or tailoring its crystal growth orientation along the a-c plane reduces the length of Li-ion migration paths, and thus allows faster Li-ion transfer, and hence better utilization of the active material. The size reduction also adversely affects the tap density and volumetric energy density, as well as the electrode/electrolyte interface stability. Ion doping aims to enhance the intrinsic electronic/ionic conductivity of LiCoPO_4 although the mechanism is still in controversy.^{310, 511-513}

The combination of the advantages of various approaches is promising for high performance LiCoPO_4 cathodes in LIBs. For example, Örnek *et al* fabricated nanostructured $\text{LiCo}_{0.95}\text{Mn}_{0.05}\text{PO}_4/\text{C}$

composite *via* sol-gel assisted carbothermal reduction reaction. The $\text{LiCo}_{0.95}\text{Mn}_{0.05}\text{PO}_4/\text{C}$ nanocomposite with particle size of 40-80 nm was coated by a homogeneous carbon layer of 5-10 nm thickness. The $\text{LiCo}_{0.95}\text{Mn}_{0.05}\text{PO}_4/\text{C}$ cathode exhibited a specific capacity of 140 mA h g^{-1} at 0.1 C with a capacity retention of 92% after 60 cycles. This was mainly attributed to the combination of advantages of size reduction, carbon coating and Mn substitution.⁴¹⁴

Table 4-9 Comparison of various approaches to improve the electrochemical performance of LiCoPO_4 .

Strategies	Catalogues	Advantages	Disadvantages
Surface modification	Carbon coating	High electronic conductivity	Low tap density and volumetric power density
	Non-carbon modification	High electronic conductivity	Non-uniform coating, high cost
Carbon network support structures	-	High electronic conductivity	Non-uniform modification, high cost
Size reduction and morphology control	Nanosized LiCoPO_4	High ion conductivity, rapid electrochemical kinetics	Low tap density and volumetric power density
	LiCoPO_4 plates	High ion conductivity	-
	3D hierarchical LiCoPO_4	-	Complex synthesis
Ion doping	Li site doping	-	Low Li-ion conductivity
	Co site doping	High ion conductivity	Controversial doping site and mechanism

4.5 Optimization of other components in high-voltage LIBs

The cycle stability and rate capability of LiCoPO_4 cathode is not only limited by the material itself but is also affected by the battery components, such as electrolytes,^{449, 514-516} separators^{77, 80, 517} and conductive additives,^{320, 356, 409, 518} as illustrated in Table 4-10.

4.5.1 Electrolyte optimisation

LiCoPO_4 high voltage cathodes with LiPF_6 -based carbonate electrolytes suffer from severe capacity fading and poor thermostability due to the oxidization of organic carbonate solvents at high potentials and decomposition of LiPF_6 , especially at elevated temperatures and in water-containing environments.^{55, 79, 320, 364, 519-522} Various efforts have been made to optimize conventional electrolytes i.e. LiPF_6 in ethylene carbonate / dimethyl carbonate / ethyl methyl carbonate (LiPF_6 -EC/DMC/EMC) for LiCoPO_4 high voltage cathodes, such as developing electrolyte additives, investigating alternatives to LiPF_6 salt or EC/DMC/EMC co-solvent, and introducing ionic liquids or solid-state electrolytes.

The electrolyte additives to optimise the conventional electrolyte LiPF_6 -EC/DMC/EMC mainly include thiophene (TPN),⁴⁰³ lithium difluoro(oxalato)borate (LiDFOB),⁵²³ tris(trimethylsilyl) borate (TMSB),⁵²⁴ lithium bis(oxalato)borate (LiBOB),³⁵³ trimethylboroxine (TMB)^{78, 525} and tris(hexafluoroisopropyl) phosphate (HFIP).^{316, 451, 501} Wei *et al* introduced TPN as an electrolyte additive to LiCoPO_4/C high voltage cathode materials. TPN is oxidised at a potential of around ~ 4.4

V vs Li/Li⁺, which is much lower than the onset potential of oxidative degradation of the conventional electrolyte (LiPF₆-EC/DMC/EMC), of around ~4.9 V vs Li/Li⁺. Therefore, TPN oxidises first, forming a protective polymer film, and thus suppresses electrolyte decomposition (Figure 4-11 a and b).⁴⁰³ It was also found that the LiDFOB electrolyte additive decomposed at 4.35 V vs Li/Li⁺ and helped to produce a stable interphase membrane, which passivated the surface of the cathode and suppressed the electrolyte decomposition.⁵²³ In addition, Qiu *et al* applied TMSB as an electrolyte additive to tackle the significantly capacity loss of LiCoPO₄ electrode at high operating voltages. The 1 wt.% TMSB remarkably enhances the cycle life of LiCoPO₄ electrode in EC-based electrolyte, which presents an initial specific capacity of 144 mA h g⁻¹ at 0.1 C with a capacity retention of 76% over 50 cycles, while only 132 mA h g⁻¹ and 45% is found for that electrolyte without TMSB. The improvement of specific capacity and cycle stability is ascribed to the SEI membrane formed in the presence of TMSB, which stabilizes the electrode/electrolyte interface, and inhibits the decomposition of conventional electrolytes at high voltages around 5 V vs. Li/Li⁺.⁵²⁴

LiBF₄ has been used as an alternative to LiPF₆ salt.^{467, 526-528} Eftekhari investigated the electrochemical performance of LiCoPO₄ electrodes protected with a thin layer of Al₂O₃ in LiBF₄-based electrolytes. It was found that both strategies remarkably enhanced the cycle stability of the cathodes which could be attributed to the improved stability of LiBF₄ and the effect of the protective Al₂O₃ layer on the cathode to avoid the side reactions at electrode/electrolyte interface.⁴⁶⁷ Drozhzhin *et al* showed that the performance of LiCoPO₄ electrodes could be improved by using solvent-in-salt electrolytes, in particular, they investigated the use of LiBF₄-propylene carbonate solutions with high salt-to-solvent molar ratio from 1:12 to 1:4.⁵²⁶

Fluorinated ethylene carbonate (FEC) has been used as an alternative to the commonly used co-solvent EC in alkyl carbonates/LiPF₆ electrolyte for LiCoPO₄ cathodes.⁵²⁹⁻⁵³¹ Markevich *et al* reported that FEC-based electrolyte leads to significantly enhanced cycle stability of LiCoPO₄ cathodes in LIBs compared to that with EC-based electrolyte (Figure 4-11 c). It was found that FEC is much more effective than the EC-based electrolyte in promoting the generation of protective film on the surface of high-voltage LiCoPO₄ electrodes, thus resulting in an improved cycling stability with 76% capacity retention at 0.2 C after 100 cycles.^{78, 83, 532}

By replacing both the salt and co-solvent in conventional electrolytes,⁵²⁸ Fukutsuka *et al* examined the compatibility of LiF combined with anion receptors in propylene carbonate (PC) electrolyte solution with high voltage cathode materials. Tripropyl borate (TPB), tris(pentafluorophenyl) borane (TPFPB) and tris(hexafluoroisopropyl) borate (THFIPB) were selected as anion receptors. The carbon- and binder-free LiCoPO₄ cathodes were fabricated *via* sol-gel process. LiCoPO₄

electrode exhibited better cycle stability in 0.1 M LiF with 0.1 M THFIPB in PC electrolyte, which was ascribed to the formation of a surface protecting layer from the reaction of F⁻-THFIPB complex.³⁰⁶

Ionic liquids have also been used as electrolytes for LiCoPO₄ cathodes, due to their high electrochemical stability window (4.0-5.7 V) and improved thermal stability.^{533, 534} For example, Chou *et al* reported that LiCoPO₄ exhibited better cycle stability and Coulombic efficiency in the room temperature ionic liquid electrolyte lithium bis(trifluoromethanesulfonyl)imide in N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (1 M LiTFSI in Pyr₁₃TFSI) compared to the conventional electrolyte (1 M LiPF₆ in EC/DEC), suggesting that the ionic liquid electrolyte is more stable in high operating voltages battery system.⁴⁵⁷ Hassoun *et al* reported LIBs fabricated by a C-coated and Fe-doped LiCoPO₄ cathode with a nano-structured Sn-C anode in an ionic liquid electrolyte lithium bis(trifluoromethanesulfonyl)imide in N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (0.2 mol kg⁻¹ LiTFSI in Pyr₁₄TFSI).⁴⁶⁴

Apart from liquid-based electrolytes, some solid-state electrolytes such as Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃,^{342, 535} Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂,²⁹⁸ Li_{3.3}PO_{3.8}N_{0.22},⁵³⁶ Li₂O-Al₂O₃-TiO₂-P₂O₅⁵³⁷ and LiTi₂(PO₄)₃⁵³⁸ have been used to improve the safety of the LIBs. For example, Nanno *et al* developed all-solid-state LIBs by mixing LiCoPO₄ cathode materials with lithium-conducting solid electrolyte Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ *via* heat treatment. It was found that the active material layer and solid electrolyte layer can be co-sintered without notable side reactions, forming an electrochemically active interface.³⁴² Also, Kunshina *et al* used a peroxide solution of Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ precursor to produce cathode materials composed of active materials with homogenously distributed conductive additives among LiCoPO₄ particles. The two-phase LiCoPO₄/Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ cathode material was achieved after heat treatment at 700 °C, which showed conductivity of two orders of magnitude higher than pure phase LiCoPO₄.⁵³⁵

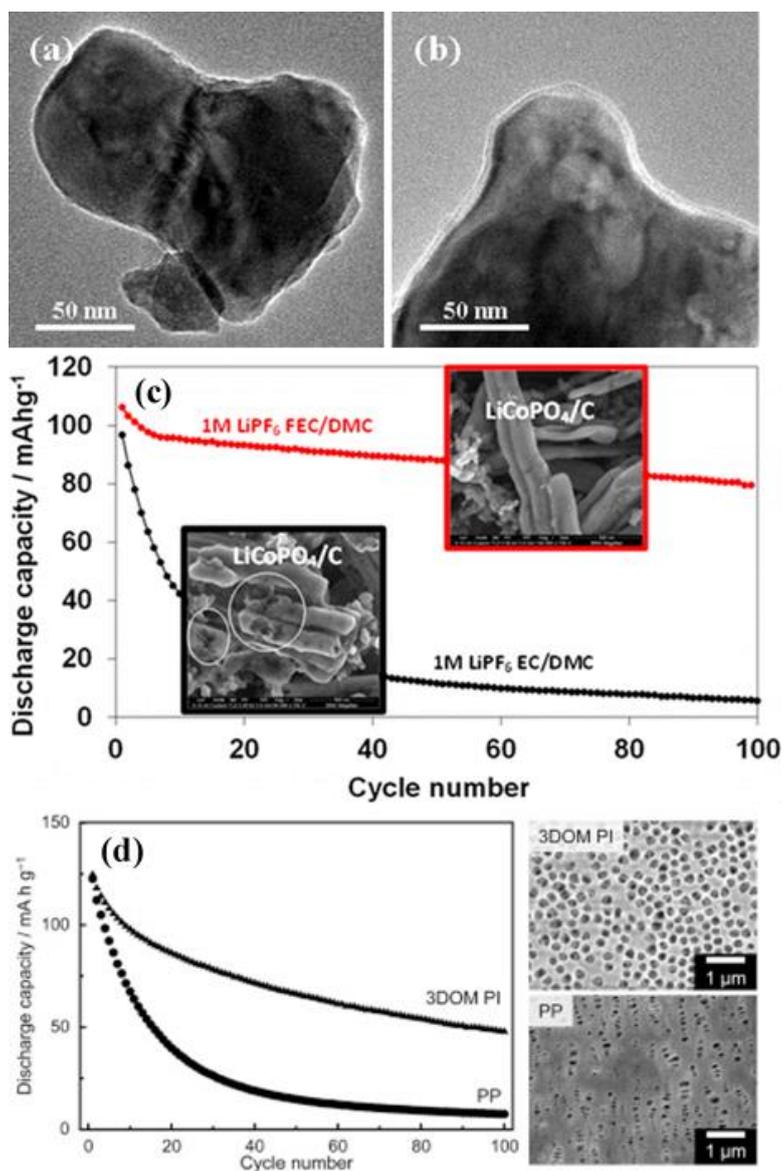


Figure 4-11 TEM images of LiCoPO₄/C cathodes (a) without and (b) with 0.1 wt.% TPN as electrolyte additive after 5 cycles of charge/discharge in LIBs. Reproduced from Ref. ⁴⁰³ with permission from Elsevier 2012. (c) Specific discharge capacity versus cycle number of LiCoPO₄/Li half cells with 1M LiPF₆ in FEC/DMC or EC/DMC as electrolytes. The cells were tested under galvanostatic cycling between 3.5 and 5.2 V at 0.2 C, and SEM images of cycled electrodes (insets) in the two electrolyte solutions, as indicated. Reproduced from Ref. ⁸³ with permission from American Chemical Society 2014. (d) Discharge capacity versus cycle number of LiCoPO₄/Li half cells with three-dimensionally ordered macroporous polyimide (3DOM PI) and polypropylene (PP) as separators. The cells were tested under galvanostatic cycling between 3.0 and 5.1 V at 0.1 C, and SEM images of 3DOM PI and PP separators. Reproduced from Ref. ⁵¹⁷ with permission from Elsevier 2017.

Table 4-10 The effects of electrolytes, separators and conductive additives on the performance of the LiCoPO₄ cathodes for LIBs.

Materials	Synthesis methods	Electrolytes ^a (v/v)	Electrolyte additives ^a	Separators / conductive additives	Rate performance, mA h g ⁻¹ (rate, C)	Cycle stability	Ref.
Li _{0.92} Co _{0.8} Fe _{0.2} P O ₄	Citrate complexation route	1 M LiPF ₆ in EC/EMC 3:7 (wt.%)	HFIP, 1 wt.%	-	121 (0.1 C), 86 (2 C)	80% capacity retention at 0.1 C after 500 cycles	451
LiCoPO ₄ /C	Sol-gel Process	1 M LiPF ₆ in EC/DMC/EMC 1:1:1	TPN, 0.05, 0.1, 0.5 wt.%	-	137 (0.1 C)	68% capacity retention at 0.1 C after 30 cycles	403
LiCoPO ₄	Solid-state reaction	1 M LiPF ₆ in EC/DEC 1:1 (wt.%)	LiBOB, 0, 0.1, 0.5, 1, 3 wt%	-	112 (0.05 C)	74% capacity retention at 0.05 C after 25 cycles	353
LiCoPO ₄	Sol-gel Process	1 M LiPF ₆ in EC/PC/EMC 1:1:3	LiDFOB, 5 wt.%	-	138 (0.1 C), 49 (0.5 C), 11 (1 C)	69% capacity retention at 0.1 C after 40 cycles	523
LiCoPO ₄ /C	Hydrothermal synthesis	1 M LiPF ₆ in FEC/DMC 1:4, 1 M LiPF ₆ in EC/DMC 1:1 (wt.%)	TMB, 0.5-1 wt.%	-	110 (0.2 C), 89 (0.8 C)	90% capacity retention at 0.2 C after 100 cycles	78
LiCoPO ₄	Solid-state reaction	1 M LiPF ₆ in EC/DMC 1:1 (wt.%)	TMB, 0.2, 0.5, 1, 3 wt.%	-	115 (0.5 C)	60 mA h g ⁻¹ at 0.5 C after 140 cycles	525
LiCoPO ₄	Solid-state reaction	1 M LiPF ₆ in EC/DMC 1:1 (wt.%)	HFIP, 1 wt.%	-	93 (0.05 C)	64 mA h g ⁻¹ at 0.05 C after 20 cycles	316
LiCoPO ₄	Sol-gel Process	1 M LiPF ₆ in EC/DMC 1:1	TMSB, 0.5, 1, 2 wt.%	-	144 (0.1C), 125 (0.2 C), 95 (0.5 C), 67 (1 C)	76% capacity retention at 0.1 C after 50 cycles	524
LiCoPO ₄ /Al ₂ O ₃	Solid-state reaction	1 M LiBF ₄ in EC/DMC 1:1	-	-	127 (0.1 C)	83% capacity retention at 0.1 C after 50 cycles	467
Li _x CoPO ₄ (x = 0.90, 0.95, 1, 1.05)	Sol-gel Process	1 M LiTFSI in Pyr ₁₃ TFSI ionic liquid, 1 M LiPF ₆ in EC/DEC 1:2	-	-	92 (0.05 C), 67 (0.2 C), 52 (0.5 C), 22 (1 C)	85% capacity retention at 0.05 C after 35 cycles	457
LiCoPO ₄ /C	Hydrothermal synthesis	1 M LiPF ₆ in EC/DMC 1:1, 1 M LiPF ₆ in FEC/DMC 1:4 (wt.%)	-	-	105 (0.2 C)	80 mA h g ⁻¹ at 0.2 C after 100 cycles	83, 532
LiFe _{0.1} Co _{0.9} PO ₄ /C	Solvothermal synthesis	0.2 mol kg ⁻¹ LiTFSI in Pyr ₁₄ TFSI ionic liquid	-	-	90 (0.05 C)	75 mA h g ⁻¹ at 0.05 C after 7 cycles	464
LiCoPO ₄ /C	Solvothermal synthesis	LiBF ₄ in PC 1:12, 1:6, 1:4, molar ratio	-	-	137 (0.1 C)	79% capacity retention at 0.1 C after 10 cycles	526
LiCoPO ₄ /C	Hydrothermal synthesis	1 M LiPF ₆ in EC/DMC 1:1	-	Separators: polyethylene, glassy paper, quartz	120 (0.2 C)	80 mA h g ⁻¹ at 0.2 C after 40 cycles	80
LiCoPO ₄ /C	Hydrothermal synthesis	1 M LiPF ₆ in EC/DMC 1:1	-	Separators: glassy fibre, polyethylene	120 (0.2 C)	78 mA h g ⁻¹ at 0.2 C after 50 cycles	77
LiCoPO ₄ /C	Hydrothermal synthesis	1 M LiPF ₆ in EC/DEC 1:2	-	Separators: 3D ordered macroporous polyimide	125 (0.1 C)	39% capacity retention at 0.1 C after 100 cycles	517
LiCoPO ₄	Solid-state reaction with high-energy ball-milling process	1 M LiPF ₆ in EC/DEC 1:1	-	Conductive additives: acetylene black, carbon black (SP270)	110 (0.05 mA cm ⁻²), 89 (0.1 mA cm ⁻²), 83 (0.2 mA cm ⁻²), 62 (0.4 mA cm ⁻²), 56 (0.8 mA cm ⁻²)	40 mA h g ⁻¹ at 0.05 mA cm ⁻² after 30 cycles	356
LiCoPO ₄	Sol-gel Process	1 M LiPF ₆ in EC/DEC 1:1	-	Conductive additives: Ketjen black	145 (0.1 mA cm ⁻²)	-	409
LiCoPO ₄ /C	Hydrothermal synthesis	1 M LiPF ₆ in EC/DEC 1:2	-	Conductive additives: acetylene black, Ketjen black	125 (0.1 C)	57% capacity retention at 0.1 C after 100 cycles	518

^a EC: ethylene carbonate; DMC: dimethyl carbonate; EMC: ethyl methyl carbonate; PC: propylene carbonate; DEC: diethyl carbonate; FEC: fluoroethylene carbonate; LiTFSI: lithium bis(trifluoromethanesulfonyl)imide; Pyr₁₃TFSI: N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide; Pyr₁₄TFSI: N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide; TPN: thiophene; LiDFOB: lithium difluoro(oxalato)borate; TMSB: tris(trimethylsilyl) borate; LiBOB: lithium bis(oxalato)borate; TMB: trimethylboroxine; HFIP: tris(hexafluoroisopropyl) phosphate.

4.5.2 Separator optimisation

The development of stable separators is also required to enhance the cycle stability of LiCoPO₄. The separators such as polyethylene and polypropylene are inert at 4 V in conventional LIBs, but they can be oxidized at around 5 V, thus affect the cycle stability of high-voltage LIBs.⁵¹⁷ Porous membranes are generally used as separators in LIBs to allow fast ion transport while mechanically

separating the anode and the cathode and hence preventing electrical short circuits. Therefore, the safety and electrochemical properties of LIBs strongly depend on the porous separator.⁵¹⁷ Some advanced porous membranes have been developed for LIBs.^{539,540} Kanamura *et al* obtained LiCoPO₄ electrode with enhanced cycle stability and Coulombic efficiency *via* applying a polyimide separator with ordered 3D macroporous structure, rather than an ordinary polypropylene separator with heterogeneous porous structure (Figure 4-11 d). The improved cycle stability of the battery using this newly developed separator is ascribed to its ordered 3D macroporous structure and good anodic stability.⁵¹⁷ Markevich *et al* achieved remarkably enhanced cycle stability of LiCoPO₄ cathodes in a 1 M LiPF₆ EC/DMC electrolyte with SiO₂-containing separators (quartz, glassy paper), compared to that achieved with conventional polyethylene separators.⁸⁰ Markevich *et al* also showed that using glass fibre separators decreases the extent of structural degradation of LiCoPO₄ electrodes.⁷⁷

4.5.3 Conductive additive optimisation

Conductive additives in the cathode are also subject to undesirable degradation reactions at high potentials.⁵⁴¹⁻⁵⁴³ Generally, high surface area carbon additives, such as acetylene black and Ketjen black, are added to electrodes to create a continuous conductive network among active materials.^{544,545} These carbon additives may be relatively inert in conventional LIBs at 4 V, but they become much more prone to anodic degradation at high voltages.⁵¹⁸ High surface area materials are required to produce a conductive network, but high surface area also leads to enhanced degradation. Kanamura *et al* examined the influence of conductive carbon additives (ketjen black and acetylene black with different surface areas) on LiCoPO₄ properties. It was found that the acetylene black with moderate specific surface area as a conductive additive for LiCoPO₄ cathode leads to better cycle stability.⁵¹⁸ Jin *et al* investigated the effect of various conductive additives such as acetylene black and carbon black (SP270) on electrochemical performance of LiCoPO₄ cathodes. It was found that the LiCoPO₄ battery with acetylene black as conductive additive exhibited better performance with an initial specific capacity of 110 mA h g⁻¹ at 0.05 mA cm⁻².³⁵⁶ Kim *et al* investigated the effect of the amount of conductive additive on the electrochemical performance of LiCoPO₄. With the increasing amount of conductive carbon (Ketjen black) from 0 to 33 wt.%, the initial discharge capacity of LiCoPO₄ improved from 103 mA h g⁻¹ to 145 mA h g⁻¹.⁴⁰⁹ Wohlfahrt-Mehrens *et al* examined the electrochemical and thermal behaviour of LiCoPO₄-based cathode. In the charging process of LiCoPO₄ cathodes, although the partially delithiated cathode exhibits good thermal stability, the fully delithiated cathode decomposes readily at 160-260 °C. The highest thermal stability was obtained by using carbon black (super-P) and graphite (KS6) as conductive additives without carbon coating.³²⁰

4.5.4 Summary of optimising other components in high-voltage LIBs

The electrolyte additives to optimise $\text{LiPF}_6\text{-EC/DMC/EMC}$ conventional electrolytes for LiCoPO_4 high-voltage LIBs are mainly target the formation of a stable interfacial films on the cathodes to decrease the decomposition of the electrolytes at high potentials. Developing alternatives to LiPF_6 salt or EC/DMC/EMC co-solvent, and introducing ionic liquid or solid-state electrolytes help to obtain LIBs with improved thermal stability and safety. Apart from electrolytes, the optimisation of separators and conductive additives are essential in the development of high voltage LIBs.

4.6 Conclusions and outlook

Olivine LiCoPO_4 is a promising candidate among the olivine phosphates family as cathode material for high-voltage LIBs due to its high redox potential of 4.8 V vs Li/Li^+ and theoretical capacity of 167 mA h g^{-1} . Various synthetic routes such as solid-state reaction, hydrothermal/solvothermal synthesis and sol-gel process have been proposed to prepare LiCoPO_4 . As the conventional method for mass production of most cathode materials for LIBs, the solid-state method is widely used for preparation of LiCoPO_4 , in spite of the drawback of poor particle size control. In contrast, wet-chemical methods like hydrothermal/solvothermal synthesis and sol-gel process provide better control of the morphology and particle size of LiCoPO_4 , although some drawbacks such as strict reaction conditions exist. Further improvements are still required to develop a simple, time and energy saving, easy to control and industrially scalable synthesis method to prepare LiCoPO_4 cathodes for LIBs with high specific capacity, good cycle stability and rate capability.

Tremendous efforts have been made to improve the electrochemical performance of LiCoPO_4 , such as surface modification (e.g. carbon coating), carbon network support structures, ion doping, size reduction and morphology control. Carbon coating on the surface of LiCoPO_4 improves the electronic conductivity of composites effectively but reduces the tap density and volumetric power density of LIBs. Carbon network structures to support LiCoPO_4 particles provides good electrical conductivity, but it's hard to achieve uniform distribution. Decreasing the particle size of LiCoPO_4 or tailoring its crystal growth orientation along the a-c plane reduces the length of Li-ion migration paths, and facilitates easier Li-ion transfer, thus better utilization of the active materials could be achieved. The size reduction also adversely affects the tap density and volumetric energy density, as well as the electrode/electrolyte interface stability. Ion doping aims to enhance the intrinsic electronic/ionic conductivity of LiCoPO_4 although the mechanism is still in controversy. In order to achieve a specific capacity close to 167 mA h g^{-1} , the combination of the advantages of various approaches is promising for high performance LiCoPO_4 cathodes in LIBs. For instance, optimization of the electrolyte components coupled to the use of tailored surface coatings and/or ion doping

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can be an effective approach to improve the chemical stability of LiCoPO_4 and mitigate degradation reactions at high potentials, and with this, improve the capacity, coulombic efficiency and cycle life. Considering the availability of Co which could limit the industrial application of LiCoPO_4 in the future, further improvement of the electrochemical performance of LiCoPO_4 is highly desirable, since despite major advances, the cycle stability and rate performance is still unsatisfactory.

Chapter 5: Solvothermal water-diethylene glycol synthesis of LiCoPO_4 and effects of surface treatments on lithium battery performance

5.1 Introduction

Development of energy storage and conversion devices is vital to address the increasing energy crisis and ecological concerns in the 21 century.⁵⁴⁶ Although a variety of renewable energy technologies such as solar cells, fuel cells and biofuels have been developed.^{334, 547-549} The need for an efficient, cheap and reliable storage device is still challenging in using renewable energies.³³⁴ Electrical energy storage like lithium batteries and supercapacitors are effective strategies in making the energy output much cleaner.⁵⁵⁰⁻⁵⁵² As one of the most efficient energy storage devices, lithium-ion batteries (LIBs) are used in portable electronic devices and large-scale electric vehicles⁵⁻⁸ due to their high energy density, high power density and light weight compared with conventional batteries.^{1, 2, 4} The olivine-structured LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$) phases have been intensively investigated as cathode materials for LIBs,^{2, 58, 285, 286} especially LiFePO_4 which has been successfully commercialised.⁶⁰⁻⁶⁵ LiCoPO_4 has also attracted significant attention due to its high redox potential (4.8 V vs. Li/Li^+) and high theoretical capacity (167 mA h g^{-1}), making it a promising future cathode material for high-voltage LIBs.^{73-75, 310, 511, 553} However, use of LiCoPO_4 as a cathode in practical applications has been hindered by its unsatisfactory cycle stability and rate capability, which could be mainly attributed to its low electronic conductivity^{211, 285, 292-296} and poor Li^+ ionic conductivity²⁹⁶⁻³⁰¹ relating to the one-dimensional ion transport channel,²⁹¹ as well as to the decomposition of electrolytes under high potentials.⁷⁶

Efforts to overcome the low electronic and ionic conductivity of LiCoPO_4 have included: (1) Size reduction and morphology control, decreasing the particle size of LiCoPO_4 or tailoring its crystal growth orientation along the a-c plane to decrease the diffusion length of lithium ions in the insertion/extraction process;^{304, 309} (2) Surface modification (e.g. carbon coating), to enhance the electronic conductivity of the composite electrode by forming a conductive network among the LiCoPO_4 particles,^{291, 307} (3) Ion doping with cations on either Li or Co sites to enhance the intrinsic electronic/ionic conductivity of LiCoPO_4 although the mechanism is still in controversy.^{74, 308} Among these approaches, the combination of size reduction and conductive agent coating (e.g. carbon coating) is regarded as an effective method to enhance the specific capacity and rate capability of LiCoPO_4 cathode.³⁷¹ Reducing the particle size of LiCoPO_4 to the nanometer size range can shorten

the Li ion transport distance, and thus reduce the time required for Li ion diffusion within the bulk LiCoPO₄ material. Carbon coating not only improves the surface electrical conductivity of LiCoPO₄ composite, which alleviates electrode polarization, but also provides effective protection from chemical attack by HF produced via electrolyte decomposition at high potentials in LiPF₆ based electrolytes.³⁷¹ Metal oxides^{75, 237, 238, 240, 241} and metal nitrides^{14-16, 370} have been combined with other electrode materials to form structured composites with improved conductivity and stability. TiN and RuO₂ are suitable for this purpose as they have good electrical conductivity, and good chemical and thermal stability.^{246, 370}

It is significant to develop facile, easily scalable and controllable, time and energy saving synthetic routes to produce LiCoPO₄ with good electrochemical performance.⁵⁵³ Various synthesis methods such as hydrothermal/solvothermal syntheses,^{291, 304} sol-gel processes^{305, 306} and solid-state reactions^{302, 303} have been proposed. Hydrothermal/solvothermal synthesis is facile and easily scalable, with mild reaction conditions and advantages of producing nanomaterials with controllable particle sizes and morphologies.³⁸⁸ Mixing an organic solvent and water as a co-solvent has been employed in the solvothermal synthesis of LiCoPO₄.^{304, 309, 376, 382, 388} The solvent mixture can be beneficial for effectively tailoring the particle size of LiCoPO₄ due to the high viscosity of the organic solvent,^{376, 388} and the water component can promote the dissolution of the reagents.³⁸⁸ However, optimisation of solvothermal conditions to achieve LiCoPO₄ cathodes with good specific capacity and cycle performance is still challenging.

Herein, a novel, simple and fast solvothermal approach towards high-performance LiCoPO₄ at relatively low temperatures (180 °C) using diethylene glycol (DEG) as a co-solvent is presented, followed by thermal treatment under Ar, air, 5%H₂/N₂ or NH₃. Surface modification of LiCoPO₄ with conductive agents like TiN, RuO₂ and carbon has been investigated. Unusually in this work the electrochemical performance of samples produced by this method does not require the use of conductive coatings (e.g. carbon) to achieve good electrochemical performance.

5.2 Experimental

5.2.1 Synthesis

Hydrothermal and solvothermal methods^{554, 555} were used to produce LiCoPO₄:

Hydrothermal synthesis: LiOH·H₂O (6.29 g, 0.15 mol, 98% purity, Fisher Scientific) was dissolved in deionised water (45 cm³), and H₃PO₄ aqueous solution (3.44 cm³, 0.05 mol, 85.3 wt% assay, Fisher Scientific) was added. CoSO₄·7H₂O (14.05 g, 0.05 mol, ≥ 99% purity, Sigma Aldrich) was dissolved in water (45 cm³) and added slowly to the LiOH solution with constant stirring, during which time a

blue suspension formed. The precursor solution was heated in a Parr 4748 Teflon-lined autoclave (125 cm³) at 180 °C for 6 h. The precipitate was then washed with deionized water and ethanol, and dried at 80 °C for 5 h under vacuum. The resulting material, which has been designated as LCP(HT), was heated at 3 °C min⁻¹ to 650 °C and maintained for 6 h under air, Ar, NH₃ or 5% H₂/N₂ to crystallise LiCoPO₄.

Solvothermal synthesis : LiOH·H₂O (0.629 g, 0.015 mol) was dissolved in deionised water (5 cm³), then DEG (diethylene glycol, 40 cm³, ≥ 99% purity, Sigma Aldrich) and H₃PO₄ aqueous solution (0.344 cm³, 0.005 mol) were added. CoSO₄·7H₂O (1.405 g, 0.005 mol) was dissolved in water (5 cm³) with DEG (20 cm³) and added slowly to the LiOH solution with constant stirring, during which time a blue suspension formed. The precursor solution was heated in a Parr 4748 Teflon-lined autoclave (125 cm³) at 180 °C for 6 h. The precipitate was then washed with deionized water and ethanol, and dried at 80 °C for 5 h under vacuum. The resulting material, which has been designated as LCP(ST), was heated at 3 °C min⁻¹ to 650 °C and maintained for 6 h under compressed air to crystallise LiCoPO₄.

Optimised solvothermal synthesis: The phase behaviour during charging of a sample made in this way has been reported.³³¹ LiOH (0.359 g, 0.015 mol, Sigma Aldrich) was dissolved/dispersed in 45 ml deionised water/diethylene glycol (H₂O/DEG) mixture, then H₃PO₄ aqueous solution (0.344 cm³, 0.005 mol, 85.3 wt% assay, Fisher Scientific) was added. CoSO₄·7H₂O (1.405 g, 0.005 mol, ≥ 99% purity, Sigma Aldrich) was dissolved in 25 ml H₂O/DEG mixture and added slowly to the LiOH solution with constant stirring, during which time a blue/purple suspension formed. The volume ratio of H₂O/DEG was set as pure H₂O, 6:1, 3:1, 1:1, 1:3, 1:6 and pure DEG. The precursor solution was heated in a Parr 4748 Teflon-lined autoclave (125 cm³) at 180 °C for 10 h. The precipitate was then washed with deionized water and ethanol, and dried at 80 °C for 5 h under vacuum. The resulting material was heated at 5 °C min⁻¹ to 600 °C and maintained for 3 h under Ar, air, NH₃ or 5% H₂/N₂ to crystallise LiCoPO₄.

To obtain carbon or RuO₂ coated LiCoPO₄ the uncrystallised or pre-fired LiCoPO₄ (0.3 g, 1.87 mmol) was manually ground in a pestle and mortar with sucrose (C₆H₁₂O₆, 0.0375 g, 0.11 mmol, Fisher Scientific) or ruthenium(III) chloride hydrate (RuCl₃·xH₂O, 0.0246g, 0.12 mmol, Sigma Aldrich) to obtain a uniform mix that was then heated under Ar as described above. The products were black powders and were ground before further characterisation. TiN modified LiCoPO₄ powders were prepared using a propylamine cross-linking sol-gel process^{265, 370, 395, 399} under nitrogen using glove box or Schlenk line conditions. Ti(NMe₂)₄ (0.21 cm³, 0.9 mmol, prepared from TiCl₄ and LiNMe₂) was dissolved in dry THF (7.5 cm³, distilled from sodium/benzophenone), and added to 0.5 g dry LiCoPO₄ powder. ⁿPrNH₂ (0.15 cm³, 1.8 mmol, distilled from BaO) was slowly added. The solution gradually

changed colour from yellow to red-orange. The suspension was stirred at room temperature for ~16 h and dried in vacuo to form a sticky powder. This was heated under Ar or NH₃ as described above for LiCoPO₄ samples.

