Understanding and development of olivine LiCoPO4 cathode materials for lithium-ion batteries

Min Zhang, Nuria Garcia-Araez and Andrew L. Hector\*

Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

Email: [A.L.Hector@soton.ac.uk](mailto:A.L.Hector@soton.ac.uk)

# Abstract

Olivine LiCoPO4 is a promising candidate as the cathode material for high-voltage lithium-ion batteries due to its high redox potential of 4.8 V *vs* Li/Li+ and a theoretical capacity of 167 mA h g-1. However, use of LiCoPO4 as a cathode in practical applications has been hindered by its unsatisfactory cycle stability, Coulombic efficiency and rate capability, which can be attributed to its low electronic conductivity, poor Li+ ion conductivity, and limited stability of electrolytes at high potentials. It is thus important to develop a simple, time and energy saving, easy to control and industrially scalable synthesis method to prepare LiCoPO4 with high specific capacity, good cycle stability and rate capability. Various synthetic routes such as solid-state reactions, hydrothermal/solvothermal synthesis and sol-gel process have been proposed and various strategies have been applied to improve the electrochemical performance. Carbon coating or the use of carbon network supports enhances the overall electronic conductivity of the composite electrode. Decreasing the particle size of LiCoPO4 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. However, carbon addition and size reduction for LiCoPO4 cathodes can reduce the volumetric energy density of lithium-ion batteries. Ion doping aims to enhance the intrinsic electronic/ionic conductivity of LiCoPO4 although the mechanism is still in controversy. Strategies to mitigate the problem of the electrolyte decomposition at high voltages have also been explored, such as optimization of the electrolyte formation and use of protective coatings, thus improving the cycle stability of LiCoPO4 cathodes in lithium-ion batteries. Understanding of olivine LiCoPO4 cathode materials development for lithium-ion batteries is crucial for further improvement.

# 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, 9, 10 Cost and safety concerns associated with the conventional cathode material, LiCoO2, have motivated the search for new high-performance materials that can be safely scaled up at reasonable cost.2, 11, 12

Olivine-structured lithium transition-metal orthophosphates LiMPO4 (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, 13 Although LiFePO4, 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,14-19 other members of the olivine family are also being researched intensively.4, 20-22 LiCoPO4 was firstly reported by Amine *et al* in 2000,23 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 LiFePO4 of 170 mA h g-1.24-26 Even though Co is more expensive than the other transition metals (e.g. Fe), the cost of LiCoPO4 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.27, 28 Applying LiCoPO4 in 18650 batteries, Howard *et al* estimated the cost of LiCoPO4 to be 142 $ kW-1 h-1, while LiCoO2 and LiFePO4 were 198 and 158 $ kW-1 h-1, respectively.29, 30

Although attractive for high energy and high power applications, use of LiCoPO4 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.25, 31-42 Also, the decomposition of electrolytes under high potentials results in poor cycle stability and coulombic efficiency.43-50 A variety of synthesis methods have been used to produce LiCoPO4, including solid-state reaction,51, 52 hydrothermal/solvothermal methods,31, 53 sol-gel synthesis,54, 55 etc. Alternate approaches like surface modification,31, 56 ion doping,25, 57 size reduction and morphology control53, 58 have also been investigated to modify the electrochemical performance of LiCoPO4. 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 LiCoPO4 (space groups: *Pnma*, *Cmcm*, and *Pna21*) have been summarised recently.59 The olivine-type *Pnma*-LiCoPO4 exhibits promising electrochemical properties as a high-voltage cathode in LIBs. Herein, we review the strategies for performance improvement with various synthesis methods for olivine LiCoPO4 cathode materials in LIBs.

# 2 Structure and properties

The olivine structured LiCoPO4 belongs to space group *Pnma* with lattice parameters of a = 10.20 Å, b = 5.92 Å, and c = 4.70 Å.23, 40, 49, 60-66 The crystal structure consists of a polyoxyanionic framework including LiO6 octahedra, CoO6 octahedra and PO4 tetrahedra,43 as illustrated in Figure *1*. Strong P-O covalent bonds in the (PO4)3- polyanion network stabilize the oxygen when fully charged and hinder O2 release at high states of charge.11, 42, 67-70 Moreover, as the fully charged state CoPO4 phase has the same olivine structure as LiCoPO4, when Li+ ions are removed from the structure during charging, Co2+ ions are oxidised to Co3+ and the lattice volume shrinks by only ~7%.43, 49, 66, 68, 71-7328, 42 Thus major volume changes during charge-discharge are avoided, resulting in a stable olivine structured LiCoPO4 cathode.