5.2.2 Characterisation and electrochemistry

Powder X-ray diffraction used a Bruker D2 Phaser with CuK_α radiation, and data was fitted using the GSAS package.²⁷⁰ Scanning electron microscopy (SEM) used a JEOL JSM-6500F (30 kV). Transmission electron microscopy (TEM) used a FEI Tecnai T12 (120 kV) with energy-dispersive X-ray (EDX) analysis (Genesis Spectrum). Brunauer-Emmett-Teller (BET) surface area and pore size distribution measurements via N₂ physisorption analysis were carried out with a Micromeritics TriStar II analyser. Electrochemical testing used a Biologics VMP-2 multichannel potentiostat. X-ray photoelectron spectroscopy (XPS) was collected with a two chamber Thermo K-alpha spectrometer with a monochromated Al K-alpha X-ray source (1486.6 eV) in constant analyser energy mode. Sample charging was prevented by use of a dual beam flood gun. X-rays were focused to a 400 μm spot at the sample surface. High resolution core peak spectra were recorded at 50 eV pass energy. Spectra were analysed using Casa XPS software. The binding energy scale was calibrated from the carbon at 285.0 eV. Core peaks were analysed with a nonlinear Shirley-type background.²⁰⁵ The peak positions and areas were optimized using a weighted least-square fitting method with 70% Gaussian and 30% Lorentzian line shapes. Several spectral analyses were applied at different positions for each sample to ensure the results were statistically reliable. Electronic and ionic conductivity was determined from the current-voltage measurement and electrochemical impedance spectroscopy on gold-coated sintered LiCoPO₄ disks (11 mm in diameter and ~0.5 mm in thickness).²¹¹⁻²¹³ Current-voltage plots were collected at 20 mV s⁻¹ over the range of -0.3 to +0.3 V (or larger voltage ranges) at room temperature. Electrochemical impedance spectroscopies were collected at 500 mV in the frequency range of 0.1 Hz to 200 kHz at room temperature.

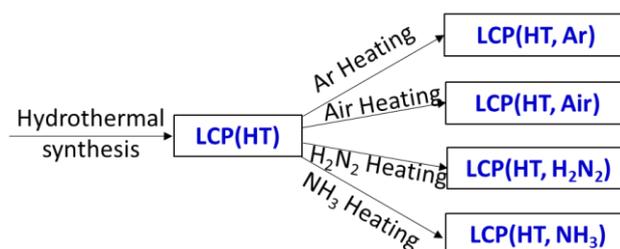
Electrode pellets for use in lithium half cells were prepared by manually mixing the LiCoPO₄ or TiN/carbon/RuO₂ coated LiCoPO₄ powders (75 wt%) with acetylene black (Shawinigan Black, 20 wt%) and polytetrafluoroethylene (6C-N, DuPont, 5 wt%) in a pestle and mortar. The resulting solid paste was hand rolled (Durston Rolling Mill) into a film of ~90 μm thickness and cut into circular disks with diameter of 11 mm. The pellet (7.5:2:0.5) was then dried at 120 °C in vacuo for 12 h to obtain the cathode with a typical mass of ~0.022 g. Alternatively electrode inks were prepared by mixing the LiCoPO₄ powders (80 wt%) with acetylene black (Shawinigan Black, 10 wt%) and poly(vinylidene fluoride) (10 wt%) dissolved in N-methyl-pyrrolidone. The slurry was cast onto Al foil (125 μm thick, Temper annealed, 99.0 % purity, Advent Research Materials) and dried at 120 °C in vacuum for 12 h. The foil was cut into circular discs with a diameter of 11 mm and pressed at 10

tons to obtain the ink (8:1:1) with a typical mass of ~ 0.037 g. The ink (7.5:2:0.5) was made by mixing three materials mentioned above with the weight ratio of 7.5:2:0.5. Swagelok cells were assembled in an argon-filled glove box with lithium foil (Rockwood Lithium GmbH) anodes and glass microfiber filter (Whatman, GF/F grade) separators soaked in 8 drops (~ 0.4 ml) of 1 mol dm^{-3} LiPF_6 in ethylene carbonate/ ethylmethyl carbonate (EC:EMC = 3:7 in weight) electrolyte (BASF, LP57). Galvanostatic testing was carried out at 25°C at various rates of charge/discharge (e.g. 0.1 C for a theoretical specific capacity of 167 mA h g^{-1} corresponds to a specific current of 16.7 mA g^{-1}) within the voltage range of $3.5\text{-}5 \text{ V}$ (vs. Li/Li^+).

5.3 Initial attempt to hydrothermal/solvothermal syntheses of LiCoPO_4 , and their electrochemical performance

5.3.1 Effect of heating environment on LiCoPO_4 prepared by hydrothermal synthesis

LiCoPO_4 samples were made by hydrothermal method, and heated under Ar, compressed air, 5% H_2/N_2 and NH_3 , respectively (Scheme 5-1).



Scheme 5-1 Hydrothermal synthesis and heating environment to LiCoPO_4 and sample labels.

Figure 5-1 shows the initial charge/discharge curves at 0.1C and cycle stability of the LCP(HT, Ar) sample which was made into inks or pellets as electrodes. The results show that LCP(HT, Ar) pellet (7.5:2:0.5) exhibited a larger capacity than inks, so that pellet type electrode was chosen to be used in the testing that followed.

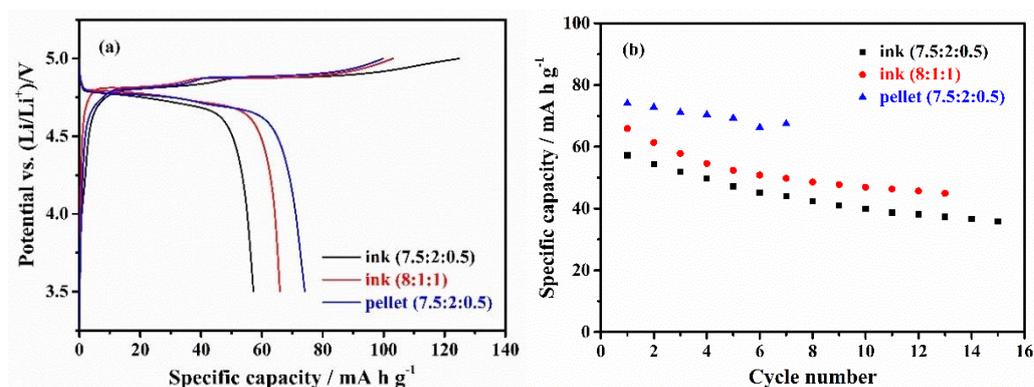


Figure 5-1 (a) The initial cycle voltage profile vs specific capacity and (b) specific capacity vs cycle number of the LCP(HT, Ar) which was made into inks or pellets as electrodes in Li half cells, cycled between 3.5 and 5 V for 7-15 cycles at a current rate of 0.1C.

Figure 5-2 shows the Rietveld fits to the XRD data of LCP(HT, Ar), LCP(HT, Air), LCP(HT, H_2N_2) and LCP(HT, NH_3) samples, which resulted in similar lattice parameters (Table 5-1) to those in the literature for LiCoPO_4 ⁵⁵⁶, indicating that the heating environment did not affect the crystal structure of LiCoPO_4 . The average LiCoPO_4 crystallite sizes are 119-191 nm.

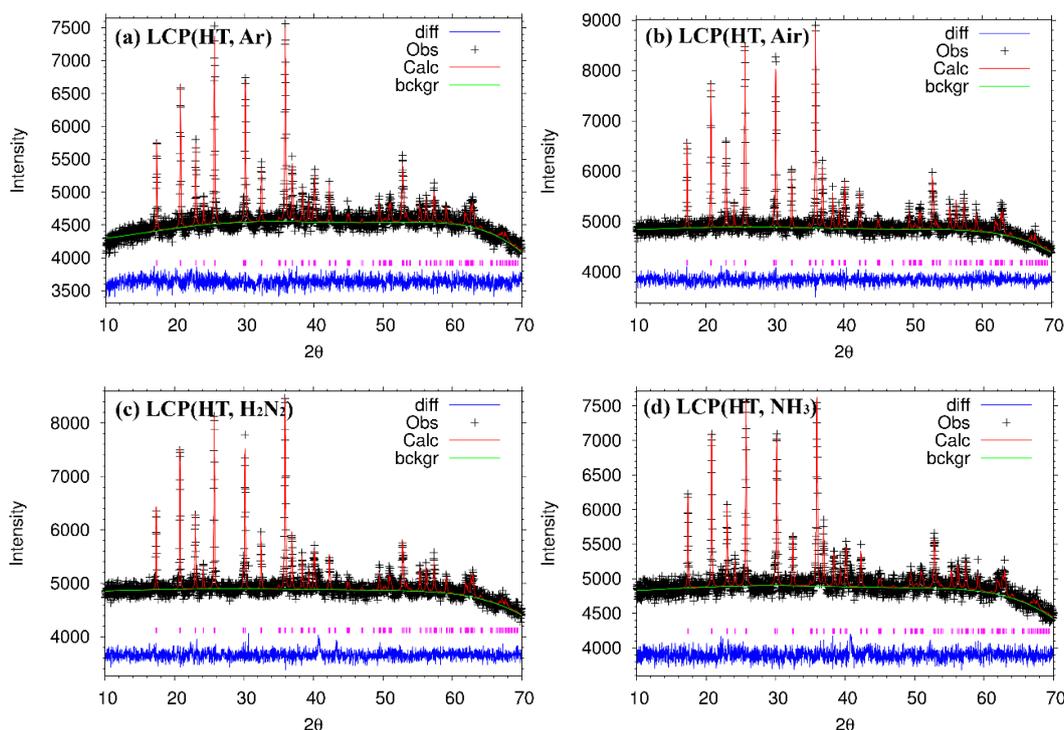


Figure 5-2 Rietveld fits to the XRD patterns of (a) LCP(HT, Ar) ($R_{\text{wp}} = 1.58\%$ and $R_{\text{p}} = 1.27\%$), (b) LCP(HT, Air) ($R_{\text{wp}} = 1.49\%$ and $R_{\text{p}} = 1.18\%$), (c) LCP(HT, H_2N_2) ($R_{\text{wp}} = 1.55\%$ and $R_{\text{p}} = 1.22\%$) and (d) LCP(HT, NH_3) ($R_{\text{wp}} = 1.50\%$ and $R_{\text{p}} = 1.19\%$) (sample labels explained in Scheme 5-1). The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for LiCoPO_4 with space group $Pnma$.

Table 5-1 Lattice parameters and crystallite sizes obtained from the Rietveld fits to the XRD patterns of the LiCoPO_4 samples (labels explained in Scheme 5-1).

Sample	a / Å	b / Å	c / Å	Crystallite size / nm
LCP(HT, Ar)	10.2046(5)	5.9214(3)	4.7020(2)	119(3)
LCP(HT, Air)	10.2026(4)	5.9198(2)	4.7001(2)	191(5)
LCP(HT, H_2N_2)	10.2009(4)	5.9216(2)	4.6994(2)	190(6)
LCP(HT, NH_3)	10.2014(6)	5.9239(3)	4.7022(3)	163(6)

Figure 5-3 shows the initial charge/discharge curves at 0.1C and cycle stability of LiCoPO_4 fired in different gases. The results show that the discharge capacity of LCP(HT, Air) (92.6 mA h g^{-1} in the initial cycle) is better than others, but it is not good enough when compared to the theoretical capacity (167 mA h g^{-1}) of LiCoPO_4 .

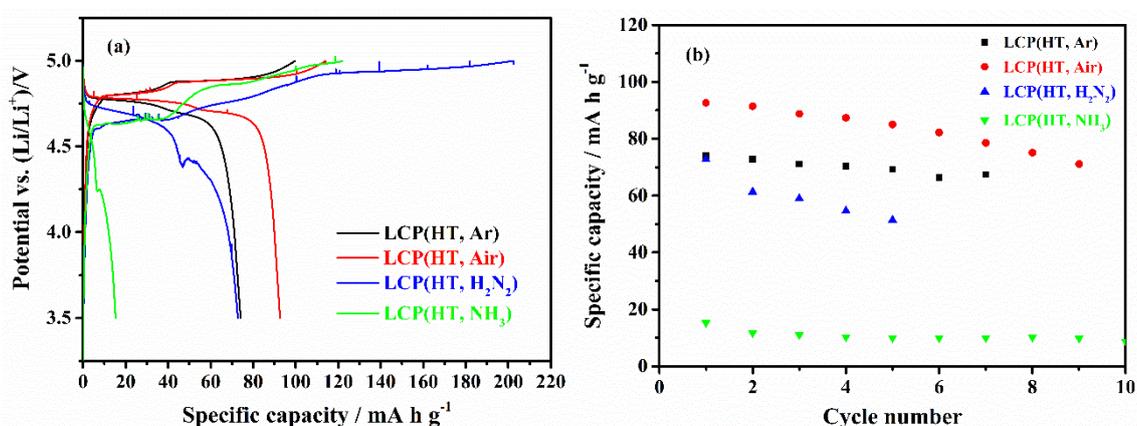


Figure 5-3 (a) The initial cycle voltage profile vs specific capacity and (b) specific capacity vs cycle number of the LiCoPO_4 / Li half cells, under galvanostatic cycling between 3.5 and 5 V at 0.1C (sample labels explained in Scheme 5-1).

5.3.2 Microstructure, morphology and electrochemistry of LiCoPO_4 prepared by hydrothermal/solvothermal syntheses

LiCoPO_4 samples were prepared by hydrothermal and solvothermal syntheses, followed by heating in air (denoted as LCP(HT, Air) and LCP(ST, Air), respectively) to compare their microstructure, morphologies and electrochemical performance.

Figure 5-4 shows the Rietveld fits to the XRD data of LCP(HT, Air) and LCP(ST, Air) samples, which yielded typical LiCoPO_4 lattice parameters (Table 5-2), suggesting that olivine structured LiCoPO_4 with $Pnma$ space group have been successfully produced via hydrothermal and solvothermal syntheses. There are no impurity elements in LCP(HT, Air) and LCP(ST, Air) according to the EDS spectra (Figure 5-5). The average crystallite sizes of LCP(HT, Air) and LCP(ST, Air) are 124 and 155 nm, which were consistent with TEM images (Figure 5-5).

Table 5-2 Lattice parameters and crystallite sizes obtained from the Rietveld fits to the XRD patterns of LiCoPO₄ samples.

Sample	a / Å	b / Å	c / Å	Crystallite size / nm
LCP(HT, Air)	10.1979(5)	5.9216(3)	4.6988(3)	124(3)
LCP(ST, Air)	10.2001(3)	5.9234(2)	4.6999(2)	155(3)

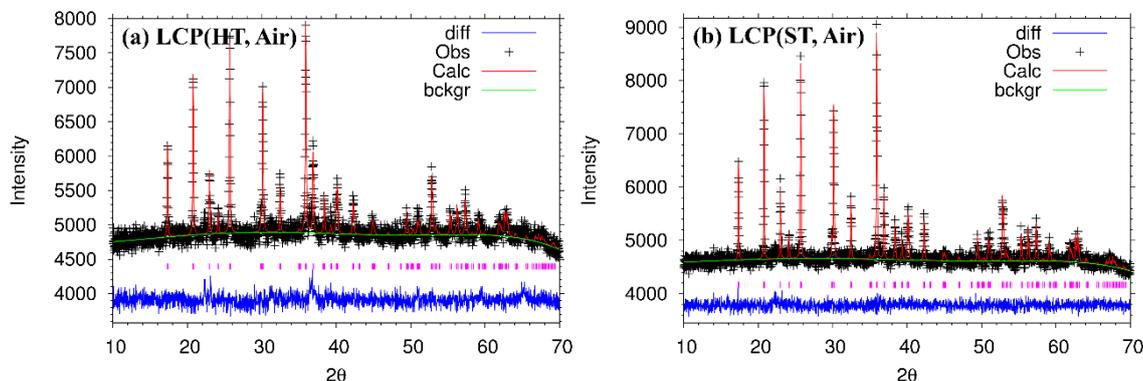


Figure 5-4 Rietveld fits to the XRD patterns of (a) LCP(HT, Air) ($R_{wp} = 1.62\%$ and $R_p = 1.26\%$) and (b) LCP(ST, Air) ($R_{wp} = 1.51\%$ and $R_p = 1.20\%$). The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for LiCoPO₄ with space group *Pnma*.

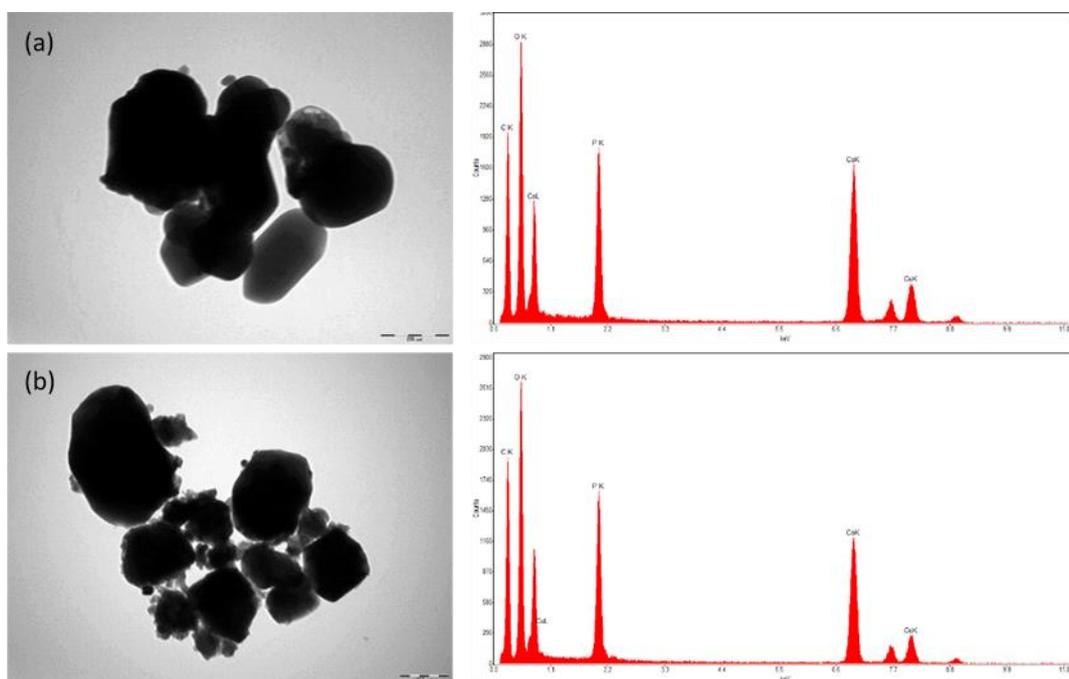


Figure 5-5 TEM images and EDS spectra of (a) LCP(HT, Air) (Scale bar = 200 nm) and (b) LCP(ST, Air) (Scale bar = 200 nm).

Figure 5-6 shows the initial charge/discharge curves at 0.1C and cycle stability of LiCoPO₄ synthesized by hydrothermal or solvothermal method and fired in compressed air. The results show

that the initial discharge capacity of LCP(ST, Air) is 127 mA h g⁻¹, which is higher than LCP(HT, Air) (107 mA h g⁻¹), but it drops quickly in the subsequent cycles. Thus, the hydrothermal/solvothermal methods need to be optimised in order to obtain LiCoPO₄ with good specific capacity and cycle stability.

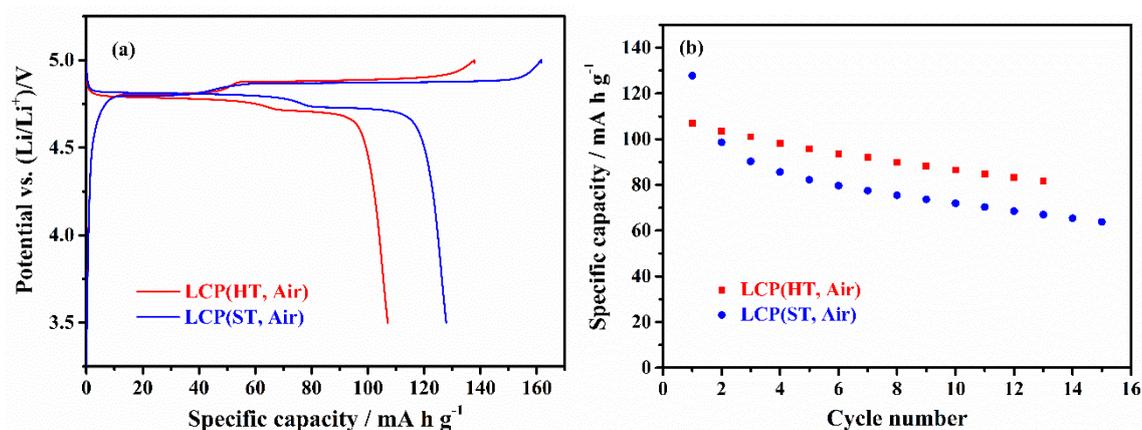


Figure 5-6 (a) The initial cycle voltage profile vs specific capacity and (b) specific capacity vs cycle number of the LiCoPO₄ / Li half cells, under galvanostatic cycling between 3.5 and 5 V at 0.1C.

5.3.3 Summary

The initial attempt to hydrothermal/solvothermal syntheses of LiCoPO₄ is presented, followed by thermal treatment under Ar, Air, 5% H₂/N₂ or NH₃. The electrochemical performance of these LiCoPO₄ samples shows the hydrothermal/solvothermal synthesis still needs further improvement. Herein, a novel, simple and fast solvothermal approach towards high-performance LiCoPO₄ will be presented in the following section.

5.4 Solvothermal water-diethylene glycol synthesis of LiCoPO₄ and effects of surface treatments

LiCoPO₄ samples were prepared by an optimised solvothermal method as described in experimental section. First, a systematic study on the effect of the solvents and heating environment to optimise the solvothermal conditions was performed. Then, LiCoPO₄ samples were coated with TiN, carbon or RuO₂ with a variety of processing conditions and thicknesses to determine whether the expected conductivity enhancement and increased surface stability improved the electrochemical behaviour of the materials.

5.4.1 Effect of solvent on LiCoPO₄ morphology in solvothermal synthesis

Uncoated LiCoPO₄ samples were produced using H₂O/DEG solvent mixtures with various volume ratios, followed by firing at 600 °C in a typical Ar environment, to determine the effect of solvents on their morphologies. The volume ratio of H₂O/DEG in solvothermal synthesis was set as pure H₂O, 6:1, 3:1, 1:1, 1:3, 1:6 and pure DEG, and the corresponding samples are referred to as LCP-H₂O(Ar), LCP-6:1(Ar), LCP-3:1(Ar), LCP-1:1(Ar), LCP-1:3(Ar), LCP-1:6(Ar), LCP-DEG(Ar), respectively. The heating temperature affects purity, crystallite/particle size distribution and specific capacity of LiCoPO₄.³⁷⁰ Most successful previous studies produce LiCoPO₄ samples at 550-700 °C,^{309, 383, 385, 407} and in this study samples were fired at 600 °C.

The SEM images (Figure 5-7) show the morphologies of LiCoPO₄ samples obtained using various ratios of H₂O/DEG. The particle size of LiCoPO₄ decreased from ~10 μm to ~80 nm with increasing DEG content (Figure 5-7 a-g), and its BET surface area increased from 1.8 to 22.6 m² g⁻¹ (Figure 5-7 h). As the ratio of H₂O/DEG decreases to less than 1:3, the particle size distribution of LiCoPO₄ becomes homogeneous (Figure 5-7 f and g). LiCoPO₄ particles readily grow to large sizes in hydrothermal (pure water) synthesis.^{291, 361, 363, 372} The pore size distribution of LiCoPO₄ samples obtained using various ratios of H₂O/DEG were investigated via N₂ physisorption analysis (Figure 5-8). The isotherms of LiCoPO₄ samples belong to the type-II, which is reflective of nonporous or macroporous structure. The density functional theory (DFT) pore size distributions calculated from the adsorption curves reveal that the main pore sizes of LiCoPO₄ samples are 4-20 nm. These mesopores are created by the interfaces between nonporous LiCoPO₄ particles. The control of particles sizes in solvent mixtures has been attributed to the increased viscosity of the solvent mixture when increasing DEG concentration, which can reduce mass transport to growing crystallite surfaces, thus results in decreasing LiCoPO₄ particle size.^{362, 376} Also, the solubility of the precursors decreases as the solvent mix becomes less polar, which increases the nucleation rate during the solvothermal process.³⁰⁹ For a given amount of precursor, more nuclei means less matter for each nucleus.^{309, 557} Therefore, larger nucleation rate in solvothermal process results in smaller LiCoPO₄ particle size.

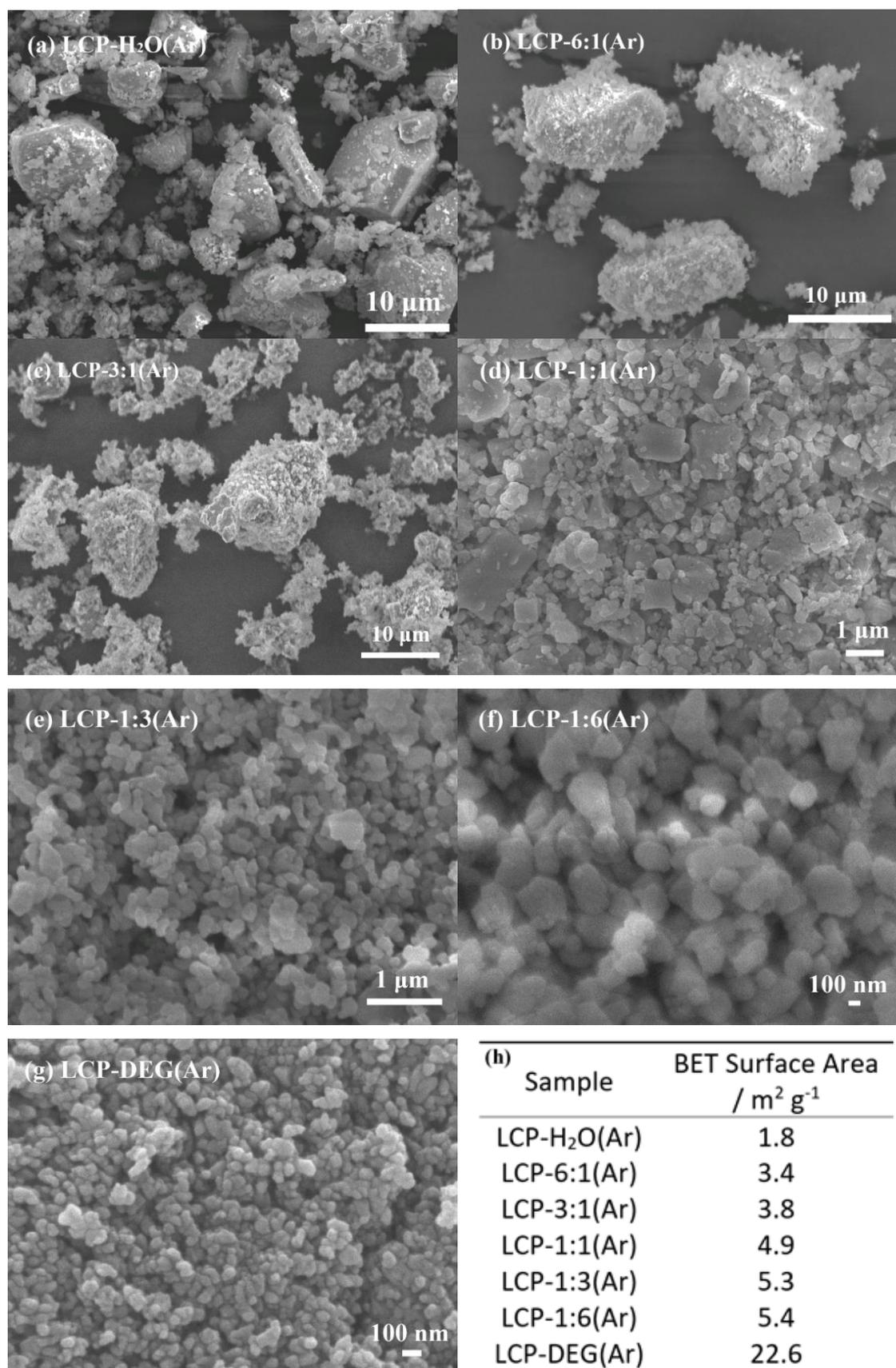


Figure 5-7 (a-g) SEM images of LiCoPO₄ samples synthesised by solvothermal method, using H₂O/DEG solvent mixture with various volume ratios, followed by firing at 600 °C in Ar. (h) BET surface area of LiCoPO₄ samples.

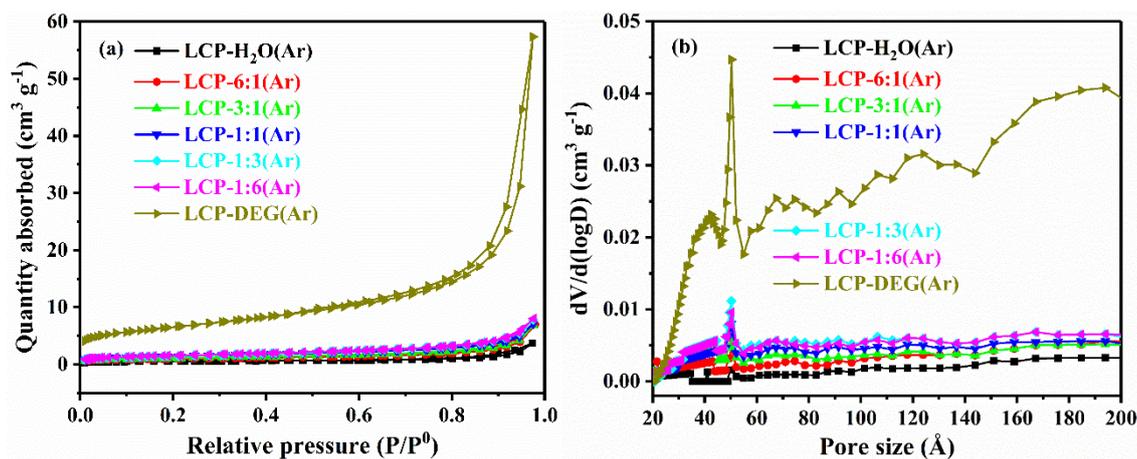
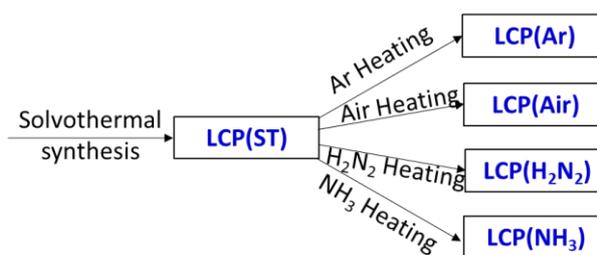


Figure 5-8 (a) N_2 physisorption isotherms and (b) pore size distribution (DFT method) curves of $LiCoPO_4$ samples obtained using various ratios of H_2O/DEG .

A review of previous work on $LiCoPO_4$ suggested that good rate capability is more likely to be achieved by $LiCoPO_4$ with particle size less than 200 nm.⁵⁵³ For example, Wei et al. synthesized carbon coated $LiCoPO_4$ with particle size of 150 nm via a microwave heating method. This nanostructured $LiCoPO_4$ provides a specific capacity of 144 mA h g^{-1} at 0.1 C, with reasonable rate capability of 116, 90 and 71 mA h g^{-1} at 5, 10 and 20 C, respectively.⁴⁴¹ In this work, sample LCP-1:6(Ar) and LCP-DEG(Ar) showed homogeneous particle size distribution with nanoparticle of less than 200 nm. This small particle size can reduce the length of Li-ion migration paths, and facilitate easier Li-ion transfer in $LiCoPO_4$ crystals, thus enhancing the rate performance of LIBs.^{309, 362, 425} However, nanosized $LiCoPO_4$ particles with high surface area can enlarge the electrode/electrolyte interface area, which leads to undesirable electrode/electrolyte by-reactions, thus resulting in a poor cycle stability.⁶¹ Hence, sample LCP-1:6(Ar) with particle size of ~ 150 nm and a relatively small surface area of 5.4 $m^2 g^{-1}$ (compared to LCP-DEG(Ar) with surface area of 22.6 $m^2 g^{-1}$) was chosen for the following studies.

5.4.2 Effect of heating environment on bare $LiCoPO_4$

Ar or air are typical heating environments in thermal treatment to crystallise $LiCoPO_4$, but the intrinsic role and effects of various heating gases on $LiCoPO_4$ has still not been fully ascertained and remains controversial.⁵⁵³ NH_3 and 5% H_2/N_2 are typical heating gases to coat TiN and carbon onto electrode materials.^{370, 371, 553} Thus, it is important to evaluate whether heating in NH_3 or 5% H_2/N_2 caused a deterioration in the $LiCoPO_4$ properties. In this section, uncoated $LiCoPO_4$ samples were produced by using the 1:6 (v/v) H_2O/DEG co-solvent optimised above, and firing at 600 °C in Ar, air, 5% H_2/N_2 or NH_3 to determine the effect of heating environment on their behaviour. Scheme 5-2 shows the labels used for different samples.



Scheme 5-2 Solvothermal synthesis to prepare LiCoPO₄, using 1:6 (v/v) H₂O/DEG co-solvent, followed by firing at 600 °C in Ar, air, 5% H₂/N₂ or NH₃.

The X-ray diffraction peaks of the resulting LiCoPO₄ samples (Figure 5-9) were consistent with the standard olivine LiCoPO₄ (JCPDS card no. 85-0002, space group *Pnma*) as expected. Table 5-3 shows the crystallographic data of LiCoPO₄ samples. The Rietveld fits²⁷⁸ to this XRD data (Figure 5-10) resulted in similar lattice parameters (Table 5-3) to those in the literature for LiCoPO₄ indicating that the heating environment did not affect the crystal structure of LiCoPO₄.³¹¹ The Lorentzian peak broadening in the Rietveld fit indicated average LiCoPO₄ crystallite sizes of 119-132 nm. These were consistent with TEM (Figure 5-11) and SEM (Figure 5-12) images of LiCoPO₄ fired in Ar, air, 5%H₂/N₂ and NH₃, which showed particle sizes of ~150 nm. No hydrogen and nitrogen (<0.1 wt.%) are detectable according to the microanalysis results (Table 5-3) with a negligible amount of carbon (< 0.5 wt.%) in the LiCoPO₄ samples.

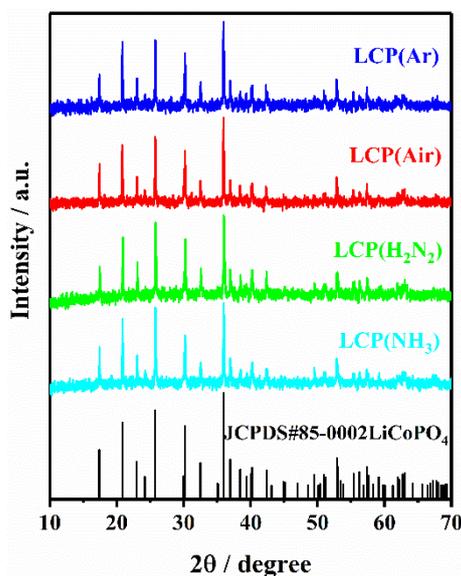


Figure 5-9 XRD patterns of LiCoPO₄ samples heated under Ar, air, 5% H₂/N₂ and NH₃, respectively, at 600 °C (labels explained in Scheme 5-2). The black stick pattern denotes the literature positions and intensities of LiCoPO₄ reflections.³⁶⁸

Table 5-3 Lattice parameters and crystallite sizes obtained from the Rietveld fits to the XRD patterns, and combustion analysis (C, H, N) results of the LiCoPO_4 samples (labels explained in Scheme 5-2).