The skeleton of PO4 polyanions in LiCoPO4 is thermally stable, but the corner-shared CoO6 octahedra of LiCoPO4 are separated by the oxygen atoms of the PO43- tetrahedra and cannot form a continuous CoO6 network.43, 53, 70, 74, 75 This makes electron delocalization difficult and thus results in the poor electronic conductivity of LiCoPO4.11, 32-37 Each PO4 tetrahedron and CoO6 octahedron shares edges with its neighbours, forming one dimensional tunnels parallel to the [010] direction down which Li-ion migration occurs preferentially (Figure 1).42, 74 The 1D channels are easily blocked by defects and impurities, which may hinder the Li+ ion diffusion.76, 77 The conductivity of sintered pellets of LiCoPO4 depends on the synthesis method, but for samples with composition close to stoichiometric LiCoPO4, values of conductivity lower than 10-9 S cm-1 have been reported,37-42 which are much lower than those of LiCoO2 (~10-3 S cm-1)78 and LiMn2O4 (~10-4 S cm-1).79

Upon charge and discharge in LIBs, LiCoPO4 undergoes two distinct two-phase reactions, both involving an intermediate Li2/3CoPO4 phase, coexisting with the fully lithiated phase at higher Li contents and with the delithiated phase at low Li contents.64-66, 71-73, 80-82 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.43, 83

A number of studies on LiCoPO4 examined the microstructure,84 structural stability,85 Li-ion intercalation86 and phase changes during charge-discharge43, 66 using first-principles methods based on density functional theory (DFT). Grey and coworkers identified the structure of the intermediate Li2/3CoPO4 formed during cycling of LiCoPO4 using first-principles solid-state DFT calculations in combination with experimental NMR and XRD data.66 It was found that both the Co3+ ions and Li vacancies are found to order along the b-axis in the lowest energy configuration. Two other low energy Li+/vacancy ordering schemes are found only 5 meV per formula unit higher in energy. All three configurations lie below the LiCoPO4-CoPO4 convex hull and they may be readily interconverted by Li+ hops along the b-direction.

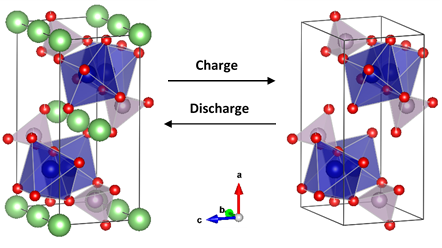


Figure 1 Unit cell of olivine-type LiCoPO4 (space group: Pnma) showing Li (green) in 1D channels along [010] between CoO6 octahedra (blue) corner-linked to PO4 tetrahedra (purple), and the olivine structure remains stable during Li-ion insertion and extraction.

# 3 Synthesis methods

To prepare LiCoPO4 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.

## 3.1 Solid-state reaction

Solid-state reaction is an economic, efficient, and scalable strategy to prepare LiCoPO4 for LIBs.87, 88 In this process, the precursors were firstly mixed and ground or milled thoroughly, then heated to 300-400 ℃ to decompose the precursors and expel the gases.39, 89-91 After that, the mixture was ground again, then calcined at elevated temperatures of 600-800 ℃ for 10-36 h.52, 66, 92, 93 As shown in Table 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.

The raw materials generally consist of a stoichiometric amount of lithium source (Li2CO3, LiOH·H2O or CH3COOLi),65, 94-96 cobalt source (Co(CH3COO)2·4H2O, Co3O4 orCoO)62, 97-99 and phosphorus source (NH4H2PO4 or (NH4)2HPO4).34, 100-102 The long and complex procedures, requiring repeated grinding and calcination, lead to undesirable particle growth and agglomeration.103-105 This can be prevented by adding growth inhibitors such as carbon or carbonate anions to obtain nanoparticles.106-109 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*.51 This electrode exhibited a capacity of 123 mA h g-1 at 0.1 C, and capacity retention of 89% after 30 cycles, as well as reasonable rate capability up to 5 C.

Table 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. |
| Li2CO3, Co3O4, NH4H2PO4 | 300 ℃, 6 h, air  780 ℃, 36 h, air | 3-10 μm | 125 (0.1 C) | 30 mA h g-1 at 0.1 C after 25 cycles | 90 |
| LiOH·H2O, CoO, (NH4)2HPO4 | 750 ℃, 8 h, air  350 ℃, 6 h, air  750 ℃,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 | 105 |
| LiOH·H2O, Co3O4, (NH4)2HPO4 | 400 ℃, 10 h, air  800 ℃, 10 h, air | 100-150 nm | 132 (0.1 C) | 92 mA h g-1 at 0.1 C after 17 cycles | 93 |
| LiOH·H2O, Co3O4, (NH4)2PO4 | 400 ℃, 10 h, air  800 ℃, 10 h, Ar | - | 128 (0.1 mA cm-2) | 70% capacity retention at 0.1 mA cm-2 after 20 cycles | 52 |
| Li2CO3, Co(CH3COO)2·4H2O, NH4H2PO4 | 350 ◦C, 6 h, air  750 ℃, 12 h, Ar | 1 μm | 109 (0.1 C)  46 (5 C) | 55 mA h g-1 at 0.1 C after 50 cycles | 101 |
| LiOH·H2O, Co3O4, (NH4)2PO4 | 400 ℃, 10 h, air  800-900 ℃, 10 h, Ar | - | 130 (0.1 C) | 117 mA h g-1 at 0.1 C after 15 cycles | 99 |
| LiOH·H2O, CoO, NH4H2PO4 | 400℃, 10 h, air  800℃, 10 h, air | 500-700 nm | 112 (0.05 C) | 83 mA h g-1 at 0.05 C after 25 cycles | 102 |
| Li2CO3, CoCO3, NH4H2PO4 | 300 ℃, 8 h, air/Ar  700 ℃, 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 | 51 |
| Li2CO3, (NH4)Co(PO4)·H2O | 600 ℃, 16 h, air  600 ℃, 8 h, air | 350-700 nm | 93 (0.05 C) | 64 mA h g-1 at 0.05 C after 20 cycles | 65 |
| Li2CO3, Co(NO3)2·6H2O, NH4H2PO4 | 350 ℃, 2 h, Ar  500 ℃, 8 h, Ar/5% H2 | 100-300 nm | 146 (0.1 C)  93 (2 C) | 92 mA h g-1 at 0.1 C after 40 cycles | 108 |
| Li2CO3, CoC2O4·2H2O, NH4H2PO4 | 375 ℃, 8 h, air  750 ℃, 12 h, Ar | 50-400 nm | 128 (0.05C) | 115 mA h g-1 at 0.05 C after 5 cycles | 109 |

## 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)58, 110, 111 and well controlled morphology (e.g., cubic, spherical, and plate-like).112-116 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.117-120 As shown in Table 2, the particle size and morphology of LiCoPO4 can be tuned by changing the stoichiometric ratio and concentrations of reactants,121-123 solvents,53, 58, 124, 125 pH values of solution,110, 126, 127 additives,31, 121, 128-130 reaction conditions65, 131-133 and sintering conditions.101, 117

Hydrothermal/solvothermal reactions can be heated in a conventional or microwave oven.134, 135 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.20, 132, 136 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.111, 123 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.121, 123, 127 For example, Nilges *et al* prepared LiCoPO4 nano-platelets *via* a facile and rapid (30 min) one-step microwave-assisted solvothermal synthesis route using a 1 : 1 (v/v) water/ethylene glycol (EG) binary solvent mixture and a temperature of 250 ℃, without additional post-annealing or carbon coating steps.137 The solvents generally play an important role in tailoring the particle size, morphology, and crystal orientation of the LiCoPO4 material.53 The as-prepared LiCoPO4 delivered an initial discharge capacity of 137 mA h g-1 at 0.1 C, and capacity retention of 68% after 100 cycles at 0.5 C.137

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.58, 138, 139 It was found that increasing the reaction temperature can minimize the unfavorable effects of Co-Li anti-site defects,18, 65, 111 and well crystallized LiCoPO4 can be obtained if high-pressure reactors are used.65, 114, 123

In hydrothermal/solvothermal synthesis, it is possible to obtain LiCoPO4 directly from the heated solution without post heat treatment.115, 116, 136, 140 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.58, 123, 124 Carbon sources used include glucose,112, 127, 141 sucrose131, 142 and ascorbic acid,125, 140 and these can also act as reducing agents to prevent the oxidation of Co2+ in hydrothermal process.31, 121