Sample	a / Å	b / Å	c / Å	Crystallite size / nm	% C	% H	% N
LCP(Ar)	10.2076(7)	5.9248(3)	4.7015(3)	132(5)	0.39	<0.10	<0.10
LCP(Air)	10.2060(6)	5.9248(3)	4.7013(3)	120(3)	0.38	<0.10	<0.10
LCP(H_2N_2)	10.2088(7)	5.9277(4)	4.7038(3)	119(4)	0.49	<0.10	<0.10
LCP(NH_3)	10.2067(7)	5.9257(4)	4.7004(3)	129(5)	0.43	<0.10	<0.10

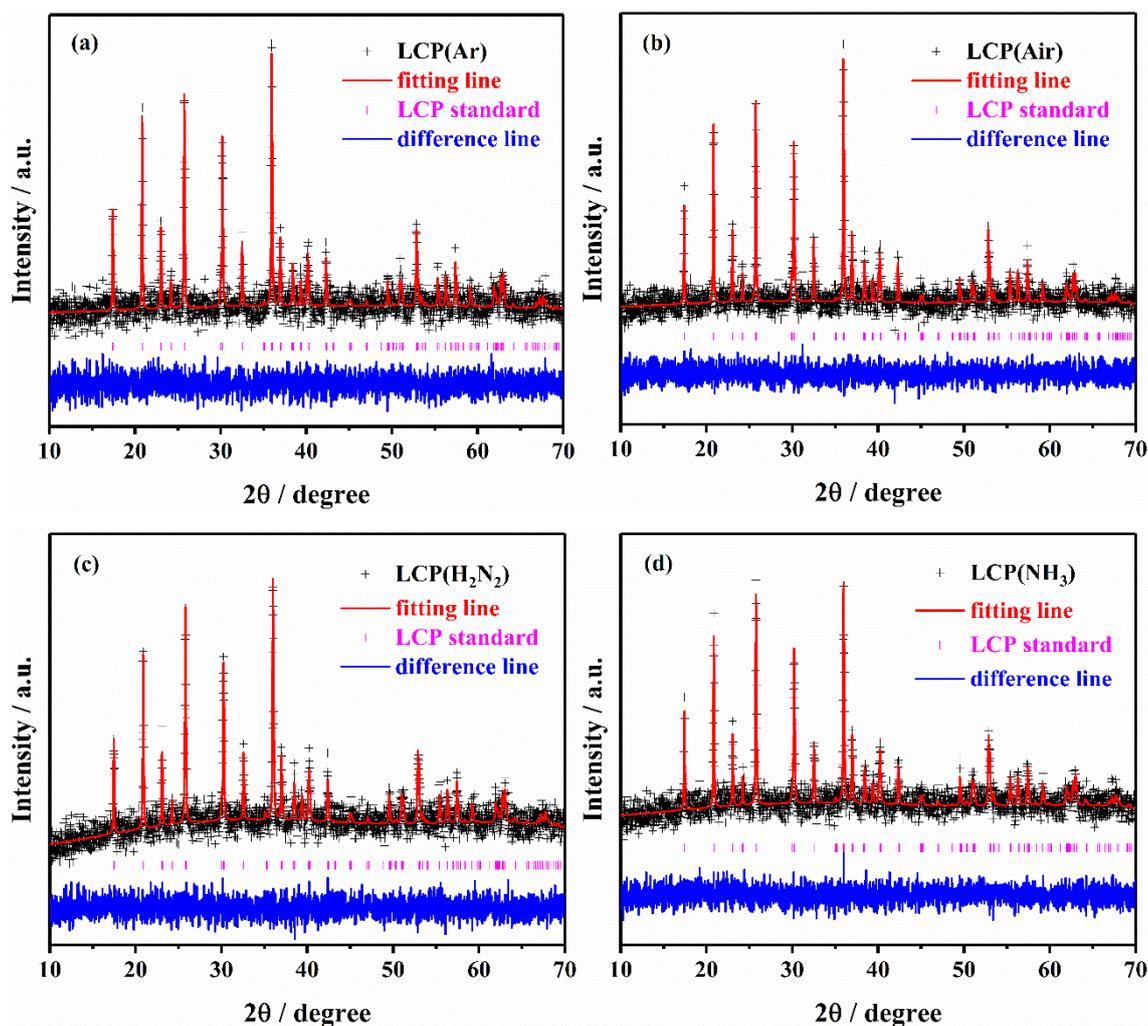


Figure 5-10 Rietveld fits to the XRD patterns of (a) LCP(Ar) ($R_{wp} = 2.81\%$ and $R_p = 2.25\%$), (b) LCP(Air) ($R_{wp} = 2.78\%$ and $R_p = 2.22\%$), (c) LCP(H_2N_2) ($R_{wp} = 2.72\%$ and $R_p = 2.15\%$) and (d) LCP(NH_3) ($R_{wp} = 2.65\%$ and $R_p = 2.12\%$) samples (sample labels explained in Scheme 5-2). The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for LiCoPO_4 with space group $Pnma$.

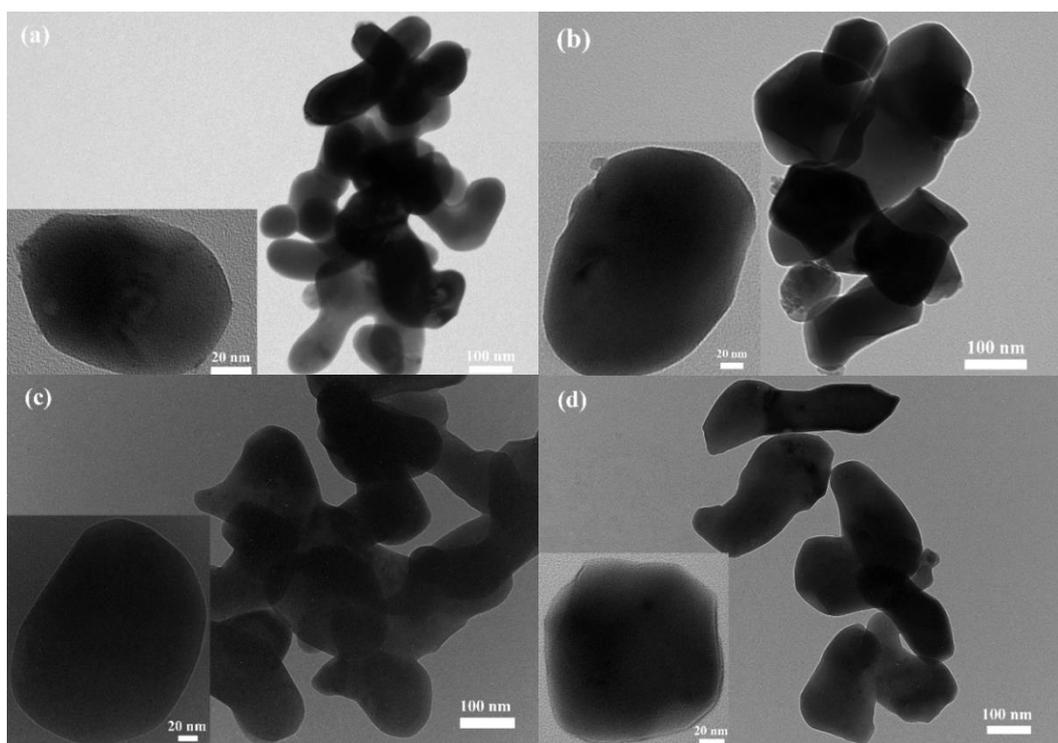


Figure 5-11 TEM images of (a) LCP(Ar), (b) LCP(Air), (c) LCP(H₂N₂) and (d) LCP(NH₃) (scale bar = 100 nm). (Inset) Magnified TEM images of single LiCoPO₄ particle (scale bar = 20 nm). Sample labels are explained in Scheme 5-2.

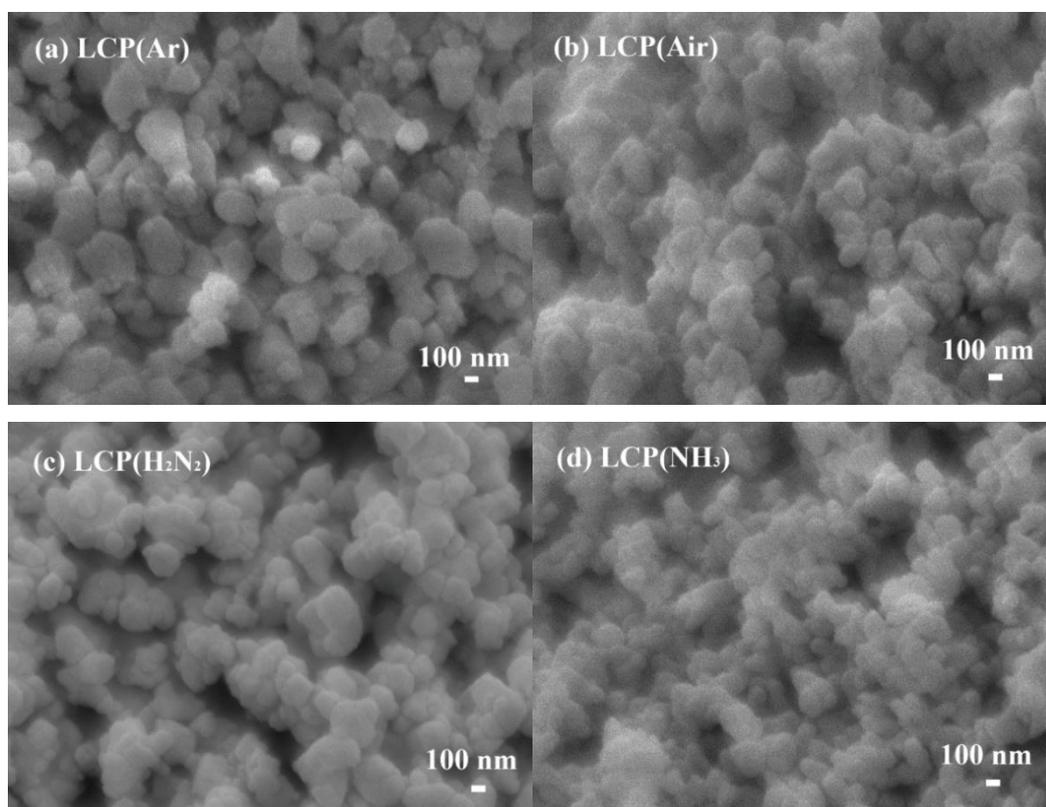


Figure 5-12 SEM images of (a) LCP(Ar), (b) LCP(Air), (c) LCP(H₂N₂) and (d) LCP(NH₃) (scale bar = 100 nm). Sample labels are explained in Scheme 5-2.

The electrochemical performance of LiCoPO_4 samples was assessed by galvanostatic cycling of Li half cells. The initial charge/discharge curves and the variations in discharge capacity and Coulombic efficiency (calculated by $\frac{\text{discharge capacity}}{\text{charge capacity}} \times 100\%$ at each cycle) over the first 40 cycles of LiCoPO_4 fired in Ar, air, 5% H_2/N_2 and NH_3 are shown in Figure 5-13. LCP(Ar), LCP(Air), LCP(H_2/N_2) and LCP(NH_3) had initial discharge capacities of 147, 130, 139 and 132 mA h g^{-1} , respectively. The capacity of LCP(Ar) decayed gradually with continuous cycling, retaining 102 mA h g^{-1} after 40 cycles, and 88 mA h g^{-1} after 57 cycles. The low Coulombic efficiency values in the first cycle for these samples are caused by the decomposition of the electrolyte during charge at high potentials.^{319, 388} The Coulombic efficiency of LCP(Ar), which improved upon cycling, was 92% in the second cycle and maintains values higher than 95% after five cycles. LiCoPO_4 fired in air or in reducing gases had lower initial discharge capacities and lost capacity more rapidly on cycling. A comparison of relevant articles using a hydrothermal/solvothermal methodology in the synthesis of LiCoPO_4 olivine phosphate cathodes is presented in Table 5-4. The obtained specific capacity and cycle stability of uncoated LCP(Ar) in this case is comparable or higher than most previous studies, even though in most of these reports LiCoPO_4 has been optimised with conductive coatings (e.g. carbon). Overall the results suggested that Ar firing was the most effective heat treatment to apply for the crystallisation of LiCoPO_4 , but since air firing is also common in this system,^{316, 353, 407, 412} both samples as well as uncrystallised LiCoPO_4 were carried forward to test the surface modification of LiCoPO_4 with TiN , RuO_2 and carbon.

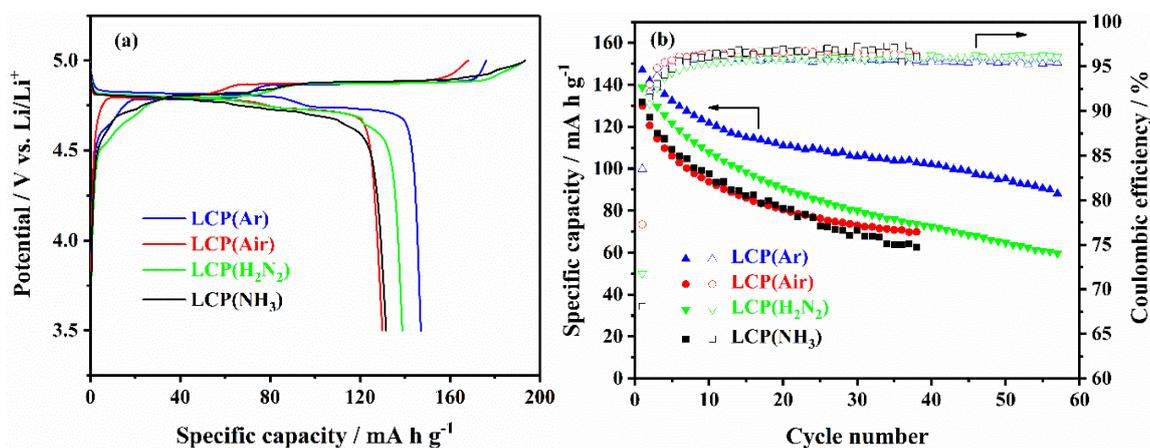


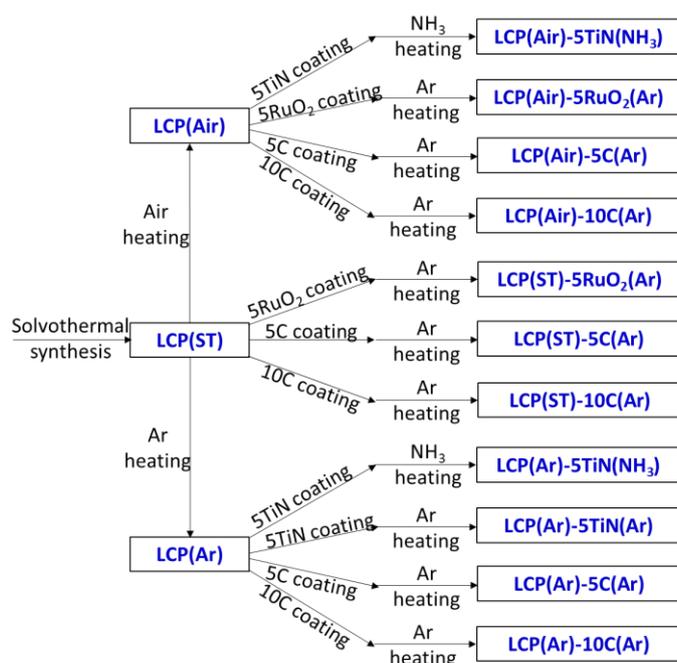
Figure 5-13 (a) The initial cycle voltage profile vs specific capacity and (b) specific capacity and coulombic efficiency vs cycle number of $\text{LiCoPO}_4/\text{Li}$ half cells under galvanostatic cycling between 3.5 and 5 V at 0.1C (sample labels explained in Scheme 5-2).

Table 5-4 Morphologies and electrochemical behaviours of LiCoPO₄ samples synthesised under hydrothermal/solvothermal conditions (shown in chronological order with the most recent study first).

Morphology, particle size	Rate performance, mA h g ⁻¹	Cycle stability	Ref.
Nanoparticles, 150 nm	147(0.1C)	102 mA h g ⁻¹ at 0.1 C after 40 cycles	This work
Irregular nanoparticle	160(0.1C) 138(1C) 120(2C) 88(5C)	138 mA h g ⁻¹ at 0.1 C after 100 cycles	385
Hexagonal platelets, 200 x 100 x 50 nm to 1.2 x 1.2 x 0.5 μm	136(0.1C) 125(0.2C) 115(0.5C) 105(1C) 95(2C)	108 mA h g ⁻¹ at 0.5 C after 15 cycles	376
Square, rhombic and hexagonal platelets, 600-800 x 400-600 x 100-150 nm to 9 x 7 x 3 μm	141(0.1C) 135(0.2C) 130(0.5C) 123(1C) 112(2C)	125 mA h g ⁻¹ at 0.5 C after 15 cycles	304
Spherical or oblong spheroid, 50-250 nm	145(0.1C)	74 mA h g ⁻¹ at 0.1 C after 20 cycles	364
Irregular particles, 390 nm-2.8 μm	135(0.1C) 132(0.5C) 125(1C) 117(2C) 101(5C)	70 mA h g ⁻¹ at 0.1 C after 30 cycles	291
Irregular particles, 200 nm-1 μm	155(0.1C) 129(1C) 98(5C) 70(10C) 51(20C)	141 mA h g ⁻¹ at 0.1 C after 80 cycles	383
Particles, 100-500 nm	97(0.1C)	82 mA h g ⁻¹ at 0.1 C after 20 cycles	368
Particles, 500 nm-10 μm	124(0.1C), 111(0.5C), 100(1C) 85(2C) 51(5C)	103 mA h g ⁻¹ at 0.1 C after 100 cycles	309
Hexagonal platelets, 400-600 x 700-800 x 100-220 nm	137(0.1C) 114(0.5C) 97(2C)	78 mA h g ⁻¹ at 0.5 C after 100 cycles	388
Hexagonal platelets, thickness <200 nm	120(0.1C) 85(0.5C) 75(1C)	90 mA h g ⁻¹ at 0.1 C after 10 cycles	382
Flower-like, 5-10 μm (compose of plate-like, 1-2 μm x 200 nm)	107(0.05C) 60(2C)	30 mA h g ⁻¹ at 0.05 C after 20 cycles	372
Hexagonal/octagonal platelet, thickness of 50-100 nm	95(0.1C) 76(0.5C)	75 mA h g ⁻¹ at 0.1 C after 10 cycles	366, 367
Nanoparticles agglomeration, 2-3 μm	105(0.2C)	95 mA h g ⁻¹ at 0.2 C after 30 cycles	392
Hedgehog-like, 5-8 μm (compose of nanorods, 40 nm x 1 μm)	136(0.1C) 85(5C)	124 mA h g ⁻¹ at 0.1 C after 50 cycles	352
Rod, 300-700 nm x 5 μm	65(0.1C)	50 mA h g ⁻¹ at 0.1 C after 10 cycles	361
Cubes, 1.2-1.5 μm x 250 nm	52(0.1C)	15 mA h g ⁻¹ at 0.1 C after 25 cycles	363

5.4.3 Synthesis, microstructure and electrochemistry of LiCoPO₄ modified with TiN, RuO₂ or C

Three kinds of LiCoPO₄ were chosen for coating, the uncrystallised LiCoPO₄ directly after solvothermal synthesis, with the advantage of a single heating step, and the LiCoPO₄ already crystallised in Ar or air (Scheme 5-3). RuO₂ and C coatings were prepared by manually grinding the precursors (RuCl₃·xH₂O or sucrose) together with LiCoPO₄, then firing under Ar.^{246, 309} This solid-state process proved to be an easy and effective method to achieve carbon coatings on LiCoPO₄.^{309, 553} TiN coating used a propylamine-crosslinked sol-gel method, then firing under Ar or NH₃. This sol-gel process has been shown to be effective to achieve TiN coatings onto LIB cathode materials according to previous research.³⁷⁰ Scheme 5-3 summarises these approaches.



Scheme 5-3 Preparation conditions and sample labels for TiN, RuO₂ or C coated LiCoPO₄ materials.

All the X-ray diffraction peaks of the resulting TiN, RuO₂ and C coated LiCoPO₄ samples (Figure 5-14) can be indexed to the standard olivine LiCoPO₄ structure. The characteristic peaks of TiN and RuO₂ were not detectable in coated LiCoPO₄ composites due to their low concentrations. Carbon coatings on battery materials are typically amorphous when heating at around 600 °C,^{302, 371, 441} and also were not visible in the diffraction data. Figure 5-15, Figure 5-16 and Figure 5-17 show the Rietveld fits to the XRD data, which yielded typical LiCoPO₄ lattice parameters (Table 5-5, Table 5-6 and Table 5-7),³¹¹ suggesting that the coating processes did not affect the crystal structure of LiCoPO₄.

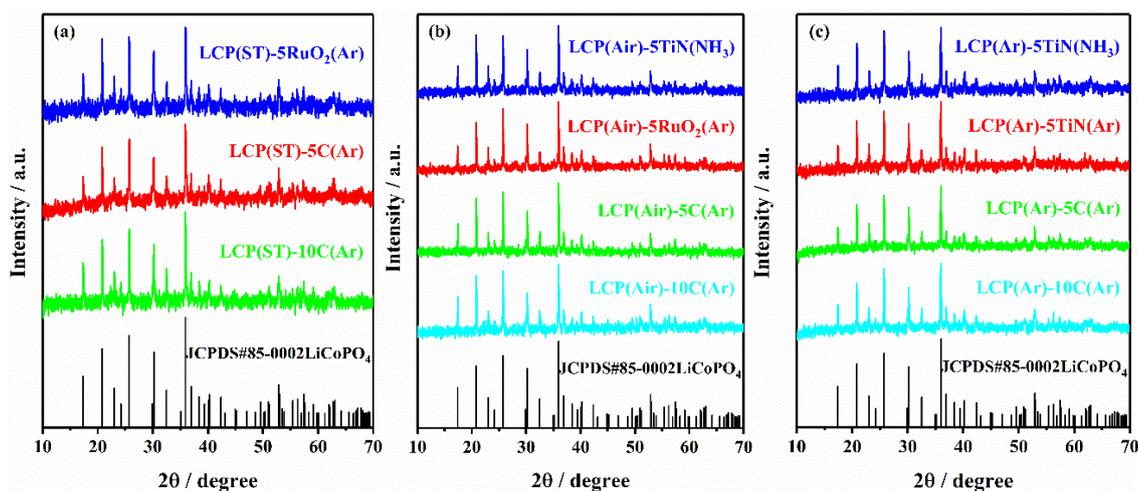


Figure 5-14 XRD patterns of uncrystallised LiCoPO₄ directly after solvothermal synthesis, and LiCoPO₄ heated under air or Ar at 600 °C, then modified with TiN, RuO₂ and carbon, respectively (labels explained in Scheme 5-3). The black stick pattern denotes the literature positions and intensities of LiCoPO₄ reflections.³⁶⁸

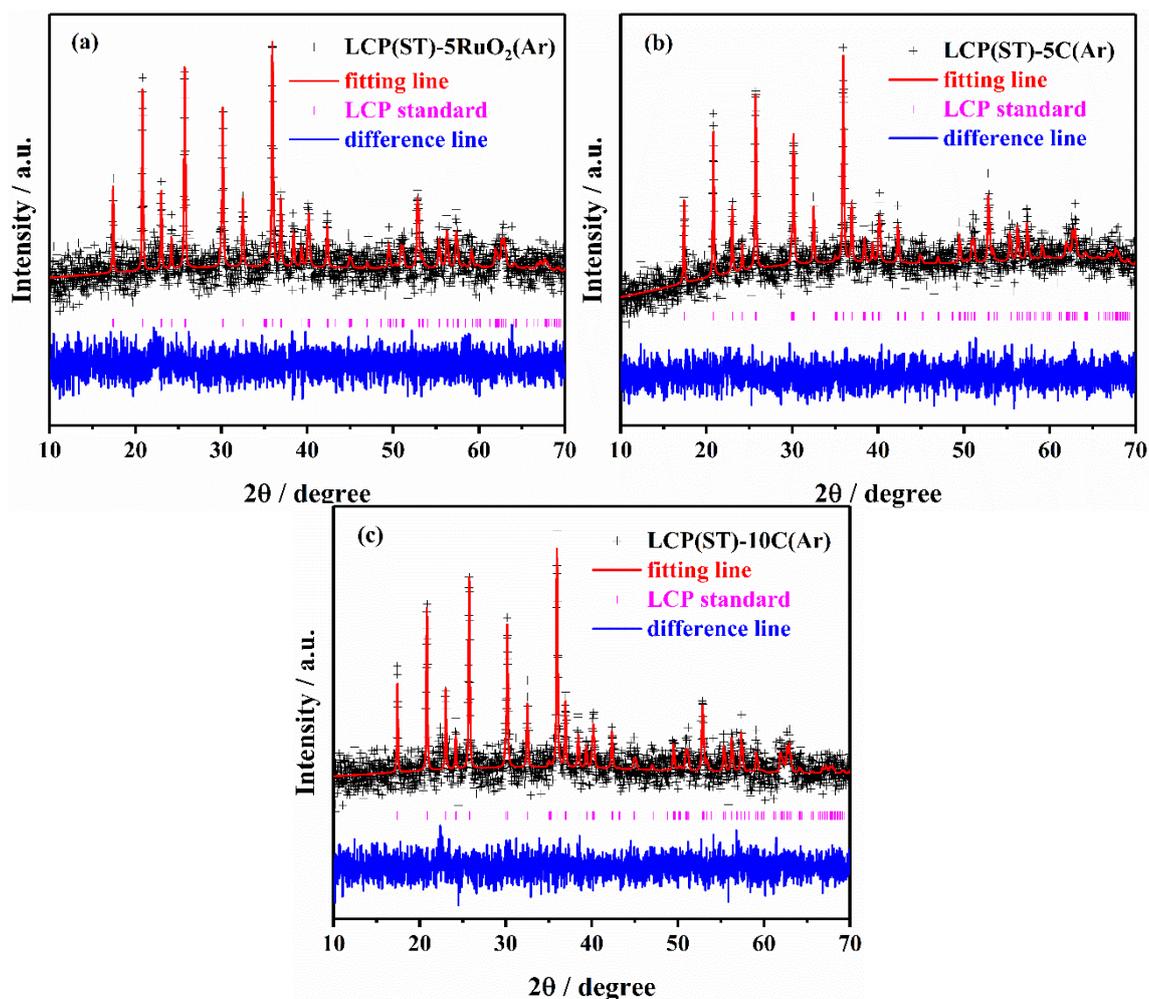


Figure 5-15 Rietveld fits to the XRD patterns of (a) LCP(ST)-5RuO₂(Ar) ($R_{wp} = 2.79\%$ and $R_p = 2.22\%$), (b) LCP(ST)-5C(Ar) ($R_{wp} = 2.81\%$ and $R_p = 2.23\%$) and (c) LCP(ST)-10C(Ar) ($R_{wp} = 2.67\%$ and $R_p = 2.10\%$) (sample labels explained in Scheme 5-3). The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for LiCoPO₄ with space group *Pnma*.

Table 5-5 Lattice parameters obtained from the Rietveld fits to the XRD patterns of the RuO₂ and C (5 or 10 wt.%) coated LiCoPO₄ samples (labels explained in Scheme 5-3).

Sample	a / Å	b / Å	c / Å
LCP(ST)-5RuO ₂ (Ar)	10.2048(11)	5.9269(5)	4.6995(5)
LCP(ST)-5C(Ar)	10.2064(16)	5.9277(9)	4.7007(9)
LCP(ST)-10C(Ar)	10.2076(10)	5.9283(5)	4.7015(5)

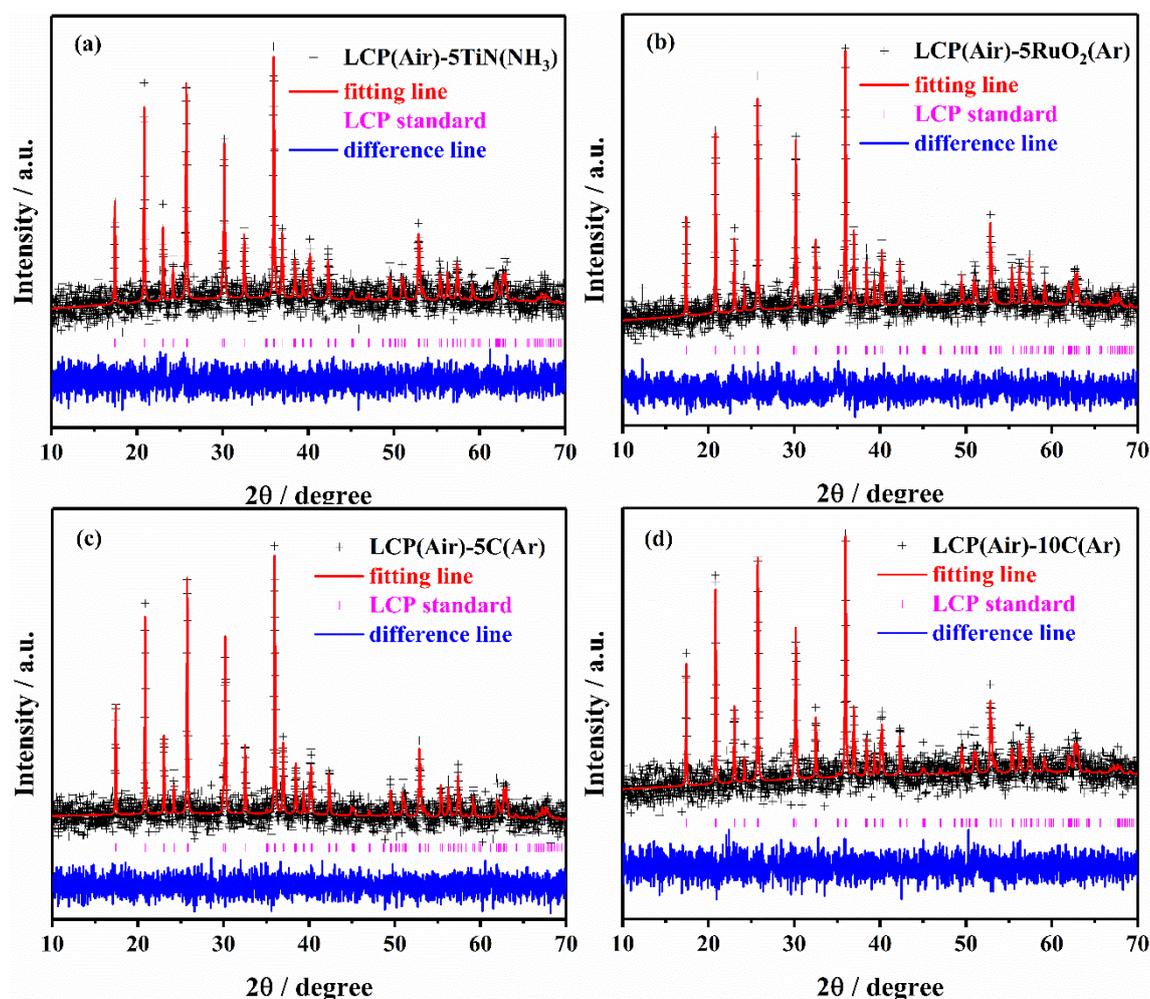


Figure 5-16 Rietveld fits to the XRD patterns of (a) LCP(Air)-5TiN(NH₃) ($R_{wp} = 2.89\%$ and $R_p = 2.32\%$), (b) LCP(Air)-5RuO₂(Ar) ($R_{wp} = 2.91\%$ and $R_p = 2.31\%$), (c) LCP(Air)-5C(Ar) ($R_{wp} = 2.68\%$ and $R_p = 2.14\%$) and (d) LCP(Air)-10C(Ar) ($R_{wp} = 2.80\%$ and $R_p = 2.23\%$) (sample labels explained in Scheme 5-3). The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for LiCoPO₄ with space group *Pnma*.

Table 5-6 Lattice parameters obtained from the Rietveld fits to the XRD patterns of the TiN, RuO₂ and C (5 or 10 wt.%) coated LiCoPO₄ samples (labels explained in Scheme 5-3).

Sample	a / Å	b / Å	c / Å
LCP(Air)-5TiN(NH ₃)	10.2053(8)	5.9268(4)	4.7005(4)
LCP(Air)-5RuO ₂ (Ar)	10.2054(6)	5.9235(3)	4.7003(3)
LCP(Air)-5C(Ar)	10.2039(6)	5.9256(3)	4.7007(3)
LCP(Air)-10C(Ar)	10.2056(8)	5.9268(4)	4.7008(4)

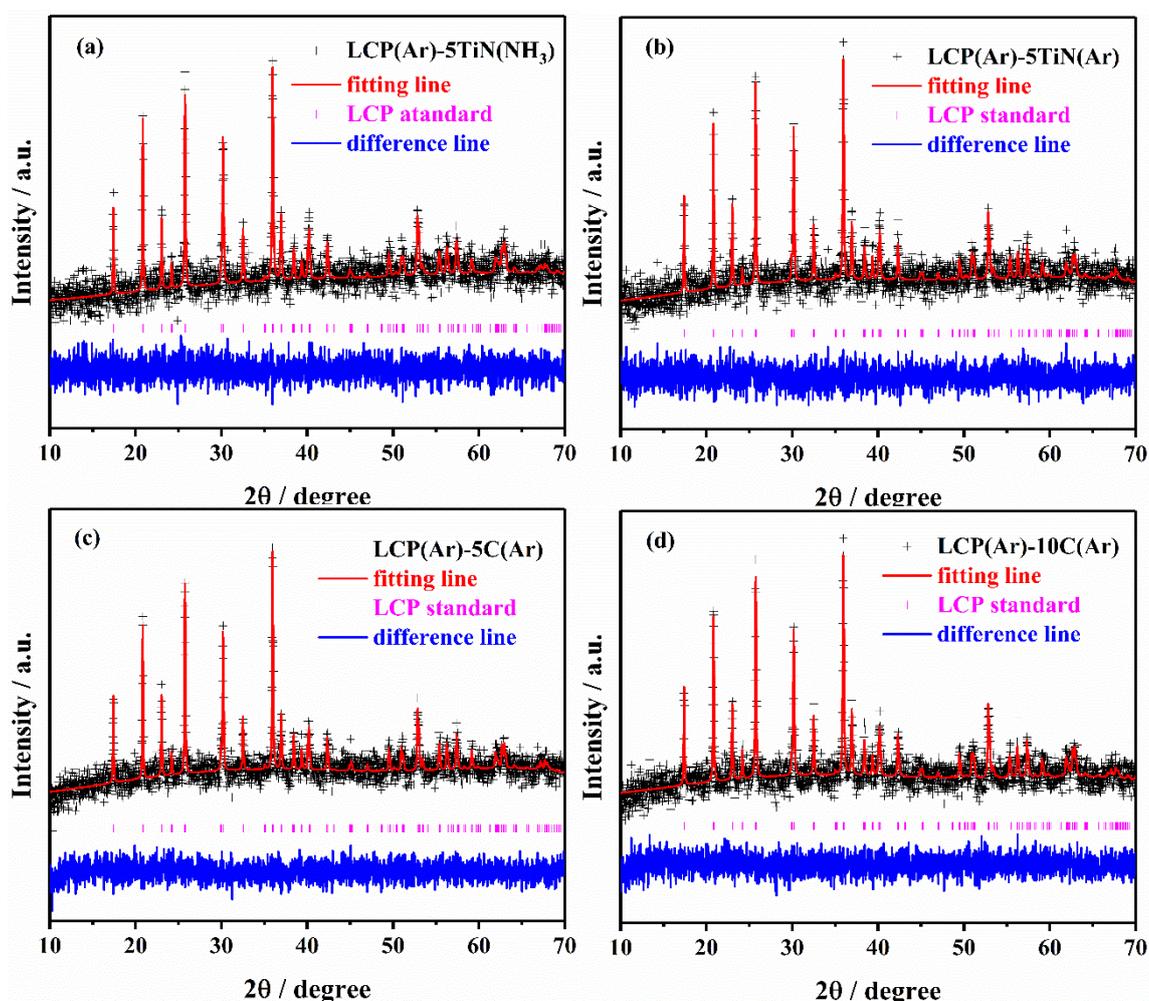


Figure 5-17 Rietveld fits to the XRD patterns of (a) LCP(Ar)-5TiN(NH₃) ($R_{wp} = 2.96\%$ and $R_p = 2.36\%$), (b) LCP(Ar)-5TiN(Ar) ($R_{wp} = 2.98\%$ and $R_p = 2.37\%$), (c) LCP(Ar)-5C(Ar) ($R_{wp} = 2.84\%$ and $R_p = 2.24\%$) and (d) LCP(Ar)-10C(Ar) ($R_{wp} = 2.73\%$ and $R_p = 2.19\%$) (sample labels explained in Scheme 5-3). The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for LiCoPO₄ with space group *Pnma*.