Table 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, CoSO4, H3PO4 | 3:1:1 | - | H2O | Glucose as reducing agent and carbon source, NH4OH to adjust pH=9.9 | 230 ℃, 15 min, 80 bar, microwave assisted: 600 W, 2.45 GHz | 700 ℃, 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 | 112 |
| LiOH⋅H2O, Co(CH3COO)2⋅4H2O, H3PO4 or (NH4)2HPO4 | 2:1:1 | 0.05 | H2O | PVPa as dispersant, NH4OH to adjust pH=8.5 | 220 or 300 ℃, 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 | 110 |
| LiOH, CoSO4·7H2O, (NH4)3PO4·3H2O | 3:1:1 | 0.1 | H2O:BAa =1:1 | Glucose as carbon source | 200 ℃, 8 h | 750 ℃, 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 | 101 |
| LiCl, Co(NO3)2·6H2O, H3PO4 | 2:2:1 | 0.325 | EGa | Glucose as carbon source, NH3·H2O as buffer, Mn doping | 200 ℃, 10 h | - | Nanoparticle agglomeration, 2-3 μm | 105 (0.2 C) | 90% capacity retention at 0.2 C after 30 cycles | 141 |
| LiOH·H2O, CoSO4·7H2O, LiH2PO4, | 2.75:1:1 | 0.1 | H2O:EGa =1:2 | Sucrose as reducing agent | 220 ℃, 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 | 115, 116 |
| CH3COOLi·2H2O, Co(CH3COO)2·4H2O, (NH4)2HPO4 | 6:1:1 | 0.04, 0.125 | H2O | L-ascorbic, citric or polyacrylic acid as organic additive, NH4OH to adjust pH=8.6-9 | 220 ℃, 30 s, microwave assisted | 650 ℃, 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 | 121 |
| LiOH, Co(NO3)2, CoSO4, Co(CH3COO)2 or CoCO3, LiH2PO4 | 1.75~2.25:1:1 | 0.1 | H2O:EGa =1:2 | Sucrose as reducing agent | 200-240 ℃, 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 | 131 |
| LiOH·H2O, CoSO4·7H2O, H3PO4 | 3:1:1 | 0.25 | H2O:EGa =1:1 | Ascorbic acid as reducing agent and buffer to adjust pH=5.5 | 250 ℃, 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 | 137 |
| Li3PO4, CoSO4·7H2O | 3:1:1 | - | EGa:H2O =0, 0.5, 1, 2, 4, 5, 10, 20 | Sucrose as carbon source | 180 ℃, 24 h | 650 ℃, 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 | 58 |
| LiOH·H2O, Co(CH3COO)2·4H2O, H3PO4 | 1:1:1 | 0.238 | TTEGa | NH4OH as additive, V3+ doping | 240 ℃, 30 min, 5 bar, microwave assisted: 850 W | 525 ℃, 12 h, 10%H2/Ar | Particles, 100-500 nm | 97 (0.1 C) | 82 mA h g-1 at 0.1 C after 20 cycles | 117 |
| LiNO3, Co(NO3)2·6H2O, (NH₄)₂HPO₄ | 1:1:1 | - | Isopropanol | Tannic acid as carbon source | 140-220 ℃, 30 min, 20 bar, microwave assisted: 2.45 GHz, 600 rpm | 650 ℃, 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 | 132 |
| Li3PO4, CoSO4·7H2O | 3:1:1 | 3 | H2O | CMCa, glucose or ascorbic acid as organic additives and carbon source | 200 ℃, 24 h, 800 rpm | 700 ℃, 1 h, Ar/3% H2 | 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 | 31 |
| LiOH·H2O, Co(CH3COO)2·4H2O, H3PO4 | 1:1:1 | 0.2 | TTEGa | V doping, LiFePO4 coating | 240 ℃, 30 min, microwave assisted: 850 W | 525 ℃, 4 h, Ar | Spherical or oblong spheroid, 50 - 250 nm | 145 (0.1 C) | 51% capacity retention at 0.1 C after 20 cycles | 113 |
| LiOH·H2O, CoSO4·7H2O, H3PO4 | 3:1:1 | - | H2O:(EG, DEG, TEG, TTEG, PEG, BA)a =1:1 | Ascorbic acid as reducing agent, pH=5.0-5.5 | 250 ℃, 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 | 53 |
| LiOH·H2O, CoSO4·7H2O, H3PO4 | 3:1:1 | 0.25 | EGa:(H2O+EGa) =0-1 | Ascorbic acid as reducing agent, pH = 5.0 | 250 ℃, 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 | 125 |
| LiNO3, Co(NO3)2·6H2O, (NH4)2HPO4 | - | - | H2O | Alginic acid as carbon source | 180 ℃, 30 min, 20 bar, microwave assisted: 15-20 W, 2.45 GHz, 600 rpm | 700 ℃, 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 | 134 |
| LiNO3, Co(NO3)2, (NH4)2HPO4 | - | - | EGa | - | 200 °C, 60 min, 20 Bar, microwave assisted: 40-50 W, 2.45 GHz, 600 rpm | 650 ℃, 6 h, Ar/5%H2 | - | 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 | 135 |
| 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. | | | | | | | | | | |

## 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.143-147 In this process, the reactants are firstly dissolved in solvents, and the resulting sol evolves gradually into a gel-like network,20, 148-152 then the gel is calcined at 500-800 ℃ to obtain LiCoPO4.153-156 As shown in Table 3, reaction parameters such as precursors,55, 157, 158 carbon sources,134, 138, 159 sintering temperature and time54, 160, 161 had significant effect on the electrochemical performance of LiCoPO4.

Various precursors and solvents are used in sol-gel synthesis to produce LiCoPO4 (Table 3).162-165 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.157, 158, 166, 167 Water is the most commonly used solvent to control the structure of LiCoPO4,134, 138, 159, 162 but organic solvents including ethanol,160 ethylene glycol,163 diethylene glycol165 and water/isopropanol co-solvent can also be used in sol-gel synthesis.155 Citric acid is widely used as a chelating agent.168-170 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.168 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.153, 168 Also, carbon deposition on the surface of LiCoPO4 can effectively suppress the particle growth during calcination.138, 153, 168 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.

Table 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. |
| LiNO3, Co(NO3)2·6H2O, (NH4)2HPO4 | Citric acid as chelating  agent and carbon source | Stirring for 3.5 h, evaporation at 85 ℃, dry at 100 ℃, pyrolysis at 350 ℃ for 2 h in Ar | 500 ℃, 4 h, air | 240-350 nm | 137 (0.1 C) | 68% capacity retention at 0.1 C after 30 cycles | 153 |
| LiNO3, Co(NO3)2, NH4H2PO4 | Citric acid as chelating agent and carbon source | Stirring at 80 ℃ for 2 h, evaporation at 120 ℃ for 12 h, pyrolysis at 350 ℃ for 2 h in air | 500 ℃, 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 | 138 |
| CH3COOLi·2H2O, Co(CH3COO)2⋅4H2O, H3PO4 | Citric acid as chelating agent | Evaporative at 80 °C for 3 h in air | 300 ℃, 5 min, air,  730 ℃, 12 h, N2 | - | 68 (0.1 C) | 15 mA h g-1 at 0.1 C after 21 cycles | 54 |
| LiNO3, Co(NO3)2·6H2O, (NH4)2HPO4 | Citric acid as chelating agent, Y doping | Evaporation at 85 °C, dry at 100 ℃ for one day | 600 ℃, 8 h, air | 500 nm | 154 (0.1 C) | 32 mA h g-1 at 0.1 C after 30 cycles | 162 |
| LiH2PO4, CH3COOLi·2H2O, Co(CH3COO)2·4H2O, NH4H2PO4 | Citric acid as chelating agent, Fe doping | Evaporation at 70 ℃ for 1 h, decompose at 300 ℃ for 5 h in air | 550 ℃, 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 | 157 |
| CH3COOLi·2H2O, Co(C5H7O2)2, H3PO4 | Ethylene glycol as solvent and carbon source | Aging for 2 days | 700 ℃, 12 h, Ar | 300 nm | 114 (2 C) | 57 mA h g-1 at 2 C after 15 cycles | 163 |
| CH3COOLi·2H2O, Co(CH3COO)2⋅4H2O, H3PO4 | Citric acid as chelating agent, graphitic carbon foam modification | Evaporation at 80 °C for 2 h | 300 ℃, 0.1 h, air,  730 ℃, 12 h, N2 | - | 100 (0.1 C) | 33 mA h g-1 at 0.1 C after 11 cycles | 158 |
| LiNO3, Co3(PO4)2, (NH4)2HPO4 | Citric acid as chelating agent, Mn doping, gallic acid as reducing agent and carbon source | Evaporation at 70 ℃ for 24 h, decompose at 350 ℃ for 3 h in air | 650 ℃, 6 h, Ar/15%H2 | 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 | 168 |
| Li2CO3, Co(CH3CO2)2·4H2O, NH4H2PO4 | Citric acid as carbon source | Evaporation at 80 ℃ for 12h, dry at 80 ℃ for 12h in vacuum | 300 ℃, 3 h, N2,  700 ℃, 10 h, N2 | - | 83 (0.5 C) | 59% capacity retention at 0.5 C after 30 cycles | 169 |
| LiNO3, Co(NO3)2·6H2O, (NH4)2HPO4 | Citric acid as chelating agent, alginic acid as carbon source | Dry at 80 ℃ | 700 ℃, 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 | 134 |

## 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. 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,171-173 such as spray pyrolysis,56, 174-178 co-precipitation,41, 107, 134, 179-181 polyol process,124, 182-186 supercritical fluid processes,139, 187-190 microwave heating84, 134, 191-194 and carbo-thermal reduction.168, 195, 196 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 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 | *In situ* coating or post-addition |
| Hydrothermal/solvothermal synthesis | Nanosize, morphology control | Strict reaction conditions (temperature, pH, time, etc.), waste liquid | Nano-size | *In situ* coating or post-addition |
| Sol-gel process | High purity and homogeneity, nanosize | Long process | Nano-size | *In situ* coating |