Table 5-7 Lattice parameters obtained from the Rietveld fits to the XRD patterns of the TiN and C (5 or 10 wt.%) coated LiCoPO₄ samples (labels explained in Scheme 5-3).

Sample	a / Å	b / Å	c / Å
LCP(Ar)-5TiN(NH ₃)	10.2084(10)	5.9287(5)	4.7018(4)
LCP(Ar)-5TiN(Ar)	10.2029(9)	5.9252(4)	4.7010(4)
LCP(Ar)-5C(Ar)	10.2075(7)	5.9255(4)	4.7005(4)
LCP(Ar)-10C(Ar)	10.2106(8)	5.9286(4)	4.7016(4)

Figure 5-18 shows the initial charge/discharge curves at 0.1C and the cycle stability of electrodes produced from the coated materials. Carbon is the most commonly used battery material coating, but RuO₂ has been used to coat electroactive materials to offer a high electronic conductivity and

quick Li permeation.⁵⁵⁸⁻⁵⁶¹ Due to its good electrical conductivity, chemical stability and thermal stability, TiN has been combined with other electrode materials to form structured composites with improved conductivity and stability.^{15, 16, 370}

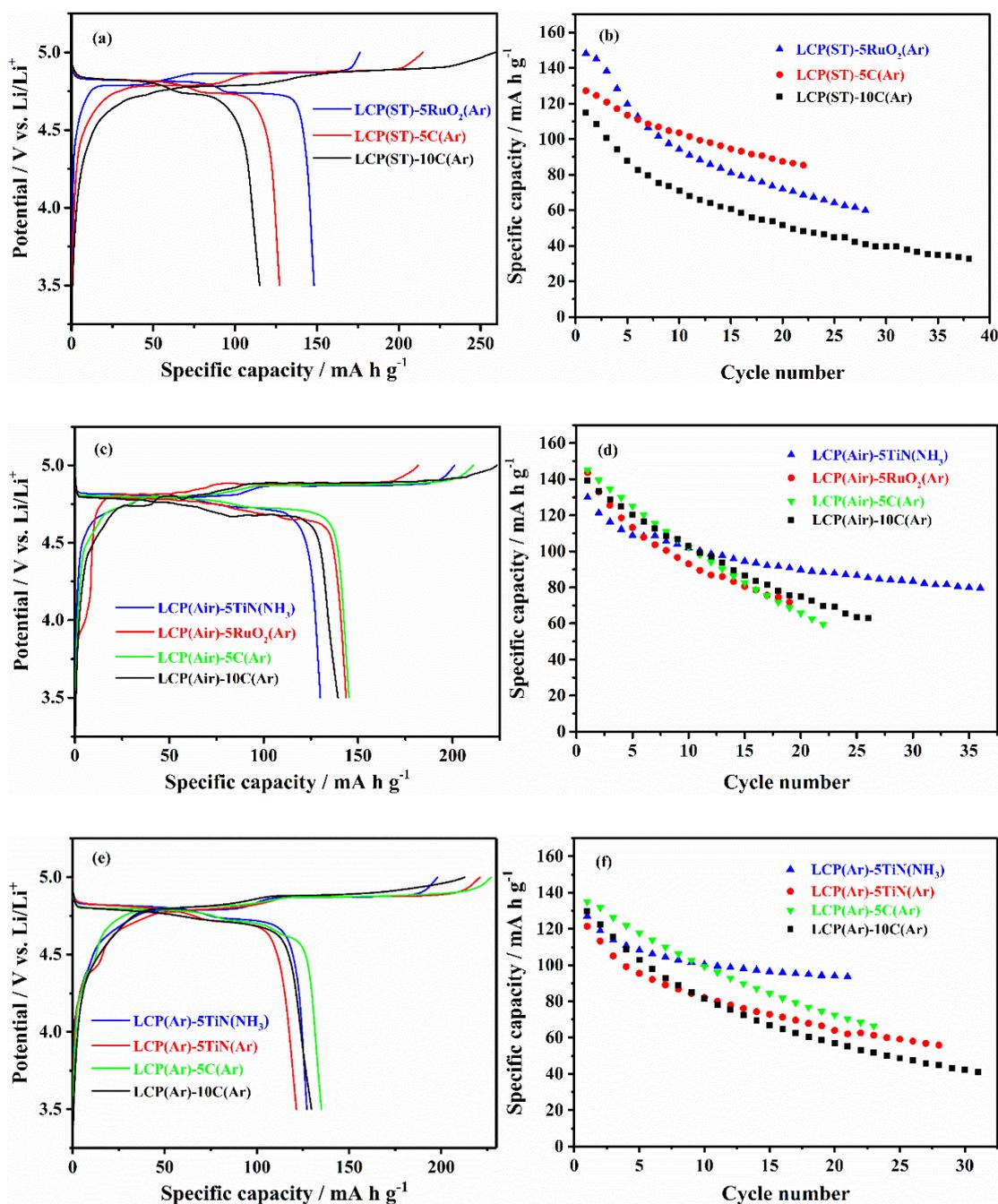


Figure 5-18 (a), (c), (e) The initial cycle voltage profile vs specific capacity, and (b), (d), (f) specific capacity vs cycle number of TiN, RuO₂ or C coated LiCoPO₄ samples made into Li half cells, under galvanostatic cycling between 3.5 and 5 V at 0.1C (sample labels explained in Scheme 5-3, with the percentage of TiN, RuO₂ or C in the composite written after the hyphen).

RuO₂ coating of the unfired LiCoPO₄ (Figure 5-18 a and b) resulted in a higher initial discharge capacity of 148 mA h g⁻¹ as expected due to the effect of RuO₂ in generating very effective mixed

conducting heterogeneous electrodes.²⁴⁶ However, its capacity drops quickly in subsequent cycles. The carbon coated samples had lower capacities than their uncoated counterparts, and the drop in capacity when C content was increased from 5% to 10% suggests that the thicker carbon coating hindered lithium diffusion.

Air fired LiCoPO₄ samples coated with TiN, RuO₂, 5wt% C or 10 wt% C (Figure 5-18 c and d) had initial discharge capacities of 130, 144, 145 and 139 mA h g⁻¹, respectively. The TiN coated sample retained a fairly large fraction of the initial capacity during continuous cycling.³⁷⁰ However, the cycle stability was quite similar to the uncoated LCP(Air) (Figure 5-13), so the coatings did not significantly improve the electrochemical performance of LiCoPO₄. Notably cycle stability was less good with RuO₂ or C coatings than with uncoated material.

A similar behaviour was observed with the Ar-fired LiCoPO₄ (Figure 5-18 e and f). The capacities of the C or TiN coated samples dropped to around 100 mA h g⁻¹ over 10 cycles, a poorer cycle stability than that of the uncoated LCP(Ar), which retained 102 mA h g⁻¹ after 40 cycles (Figure 5-13). The coatings did not deliver the expected improvement in electrochemical performance of LiCoPO₄. However, the purpose of the conductive agent coating was to create a conductive network among the LiCoPO₄ particles to improve the conductivity of the composites. These results infer that, using this novel and optimised solvothermal conditions, the conductivity of bare LCP(Ar) sample is good enough to provide competitive specific capacity and cycle stability.

5.4.4 Further investigation of LiCoPO₄ fired in Ar and air

The electronic and ionic conductivity of LiCoPO₄ powders fired in Ar and air was evaluated with current-voltage measurements and electrochemical impedance spectroscopy. LiCoPO₄ samples were pressed, sintered and gold-coated to produce self-standing LiCoPO₄ disks, which were dry contacted with two silver paste electrodes. The produced linear current-voltage plots (Figure 5-19), showing that the LCP(Ar) pellet behaves as a resistor and the current-voltage relationship is given by Ohm's law: $V = IR$. Hence, the resistance of the LiCoPO₄ samples can be estimated as being equal to the inverse of the slope of the current-voltage plot. The conductivity of the samples is given by $\sigma = \frac{1}{R} \frac{l}{A}$, where σ is the conductivity, l is the thickness of the LiCoPO₄ pellets (0.48 mm for LCP(Ar) and 0.64 mm for LCP(Air) sample), A is the area of the LiCoPO₄ pellets (95 mm²), and R is the resistance (42.2 Ω for LCP(Ar) and $1.7 \times 10^7 \Omega$ for LCP(Air) sample). The conductivities of LCP(Ar) and LCP(Air) are calculated to be $\sim 10^{-3} \text{ S cm}^{-1}$ and $\sim 10^{-9} \text{ S cm}^{-1}$, respectively. Current-voltage plots with larger voltage ranges are shown in Figure 5-20, and they are in agreement with those in Figure 5-19.

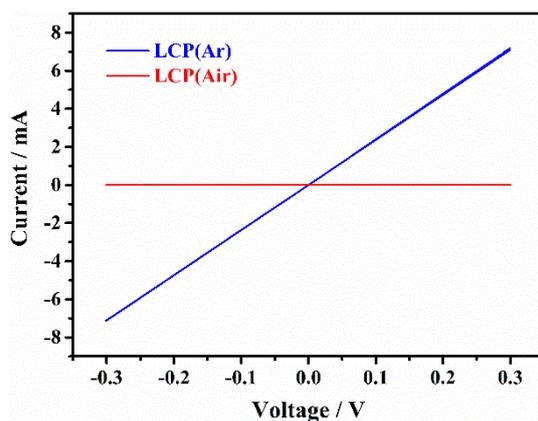


Figure 5-19 Current-voltage plots (3 cycles each) for LiCoPO_4 samples fired in Ar and air, respectively, cycling at scanning rate of 20 mV s^{-1} , showing the ohmic behaviour of the samples (labels explained in Scheme 5-2).

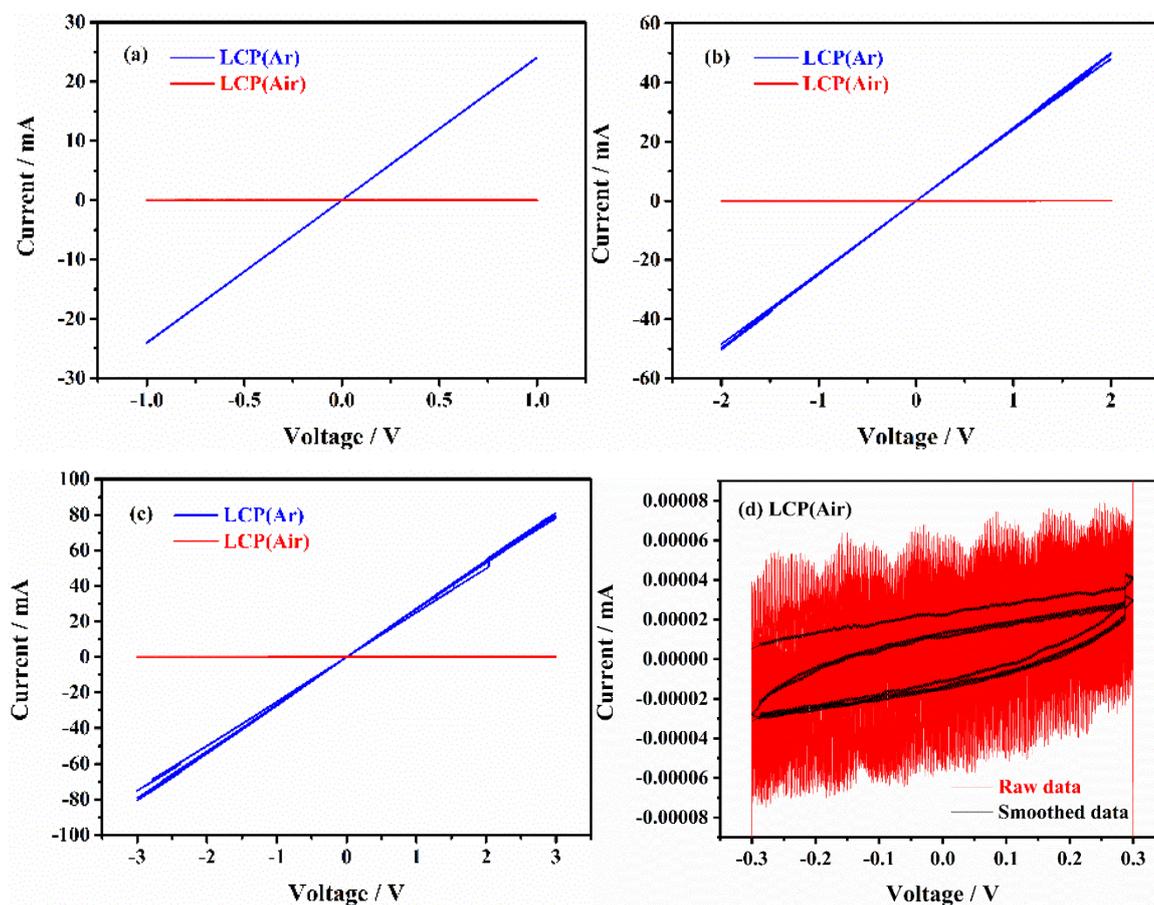


Figure 5-20 Current-voltage plots (3 cycles each) for LiCoPO_4 samples fired in Ar and air, respectively, cycling at scanning rate of 20 mV s^{-1} , showing the ohmic behaviour of the samples (labels explained in Scheme 5-2).

These conductivity results can be confirmed by electrochemical impedance spectroscopy measurements of the gold-coated pressed LiCoPO_4 pellets, as presented in Figure 5-21. The impedance of the LCP(Ar) sample shows purely resistor behaviour (Figure 5-21 a). This is in

agreement with the fact that this sample has reasonably high electronic conductivity of $\sim 10^{-3} \text{ S cm}^{-1}$, estimated from the value of the resistance and taking into account the dimension of the pellet. On the other hand, the LCP(Air) sample shows much higher values of impedance (Figure 5-21 b). This is ascribed to the fact that this sample has much higher electronic resistance, thus it behaves as a resistor coupled to a capacitor (or a constant phase element) in parallel. In addition, the surface of the pellet cannot be polished prior to gold coating (due to the fragility of the pellet), thus the LiCoPO_4 -gold interphase behaves as a Warburg element, rather than a capacitor or a constant phase element. By fitting the data to the equivalent circuit shown in Figure 5-21 b, the electronic conductivity of the LCP(Air) sample is estimated to $\sim 10^{-9} \text{ S cm}^{-1}$. This is in agreement with the estimation of the total conductivity of the samples by using current-voltage measurements, and the dramatic difference in conductivity between these two samples explains the fact that the sample fired in Ar showed better specific capacity and cycling performance.

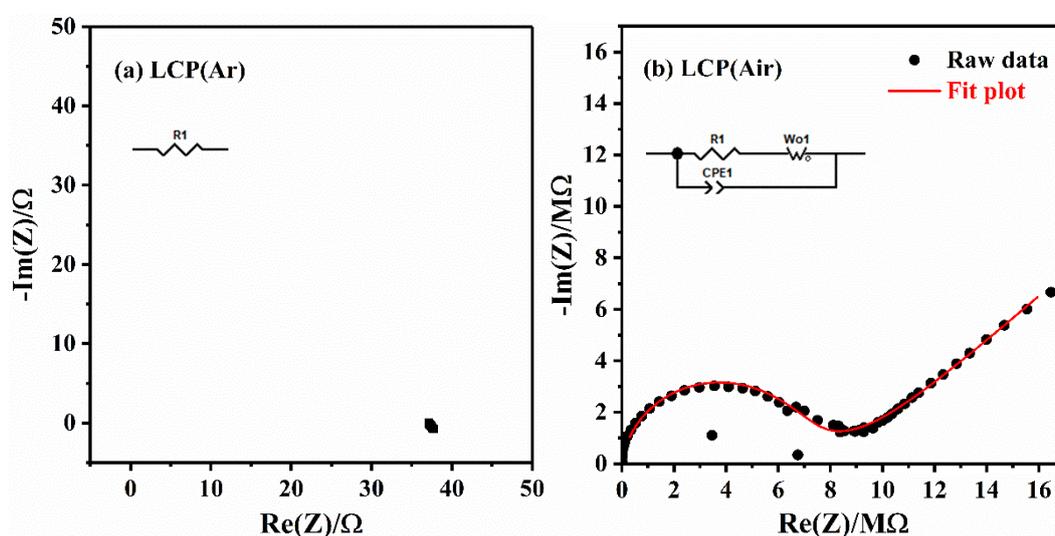


Figure 5-21 Electrochemical impedance spectroscopy (Nyquist plots) of (a) LCP(Ar) and (b) LCP(Air) samples, collected at 500 mV in the frequency range of 0.1 Hz to 200 kHz. The insets show equivalent circuits used to fit the data (labels explained in Scheme 5-2).

Wolfenstine et al. investigated the effect of added carbon on the electronic conductivity and specific capacity of LiCoPO_4 , and found that the added carbon was partly consumed to reduce the LiCoPO_4 surface layers to Co_2P during heating under Ar atmosphere.^{293, 294} The formation of highly conductive ($\sim 10^{-1} \text{ S cm}^{-1}$) Co_2P phase in LiCoPO_4 cathode led to improved electrochemical performance. As the amount of the Co_2P phase increased to 4 wt.%, the electronic conductivity increased to $\sim 10^{-4} \text{ S cm}^{-1}$ with a maximum discharge capacity of $\sim 120 \text{ mA h g}^{-1}$ obtained. However, for LiCoPO_4 cathodes with higher concentrations of Co_2P , the capacities dropped rapidly due to the electrochemically inert Co_2P phase, which improves the electronic conductivity but tends to hinder the Li^+ insertion/extraction. Similar phenomena were also observed by Xu³⁴⁰ and Indris et al.³¹⁶ Ma

et al. demonstrated that the presence of Co_2P can accelerate the electrolyte decomposition at high voltage in the charge process for LiCoPO_4 due to the catalytic property of Co_2P .⁵⁶² Dimesso et al. suggested that the formation of Co_2P occurs due to reduction reactions at the grain boundaries of the LiCoPO_4 crystalline phase during annealing at high temperatures.^{406, 408, 411, 419, 462, 463, 470} Brutti et al. synthesized LiCoPO_4 via a solvothermal synthesis followed by heating under Ar atmosphere. It was found that the heating promotes Co_2P precipitation on the LiCoPO_4 particles surface together with loss of organic by-products formed in the solvothermal synthesis.⁴⁵⁸ Nallathamby et al. confirmed that the presence of Co_2P as a second phase enhanced the conductivity and electrochemical performance of LiCoPO_4 . It was found that the Co_2P is achievable only in an inert atmosphere. The LiCoPO_4 cathode showed a discharge capacity of 123 mA h g^{-1} at 0.1 C with capacity retention of 89% after 30 cycles, and rate capability of 81 mA h g^{-1} at 5 C.³⁰²

Based on the discussion above, the better conductivity of LiCoPO_4 heated in Ar was considered likely to be due to the presence of Co_2P on the surface on LiCoPO_4 . X-ray photoelectron spectroscopy (XPS) spectra of LiCoPO_4 samples fired under Ar and air are shown in Figure 5-22. These two samples had similar Li 1s and C 1s spectra (Figure 5-23). Particularly, for the LiCoPO_4 fired under Ar, the Li 1s signal located at 55.7 eV is well in accordance with the value reported for LiCoPO_4 .³⁰² The C 1s spectrum consists of three peaks, with the main component at 285.0 eV corresponding to C-C, and the other two peaks observed at 287.1 eV and 289.0 eV attributed to C-O and O=C-O environments of carbon.⁵⁶³ Figure 5-22 shows clear differences between the chemical environments present in the P 2p and O 1s spectra of these samples. For the LiCoPO_4 fired under Ar, the O 1s spectrum with a binding energy of 531.6 eV is in agreement with the air-fired sample and with the $(\text{PO}_4)^{3-}$ environment in LiCoPO_4 ,³⁰² but an additional weak peak at 529.1 eV demonstrates the presence of a small amount of metal oxide (e.g. Li_2O with binding energy of 528.6 eV for O 1s spectrum).⁵⁶⁴⁻⁵⁶⁶ The P 2p spectrum ($2p_{3/2}$ and $2p_{1/2}$ doublet) shows the main component at 133.5-134.4 eV in accordance with LiCoPO_4 ,³⁶⁶ and a doublet at lower binding energy (130.9-131.8 eV) that corresponds to Co_2P .⁵⁶⁷ A small shift in binding energy of P 2p in Co_2P (expected at around 129 eV) is likely to be due to a differential charging effect resulting from the different electrical conductivities at the surfaces of LiCoPO_4 and Co_2P .⁵⁶⁷⁻⁵⁶⁹ Co_2P formation in Ar fired LiCoPO_4 is attributed to the carbon-containing organic solvent (DEG) chosen for the synthesis, which can decompose at high temperature and the resulting carbon can cause carbothermal reduction to reduce the LiCoPO_4 surface layers to Co_2P during heating under inert atmosphere.^{293, 294, 302, 411, 458, 462} This process also explains the relatively low carbon content measured in these samples by microanalysis. The Co 2p spectra are not fitted due to the complexity of the 2p spectra resulting from peak asymmetries, complex doublet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies.⁵⁷⁰ For the LiCoPO_4 fired under Ar, the $2p_{3/2}$ and $2p_{1/2}$

doublet in the Co 2p spectrum has binding energy values of 781.5 and 797.6 eV, respectively. In LCP(Air) these peaks are observed at 782.1 eV and 798.1 eV ($2p_{3/2}$ and $2p_{1/2}$). The shift to lower binding energy can be attributed to the presence of Co_2P in LCP(Ar).⁵⁶⁷ The difference of binding energy between Co $2p_{3/2}$ and its satellite peak is in agreement with the Co^{2+} environment in LiCoPO_4 .^{366, 570} For the LiCoPO_4 fired under air, a new chemical environment corresponding to P_2O_5 is identified with additional peaks in the P 2p (135.3-136.1 eV) and O 1s (533.3 eV) spectra.^{571, 572}

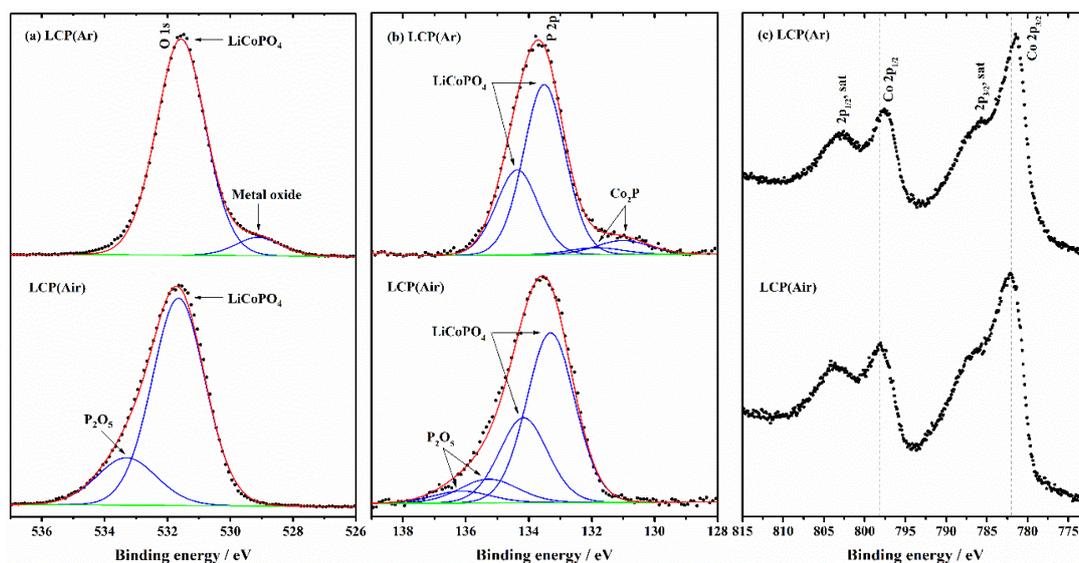


Figure 5-22 P 2p, O 1s and Co 2p XPS spectra of LiCoPO_4 samples fired in Ar and air, respectively (labels explained in Scheme 5-2). The data points and enveloped fitting plot are overlaid in black dots and a red line, respectively. The fitting peaks and background are shown in blue and green, respectively.

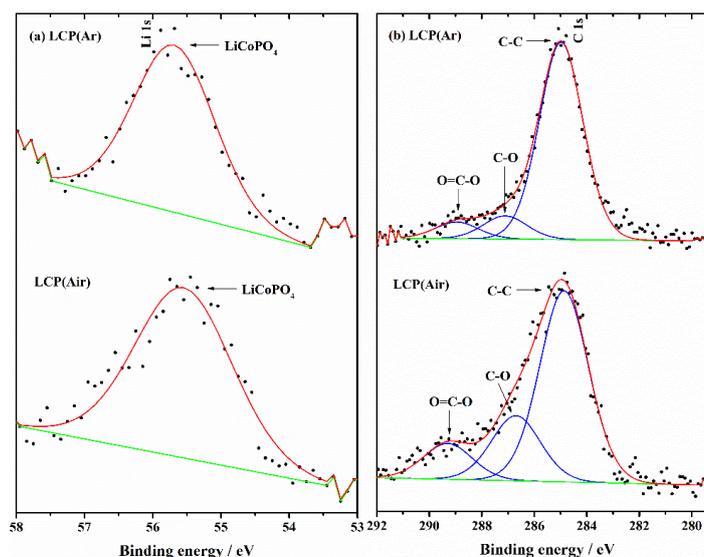


Figure 5-23 Li 1s and C 1s XPS spectra of LiCoPO_4 samples fired in Ar and air, respectively (labels explained in Scheme 5-2). The data points and enveloped fitting plot are overlaid in black dots and a red line, respectively. The fitting peaks and background are shown in blue and green, respectively.

The best specific capacity (147 mA h g^{-1}) and cycling performance of LiCoPO_4 shown in Figure 5-13, achieved by heating in Ar, can be attributed to the good electronic conductivity ($\sim 10^{-3} \text{ S cm}^{-1}$) of LiCoPO_4 due to the presence of Co_2P after firing under Ar. Also, the nanosized LiCoPO_4 obtained from DEG promoted solvothermal synthesis provides short Li-ion migration paths, and facilitates easier Li-ion transfer within the material. The LiCoPO_4 fired in air showed relatively low initial specific capacity of 130 mA h g^{-1} . This could be attributed to the poor electric conductivity of $\sim 10^{-9} \text{ S cm}^{-1}$ (Figure 5-19 and Figure 5-20) as there is no evidence of the presence of Co_2P in this sample.

5.5 Conclusions

A facile solvothermal synthesis to prepare olivine-structured LiCoPO_4 for high-voltage cathodes in LIBs has been developed, using various ratios of water/diethylene glycol as solvent, followed by thermal treatment under Ar, air, $5\% \text{H}_2 + \text{N}_2$ or NH_3 . The diethylene glycol plays an important role in tailoring the particle size of LiCoPO_4 . It is found that using a ratio of water/diethylene glycol of 1:6 (v/v), LiCoPO_4 is obtained with a homogenous particle size of $\sim 150 \text{ nm}$. The LiCoPO_4 prepared after heating in Ar exhibits high initial discharge capacity of 147 mA h g^{-1} at 0.1 C with capacity retention of 70% after 40 cycles. This is attributed to the enhanced electronic conductivity of LiCoPO_4 due to the presence of Co_2P after firing under Ar. The specific capacity and cycle stability of carbon, TiN and RuO_2 coated LiCoPO_4 were also examined, but did not improve the performance of the material. Hence, under the optimised solvothermal synthesis conditions, LiCoPO_4 with good discharge capacity and cycle stability, without need for separate conductivity coatings, were produced.

Chapter 6: Surface treatments and electrochemical behaviour of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes for lithium-ion batteries

6.1 Introduction

Lithium-ion batteries (LIBs) are one of the most promising power sources for energy storage system due to their high energy density, high power density, and light weight.^{19, 573} The anode material plays an important role in the cycle life, safety and cost of LIBs.²³⁻²⁵ Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a superior cycling stability owing to its negligible volume change during charge/discharge process, high potential of ~ 1.55 V vs. Li/Li^+ , high thermal stability and good safety.^{87, 88} This makes it a promising anode material for LIBs used for large-scale applications such as electric vehicles (EVs) or hybrid electric vehicles (HEVs).⁸⁹⁻⁹¹ However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ suffers from a low electrical conductivity ($\sim 10^{-13}$ to 10^{-8} S cm^{-1})⁹²⁻⁹⁴ and lithium diffusion coefficient ($\sim 10^{-13}$ $\text{cm}^2 \text{ s}^{-1}$),⁹⁵⁻⁹⁹ which results in poor rate capability in LIBs.

As illustrated in Figure 6-1,⁵⁷⁴ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a spinel structure with a cubic space group $Fd3m$ and lattice parameter between $a = 8.352$ and 8.370 Å.⁵⁷⁵⁻⁵⁸¹ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be denoted as $[\text{Li}_3]_{8a}[\text{LiTi}_5]_{16d}[\text{O}_{12}]_{32e}$ because three Li atoms occupy the tetrahedral 8a sites, one Li atom and five Ti atoms occupy the octahedral 16d sites, and all of the O atoms occupy the 32e sites.^{582, 583} Upon discharge in LIBs, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ converts to rock salt structured $\text{Li}_7\text{Ti}_5\text{O}_{12}$ with little cell volume change ($< 0.2\%$).⁵⁸⁴ $\text{Li}_7\text{Ti}_5\text{O}_{12}$ can be denoted as $[\text{Li}_6]_{16c}[\text{LiTi}_5]_{16d}[\text{O}_{12}]_{32e}$ because the inserted three Li atoms occupy the empty 16c sites and three Li atoms initially locate at the 8a sites also migrate to the 16c sites due to electrostatic repulsion effects.⁵⁸⁵ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be further converted to $\text{Li}_9\text{Ti}_5\text{O}_{12}$ because more than three Li atoms can be inserted to occupy the 8a, 8b and 48f sites.^{586, 587}

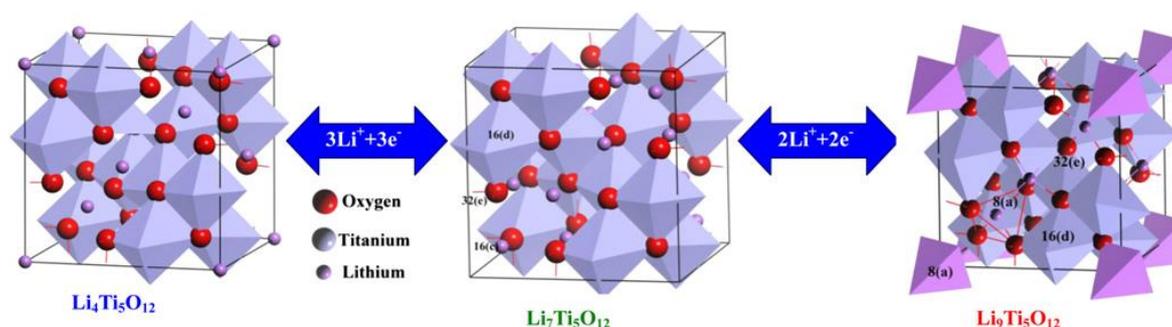


Figure 6-1 Structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_7\text{Ti}_5\text{O}_{12}$ and $\text{Li}_9\text{Ti}_5\text{O}_{12}$. Reproduced from Ref. ⁵⁷⁴ with permission from Elsevier 2012.

6.2 Synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via solid-state reaction

Various methods have been developed to synthesize $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes for LIBs with good electrochemical performance and low cost. For instance, solid-state reaction, hydrothermal synthesis, sol-gel synthesis, molten-salt synthesis, and microwave processing. Solid-state reaction is the most commonly used method to prepare electrode materials. Typically, a stoichiometric ratio of Li_2CO_3 and TiO_2 are mixed evenly via grinding or ball-milling, then heated at temperature from 600 °C to 1000 °C in air to obtain $\text{Li}_4\text{Ti}_5\text{O}_{12}$.⁸⁷ Although this solid-state method suffers from issues such as inhomogeneity, uncontrollable morphology and large particle size, it is a scalable strategy for commercial application owing to its simple and easy synthesis process and low cost.⁸⁷

Yoon et al. synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by a solid-state reaction with Li_2CO_3 and anatase TiO_2 as starting materials. Different sizes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles were obtained by varying the size of ZrO_2 beads during high energy milling. The smaller ZrO_2 beads resulted in finer $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with particle size of 162 nm, which showed a discharge capacity of 174 mA h g^{-1} at 0.1 C and rate capability of 139 mA h g^{-1} at 10 C.⁵⁸⁸ Michalska et al. found that the average grain sizes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ could be reduced by increasing the ball-milling time in solid-state reaction, which results in a capacity retention of 94% at 1 C after 50 cycles.⁵⁸⁹

6.3 Surface modification to improve the performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Due to poor electronic conductivity and Li^+ ionic diffusivity, the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits poor rate capability especially at high rates. Tremendous efforts have been made to tackle these issues such as surface modification, ion doping, size reduction and morphology control.⁸⁷⁻⁸⁹ Surface modification has been intensively investigated to improve the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes in LIBs. The surface modification materials mainly include carbon, metal, metal oxide and other conductive agents.