# 4 Strategies for performance improvement

Olivine LiCoPO4 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 LiCoPO4, using approaches such as surface modification (e.g. carbon coating), carbon network support structures, ion doping, size reduction and morphology control.32-42 The poor capacity and cycle stability of LiCoPO4 electrodes in conventional LiPF6-containing electrolyte solutions has been attributed to degradation of the olivine structure.44-48 Bramnik *et al* investigated the thermal stability of LiCoPO4 cathodes charged to low lithium contents using synchrotron diffraction and differential thermal analysis. It was found that CoPO4 appearing during the delithiation of LiCoPO4 is unstable upon heating and decomposes readily at temperatures of 100-200 °C.68 Similar observations were reported by Wohlfahrt-Mehrens *et al* who found that the fully charged cathode decomposes at 160-260 °C.69 Unlike other phosphates with Co3+ in octahedral coordination, Bramnik *et al* found that Co3+ is present in a high-spin configuration in delithiated (charged) CoPO4, which could explain the fact that CoPO4 is unstable in contact with air or moisture and undergoes amorphisation.64 Using *in situ* synchrotron diffraction, Bramnik *et al* also demonstrated the electrochemical extraction of lithium is accompanied by significant electrolyte decomposition, contributing to the capacity loss upon cycling.49 This is in agreement with a first-principles investigation on LiCoPO4 by Major *et al*, who found that fully delithiated CoPO4 is energetically unstable.197 Markevich *et al* found this delithiated CoPO4 phase to be prone to nucleophilic attack by F- anions (produced by electrolyte decomposition at high voltages) on the P atoms to beak the P-O bonds of the phosphate anions.46 This process leads to the surface degradation of LiCoPO4 (interfaced with the electrolyte solution),50 accompanied by the cobalt dissolution,198 olivine structure degradation,44 formation of cracks in crystals after charging,199, 200 and Li depletion due to the reformation of the solid-electrolyte interface (SEI),47 thus resulting in a fast capacity fading upon cycling. Brutti *et al* suggested that the self-discharge in LiCoPO4 electrodes is a self-feeding process that occurs with the spontaneous transfer of electrons from the electrolyte to the Co3+ ions in the delithiated electrode, mediated by a porous and partially reactive SEI film that is unable to fully passivate the electrode surface.199 Recently, Ikuhara *et al* investigated atomic level changes during capacity fade in highly oriented thin films of LiCoPO4.43 It was found that many cation exchange (antisite) defects were formed in the surface after only three cycles. The concentration of these defects increases upon further cycling, with significant capacity fading. The formation of cation exchange defects is associated with oxygen loss and deformation of PO4 tetrahedra, leading to structural degradation detrimental to the cycle stability of LiCoPO4 electrodes.

Surface modification is an important strategy to improve the cycle stability of LiCoPO4 electrodes by protecting LiCoPO4 from direct contact with electrolyte thus avoiding surface degradation caused by HF attack produced from electrolyte decomposition.56, 185, 198 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.201

## 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.35, 52, 56, 185, 198, 202 The classical conductive agent introduced to modify electrode materials is carbon, which possesses high conductivity, low cost and good stability in batteries.14, 120 Relevant examples of the electrochemical performance of LiCoPO4 after surface modification are shown in Table 5.

4.1.1 Carbon coating. In general, the main role of carbon coating is to enhance the electronic conductivity of LiCoPO4.56, 109, 153, 171, 177, 183, 198 For example, Wei *et al* synthesized a core-shell LiCoPO4/C nanocomposite *via* microwave heating. LiCoPO4 with an average particle size of ~150 nm was coated with a uniform amorphous carbon film of ~10 nm thickness.191 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.34, 35, 51, 65 Wolfenstine *et al* investigated the effect of added carbon on the electronic conductivity and discharge capacity LiCoPO4. 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 a maximum discharge capacity of ∼120 mA h g−1 obtained.34, 35 Nallathamby *et al* confirmed that the presence of Co2P as a second phase improved the conductivity and electrochemical properties of the parent LiCoPO4. The formation of Co2P is found to be achievable only in an inert atmosphere.51

Meanwhile, carbon coating reduces the particle size and alleviates the aggregation of LiCoPO4 particles by inhibiting undesirable particle growth.31, 58, 198 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.14, 203

In addition, carbon coating can protect LiCoPO4 from direct contact with electrolyte thus avoiding surface degradation caused by HF attack produced from electrolyte decomposition.56, 185, 198 For batteries using LiPF6 based electrolyte, LiCoPO4 may suffer from partial dissolution due to the presence of HF, which is produced by LiPF6 hydrolysis with trace water impurities.14, 204, 205 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 LiCoPO4 lattice.14, 89 Therefore, the coating on the surface of LiCoPO4 should be thin, uniform and intact.154, 155, 194 Also, the addition of carbon reduces the tap density of LiCoPO4 cathodes and thus decreases the volumetric energy density of LIBs. Taking these into consideration, the optimum carbon contents depends on various coating strategies.14, 47, 132, 198, 206

Table 5 The effects of carbon and other surface coatings on the performance of LiCoPO4 composites.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Carbon | | | |  | |  |
| Synthesis methods | Precursors | Coating techniques | Content (wt.%) | Thickness (nm) | Rate performance, mA h g-1 (rate, C) | Cycle stability | Ref. |
| Microwave heating | Acetylene black | *In situ* | 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 | 191 |
| Spray pyrolysis | Citric acid | *In situ* | 2.4 | 3-5 nm | 123 (0.1 C), 82 (5 C) | 95% capacity retention at 0.1 C after 20 cycles | 174 |
| Solvothermal synthesis | Glucose | *In situ* | 3.4, 5.1 | 8 nm | 136 (0.1 C), 85 (5 C) | 91% capacity retention at 0.1 C after 50 cycles | 101 |
| 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 | 175 |
| Sol-gel process | Citric acid | *In situ* | 0.52 | - | 137 (0.1 C) | 68% capacity retention at 0.1 C after 30 cycles | 153 |
| Planetary ball mill | Acetylene black | *In situ* | 3, 5, 10 | - | 145 (0.1 C), 72 (5 C) | 70% capacity retention at 0.1 C after 50 cycles | 198 |
| 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 | 177 |
| Solvothermal synthesis | Glucose, Mn doping | *In situ* | 12 | - | 105 (0.2 C) | 90% capacity retention at 0.2 C after 30 cycles | 141 |
| Sol-gel process | Citric acid, acetylene black | *In situ*, *ex situ* | 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 | 206 |
| 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 | 179 |
| Sol-gel process | Citric acid | *In situ* | ＜ 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 | 207 |
| 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 | 51 |
| Emulsion drip combustion, ball mill | Kerosene, heptane | *In situ* | 3, 8, 35, 37, 66, | 10 nm | 128 (0.1 C) | 87% capacity retention at 0.1 C after 25 cycles | 171 |
| Microwave-assisted ball mill | Acetylene black | *In situ* | 3.1 | - | 161 (1 C) | 83% capacity retention at 1 C after 1700 cycles | 194 |
| Solvothermal synthesis | Sucrose | *In situ* | 0.13-0.23 | - | 120 (0.1C) | 78% capacity retention at 0.1 C after 20 cycles | 208 |
| 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 | 56 |
| 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 | 58 |
| 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 | 108 |
| Sol-gel assisted carbothermal reduction | Citric acid | *In situ* | 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 | 168 |
| PVPa 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 | 185 |
| Microwave-solvothermal synthesis | Tannic acid | *In situ* | 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 | 132 |
| One-pot hydrothermal synthesis | CMCa, glucose, ascorbic acid | *In situ* | 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 | 31 |
| Microwave-hydrothermal synthesis | Alginic acid | *Ex situ* | 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 | 134 |
| Sol-gel process | Citric acid | *In situ* | 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 | 209 |
| Solid-state reaction | LiFePO4 coating | Sol-gel route | 10 | 2-3 nm | 132 (0.1 C) | 92 mA h g-1 at 0.1 C after 17 cycles | 93 |
| Solid-state reaction | LiFePO4 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 | 52 |
| Microwave-assisted solvothermal synthesis | LiFePO4 coating, V doping | *Ex situ* | 5, 10 | 3-5 nm | 145 (0.1 C) | 51% capacity retention at 0.1 C after 20 cycles | 113 |
| 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 | 26 |
| Sol-gel process | AlF3 coating | *Ex situ* | 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 | 202 |
| a: PVP: polyvinylpyrrolidone; CMC: carboxymethylcellulose sodium salt. | | | | | | | |

4.1.2 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)31, 56, 132, 168, 174, 185 and inorganic sources (e.g. carbon nanofibres, carbon nanotubes, graphene and acetylene black).109, 160, 166, 194, 198, 210