6.3.1 Carbon coating

Carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized by Wu et al. via heat-treating the mixture of TiO_2 , Li_2CO_3 and sugar. It was found that carbon coating reduced the size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle by inhibiting the agglomeration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in heating process. This uniformly coated carbon nanolayer enhanced the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and favoured Li^+ ion diffusion, thus resulting in a reversible capacity of ~ 160 mA h g^{-1} at 0.1 C rate.⁵⁹⁰ Xia et al. prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with a uniform 5 nm thickness graphitized-carbon coating via a chemical vapour decomposition method. The carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited much higher electrical conductivity of 2.05 S cm^{-1} than the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of

less than $10^{-13} \text{ S cm}^{-1}$.⁵⁹¹ Also, Xia et al. synthesized carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with different morphologies like nanoparticles, nanorods and hollow spheres, which showed improved rate capability due to their good electronic conductivity.⁵⁹²

As shown in Figure 6-2, a solid-state reaction was developed by Amine et al. to prepared microscale spherical carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ using TiO_2 and Li_2CO_3 as raw materials, and pitch as carbon source. It has been reported that this highly conducting carbon coating improved the electronic conductivity of composites, inhibited the growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles to maintain the spherical morphology, and enabled partial reduction of the Ti^{4+} to Ti^{3+} . This carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited high rate capabilities of 165, 160, and 123 mA h g^{-1} at 1 C, 10 C, and 100 C, respectively, as well as almost no capacity fading over 100 cycles at 1C, 5C and 10 C (Figure 6-2).⁵⁹³ Yang et al. employed a sol-gel method with citric acid as the chelating agent and carbon resource for in situ carbon coating. The carbon (3.5 wt%) coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits capacities of 143.6 and 133.5 mA h g^{-1} at 0.5 C and 1 C, respectively, without obvious capacity fading over 50 cycles.⁵⁹⁴ Yin et al. prepared carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via solid-state reaction using polyacrylonitrile (PAN) as carbon source. It was found that the particle size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is reduced and its electrical conductivity is enhanced after carbon coating. The carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained with 10 wt% PAN showed higher initial specific capacities of 158, 138 and 121 mA h g^{-1} at 0.2 C, 1/3 C and 3C, respectively.⁵⁹⁵

Liu et al. investigated the effects of different carbon sources (conductive graphite KS-6 and sucrose) on the electrochemical properties of carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites, which were prepared by a solid-state reaction with Li_2CO_3 and TiO_2 as raw materials. The sucrose formed carbon was uniformly coated on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles, while the KS-6 formed carbon was embedded among the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. The carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite with both KS-6 and sucrose as carbon sources showed an initial specific capacity of 152.5 mA h g^{-1} at 0.2 C, good cycle stability with 96.8% capacity retention over 1000 cycles at 1 C, and rate capability of 123.6 mA h g^{-1} at 10 C.⁵⁹⁶ Zhang et al. prepared carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorods with glucose as carbon source via hydrothermal treatment. The carbon coating inhibited the particle growth and improved the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, thus enabling faster ion and electron transport comparing to pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$.⁵⁹⁷ Zhang et al. synthesized carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via spray drying with polyvinyl pyrrolidone (PVP) as binder and carbon source. The nano-sized primary $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles were aggregated to form spherical secondary particles with micron sizes. It was found that the secondary particle size, tap density and degree of spherical morphology for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ increases when increasing the amount of PVP. The carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited enhanced rate capacity due to its higher electrical conductivity and smaller primary particle sizes comparing to bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$.⁵⁹⁸

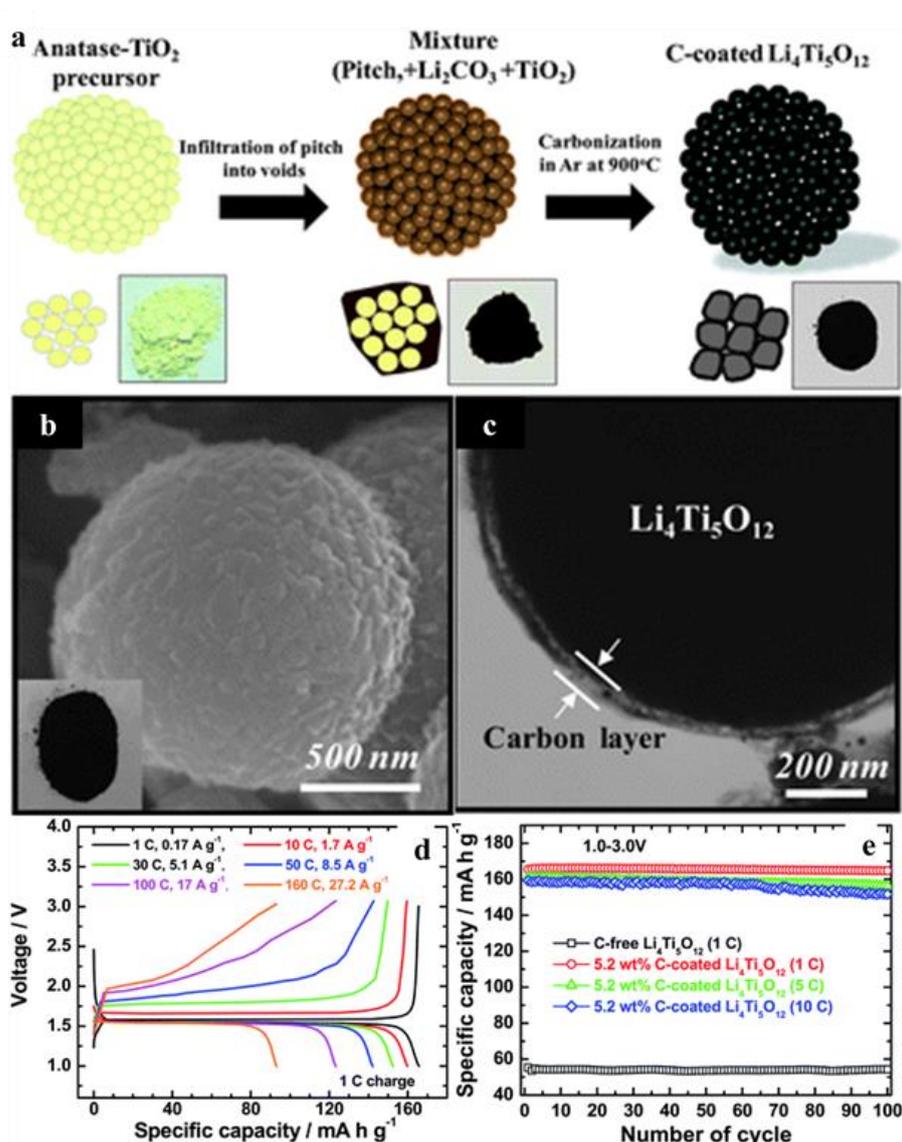


Figure 6-2 (a) Schematic illustration in preparation of microscale spherical carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and photographs of powders produced in process. (b) SEM and (c) TEM images of carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$. (d) Rate capability of carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in Li half cells, cycled at various rates from 1 C to 160 C. (e) Cycle stability of carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cycled at 1 C, 5 C and 10 C, in comparison with uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 1 C over 100 cycles. Reproduced from Ref. ⁵⁹³ with permission from the Royal Society of Chemistry 2011.

6.3.2 Metal coating

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Ag composites were synthesized by Wen et al. via thermal decomposition of AgNO_3 . The 5 wt% Ag coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ delivered a reversible capacity of $184.2 \text{ mA h g}^{-1}$ at 2C after 50 cycles with a capacity retention of higher than 96.5%.⁵⁹⁹ Sun et al. synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Ag composite by an electroless deposition method with Ag nanoparticles ($< 10 \text{ nm}$) distributed on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles ($\sim 90 \text{ nm}$). This $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Ag composite showed high rate capability of 131 mA h g^{-1}

¹ at 30 C, with 98% capacity retention over 120 cycles at 1 C to 30 C rates.⁶⁰⁰ As shown in Figure 6-3, Czerwinski et al. prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Ag composite via a solid-state reaction with 2-10 nm size Ag nanoparticles deposited on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Ag composite exhibited a capacity retention of > 94% over 50 cycles at 1 C, and maintained > 86% of initial capacity after increasing the charge/discharge rate from 1 C to 10 C.⁶⁰¹

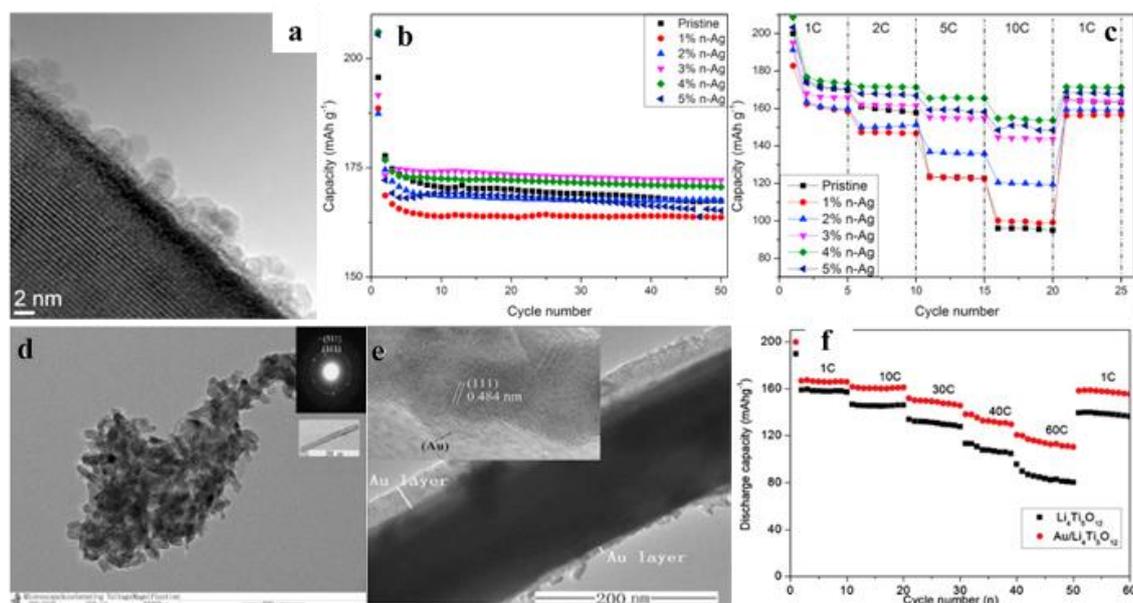


Figure 6-3 (a) HRTEM image of 5% Ag modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b) cycle stability and (c) rate capability of pristine and Ag modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Reproduced from Ref.⁶⁰¹ with permission from Elsevier 2014. (d) TEM image of Au coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorod aggregates. The insets in (d) are the electron diffraction of selected area and TEM image of a single nanorod. (e) TEM image of an Au coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorod. The inset in (e) is HRTEM image of Au coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ corresponding to spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (111) plane spacing. (f) The rate capabilities of bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Au coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in Li half cells, cycled at various sequential rates from 1 C to 60 C. Reproduced from Ref.⁶⁰² with permission from Elsevier 2014.

Cu particles were deposited onto the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by Wen et al. via electroless deposition. The conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Cu composite is two orders magnitude higher than that of bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which resulted in improved rate capability and cycle stability.⁶⁰³ Wang et al. prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with Cu modification on the surface via electroplating process. The Cu coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite showed better rate capability and cycle stability than bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ due to the improved charge transfer reaction.⁶⁰⁴ Liu et al. dispersed Cu nanoparticles onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via hydrothermal synthesis followed by heat treatment. It was found that Cu nanoparticles improved the electronic conductivity of composites and prevented the agglomeration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles.⁶⁰⁵ Li et al. synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Cu composites via a solvothermal method with Cu nanoparticles dispersed in the matrix of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Cu composite with 15 wt% Cu showed the best rate capability

of $122.9 \text{ mA h g}^{-1}$ at 20 C with 87% capacity retention after 1000 cycles. The improved rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite after Cu modification could be attributed to the increased electrical conductivity and reduced polarization during charge/discharge process.⁶⁰⁶

As shown in Figure 6-3, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Au nanorod aggregates were produced by Guo et al., which exhibited a Li^+ diffusion coefficient of $7.32 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. This material delivered a rate capability of $\sim 120 \text{ mA h g}^{-1}$ up to 60 C , which is much higher than that of bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This could be ascribed to the nanorod morphology enabling easier Li^+ ion transfer and Au coating improving the electrical conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite.⁶⁰² Hsieh et al. deposited Zn nanolayers with 1-10 nm thicknesses onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles via microwave-assisted synthesis. The Zn coating on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ enhanced the electronic conductivity and reduced battery polarization, thus resulting in a better rate capability.⁶⁰⁷

6.3.3 Metal oxide coating

Rutile- TiO_2 nanocoating on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets has been achieved by Guo et al. via a solution-based method. This composites were investigated at atomic resolution by an advanced spherical aberration imaging technique as shown in Figure 6-4. The carbon-free nanocoating of rutile- TiO_2 on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles enhanced the kinetics for fast Li^+ transfer at high rates. The rutile- TiO_2 coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets showed high cycle stability up to 20 C and delivered a specific capacity of 110 mA h g^{-1} at 60 C , which is much higher than bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (10 mA h g^{-1} at 60 C).⁶⁰⁸ Chen et al. prepared anatase- TiO_2 coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorod by a microemulsion-assisted hydrothermal method. It was found that the anatase- TiO_2 nanocoating layer contributes some capacity and delivered a good cycle stability with 96% of capacity retention after 100 cycles at a current density of 1.75 A g^{-1} .⁶⁰⁹ It was found that the TiO_2 modification enhanced the electronic conductivity and electrochemical activity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, which showed lower charge transfer resistance than that of pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$, thus resulting in better rate capability.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ - SnO_2 composites with various amounts of nano-sized SnO_2 distributed evenly on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were synthesized by Lai et al. via an in situ deposition method. The SnO_2 as active Li storage compound presented a synergistic interaction with $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which enhanced the overall specific capacity of the composites. The 5% SnO_2 modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ showed the best cycling stability, which delivered a specific capacity of 189 mA h g^{-1} after 42 cycles at a current density of 0.5 mA cm^{-1} .⁶¹⁰ Shao et al. synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Sn oxide composites via cellulose-assisted combustion method, which maintained a capacity of 224 mA h g^{-1} after 50 cycles at a current density of 100 mA g^{-1} .⁶¹¹

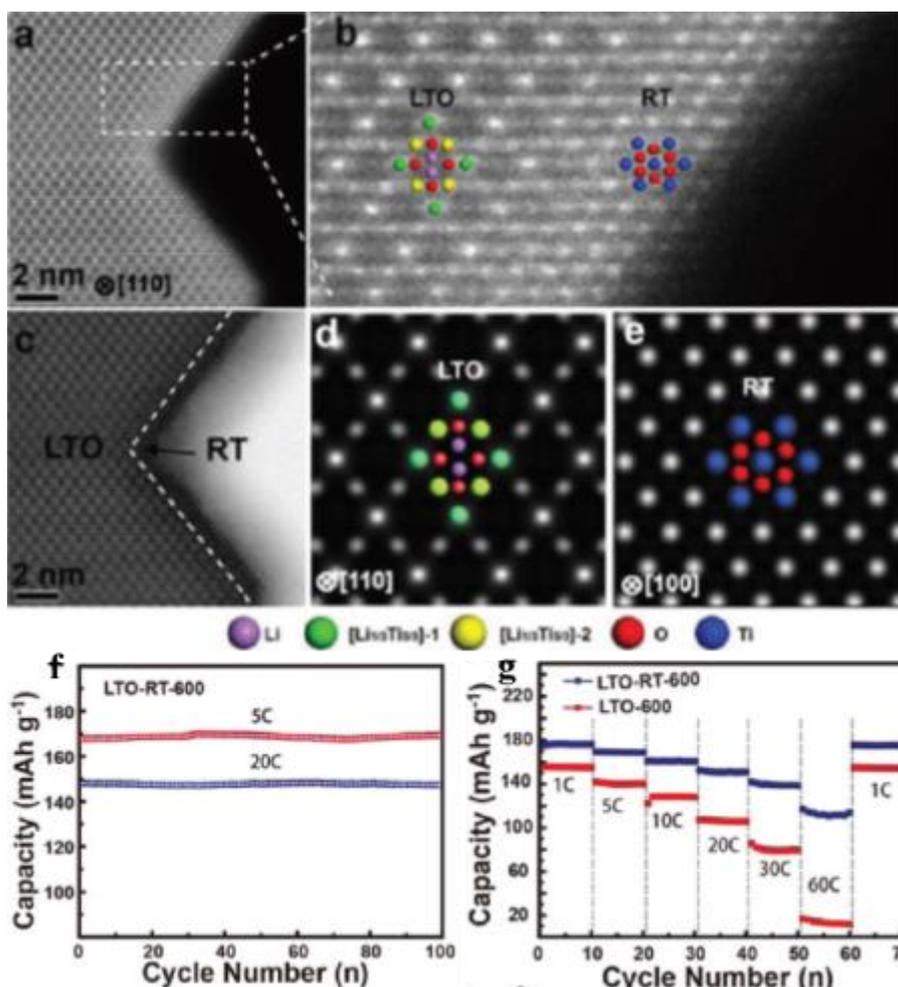


Figure 6-4 STEM images of Rutile-TiO₂ coated Li₄Ti₅O₁₂ nanosheets (denoted as LTO-RT-600) made by solution-based method and heat treated at 600 °C: (a, b) High-angle annular-dark-field (HAADF) and (c) corresponding annular-bright-field (ABF) images of LTO-RT-600 nanosheets. The simulated HAADF images of (d) Li₄Ti₅O₁₂ projected from [110] direction and (e) rutile-TiO₂ projected from [100] direction. The insets exhibit the atom configuration. (f) Cycle stability and (g) rate capability of Rutile-TiO₂ coated Li₄Ti₅O₁₂ nanosheets and uncoated Li₄Ti₅O₁₂ in Li half cells, cycled at various rates from 1 C to 60 C. Reproduced from Ref. ⁶⁰⁸ with permission from American Chemical Society 2012.

Sun et al. deposited an ultrathin layer of ZrO₂ onto Li₄Ti₅O₁₂ via an atomic layer deposition method. The ZrO₂ coated Li₄Ti₅O₁₂ anodes showed better cycle stability and rate capability, which could be ascribed to the enhanced electronic conductivity after ZrO₂ coating.⁶¹² Core-shell Li₄Ti₅O₁₂-CeO₂ nanosphere was prepared by Huang et al. via an one-pot co-precipitation method, which showed reversible capacity of 153 mA h g⁻¹ over 180 cycles at 10 C, with good rate capability of 128.4 mA h g⁻¹ at up to 40 C rate. This could be attributed to the improved electronic conductivity and lithium ion diffusivity of Li₄Ti₅O₁₂-CeO₂ composite.⁶¹³ Chen et al. synthesized SiO₂ modified Li₄Ti₅O₁₂ via sol-gel method. It was found that the SiO₂ coating could enhance the kinetics of Li⁺ transfer and reduce the electrode polarization during charge/discharge. The 2.5 % SiO₂ coated Li₄Ti₅O₁₂ showed the best

rate capability of $155.4 \text{ mA h g}^{-1}$ with a capacity retention of 99.6% and $141.7 \text{ mA h g}^{-1}$ with 96.4% capacity retention over 100 cycles at 1 C and 10 C, respectively.⁶¹⁴ Li et al. found that the ZnO coating on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ not only enhanced the electronic conductivity and Li^+ ion diffusion, but also suppressed the interfacial reactions between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode and electrolyte solution. This contributes to an improved rate capability and cycle stability for LIBs.⁶¹⁵

$\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-Fe}_2\text{O}_3$ composites were synthesized by Wang et al. via a hydrolysis synthesis, which delivered a specific capacity of $109.4 \text{ mA h g}^{-1}$ at 10 C, and a capacity retention of 93% after 300 cycles of charge/discharge at 2 C rate.⁶¹⁶ Jiang et al. prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-Fe}_2\text{O}_3$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-CuO}$ composites via solution-combustion methods. Both composites showed reversible capacity of 172 mA h g^{-1} over 100 cycles at 1 C, and the $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-CuO}$ delivered good rate capability of 106 mA h g^{-1} up to 20 C.⁶¹⁷

6.3.4 Other conductive additive coatings

Conductive polymers have been used to coat on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to enhance the electrical conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Xie et al. synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-polyacene}$ composite with polyacene evenly distributed between the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. The modification of polyacene led to much higher electronic conductivity of $10^{-1} \text{ S cm}^{-1}$ than the bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($10^{-9} \text{ S cm}^{-1}$). This resulted in a capacity retention of 88% over 200 cycles at 3 C, and good rate capability up to 10 C.⁶¹⁸ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorods coated with a poly (3,4-ethylenedioxythiophene) layer were prepared by Zhang et al. This composite maintained a specific capacity of $168.7 \text{ mA h g}^{-1}$ at 1 C with a high capacity retention of 99.5% over 100 cycles, which could be ascribed to the highly conductive polymer coating to enhance the electronic conductivity of the composites.⁶¹⁹

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers coated with a layer of conductive $\text{TiN/TiO}_x\text{N}_y$ were synthesized by Paik et al. The conductive coating enabled fast electron transport, thus resulting in better specific capacity especially at high rates compared to bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$.⁶²⁰ Qu et al. found that the AlF_3 modification on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can suppress the gas generation during charge/discharge and enhance the rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials.⁶²¹

In conclusion, surface modification is an effective method to improve the cycle stability and rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes in LIBs. Conductive coating on the surface on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can improve the electronic conductivity of composite electrodes, protect active materials from directly contact with the electrolyte, and prevent the dissolution of metal ions in the electrolyte.^{87, 593} Due to its good electrical conductivity, low cost, and good chemical and thermal stability, TiN has been chosen to coat onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles to improve the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites. Carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been prepared as comparison.

6.4 Experimental

6.4.1 Synthesis

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared via a solid-state reaction using Li_2CO_3 (0.5 g, 0.0677 mol, $\geq 99\%$ purity, Acros Organics) and anatase TiO_2 (1.351 g, 0.0169 mol, $\geq 99\%$ purity, Sigma Aldrich) with a stoichiometric Li/Ti molar ratio of 4:5. The ratio of precursors was varied with 0 %, 2 %, 4 % and 6 % excess of Li. The precursors were manually ground in motor and pestle, then further homogenised via planetary ball milling (Mixer Mill MM200) with acetone medium (~ 1 ml) for 3 h. This mixture was dried in a vacuum oven at 80 °C for 0.5 h, then calcined in a muffle furnace (Carbolite CWF 1200) at 800 °C for 0.5 h in air to crystallise $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The products were white powders and were ground before characterization. This crystallised $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was heated at 3 °C min^{-1} to 650 °C and maintained for 6 h under 5% H_2/N_2 or NH_3 to check the effect of heating environment on $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

To obtain carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the crystallised $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (0.5 g, 1.089 mmol) was manually ground in a pestle and mortar with sucrose ($\text{C}_6\text{H}_{12}\text{O}_6$, 0.132 g, 0.385 mmol, Fisher Scientific) to obtain a uniform mix that was then heated at 3 °C min^{-1} to 650 °C and maintained for 6 h under 5% H_2/N_2 . The products were black powders and were ground before further characterisation. Bare carbon was prepared using sucrose as a precursor via the same method as described above.

TiN modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were prepared using a propylamine cross-linking sol-gel process^{265, 370, 395, 399} under nitrogen using glove box or Schlenk line methods. $\text{Ti}(\text{NMe}_2)_4$ (0.213 cm^3 , 0.898 mmol, prepared from TiCl_4 and LiNMe_2) was dissolved in dry THF (7.5 cm^3 , distilled from sodium/benzophenone), and added to 0.5 g dry $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder. $^n\text{PrNH}_2$ (0.148 cm^3 , 1.796 mmol, distilled from BaO) was slowly added. The solution gradually changed colour from yellow to orange. The suspension was stirred at room temperature for ~ 16 h and dried *in vacuo* to form a sticky powder. This was heated at 3 °C min^{-1} to 650 °C and maintained for 6 h under NH_3 . Bare TiN was prepared via the same method as described above.

6.4.2 Characterisation and electrochemistry

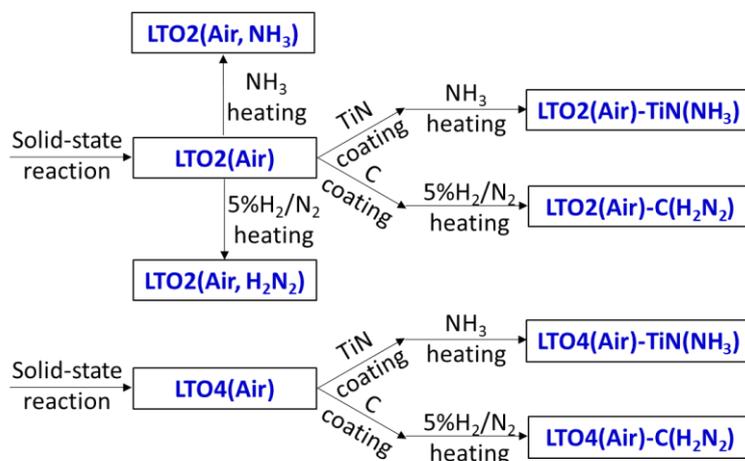
Powder X-ray diffraction used a Bruker D2 Phaser with $\text{CuK}\alpha$ radiation.²⁷⁰ Transmission electron microscopy (TEM) was carried out with a FEI Tecnai T12 (120 kV). Combustion (C, H, N) analysis was outsourced to Medac Ltd. Electrochemical testing used a Biologics VMP-2 multichannel potentiostat.

Electrodes for use in lithium half cells were prepared by mixing the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or C coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder (80 wt%) with acetylene black (10 wt%) and poly(vinylidene fluoride) (10

wt%) dissolved in N-methyl-pyrrolidone. The slurry was cast onto Al foil (125 μm thick, Temper annealed, 99.0 % purity, Advent Research Materials) and dried at 120 $^{\circ}\text{C}$ in vacuum for 12 h. The foil was cut into circular discs with a diameter of 11 mm and pressed at 10 tons to obtain the cathode with a typical mass of ~ 0.037 g. Swagelok cells were assembled in an argon-filled glove box with lithium foil (Rockwood Lithium GmbH) electrodes and glass microfiber filter (Whatman, GF/F grade) separators soaked in 8 drops of 1 mol dm^{-3} LiPF_6 in ethylene carbonate/dimethyl carbonate (EC: DMC = 1:1 in volume) electrolyte (BASF, LP30). Galvanostatic testing was carried out at 25 $^{\circ}\text{C}$ at 0.1 C rate of charge/discharge (0.1 C is a current calculated for $0.1\times$ the theoretical capacity per hour) within the voltage range of 0.8-2.5 V (vs. Li^+/Li).

6.5 Results and discussion

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were prepared by a solid-state reaction. First, the effect of the impurities and heating environment on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were investigated. Then, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were coated with TiN or carbon to check if the expected increased conductivity and surface stability enhanced the discharge capacity and cycle stability of the composites. Scheme 6-1 shows the labels used for different samples.



Scheme 6-1 Preparation conditions and sample labels for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and C coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials.

6.5.1 Effect of impurities on bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were prepared using a stoichiometric ratio of Li_2CO_3 and anatase TiO_2 precursors with various Li excess, followed by firing at 800 $^{\circ}\text{C}$ in air, to determine the effect of impurities on their properties. The Li excess amount was set as 0%, 2%, 4% and 6%, which is corresponding to sample defined as LTO0(Air), LTO2(Air), LTO4(Air), LTO6(Air), respectively.

The X-ray diffraction peaks of the resulting $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples (Figure 6-5) were mainly consistent with the standard spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (JCPDS card no. 49-0207, space group $Fd3m$). However, some impurity phases are detected in these samples, which can be indexed to anatase TiO_2 (JCPDS card no. 21-1272) and rutile TiO_2 (JCPDS card no. 21-1276). It has been reported that Li loss leads to anatase TiO_2 which can convert to rutile TiO_2 at 800 °C.^{622, 623} The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample prepared with 2% Li excess showed negligible impurity reflection peaks. The TEM images (Figure 6-10 a and b) of this $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples exhibited particle sizes of ~ 200 nm. This small particle size can reduce the length of Li-ion migration paths, and facilitate easier Li-ion transfer in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystals.⁵⁵³ No carbon, hydrogen and nitrogen (<0.1 wt.%) are detectable according to the microanalysis result (Table 6-1) for this $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample.

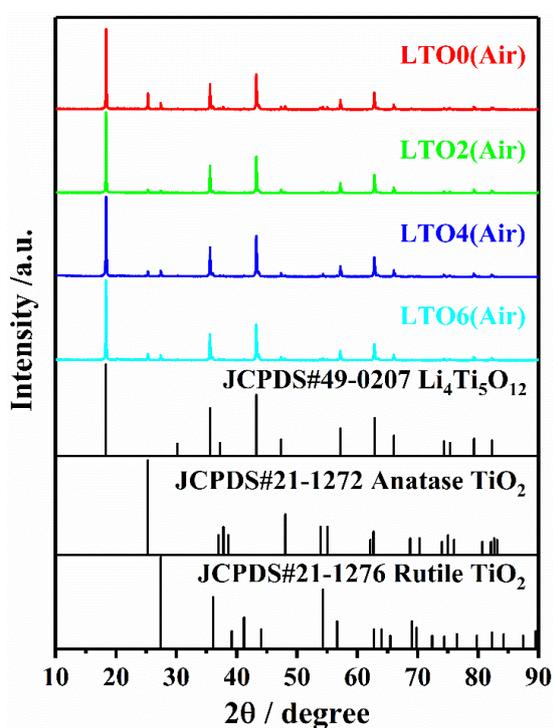


Figure 6-5 XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples prepared with various Li excess amount of 0%, 2%, 4% and 6%, respectively, then heated under air at 800 °C. The black stick pattern denotes the literature positions and intensities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, anatase TiO_2 and rutile TiO_2 reflections.

The electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes were tested by galvanostatic cycling in Li half cells. Figure 6-6 showed the initial charge/discharge curves at 0.1 C and the variations in charge capacity over the first 50 cycles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with 0%, 2% and 4% Li excess. The LTO2(Air) sample had much higher initial charge capacity of 165 mA h g^{-1} than LTO0(Air) (132 mA h g^{-1}) and LTO4(Air) (130 mA h g^{-1}) samples. This could be attributed to a lower amount of impurities in LTO2(Air). The capacity of LTO2(Air) maintained steadily during the initial 10 cycles, but dropped quickly in the following 10 cycles, then decayed gradually with continuous cycling, retaining 80 mA h g^{-1} after 50 cycles. LTO4(Air) had lower initial charge capacity compare to LTO2(Air), but it maintained steadily

during the initial 20 cycles, and lost capacity less rapidly with continuous cycling, retaining 75 mA h g⁻¹ after 50 cycles. It has been reported that TiO₂ is an active material in Li half cells which produces an oxidation peak at ~2.1 V vs Li/Li⁺ and a reduction peak at ~1.6 V vs Li/Li⁺ in cyclic voltammetry.⁶²⁴ These correspond to the extra plateaus at 2.1 V in the charge profile and 1.6 V in the discharge profile for LTO0(Air) and LTO4(Air) samples, which showed TiO₂ impurity peaks in the XRD patterns (Figure 6-5). However, it has been reported that the TiO₂ impurities have a negative effect on the Li ion diffusion coefficient of Li₄Ti₅O₁₂ composites, which can result in poor electrochemical performance.⁶²⁵

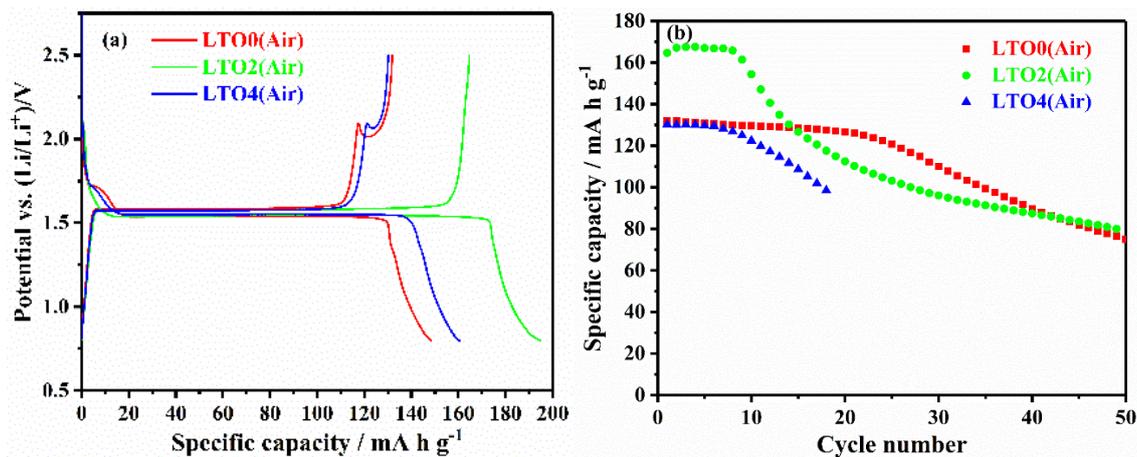


Figure 6-6 (a) The initial cycle of voltage profile vs specific capacity and (b) specific capacity vs cycle number of Li₄Ti₅O₁₂/Li half cells under galvanostatic cycling between 0.8 and 2.5 V at 0.1 C (sample labels explained in Scheme 6-1).

6.5.2 Effect of heating environment on bare Li₄Ti₅O₁₂

Li₄Ti₅O₁₂ samples were prepared by firing at 650 °C in NH₃ or 5%H₂/N₂ to check the effect of heating environment on their properties. The sample labels were shown in Scheme 6-1. The resulting Li₄Ti₅O₁₂ samples showed similar X-ray diffraction peaks (Figure 6-7), which were mainly consistent with the standard spinel Li₄Ti₅O₁₂. There are some impurity reflection peaks detectable in these samples, which correspond to anatase TiO₂ and rutile TiO₂.

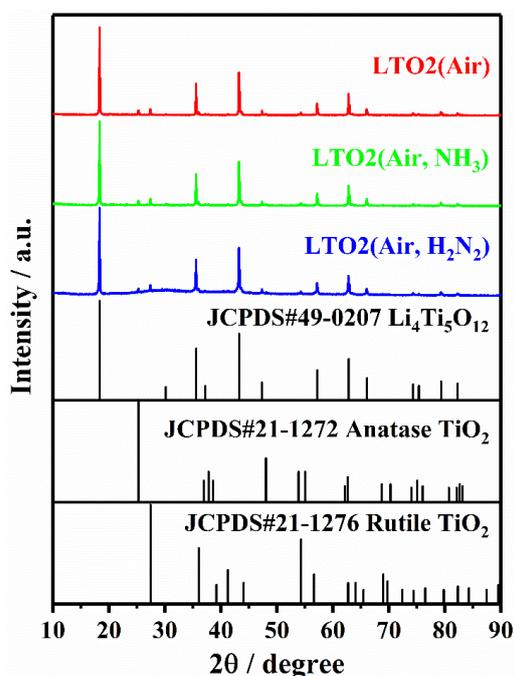


Figure 6-7 XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples prepared with 2% Li excess and heated under NH_3 and 5% H_2/N_2 , respectively, at 650 °C (labels explained in Scheme 6-1). The black stick pattern denotes the literature positions and intensities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, anatase TiO_2 and rutile TiO_2 reflections.

Figure 6-8 shows the initial charge/discharge curves and the cycle stability at 0.1 C over the first 50 cycles for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples fired in NH_3 and 5% H_2/N_2 . LTO2(Air), LTO2(Air, NH_3) and LTO2(Air, H_2N_2) had initial charge capacities of 165, 154 and 150 mA h g^{-1} , respectively. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ fired in H_2N_2 had lower initial charge capacity than LTO2(Air) and it dropped quickly in the following cycles. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ fired in NH_3 showed less initial charge capacity but it decayed less rapidly over the first 20 cycles compared to LTO2(Air). The NH_3 and 5% H_2/N_2 heating environments were carried forward to the surface modification of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with TiN and carbon coatings, respectively.

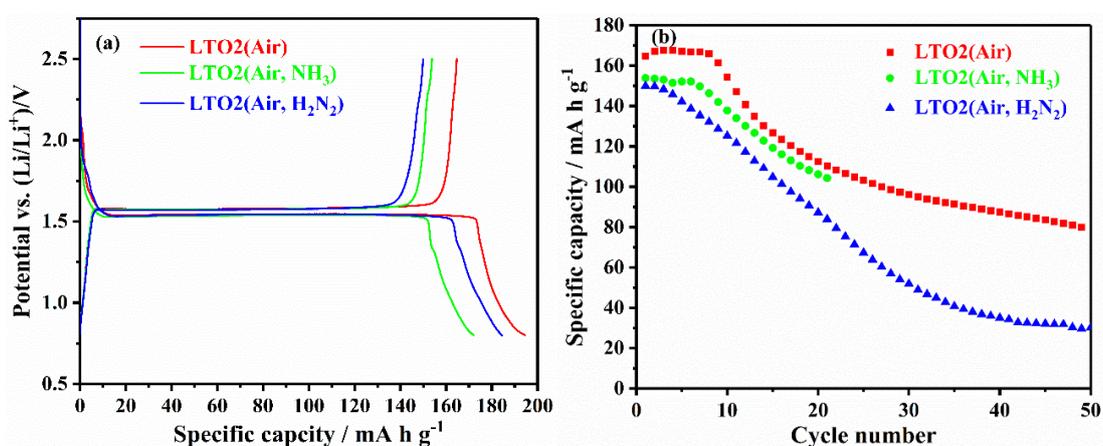


Figure 6-8 (a) The initial cycle of voltage profile vs specific capacity and (b) specific capacity vs cycle number of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ half cells under galvanostatic cycling between 0.8 and 2.5 V at 0.1 C (sample labels explained in Scheme 6-1).

6.5.3 Synthesis, microstructure and electrochemistry of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ modified with TiN or C

The LTO2(Air) and LTO4(Air) samples with relatively better cycle performance at 0.1 C were chosen for coating (Scheme 6-1). Carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was obtained by mixing sucrose and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via grinding then heating in 5% H_2/N_2 . This solid-state reaction is an effective and simple strategy to coat carbon onto electrodes in LIBs.^{309, 553} TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was achieved via a propylamine-crosslinked sol-gel method, then heating in NH_3 , which has been proved to be an effective method to obtain TiN coated electrodes for LIBs in previous research.³⁷⁰ These approaches are summarised in Scheme 6-1.

Figure 6-9 showed the X-ray diffraction patterns of TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples, which were mainly consistent with the standard spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structure, with some impurity reflection peaks corresponding to anatase TiO_2 and rutile TiO_2 . As shown in Table 6-1, the combustion analysis for the TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample with 2% Li excess showed it to contain 0.22 wt% C, 0.88 wt% H and 2.39 wt% N, which is calculated to be 10 wt% TiN coating onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The corresponding carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample contains 2.53 wt% of carbon in the composite (Table 6-1). The TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples with 4% Li excess contain 12 wt% TiN and 3.99 wt% carbon coatings, respectively (Table 6-1).

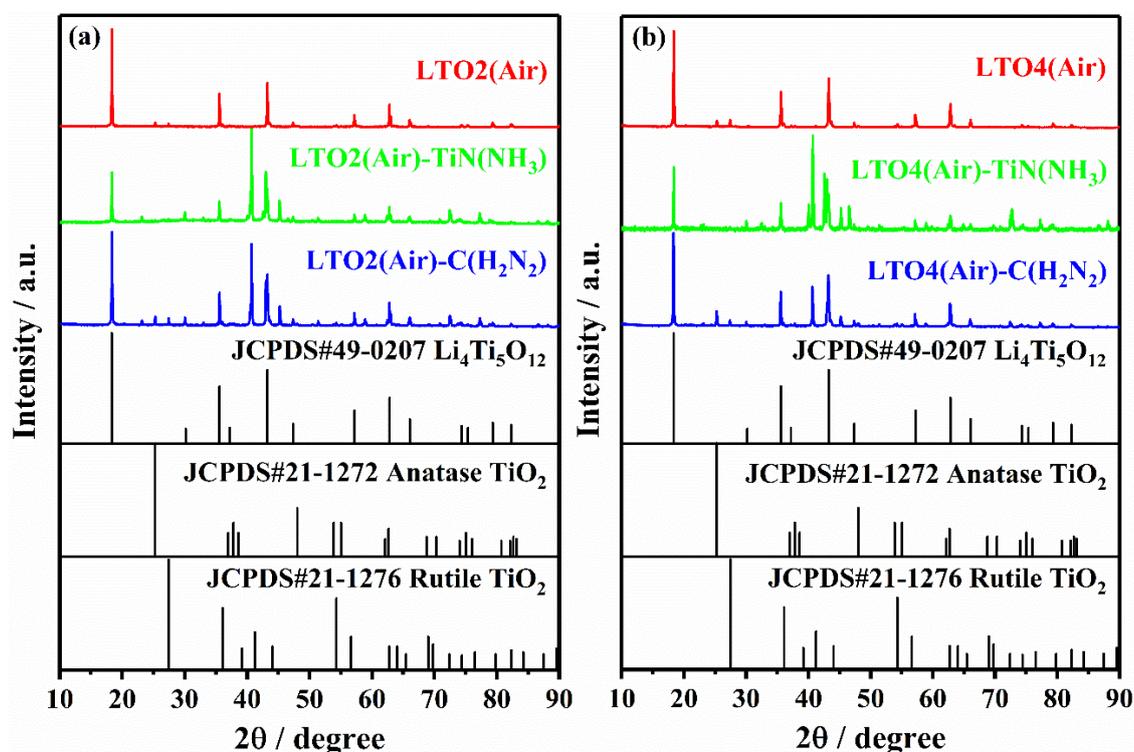


Figure 6-9 XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared with (a) 2% and (b) 4% Li excess and heated under air, then modified with TiN and carbon, respectively (labels explained in Scheme 6-1). The black stick pattern denotes the literature positions and intensities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, anatase TiO_2 and rutile TiO_2 reflections.

Table 6-1 Combustion analysis (C, H, N) results of the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiN or carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples (labels explained in Scheme 6-1).

Sample	% C	% H	% N
LTO2(Air)	<0.10	<0.10	<0.10
LTO2(Air)-TiN(NH_3)	0.22	0.88	2.39
LTO2(Air)-C(H_2N_2)	2.53	<0.10	1.70
LTO4(Air)-TiN(NH_3)	0.20	0.94	2.76
LTO4(Air)-C(H_2N_2)	3.99	<0.10	1.73

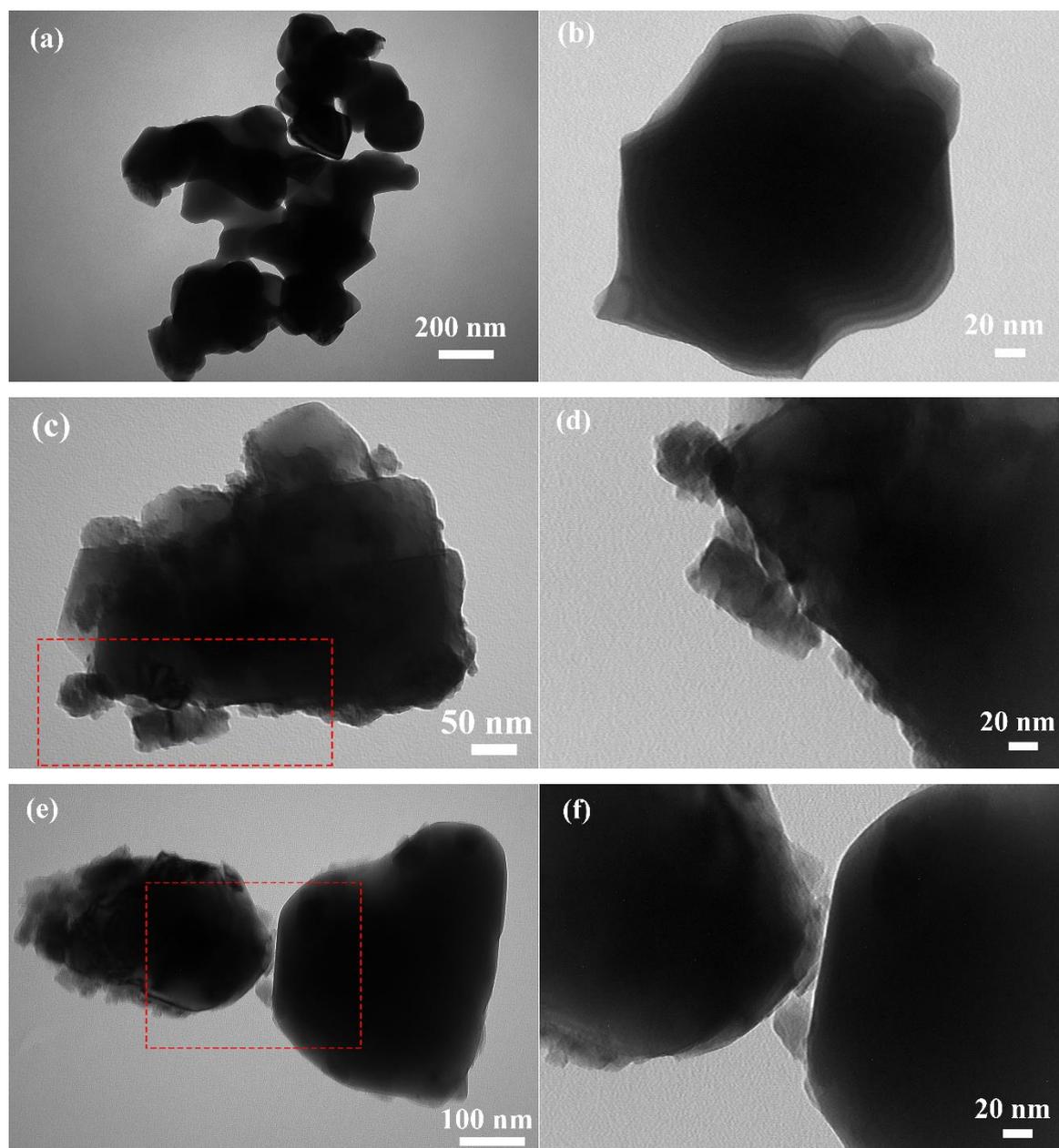


Figure 6-10 TEM images of (a) and (b) LTO2(Air), (c) and (d) LTO2(Air)-TiN(NH_3), (e) and (f) LTO2(Air)-C(H_2N_2) samples. The enlarged view of the regions marked by the red boxes in (c) and (e) are displayed in (d) and (f), respectively. Sample labels are explained in Scheme 6-1.

TEM images of the bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample (Figure 6-10 a and b) exhibited a smooth surface. TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Figure 6-10 c and d) showed TiN nanoparticles were aggregated to some extent and distributed across the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It is challenging to form a thin and uniform TiN nanolayer with full coverage on $\text{Li}_4\text{Ti}_5\text{O}_{12}$. TEM images of carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample (Figure 6-10 e and f) showed the carbon layer partially coated on the surface acted to separate the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. The presence of the TiN and carbon on the surface provides a conducting network between the particles which is supposed to improve the electrical conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites.

The electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites are supposed to be improved after TiN and carbon coatings due to the enhanced conductivity and surface stability. However, TiN and carbon themselves can undergo conversion reactions at low potentials to contribute to capacities in LIBs.¹² Therefore, bare TiN and carbon were employed as the active materials to check their contributions. Bare TiN and carbon samples were prepared in the same way as achieving coatings on $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Figure 6-11 showed the X-ray diffraction pattern of the TiN sample, which can be indexed to the standard cubic TiN structure (JCPDS Card No. 65-0414). The carbon sample was mainly amorphous.

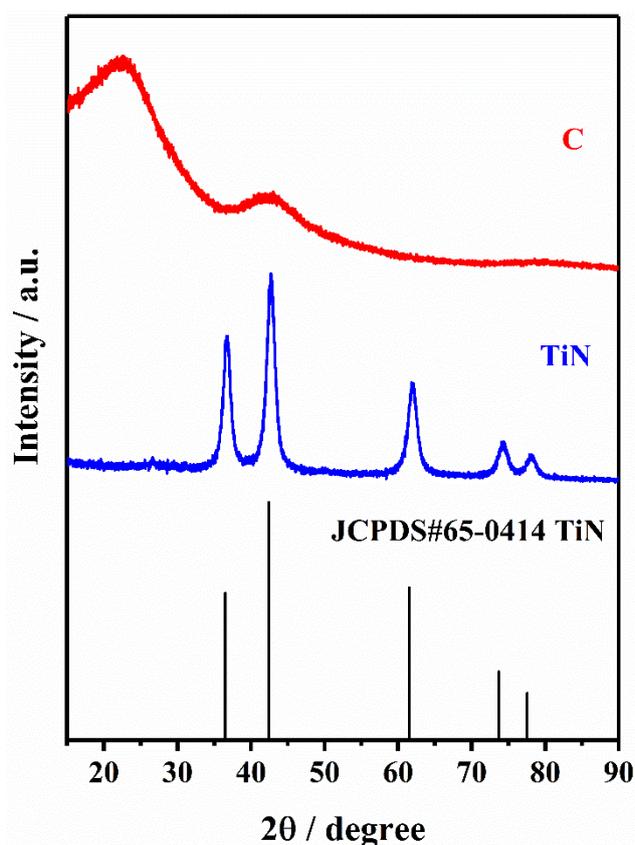


Figure 6-11 XRD patterns of bare TiN and carbon, respectively (labels explained in Scheme 6-1). The black stick pattern denotes the literature positions and intensities of TiN reflections.

TiN and carbon electrodes were fabricated and Li half cells were assembled in the same way as the TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples. The cyclic voltammetry of TiN (Figure 6-12) and carbon (Figure 6-13) were presented over the potential range in which the TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ batteries are operated. The results exhibited very low currents over 100 cycles, which could be confirmed by the plots of potential against charge/discharge capacity for TiN (Figure 6-12) and carbon (Figure 6-13). This galvanostatic cycling was tested at a current density of 175 mA g^{-1} , which is 10 times larger than that used in the TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes, to keep the same specific current for the coating content. TiN and carbon showed specific charge capacities of lower than 1.6 and 1.7 mA h g^{-1} over 100 cycles, respectively, which indicated that the TiN and carbon were almost electrochemically inert in LIBs.

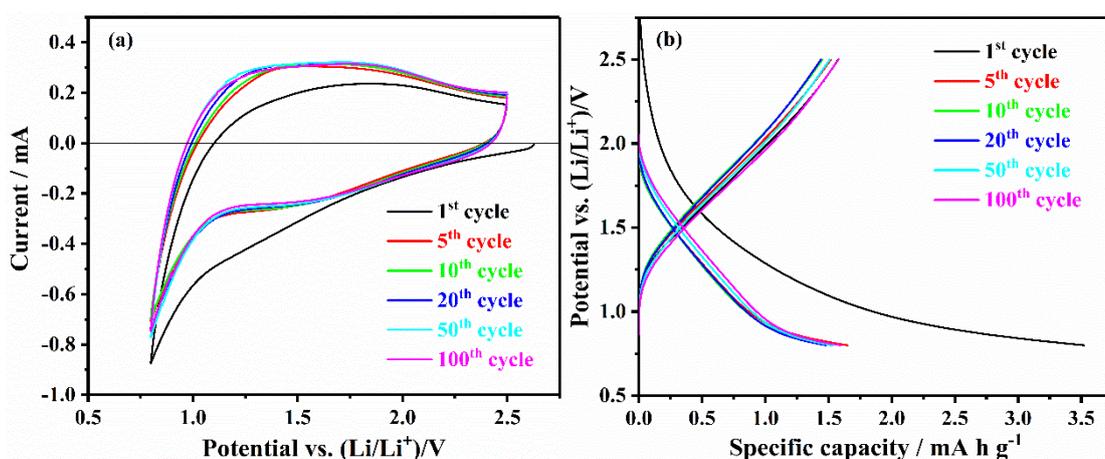


Figure 6-12 (a) Cyclic voltammetry plots of TiN/Li half cell at 20 mV s^{-1} over the range of 0.8 to 2.5 V at room temperature; (b) The voltage profile against specific capacity of TiN/Li half cell under galvanostatic cycling between 0.8 and 2.5 V for 100 cycles.

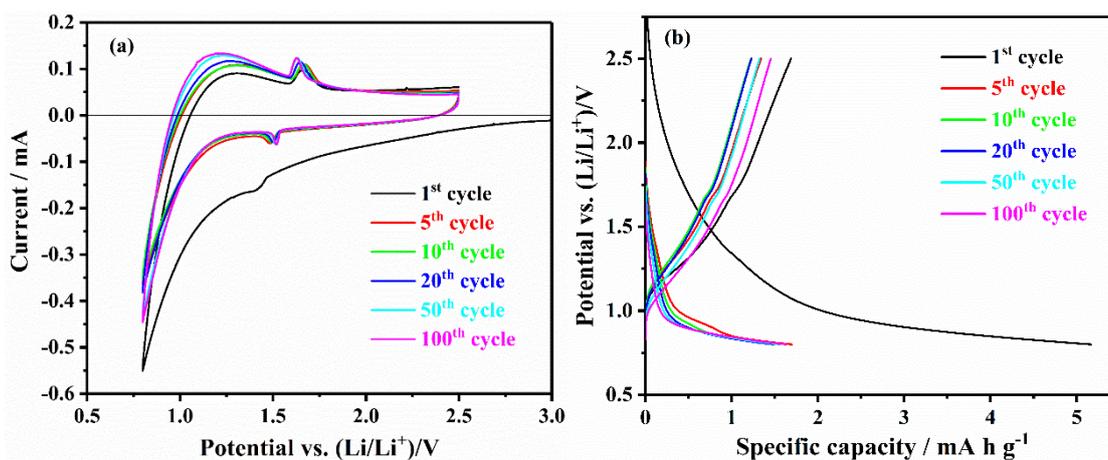


Figure 6-13 (a) Cyclic voltammetry plots of carbon/Li half cell at 20 mV s^{-1} over the range of 0.8 to 2.5 V at room temperature; (b) The voltage profile against specific capacity of carbon/Li half cell under galvanostatic cycling between 0.8 and 2.5 V for 100 cycles.

The charge/discharge profiles in the initial cycle and the variations in charge capacity at 0.1 C rate over 50 cycles for TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with 2% Li excess are shown in Figure 6-14. LTO2(Air), LTO2(Air)-TiN(NH_3) and LTO2(Air)-C(H_2N_2) had initial charge capacities of 165, 174 and 157 mA h g^{-1} , respectively. The carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ had lower initial charge capacity than LTO2(Air) and it dropped quickly in the following cycles. The TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ had higher initial charge capacity but it decayed more rapidly over the 50 cycles compared to LTO2(Air).

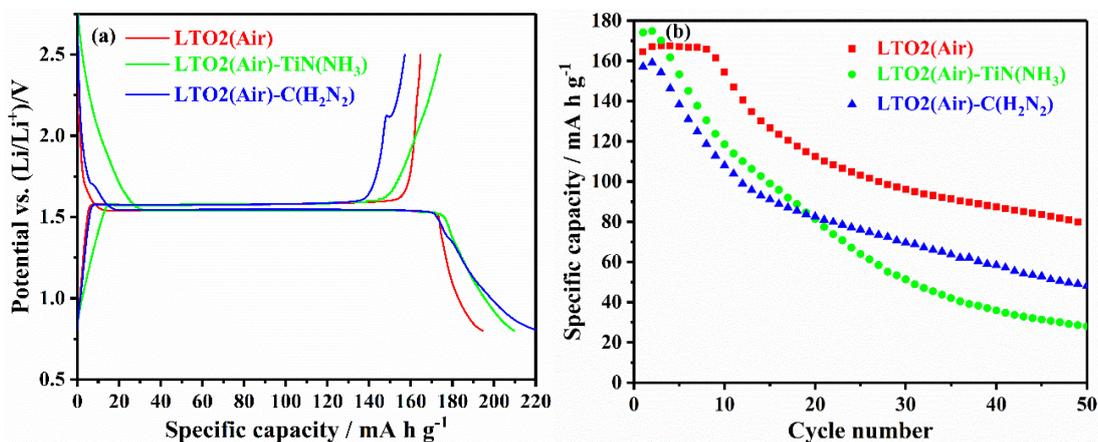


Figure 6-14 (a) The initial cycle of voltage profile vs specific capacity and (b) specific capacity vs cycle number of uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiN or carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in Li half cells under galvanostatic cycling between 0.8 and 2.5 V at 0.1 C (sample labels explained in Scheme 6-1).

Figure 6-15 shows the initial charge/discharge plots at 0.1 C and the cycle stability over the first 50 cycles of TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with 4% Li excess. LTO4(Air), LTO4(Air)-TiN(NH_3) and LTO4(Air)-C(H_2N_2) exhibited specific capacities of 130, 144 and 146 mA h g^{-1} at 0.1 C in initial cycle, respectively. The TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ showed higher initial charge capacities than LTO4(Air), but these dropped quickly over 50 cycles.

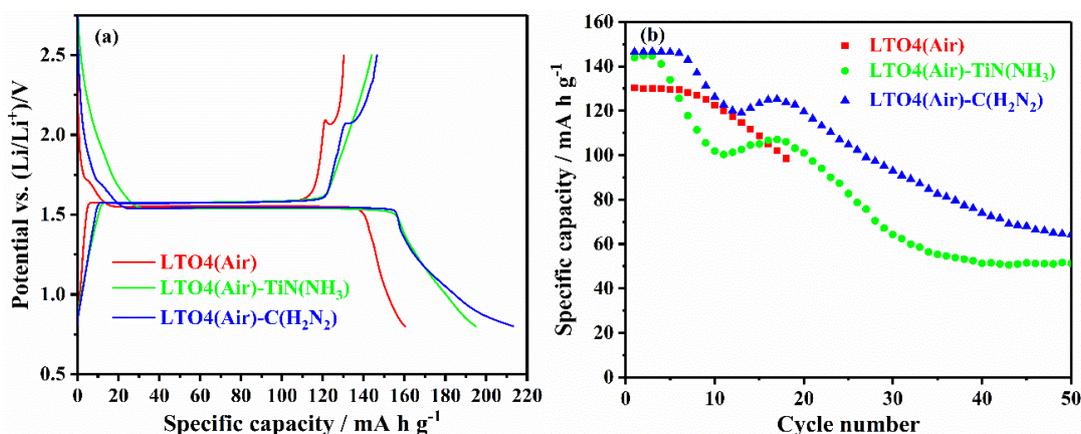


Figure 6-15 (a) The initial cycle of voltage profile vs specific capacity and (b) specific capacity vs cycle number of uncoated $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiN or carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in Li half cells under galvanostatic cycling between 0.8 and 2.5 V at 0.1 C (sample labels explained in Scheme 6-1).

The TiN and carbon conductive coatings did not deliver the expected improvement in cycle performance for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes in LIBs. These preliminary electrochemical properties data presented above for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ requires further characterisation. Even though TiN and carbon coatings on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ could improve the conductivity between particles, these nanoparticles aggregated together to form partial coating and thick layer (Figure 6-10), which could inhibit the Li-ion transfer in the composites. Further optimisation of TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites are required to achieve a uniform, thin and intact conductive coating for the improvement of electrochemical performance in LIBs.

6.6 Conclusions

A series of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples with Li excesses of 0% to 6% were synthesized via solid-state reaction. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared with 2% Li excess were found to have minimum TiO_2 impurities, which delivered a high initial capacity of 165 mA h g^{-1} . This $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited a small particle size of $\sim 200 \text{ nm}$, which ensures short Li-ion migration paths in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystals to facilitate easier Li-ion transfer. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were post-heated in NH_3 and $5\% \text{H}_2/\text{N}_2$ at $650 \text{ }^\circ\text{C}$ to investigate the effect of heating environment on their properties. TiN and carbon were successfully coated onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The specific capacity and cycle stability of TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were examined. TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited improved initial capacity of 174 mA h g^{-1} , close to theoretical capacity of 175 mA h g^{-1} , but these coatings did not deliver the expected improvement in cycle stability for $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Further improvement are required for the application of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials in lithium-ion batteries.

Chapter 7: Sol-gel routes and evaporation induced self-assembly to nanostructured titanium nitride as a cathode for lithium-sulfur batteries

7.1 Introduction

Lithium-sulfur (Li-S) batteries are promising energy storage system for large scale industrial application, due to their high energy density, low cost and environmental benignity.⁹ The practical use of Li-S batteries has been inhibited by the poor conductivity of sulfur and lithium sulfide, the large volume expansion of the sulfur cathode in discharge (~80%), the shuttle effect caused by the dissolution and diffusion of intermediate long-chain lithium polysulfides in electrolytes (Figure 7-1), as well as safety issues of lithium metal anodes.¹¹⁸ Tremendous efforts have been applied to tackle these issues, such as encapsulating sulfur cathodes with conductive host materials like porous carbon, polymeric and inorganic materials. The host materials can improve the conductivity of the sulfur cathode, confine lithium polysulfides within the host and buffer the volume change of sulfur cathode during charge/discharge process.¹¹⁵

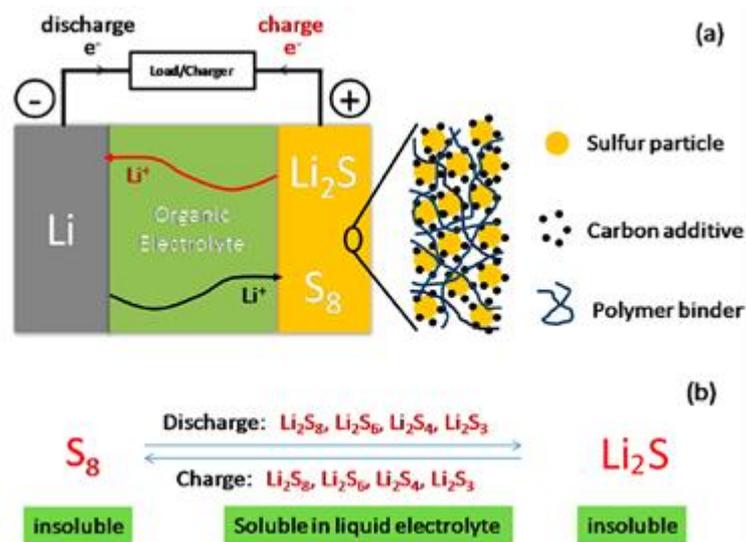


Figure 7-1 (a) Illustration of the charge (red) and discharge (black) process in a Li-S battery composed of sulfur composite cathode, lithium metal anode and organic electrolyte. (b) The formation of soluble lithium polysulfides (Li₂S₈, Li₂S₆, Li₂S₄, and Li₂S₃) and insoluble Li₂S in the charge/discharge process. Reproduced from Ref. ¹¹¹ with permission from American Chemical Society 2013.

Efforts to improve the electrochemical performances of Li-S batteries have been focused on the development of carbon-based sulfur composites. Porous carbon-sulfur composites have been prepared by Gao et al. via thermal treatment of sublimed sulfur and microporous carbon spheres. A sulfur-carbon composite with 42 wt% sulfur loading exhibited a reversible capacity of $\sim 650 \text{ mA h g}^{-1}$ after 500 cycles at current density of 400 mA g^{-1} . As illustrated in Figure 7-2, the micropores ($< 2 \text{ nm}$) confined sulfur and lithium polysulfides to prevent them from releasing into the electrolyte, thus the electrochemical reaction of the sulfur cathode was constrained within the narrow micropores, resulting in an improved cycle stability of Li-S batteries.¹¹⁹ Mesoporous materials (2-50 nm) with increased pore sizes over micropores could contribute to improved sulfur loading and allow easy access to sulfur by liquid electrolytes for facile Li^+ migration.⁹ Li et al. prepared mesoporous carbon-sulfur composite cathodes for Li-S batteries with tunable pore sizes ranging from 3 nm to 22 nm. It was found that the partial sulfur-filling composites exhibited higher initial discharge capacity and better cycle stability as full sulfur-filling in mesopores hinders the access of electrolyte and ion transport. An initial specific capacity of $\sim 1390 \text{ mA h g}^{-1}$ at 0.1 C rate and good cycle stability of $\sim 840 \text{ mA h g}^{-1}$ over 100 cycles were achieved via optimising the pore size of mesoporous carbon (22 nm) and sulfur loading (50 wt%).¹²⁰

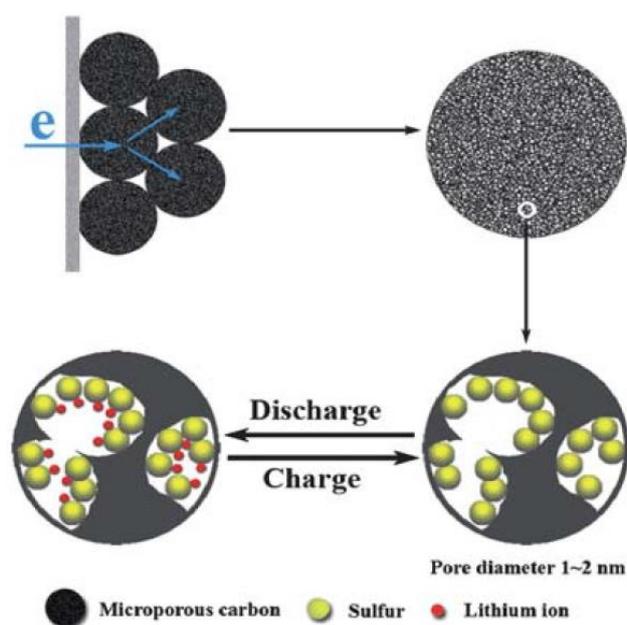


Figure 7-2 Schematic illustration of the electrochemical reaction constrained within the micropores of the sulfur-carbon sphere composite cathode. Reproduced from Ref. ¹¹⁹ with permission from the Royal Society of Chemistry 2010.

TiN with high conductivity and unique morphology such as porous structure or hollow sphere are promising host materials for sulfur cathodes in Li-S batteries. As shown in Figure 7-3, Goodenough et al. reported the mesoporous TiN-enabled highly stable Li-S batteries, which showed a discharge

capacity of 988 mA h g^{-1} at 0.5 C , with capacity retention of 644 mA h g^{-1} after 500 cycles. This can be ascribed to the high electrical conductivity, robust porous framework and favourable adsorption properties of TiN.¹⁵⁵ Also, Zheng et al. prepared hollow porous TiN tubes with high conductivity as a sulfur host cathode material for Li-S batteries. The TiN not only reduces the shuttle effect in charge/discharge process due to the strong interaction between TiN and lithium polysulfides, but also acts as a catalyst to facilitate the oxidation process in Li-S batteries. The TiN-S cathodes delivered a reversible capacity of 840 mA h g^{-1} at 0.5 C after 450 cycles, and a rate capability of 1026 mA h g^{-1} at 5 C .¹⁵⁴

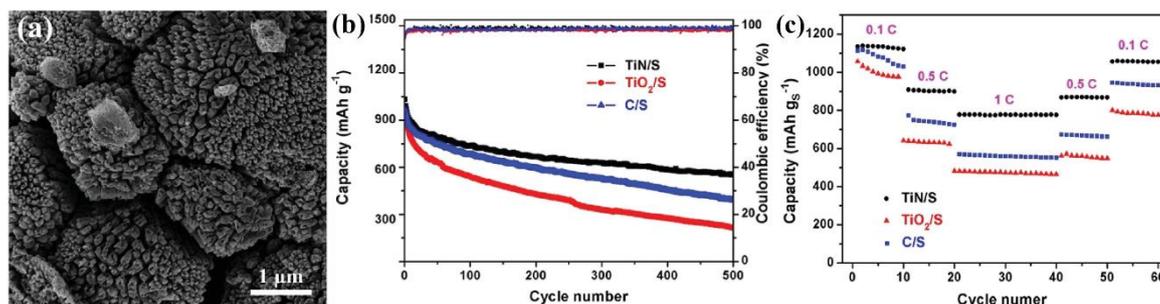


Figure 7-3 (a) SEM image of mesoporous TiN. (b) Cycle stability of TiN-S, TiO_2 -S and Vulcan C-S cathodes at 0.5 C over 500 cycles. (c) Rate capability of TiN-S, TiO_2 -S and Vulcan C-S cathodes in Li-S batteries, cycled at various sequential rates from 0.1 C to 1 C . Reproduced from Ref. ¹⁵⁵ with permission from John Wiley and Sons 2016.

In this chapter, an attempt was made to introduce mesoporous TiN as a sulfur host material to enhance the conductivity of sulfur cathodes, buffer the volume change and reduce the shuttle effect during charge/discharge process. Nanostructured TiN was synthesized by a cross-linked sol-gel route or evaporation induced self-assembly method with surfactants to achieve a porous structure. Carbon has been treated as a comparison in this work.

7.2 Experimental

7.2.1 Synthesis

(1) HDA assisted cross-linked sol-gel method⁶²⁶ to prepare TiN

Preparation of TiN-HDA-I and TiN-HDA-M: Titanium amides and the sol-gel intermediates were handled under nitrogen using glove box or Schlenk line methods. 2.704 g of hexadecylamine (HDA, distilled from BaO) was dissolved in 20 ml (7.5 ml for TiN-HDA-M) of dry THF (distilled from sodium/benzophenone) and stirred for 4 h. $\text{Ti}(\text{NMe}_2)_4$ (2.65 cm^3 , 11.2 mmol, Epichem) was added and stirred for 2 h. The solution changed colour from transparent to dark red. 0.92 ml $^n\text{PrNH}_2$

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(distilled from BaO) was added twice to the solution 2 h apart (1.84 ml $^n\text{PrNH}_2$ was added once for TiN-HDA-M). The solution was stirred at room temperature overnight and pumped off to form viscous gels. This was then heated under a flow of NH_3 (dried with a column of molecular sieves) at $1\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$ and maintained for 10 h ($3\text{ }^\circ\text{C min}^{-1}$ to $650\text{ }^\circ\text{C}$ and maintained for 6 h for TiN-HDA-M) before cooling. The product was a black powder and was ground in a pestle and mortar before further characterisation.

Preparation of TiN-HDA-I2 and TiN-HDA-M2: the procedures are the same as above. The only difference is much higher NH_3 flow rate during heating.

(2) P123 assisted cross-linked sol-gel method⁶²⁶ to prepare TiN

Preparation of TiN-P123-1, TiN-P123-2 and TiN-P123-3: The HDA surfactant was replaced with PEG-PPG-PEG (Pluronic P-123, Sigma-aldrich). The prepared gel was heated under a flow of NH_3 at $1\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$ and maintained for 10 h for TiN-P123-1 sample ($1\text{ }^\circ\text{C min}^{-1}$ to $650\text{ }^\circ\text{C}$ and maintained for 10 h for TiN-P123-2, $3\text{ }^\circ\text{C min}^{-1}$ to $650\text{ }^\circ\text{C}$ and maintained for 17 h for TiN-P123-3).

Preparation of TiN-P123-700 to TiN-P123-1000 series samples: the procedures are the same as above. The prepared gels were heated under a flow of NH_3 at $3\text{ }^\circ\text{C min}^{-1}$ to $700\text{-}1000\text{ }^\circ\text{C}$ and maintained for 24 h.

(3) PEO-b-PS assisted evaporation induced self-assembly (EISA) method¹⁵² to prepare TiN

Poly(ethylene oxide)-block-polystyrene (PEO-b-PS) was prepared by an atom transfer radical polymerization (ATRP) method.⁶²⁷ The method consists of the preparation of PEO-Br macroinitiator and polymerization of styrene to form PEO-b-PS. To prepare the PEO-Br macroinitiator, poly(ethylene oxide) methyl ether (PEO-OH, average $M_n = 5\text{ kg mol}^{-1}$, 20 g) was dissolved in dichloromethane (CH_2Cl_2 , 100ml), then trimethylamine (TEA, 5 ml) was added. The mixture was cooled in an ice water bath, and 2-bromoisobutylbromide (1.48 ml) was injected dropwise under stirring. The ice bath was removed and the mixture was stirred at room temperature overnight. The obtained yellowish solution was extracted in water and precipitated in cold ether twice, then dried under vacuum at room temperature overnight to obtain the PEO-Br macroinitiator. To polymerize styrene, PEO-Br (2.539 g, 0.5 mmol), styrene (20 g, 192 mmol, filtered by using neutral alumina column to remove the inhibitor), pentamethyldiethylenetriamine (PMDETA, 0.085 g, 0.5 mmol) and copper bromide (CuBr , 0.071 g, 0.5 mmol, purified by stirring in acetic acid, and washed with ethanol and diethyl ether) were placed in a 50 ml round bottom flask. After three cycles of freeze-pump-thaw, the mixture was reacted at $110\text{ }^\circ\text{C}$ for 12 h in an oil bath. The obtained gel-like product was dissolved in THF and filtered through neutral alumina column to remove the copper catalyst.

The resulting solution was added to cold methanol to precipitate white PEO-b-PS, then dried under vacuum at room temperature overnight.

Preparation of TiO₂-(PEO-b-PS)-1 and TiN-(PEO-b-PS)-1: titanium(IV) isopropoxide (TTIP, 1.2 g, 99.999% purity, Sigma Aldrich) was added to 4.4 g of the polymer solution consisting of PEO-b-PS block co-polymer, HCl, H₂O and THF in a mass ratio of 1:1.1:1.9:18, and stirred for 1 h. The solution was then poured into a glass Petri dish with a cover and heated at 50 °C on a hot plate. Once the solvent evaporated, the resulting polymer/inorganic hybrid film was placed inside an oven at 100 °C for 12 h to cure the film. The obtained product was scraped and crushed into a powder. This was then heated under air at 1 °C min⁻¹ to 500 °C and maintained for 3 h before cooling. The resulting TiO₂-(PEO-b-PS)-1 was heated again under a flow of NH₃ at 1 °C min⁻¹ to 700 °C and maintained for 10 h to convert TiO₂ to TiN, and the final TiN-(PEO-b-PS)-1 sample was obtained.

Preparation of TiO₂-(PEO-b-PS)-2 and TiN-(PEO-b-PS)-2: the procedures were the same as above while the solvent evaporation process was much slower. The solvent was evaporated in a fume hood at room temperature overnight. The resulting film was then placed on a hot plate at 25 °C, 50 °C and 80 °C for one day each to cure the film.

(4) Melt-diffusion method to prepare S-TiN or S-AB composites

25 wt% sulfur was well mixed with 75 wt% TiN or acetylene black. The mixture was sealed in a Teflon container and heated at 155 °C for 15 h to incorporate sulfur into the porous TiN or acetylene black. After cooling to room temperature, S-TiN or S-AB composites were obtained.

7.2.2 Characterisation and electrochemistry

Powder X-ray diffraction (XRD) used a Bruker D2 Phaser with CuK_α radiation. Small-angle X-ray scattering (SAXS) used a Rigaku Smartlab diffractometer with a parallel beam of CuK_α X-rays, and samples placed in 0.7 mm capillaries. Scanning electron microscopy (SEM) used a JEOL JSM-6500F (30 kV). Transmission electron microscopy used a FEI Tecnai T12 (120 kV). Brunauer-Emmett-Teller (BET) surface area measurements were carried out with a Micromeritics TriStar II analyser. ¹H NMR spectra were obtained with a Bruker AVIIIHD500 FT-NMR spectrometer with CDCl₃ as the solvent. Electrochemical testing used a Biologics VMP-2 multichannel potentiostat.

Conductivity measurements were carried out on TiN pellets made by manually mixing 90 wt% TiN powder with PTFE in a pestle and mortar. The resulting solid lump was hand rolled (Durston Rolling Mill) into a film and cut into disks with diameter of 10 mm, and then the pellet was assembled into a Swagelok cell without any electrolyte. Cyclic voltammograms (CV) were collected at 20 mV s⁻¹ over the range of -0.3 to +0.3 V (-0.1 to +0.1 V for more conductive samples) at room temperature.

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S-TiN Electrodes (inks) for use in lithium half cells were prepared by mixing the S-TiN composite powders (80 wt%) with acetylene black (Shawinigan Black, 10 wt%) and poly(vinylidene fluoride) (10 wt%) in N-methyl-pyrrolidone. The slurry was cast onto Al foil (125 μm thick, Temper annealed, 99.0 % purity, Advent Research Materials) and dried at 40 $^{\circ}\text{C}$ in vacuum for 12 h. The foil was cut into circular discs with a diameter of 11 mm and pressed at 10 tons to obtain the ink with a typical mass of ~ 0.037 g.

S-AB electrode pellets for use in lithium half cells were prepared by manually mixing the sulfur (25 wt%) with acetylene black (75 wt%) in a pestle and mortar. The resulting mixture was ball milled continuously for 30 mins at 20 rps using a stainless steel vessel (10 ml) with a stainless steel ball ($\phi = 10$ mm). The ball milled composite (90 wt%) and polytetrafluoroethylene (PTFE, 6C-N, DuPont, 10 wt%) were ground together and the resulting solid paste was hand rolled into a film of 80-120 μm thickness and cut into circular disks with diameter of 11 mm. The disk was then dried at 40 $^{\circ}\text{C}$ in vacuum for 12 h to obtain the pellet with a typical mass of ~ 0.012 g.

Swagelok cells were assembled in an argon-filled glove box with lithium foil (Rockwood Lithium GmbH) anodes and a glass microfiber filter (Whatman, GF/F grade) separator soaked in 60 μl of electrolyte. The electrolyte was composed of 1 mol dm^{-3} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane / dimethoxymethane (DOL/DME = 1:1 in volume) with 0.2 mol dm^{-3} LiNO_3 . Galvanostatic testing was carried out at 25 $^{\circ}\text{C}$ at various rates of charge/discharge (e.g. 0.1 C is a current calculated for 0.1 \times the theoretical capacity per hour) within the voltage range of 1.7-2.8 V (vs. Li^+/Li).

7.3 Results and discussion

Titanium nitride was initially made by a cross-linked sol-gel method with HDA or P123 as a surfactant, or an evaporation induced self-assembly method with PEO-b-PS as a surfactant, then heated under NH_3 at a variety of processing conditions. The samples were characterized by BET and electrochemical measurements of the effective conductivity, and the main results are summarized in Table 7-1.

Table 7-1 Synthesis conditions, conductivities, BET specific surface area, pore volume and pore size distribution of the TiN and TiO₂ samples.

Sample	Heating conditions	Conductivity / S m ⁻¹	BET surface area / m ² g ⁻¹	BJH pore volume / cm ³ g ⁻¹	DFT pore size / nm
TiN-HDA-I	1 °C min ⁻¹ to 500 °C for 10 h in NH ₃	5.9 x 10 ⁻⁹	299.35	0.07	2-3
TiN-HDA-M	3 °C min ⁻¹ to 650 °C for 6 h in NH ₃	1.9 x 10 ⁻⁶	40.67	0.01	2-3
TiN-HDA-I2	1 °C min ⁻¹ to 500 °C for 10 h in NH ₃	2.7 x 10 ⁻⁹	307.66	0.10	2-3
TiN-HDA-M2	3 °C min ⁻¹ to 650 °C for 6 h in NH ₃	4.4 x 10 ⁻⁶	185.57	0.08	2-3
TiN-P123-1	1°C min ⁻¹ to 500°C for 10h in NH ₃	8.3 x 10 ⁻⁸	79.52	0.10	5
TiN-P123-2	1°C min ⁻¹ to 650°C for 10h in NH ₃	1.1 x 10 ⁻⁵	44.67	0.08	5
TiN-P123-3	3°C min ⁻¹ to 650°C for 17h in NH ₃	7.0 x 10 ⁻⁷	82.69	0.11	5
TiN-P123-700	3°C min ⁻¹ to 700°C for 24h in NH ₃	2.3 x 10 ⁻⁸	32.32	0.05	5
TiN-P123-750	3°C min ⁻¹ to 750°C for 24h in NH ₃	2.1 x 10 ⁻³	71.75	0.11	5
TiN-P123-800	3°C min ⁻¹ to 800°C for 24h in NH ₃	3.2 x 10 ⁻²	70.10	0.11	5
TiN-P123-850	3°C min ⁻¹ to 850°C for 24h in NH ₃	9.4 x 10 ⁻¹	55.09	0.09	5
TiN-P123-900	3°C min ⁻¹ to 900°C for 24h in NH ₃	1.07	33.01	0.05	5
TiN-P123-950	3°C min ⁻¹ to 950°C for 24h in NH ₃	2.41	16.37	0.02	5
TiN-P123-1000	3°C min ⁻¹ to 1000°C for 24h in NH ₃	1.56	3.79	0.004	5
TiO ₂ -PEO-b-PS-1	1°C min ⁻¹ to 500°C for 3h in air	/	66.38	0.11	5
TiN-PEO-b-PS-1	1°C min ⁻¹ to 700°C for 10h in NH ₃	/	46.66	0.07	5
TiO ₂ -PEO-b-PS-2	1°C min ⁻¹ to 500°C for 3h in air	/	/	/	20
TiN-PEO-b-PS-2	1°C min ⁻¹ to 700°C for 10h in NH ₃	/	/	/	20
Acetylene black	/	0.73	73.92	0.10	3-5

7.3.1 Synthesis, microstructure and electrochemistry of TiN prepared with HDA as a surfactant

Titanium nitride was made by a sol-gel cross-linking method with HDA as a surfactant, and heated under NH_3 at different conditions as shown in Table 7-1. TiN-HDA-I2 and TiN-HDA-M2 were heated under NH_3 with a higher NH_3 flow rate.

The XRD patterns of TiN-HDA-I and TiN-HDA-I2 (Figure 7-4) showed noisy backgrounds and broad extra features beyond those of TiN, which indicates poor crystallinity and some amorphous carbon incorporated into the samples. This could be verified by TEM images showed in Figure 7-5, these very small TiN-HDA-I2 particles dispersed among a large amount of amorphous carbon. The presence of surface impurities could reduce the conductivity of TiN samples ($\sim 10^{-9} \text{ S m}^{-1}$) as shown in Figure 7-6. The nitrogen adsorption/desorption isotherms and pore size distribution curves of TiN samples were displayed in Figure 7-7. Pore volume and pore size distributions are resolved by Barrett-Joyner-Halenda (BJH) method and density functional theory (DFT), respectively. The BET specific surface area of TiN-HDA-I and TiN-HDA-I2 samples are about $300 \text{ m}^2 \text{ g}^{-1}$ (Table 7-1), this high surface area could be attributed to the presence of amorphous carbon. Pore size distribution curves in Figure 7-7 shows that the pore sizes mainly fall in the range of 2-3 nm. However, the small BJH pore volume ($\leq 0.1 \text{ cm}^3 \text{ g}^{-1}$) shown in Table 7-1 indicate these samples were probably not porous materials but particles with very small size.

The X-ray diffraction peaks of the TiN-HDA-M and TiN-HDA-M2 samples (Figure 7-4) were mainly consistent with the standard cubic TiN structure (JCPDS card no. 65-0414). Impurity peaks were detected, which could be indexed to anatase TiO_2 (JCPDS card no. 21-1272). Heating at higher temperature ($650 \text{ }^\circ\text{C}$) reduces the amount of surface impurities which could increase the conductivity ($\sim 10^{-6} \text{ S m}^{-1}$) of the samples (Figure 7-6), but it was not good enough for use in Li-S batteries. The BET specific surface area and BJH pore volume of TiN-HDA-M2 (Figure 7-7) is much higher than TiN-HDA-M as shown in Table 7-1, which could be attributed to the higher NH_3 flow rate during heating that helps to get rid of the residual surface organic groups.

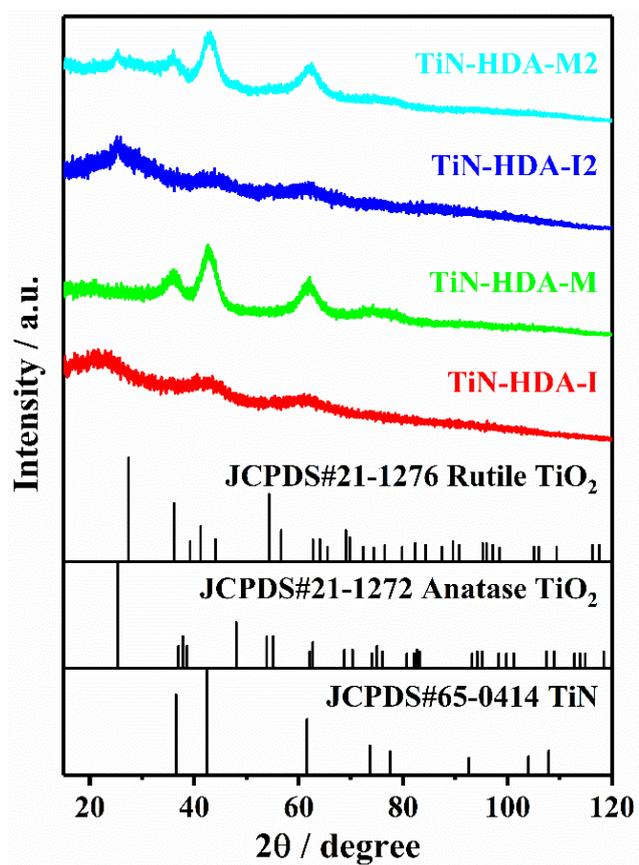


Figure 7-4 XRD patterns of TiN series samples prepared using the HDA assisted sol-gel route and heated under NH₃ with different heating conditions (labels explained in Table 7-1). The black stick patterns denote the literature TiN, anatase TiO₂ and rutile TiO₂ reflection positions and intensities.

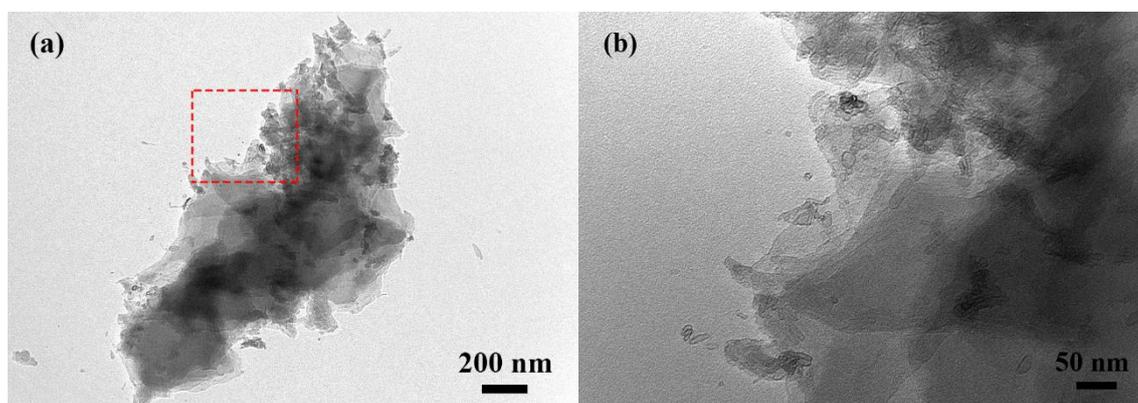


Figure 7-5 (a) TEM images of TiN-HDA-I2 (scale bar = 200 nm) and (b) enlarged view of the region marked by the red box (scale bar = 50 nm). Sample label is explained in Table 7-1.

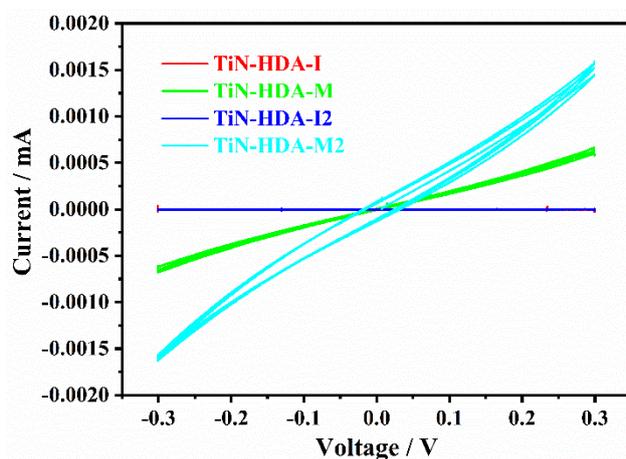


Figure 7-6 Current-voltage plots (3 cycles each) for dry TiN samples at scanning rate of 20 mV s^{-1} , showing the ohmic behaviour of the samples (labels explained in Table 7-1). Note that the red line is coincident with the blue line.

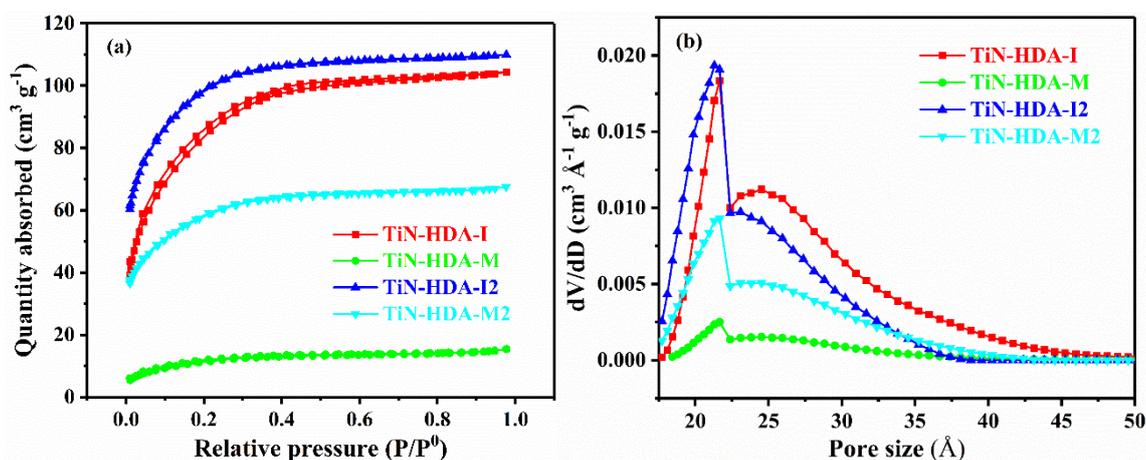


Figure 7-7 (a) nitrogen adsorption/desorption isotherms and (b) pore size distribution (DFT method) curves of mesoporous TiN samples (labels explained in Table 7-1).

7.3.2 Synthesis, microstructure and electrochemistry of TiN prepared with P123 as a surfactant

Titanium nitride was made by a cross-linked sol-gel method with P123 as a surfactant, and heated under NH_3 at different conditions as shown in Table 7-1. Figure 7-8 shows the XRD patterns of TiN-P123-1, TiN-P123-2 and TiN-P123-3 samples which suggests that these samples are composites of osbornite TiN, anatase TiO_2 and rutile TiO_2 . Figure 7-9 shows the conductivity of TiN-P123-2 is much higher than TiN-P123-1 (Table 7-1) which indicates heating at higher temperature could result in better conductivity, but it was also affected by the heating time when taking TiN-P123-3 in consideration. The nitrogen adsorption/desorption isotherms and pore size distribution curves of TiN samples are displayed in Figure 7-10. The BET specific surface area of TiN-P123-1, TiN-P123-2

and TiN-P123-3 samples were at a range of 44-83 m² g⁻¹ (Table 7-1), with BJH pore volume of about 0.1 cm³ g⁻¹. Pore size distribution curves in Figure 7-10 show that the pore sizes were about ~5 nm.

Among these three samples, TiN-P123-2, which had the best conductivity, was chosen to be the cathode material with sulfur and made into Li-S batteries to do electrochemical tests. Figure 7-11 shows the initial charge/discharge curves and cycle stability at 0.1C as well as rate capability of TiN-P123-2 sample. The results show that the initial discharge capacity of TiN-P123-2 is 1039 mA h g⁻¹, but it drops quickly over 20 cycles.

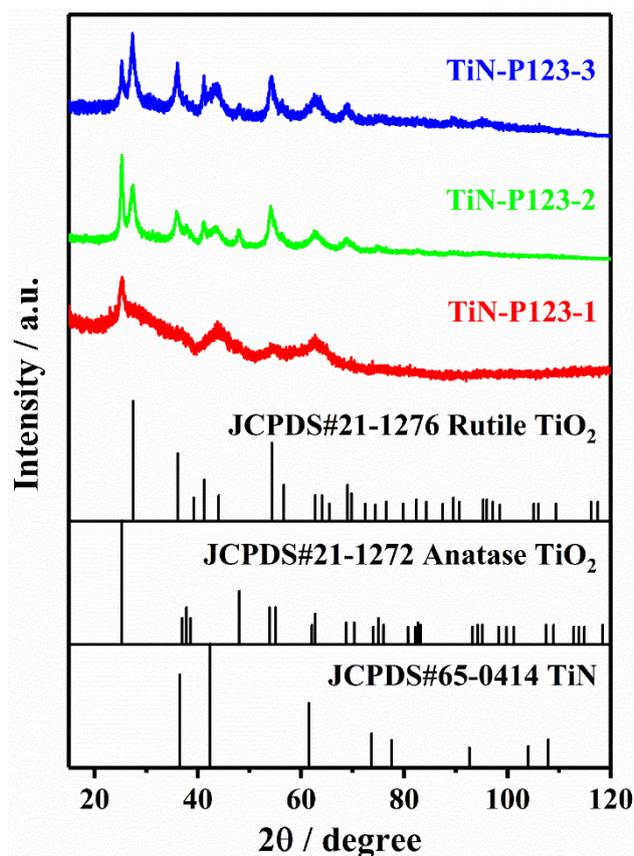


Figure 7-8 XRD patterns of TiN series samples prepared using the P123 assisted sol-gel route and heated under NH₃ with different heating conditions (labels explained in Table 7-1). The black stick patterns denote the literature TiN, anatase TiO₂ and rutile TiO₂ reflection positions and intensities.

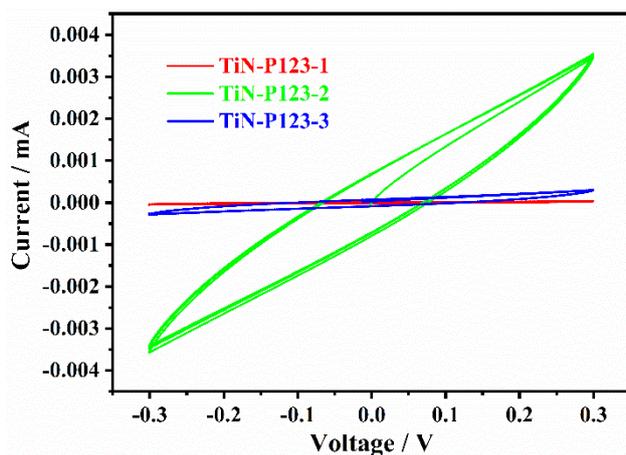


Figure 7-9 Current-voltage plots (3 cycles each) for dry TiN samples at scanning rate of 20 mV s^{-1} , showing the ohmic behaviour of the samples (labels explained in Table 7-1).

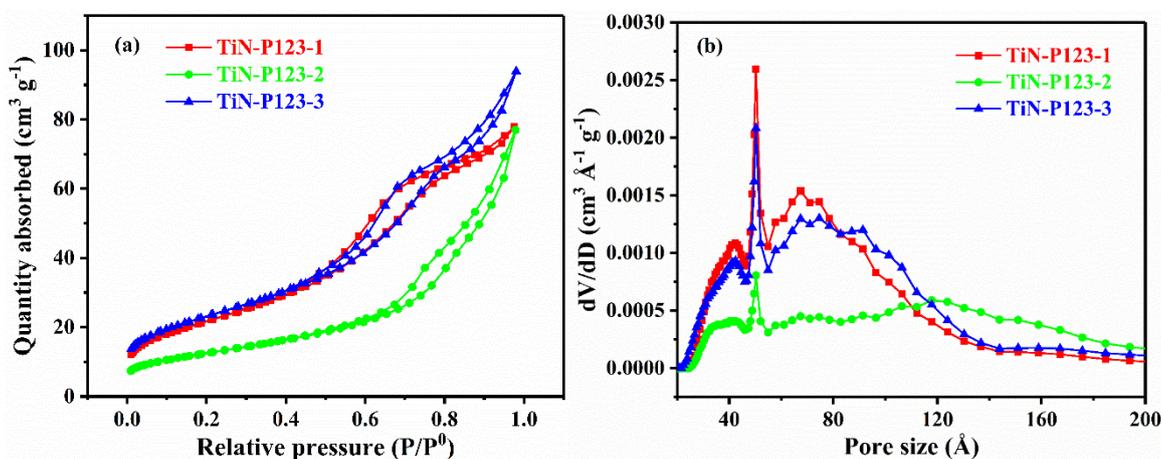


Figure 7-10 (a) nitrogen adsorption/desorption isotherms and (b) pore size distribution (DFT method) curves of mesoporous TiN samples (labels explained in Table 7-1).

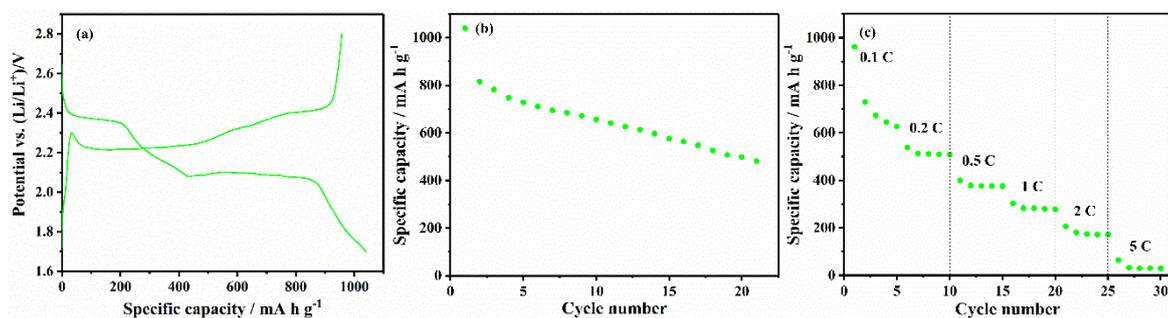


Figure 7-11 (a) The initial cycle of voltage profile vs. specific capacity and (b) specific capacity vs. cycle number, cycle at 0.1C rate, (c) The discharge specific capacity vs. cycle number of TiN-P123-2 in Li half cells, cycle at various sequential rates from 0.1C to 5C, between 1.7 and 2.8 V (labels explained in Table 7-1).

7.3.3 Effect of heating temperature on TiN prepared with P123 as a surfactant

Titanium nitride was made by cross-linked sol-gel method with P123 as a surfactant, and heated under NH_3 at 3°C min^{-1} to 700-1000°C for 24h as shown in Table 7-1 to check the effect of heating temperature on TiN properties.

Figure 7-12 shows the XRD patterns of TiN-P123-700 to TiN-P123-1000 samples which show these samples are composites of osbornite TiN and rutile TiO_2 . At higher temperature the TiO_2 is more likely to convert into TiN. The TEM images of TiN-P123-700 and TiN-P123-850 showed in Figure 7-13 indicate these very small particles were aggregated together. As shown in Figure 7-14, the conductivity of the TiN samples increases when the heating temperature increases (Table 7-1), which could be attributed to the increasing amount of TiN. The nitrogen adsorption/desorption isotherms and pore size distribution curves of TiN samples are displayed in Figure 7-15. The BET specific surface area and BJH pore volume of TiN-P123-700 to TiN-P123-1000 samples tend to reduce as the heating temperature increases (Table 7-1). Pore size distribution curves in Figure 7-15 shows that the pore sizes are about 5 nm.

These TiN samples have been used as a cathode materials with sulfur and made into Li-S batteries to do electrochemical tests. Figure 7-16 shows the initial charge/discharge curves at 0.1C of TiN-P123-700 to TiN-P123-1000 samples with initial discharge capacities of 817, 974, 903, 851, 879, 868 and 772 mA h g^{-1} , respectively. The discharge capacity of these samples decayed gradually with continuous cycling, retaining $\sim 400 \text{ mA h g}^{-1}$ after 40 cycles (Figure 7-16). The rate capability of these samples showed the capacity drops quite significantly at higher rates which suggests that the TiN still needs to be further optimised to provide the fastest kinetics.

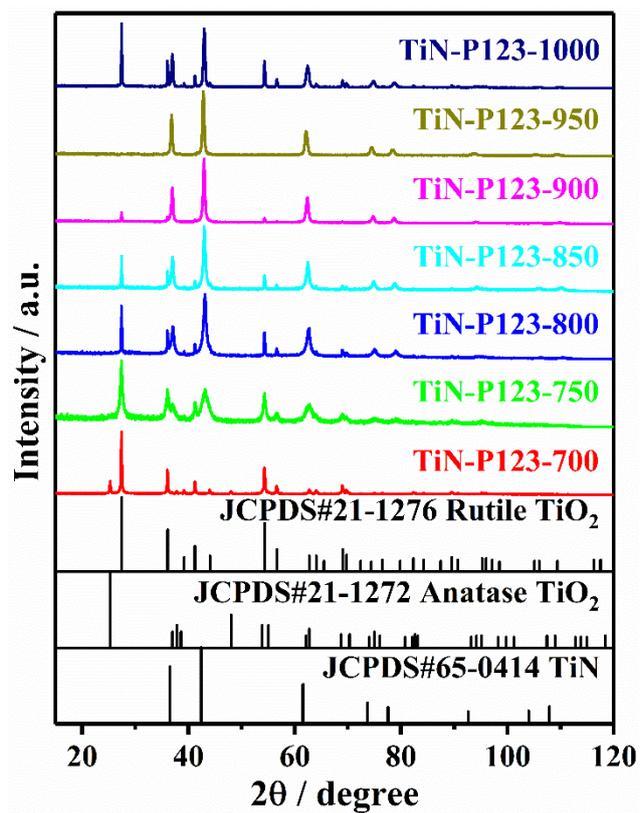


Figure 7-12 XRD patterns of TiN series samples prepared using the P123 assisted sol-gel route and heated under NH₃ with heating temperature range from 700 to 1000 °C (labels explained in Table 7-1). The black stick patterns denote the literature TiN reflection positions and intensities.

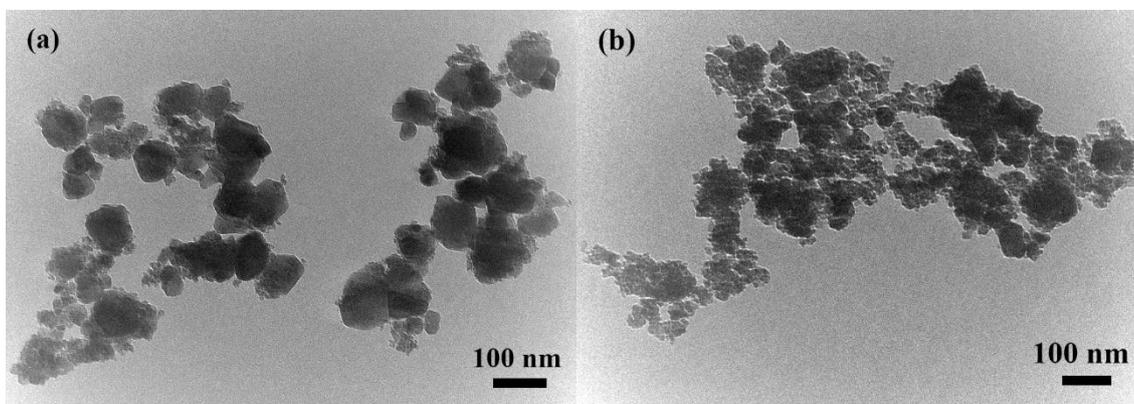


Figure 7-13 TEM images of (a) TiN-P123-700 and (b) TiN-P123-850 (scale bar = 100 nm). Sample labels are explained in Table 7-1.

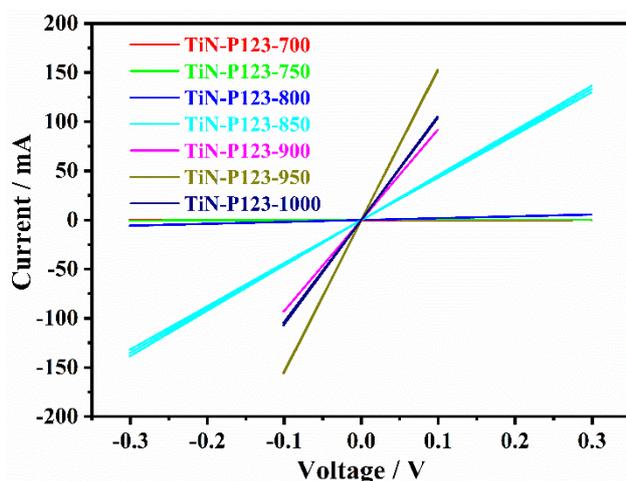


Figure 7-14 Current-voltage plots (3 cycles each) for dry TiN samples at scanning rate of 20 mV s^{-1} , showing the ohmic behaviour of the samples (labels explained in Table 7-1). Note that the red and green lines are coincident with the blue line.

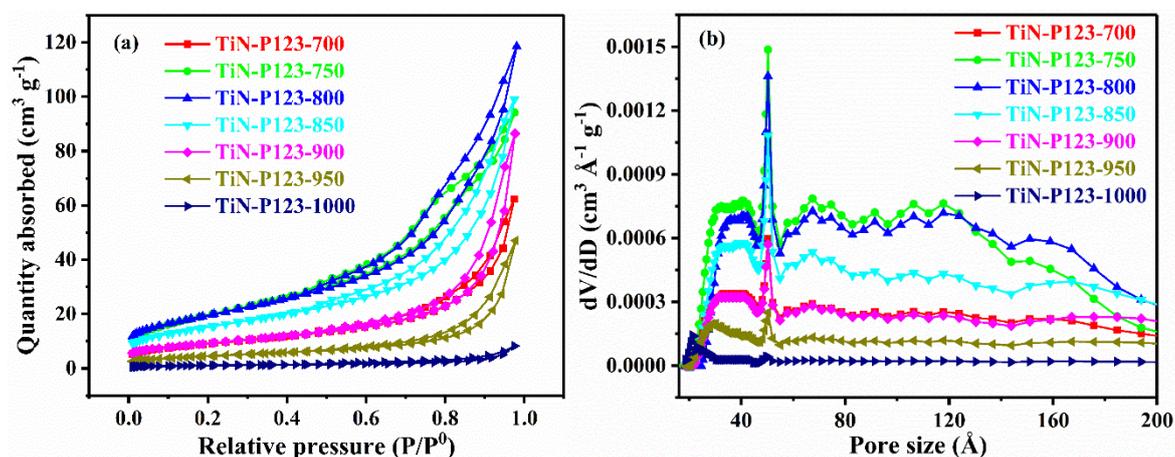


Figure 7-15 (a) nitrogen adsorption/desorption isotherms and (b) pore size distribution (DFT method) curves of mesoporous TiN samples (labels explained in Table 7-1).

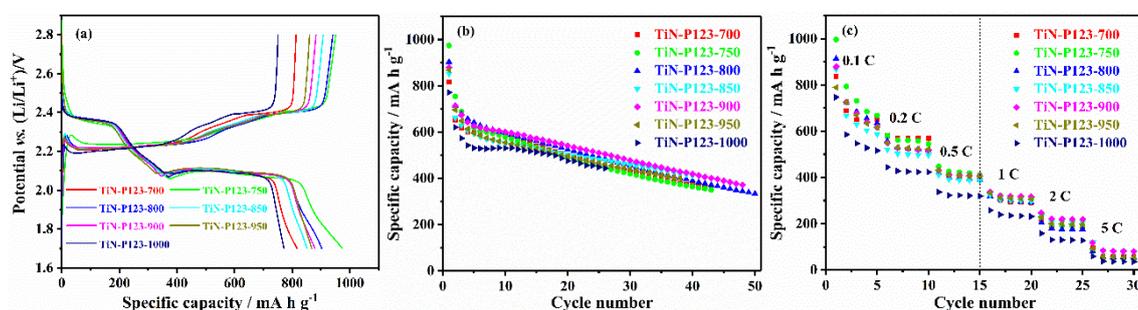


Figure 7-16 (a) The initial cycle of voltage profile vs. specific capacity and (b) specific capacity vs. cycle number, cycle at 0.1C rate, (c) The discharge specific capacity vs. cycle number of TiN samples in Li half cells, cycle at various sequential rates from 0.1C to 5C , between 1.7 and 2.8 V (labels explained in Table 7-1).

7.3.4 Synthesis, microstructure and electrochemistry of TiN prepared with PEO-b-PS as a surfactant

The PEO-b-PS copolymer was prepared by an atom transfer radical polymerization (ATRP) method. ^1H NMR spectrum (Figure 7-17) was used to determine the molar mass of PEO-b-PS copolymer, which was calculated to be 30 kg mol^{-1} according to Equation 7-1:

$$M_{\text{PEO-b-PS}} = \frac{A_{\text{PS}}/5}{A_{\text{PEO}}/4} \times \frac{M_{\text{PEO}}}{44} \times 104 + M_{\text{PEO}} + 80 \quad \text{Equation 7-1}$$

Equation 7-1 $M_{\text{PEO-b-PS}}$ and M_{PEO} (5 kg mol^{-1}) are the molar mass of PEO-b-PS and PEO, respectively. A_{PS} and A_{PEO} are the integral areas of the peaks at 6.30-7.30 ppm for aromatic protons ($-\text{C}_6\text{H}_5$) on the PS block and at 3.53-3.70 ppm for methylene group protons ($-\text{CH}_2\text{CH}_2\text{O}$) on the PEO block, respectively (Figure 7-17). The value of 44 and 104 are the molecular weights of ethylene oxide and styrene monomeric units, respectively.⁶²⁸

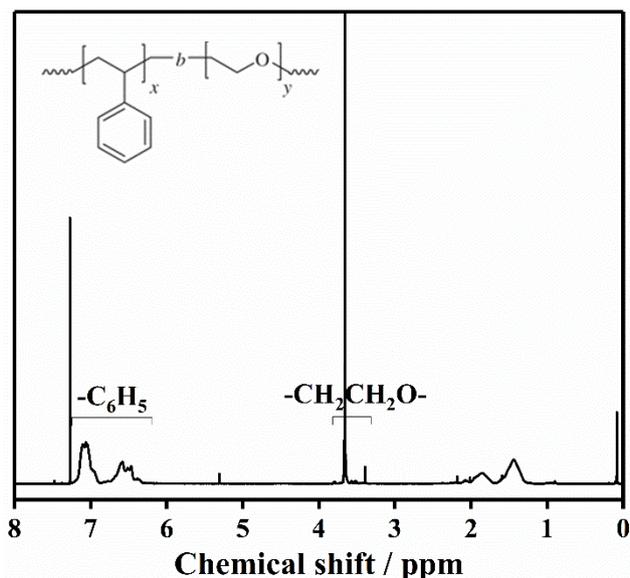


Figure 7-17 ^1H NMR spectrum of PEO-b-PS copolymer (in CDCl_3 solvent). (Inset) Chemical structure of PEO-b-PS.⁶²⁹

Titanium nitride was made by evaporation induced self-assembly (EISA) method with PEO-b-PS as a surfactant.¹⁵² The resulting TiO_2 precursor after solvent evaporation was heated to $500 \text{ }^\circ\text{C}$ in air to obtain TiO_2 , then it was converted to $\text{TiN}-(\text{PEO-b-PS})-1$ via heating to $700 \text{ }^\circ\text{C}$ under a flow of NH_3 . $\text{TiN}-(\text{PEO-b-PS})-2$ was made by the same method with a slower solvent evaporation process.

Figure 7-18 shows the XRD pattern of TiO_2 precursor, $\text{TiO}_2\text{-PEO-b-PS-1}$ and TiN-PEO-b-PS-1 samples. All the X-ray diffraction peaks of TiO_2 were consistent with the standard anatase structure, while the XRD pattern of TiO_2 precursor directly after evaporation induced self-assembly process showed a noisy background. These suggest the organic components in TiO_2 precursor has been removed

during heat treatment at 500 °C in air. Anatase TiO₂ could be partly converted into TiN after firing in NH₃ at 700 °C (Figure 7-18). The structure of TiO₂ precursor was further investigated by SAXS analyses (Figure 7-19), which showed reflections at the scattering wave vector (q) corresponding to the primary 100 peak with the 200 orientation. The d-spacing is related to the peak position q according to $d = 2\pi/q$. After heat treatment, the 100 peak of TiO₂ shifted to a larger q value comparing to TiO₂ precursor, reflecting a reduced d-spacing in the pore arrangement, which is due to the removal of organic components after firing.¹⁵² The TEM images of TiO₂ and TiN samples shown in Figure 7-20 indicate these nano-sized particles were aggregated together to form pores between particles. The nitrogen adsorption/desorption isotherms and pore size distribution curves of TiO₂ and TiN samples were displayed in Figure 7-21. The BET specific surface area and BJH pore volume of TiN sample is less than TiO₂ (Table 7-1). The pore size distribution curves in Figure 7-21 show that the pore sizes of TiO₂ and TiN samples are about ~5 nm.

The TiN samples were used as cathode materials with sulfur and made into Li-S batteries for electrochemical testing. Figure 7-22 shows the initial charge/discharge curves and cycle stability at 0.1C as well as rate capability of TiN-PEO-b-PS-1 sample. The results show that the initial discharge capacity of TiN-PEO-b-PS-1 is 927 mA h g⁻¹, which quickly drops to 472 mA h g⁻¹ after 20 cycles, and decayed gradually with continuous cycling, retaining ~300 mA h g⁻¹ over 100 cycles (Figure 7-22).

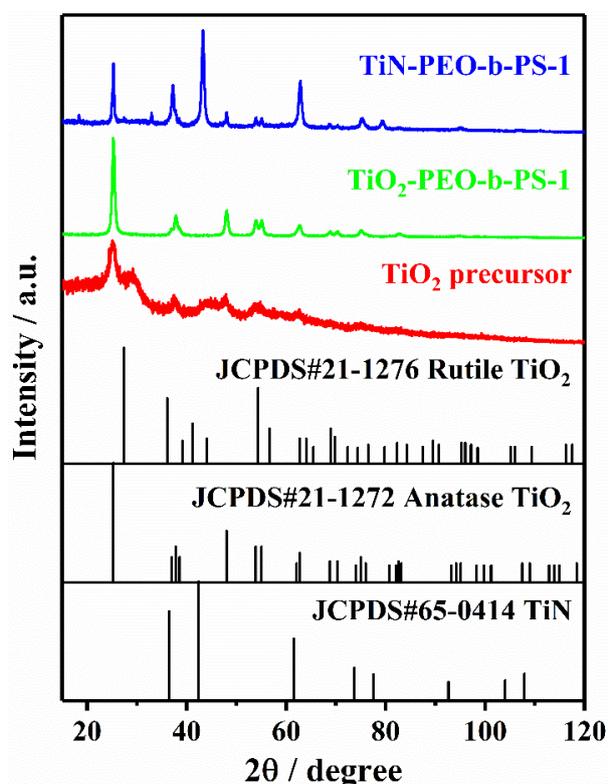


Figure 7-18 XRD patterns of TiO₂ precursor, TiO₂ and TiN samples prepared using the PEO-b-PS assisted EISA method, then heating under air and NH₃ (labels explained in Table 7-1). The black stick patterns denote the literature TiN, anatase TiO₂ and rutile TiO₂ reflection positions and intensities.

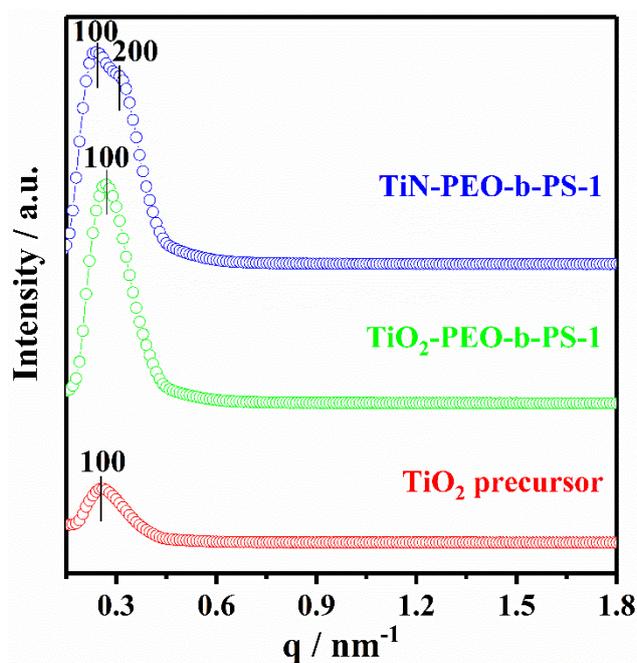


Figure 7-19 SAXS patterns of TiO_2 precursor, TiO_2 -PEO-b-PS-1 and TiN-PEO-b-PS-1 samples. Sample labels are explained in Table 7-1.

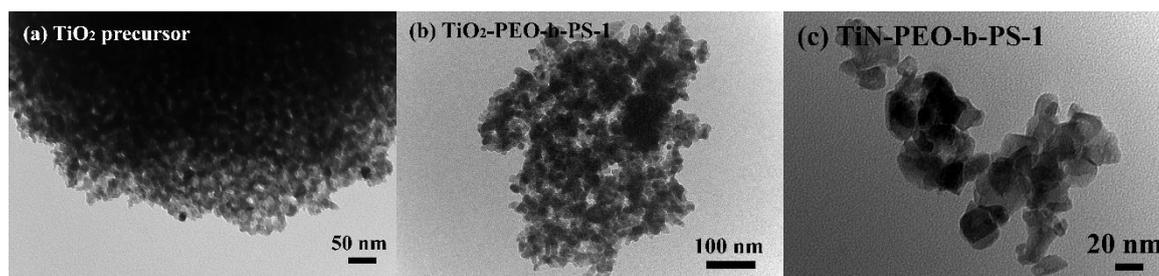


Figure 7-20 TEM images of (a) TiO_2 precursor (scale bar = 50 nm), (b) TiO_2 -PEO-b-PS-1 (scale bar = 100 nm) and (c) TiN-PEO-b-PS-1 (scale bar = 20 nm). Sample labels are explained in Table 7-1.

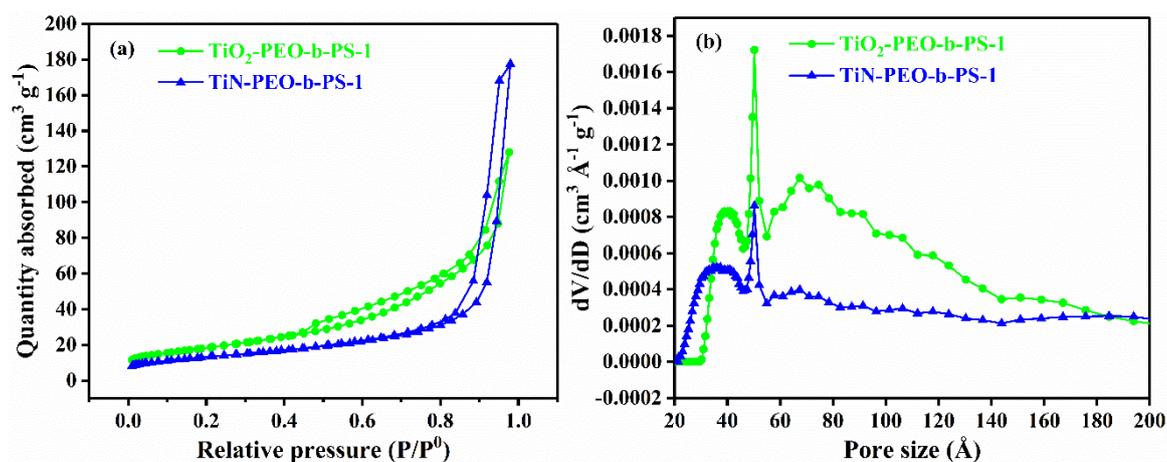


Figure 7-21 (a) nitrogen adsorption/desorption isotherms and (b) pore size distribution (DFT method) curves of mesoporous TiO_2 and TiN samples (labels explained in Table 7-1).

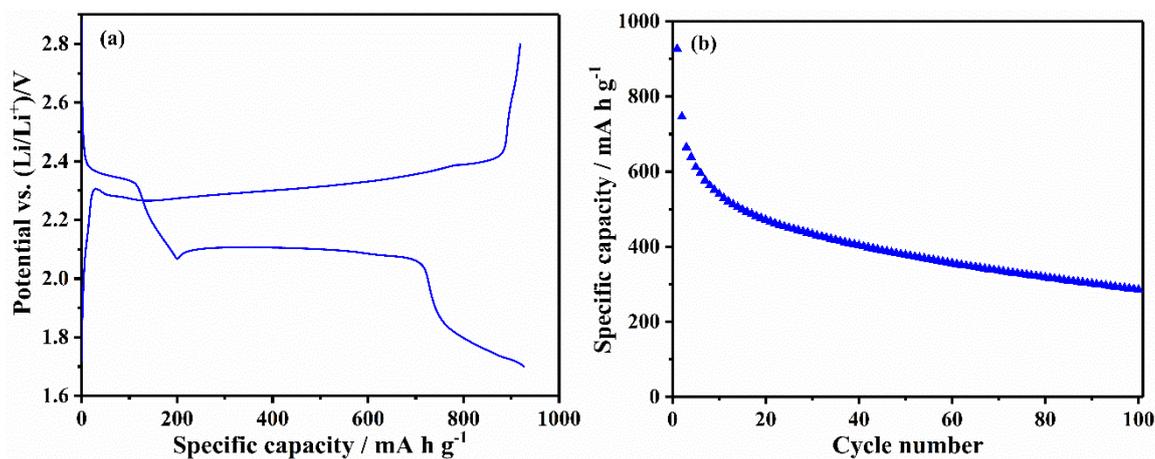


Figure 7-22 (a) The initial cycle of voltage profile vs. specific capacity and (b) specific capacity vs. cycle number of TiN sample in Li half cells, cycle at 0.1C rate, between 1.7 and 2.8 V (labels explained in Table 7-1).

The TiO₂-(PEO-b-PS)-2 and TiN-(PEO-b-PS)-2 samples were made by the same evaporation induced self-assembly method as described above but with a slower solvent evaporation process. As shown in Figure 7-23, the SEM images of TiO₂ and TiN samples exhibited a mesoporous structure with worm-like pores and pore width of about 20 nm. This TiN is expected to be a promising host material for sulfur as it could confine sulfur and polysulfides within the pores or layers by physical interactions, thus reducing the “shuttle effect” and volume change during charge/discharge process in lithium-sulfur batteries.

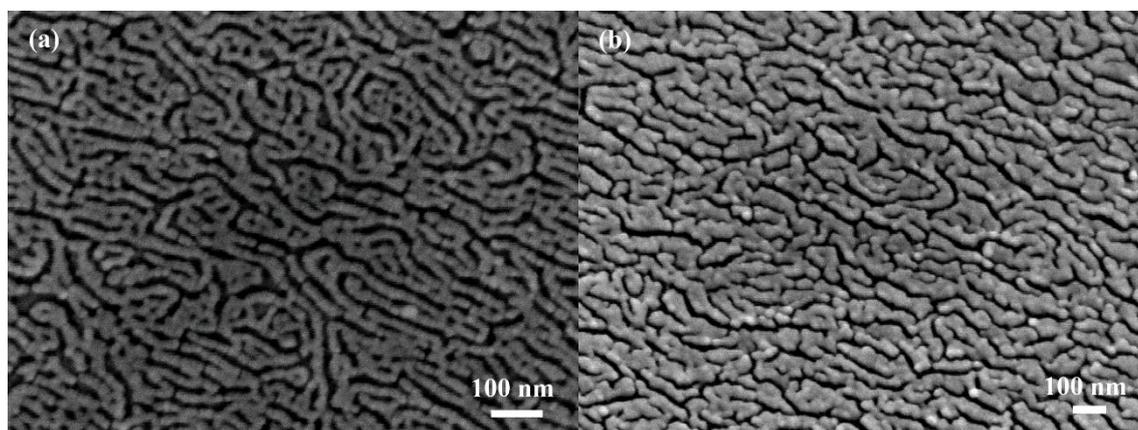


Figure 7-23 SEM images of (a) TiO₂-PEO-b-PS-2 and (b) TiN-PEO-b-PS-2 (scale bar = 100 nm). Sample labels are explained in Table 7-1.

7.3.5 Microstructure and electrochemistry of acetylene black

As carbon has been commonly used as the host materials of sulfur to enhance its conductivity and reduce the “shuttle effect” in Li-S batteries.⁹ Acetylene black has been treated as a comparison in

this work. Figure 7-24 shows the acetylene black has a good conductivity of 0.73 S m^{-1} . The nitrogen adsorption/desorption isotherm and pore size distribution curve of acetylene black were displayed in Figure 7-25. The BET specific surface area and pore volume of acetylene black is $73.92 \text{ m}^2 \text{ g}^{-1}$ and $0.1 \text{ cm}^3 \text{ g}^{-1}$, respectively (Table 7-1). The pore sizes of acetylene black mainly fall in the range of 3-5 nm. This acetylene black has been used as a cathode material with sulfur and made into Li-S batteries to do electrochemical tests. Figure 7-26 shows the initial charge/discharge curves and cycle stability at 0.1C of acetylene black. The results show that the initial discharge capacity of acetylene black is 1359 mA h g^{-1} , and retains 941 mA h g^{-1} over 19 cycles.

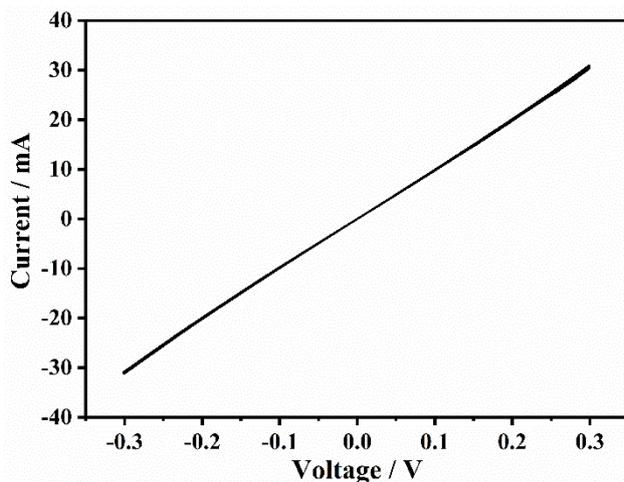


Figure 7-24 Current-potential plots (3 cycles each) for acetylene black at scanning rate of 20 mV s^{-1} , showing the ohmic behaviour of the sample.

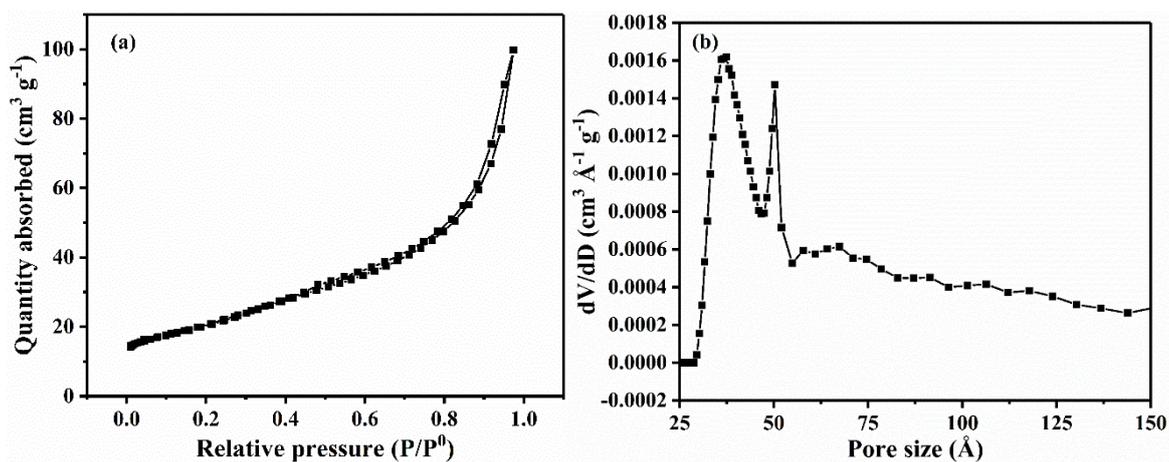


Figure 7-25 (a) nitrogen adsorption/desorption isotherms and (b) pore size distribution (DFT method) curves of acetylene black.

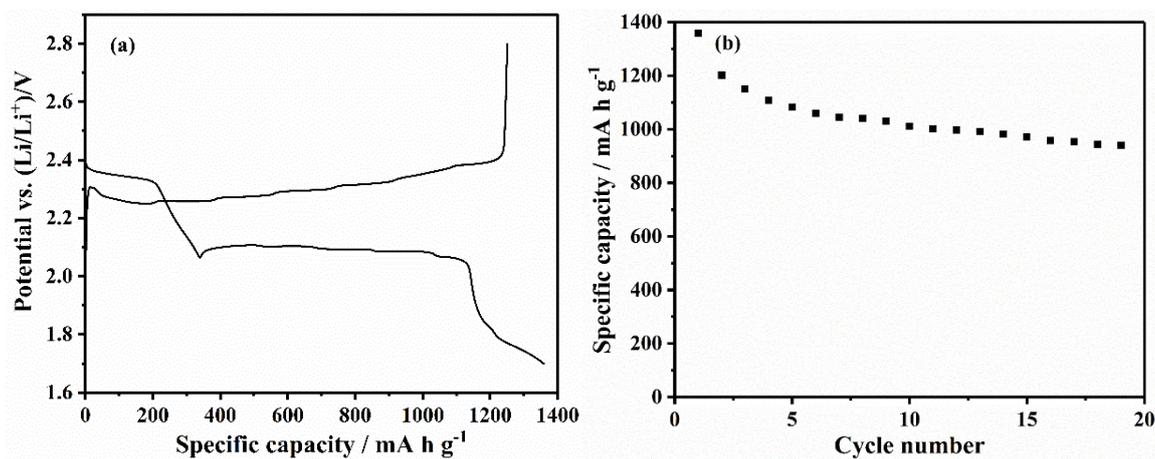


Figure 7-26 (a) The initial cycle of voltage profile vs. specific capacity and (b) specific capacity vs. cycle number of acetylene black in Li half cells, cycle at 0.1C rate, between 1.7 and 2.8 V.

7.4 Conclusions

Titanium nitride samples were prepared by a cross-linked sol-gel method with HDA or P123 as a surfactant, or evaporation induced self-assembly method with PEO-b-PS as a surfactant, and heated under NH₃ at a variety of processing conditions. The heating temperature and NH₃ flow rate during heat treatment have been found to affect the conductivity and porosity of prepared TiN. Selected TiN samples have been used as cathode materials with sulfur and made into Li-S batteries, but these still need further improvement as the TiN showed less capacity than carbon as sulfur host materials. The evaporation induced self-assembly method with slow solvent evaporation rate has been found to be a promising strategy to obtain mesoporous TiN with worm-like morphology and pore size of ~20 nm. Further characterization are required to investigate the conductivity properties and electrochemical performance of this mesoporous TiN.

Chapter 8: Conclusions and future work

8.1 Conclusions

The principle, cathodes and anodes for lithium-ion and lithium-sulfur batteries, and the application of nanostructured titanium nitride in high energy and high capacity battery systems have been investigated.

Sol-gel approaches to the coating of battery materials with TiN have been explored. A propylamine cross-linking method gave higher electronic conductivity materials than ammonia cross-linking, and hence was used to produce the coatings. Firing in ammonia also resulted in lower carbon contents, so LiFePO_4 was examined after firing in ammonia and found to be comparable with the material fired more conventionally in a dilute hydrogen mix. TiN-coated LiFePO_4 performed well as an electrode material in lithium half cells, with capacities, cycling performance and rate capabilities in the best cases that were competitive with other coating materials. LiFePO_4 modified with 10 wt% TiN from the propylamine cross-linking method and fired in ammonia exhibits a maximum discharge capacity of 159 mA h g^{-1} , that is 93% of the theoretical capacity (170 mA h g^{-1}), at the rate of 0.1 C. The results demonstrate the suitability of this new route to produce TiN coatings, which could also be applied to high voltage materials or for materials to be operated at high temperatures, where corrosion or degradation of other coating materials (e.g. carbon) would be problematic.

Understanding and development of olivine LiCoPO_4 cathode materials for lithium-ion batteries have been reviewed systematically. Various synthetic routes such as solid-state reactions, hydrothermal/solvothermal synthesis and sol-gel process to prepare LiCoPO_4 have been discussed. The strategies of surface modification, carbon network support structures, ion doping, size reduction and morphology control to improve the electrochemical performance of LiCoPO_4 have been systematically summarised. Optimization of electrolytes, separators and conductive additives are essential in the development of high voltage LIBs.

A facile solvothermal synthesis to prepare olivine-structured LiCoPO_4 for high-voltage cathodes in LIBs has been developed, using various ratios of water/diethylene glycol as solvent, followed by thermal treatment under Ar, air, 5% H_2 + N_2 or NH_3 . The diethylene glycol plays an important role in tailoring the particle size of LiCoPO_4 . It is found that using a ratio of water/diethylene glycol of 1:6 (v/v), LiCoPO_4 is obtained with a homogenous particle size of $\sim 150 \text{ nm}$. The LiCoPO_4 prepared after heating in Ar exhibits high initial discharge capacity of 147 mA h g^{-1} at 0.1 C with capacity retention of 70% after 40 cycles. The obtained specific capacity and cycle stability of uncoated LCP(Ar) in this case is comparable or higher than most previous studies, even though in most of these reports

LiCoPO_4 has been optimised with conductive coatings (e.g. carbon). This is attributed to the enhanced electronic conductivity of LiCoPO_4 due to the presence of Co_2P after firing under Ar. The specific capacity and cycle stability of carbon, TiN and RuO_2 coated LiCoPO_4 were also examined, but did not improve the performance of the material. Hence, under the optimised solvothermal synthesis conditions, LiCoPO_4 with good discharge capacity and cycle stability, without need for separate conductivity coatings, were produced.

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a promising anode material for LIBs used for large-scale applications. A series of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples with Li excesses of 0% to 6% were synthesized via solid-state reaction. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared with 2% Li excess were found to have minimum TiO_2 impurities, which delivered a high initial capacity of 165 mA h g^{-1} . This $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited a small particle size of $\sim 200 \text{ nm}$, which ensures short Li-ion migration paths in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystals to facilitate easier Li-ion transfer. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were post-heated in NH_3 and $5\% \text{H}_2/\text{N}_2$ at $650 \text{ }^\circ\text{C}$ to investigate the effect of heating environment on their properties. TiN and carbon were successfully coated onto $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The specific capacity and cycle stability of TiN and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were examined. TiN coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited improved initial capacity of 174 mA h g^{-1} , close to theoretical capacity of 175 mA h g^{-1} , but these coatings did not deliver the expected improvement in cycle stability for $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Further improvement are required for the application of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials in lithium-ion batteries.

Sol-gel routes and evaporation induced self-assembly to nanostructured TiN as a cathode for lithium-sulfur batteries were investigated. TiN samples were prepared by a cross-linked sol-gel method with HDA or P123 as a surfactant, or evaporation induced self-assembly method with PEO-b-PS as a surfactant, and heated under NH_3 at a variety of processing conditions. The heating temperature and NH_3 flow rate during heat treatment have been found to affect the conductivity and porosity of prepared TiN. Selected TiN samples have been used as cathode materials with sulfur and made into Li-S batteries, but these still need further improvement as the TiN showed less capacity than carbon as sulfur host materials. The evaporation induced self-assembly method with slow solvent evaporation rate has been found to be a promising strategy to obtain mesoporous TiN with worm-like morphology and pore size of $\sim 20 \text{ nm}$. Further characterization are required to investigate the conductivity properties and electrochemical performance of this mesoporous TiN.

8.2 Future work

Lithium-ion batteries and lithium-sulfur batteries are promising reversible energy storage devices for large scale industrial application. Metal nitrides have been used as electrode materials for batteries and supercapacitors, and have also been combined with other electrode materials to form

structured composites with improved conductivity and stability. TiN is suitable for these purposes as it possesses good electrical conductivity, low cost, and good chemical and thermal stability. There is room to further improve the performance of TiN coatings on cathodes and anodes for lithium-ion batteries. Due to the coating, Li-ions have to migrate through the surface layer before diffusing in and out of the active material lattice. Therefore, it is important to optimize the coating strategies to obtain electrode material with a thin, uniform and intact TiN surface layer. TiN coatings may provide good options for batteries used in non-standard conditions like high temperature cycling due to its high thermal and chemical stability. In this work, TiN have been coated on the surface of LiFePO_4 , LiCoPO_4 cathodes and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode to achieve improved electrochemical performance in some cases due to the enhanced electrical conductivity. Other electrode materials in lithium-ion batteries such as LiMnPO_4 , LiNiPO_4 and LiMn_2O_4 also suffer from poor electrical conductivity and can benefit from TiN coating to enhance the electron transport.

Nanostructure mesoporous TiN with high conductivity are promising host materials for sulfur cathodes in lithium-sulfur batteries, which can improve the conductivity of the sulfur cathode, confine lithium polysulfides within the host and buffer the volume change of sulfur cathode during the charge/discharge process. In this work, the evaporation induced self-assembly method has been found to be a promising strategy to obtain mesoporous TiN with worm-like morphology and pore size of ~ 20 nm. Further improvement and characterisation (e.g. optimised method for impregnation of sulfur into the mesoporous structure) are required to investigate the conductivity properties and electrochemical performance of this mesoporous TiN.

TiN has good activity as an oxygen reduction reaction electrocatalyst in lithium-oxygen batteries. With the developed synthetic strategy in this work, there are opportunities to obtain stable, high surface area electrodes by assembling 3-dimensional TiN nanostructures with controlled surface chemistry. It is thus promising to apply this nanostructured mesoporous TiN as a stable air-cathode backbone in lithium-oxygen battery, which could result in high specific capacity, good cycle stability and Columbic efficiency due to the porous structure and good electric conductivity of TiN.

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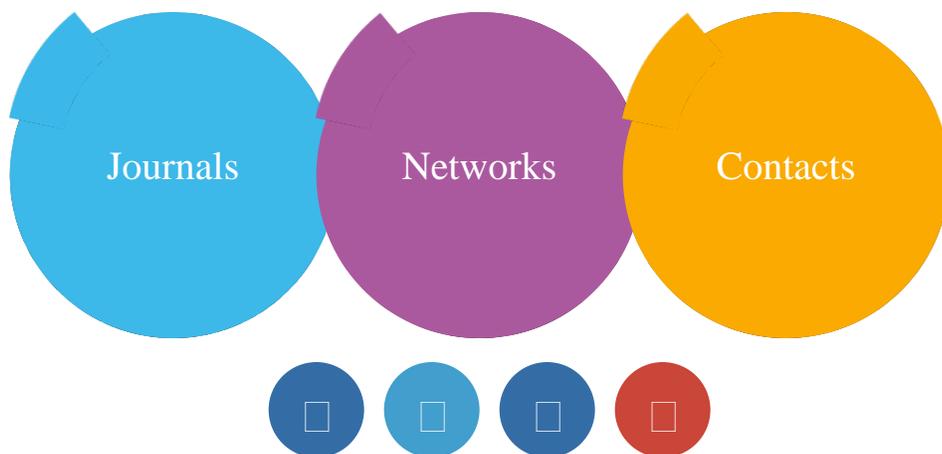


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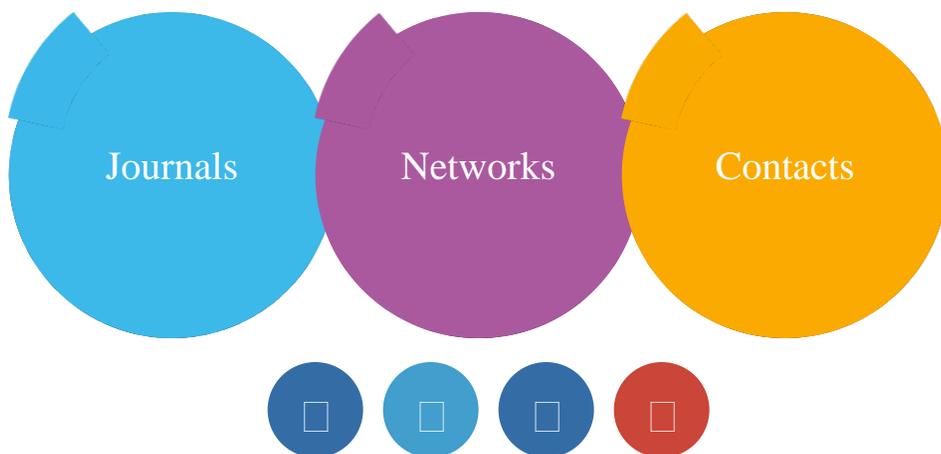


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