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).15, 134, 141 Passerini *et al* reported that the choice of carbon source, such as sucrose, polyacrylic acid and Tween 80® has a major impact on the purity, particle size, morphology and electrochemical performance of LiCoPO4. With 20wt. % sucrose as carbon source, TEM image showed a homogeneous coating layer with a well-defined thickness of about 3 nm (Figure 2 a). When reducing the sucrose amount to 10 wt.%, it showed a carbon layer on the entire surface but not homogeneous in thickness (Figure 2 b). The LiCoPO4/C composites showed partially uncoated areas with polyacrylic acid or Tween 80® as carbon sources (Figure 2 c and d). Although carbon coating improves the conductivity of LiCoPO4 and protects the LiCoPO4 particles from direct contact with the electrolyte, a decrease of capacity with cycling is still observed, probably associated with electrolyte decomposition at high operating voltages.56 As shown in Figure 2 e-h, Kanamura *et al* synthesized LiCoPO4/C particles by one-pot hydrothermal process using three different organic additives as carbon sources i.e. carboxymethylcellulose sodium salt (CMC), glucose and ascorbic acid. CMC played an important role to decrease the LiCoPO4 particle size to 390 nm and form a continuous carbon coating on the surface. LiCoPO4/C prepared with CMC delivered higher initial discharge capacity of 135 mA h g-1 at 0.1 C, and showed better rate capability and cycle performance than the other samples.31

Inorganic carbons offer an alternative approach to increase the conductivity of LiCoPO4 electrodes.211 Using inorganic carbons such as carbon nanotubes or nanofibres,114, 210 graphene and acetylene black,106, 175, 177, 179, 191, 194, 198, 206 a 3D conductive network can be obtained in the LiCoPO4 electrode. As shown in Figure 2 i-k, Jin *et al* fabricated LiCoPO4-multiwall carbon nanotube nanocomposites by dispersing carbon nanotubes during the gelation step of LiCoPO4 synthesis. The uniform distributions of carbon nanotubes within LiCoPO4 particles could enhance the electrical conductance between LiCoPO4 particles, thus improving its specific capacity.210

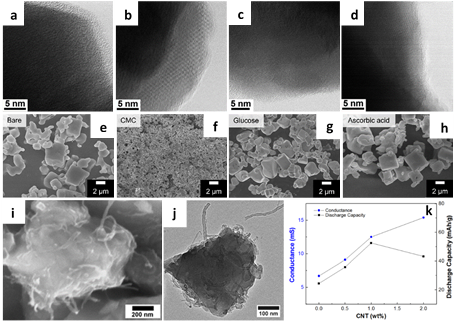


Figure 2 TEM images of LiCoPO4/C particles prepared using (a) 20 wt.% sucrose, (b) 10 wt.% sucrose, (c) 20 wt.% polyacrylic acid and (d) 40 wt.% Tween 80® as carbon sources; Reproduced from Ref. 56 with permission from the Royal Society of Chemistry 2016. SEM images of (e) bare LiCoPO4 and LiCoPO4/C prepared using (f) CMC, (g) glucose and (h) ascorbic acid as carbon sources; Reproduced from Ref. 31 with permission from Elsevier 2017. (i) SEM and (j) TEM images of LiCoPO4-multiwall carbon nanotube (LiCoPO4-MWCNT) nanocomposite, (k) MWCNT amounts vs conductance or discharge capacity of bare LiCoPO4 and LiCoPO4-MWCNT cathodes for LIBs. Reproduced from Ref. 210 with permission from Springer Nature 2016.

4.1.3 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 LiCoPO4. Too thin carbon coating cannot cover the LiCoPO4 particle uniformly, but too thick carbon layer will limit Li-ion diffusion and decrease the volumetric energy density of the battery materials.15 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 LiCoPO4.45 Thus pure LiCoPO4 can be obtained before carbon coating to improve the purity of the composite.11, 69, 107 Also, various kinds of carbon materials especially graphitic carbon can be chosen to improve the quality of coating layer.158, 167, 212, 213 However, it is often a challenge to obtain a uniform carbon coating.211 Gao *et al* compared three techniques, pyrolysis of sucrose, spray of acetylene black, and propane vapour deposition, to *ex situ* coat carbon onto the surface of LiCoPO4 particles. Figure 3 a and b shows the vapour deposition technique helps developing a more homogeneous carbon coating layer on LiCoPO4, thus enabling the active composite to deliver a specific capacity of 130 mA h g-1 at 0.06 C and maintain 80% of that after 30 cycles (Figure 3 c).179

Some *in situ* carbon coating methods, such as the sol-gel168, 206, 207, 209 or solvothermal synthesis101, 128, 132, 208, 214 can generate uniform, compact, and intact carbon layers with appropriate thickness on LiCoPO4.32, 174, 215 Gao *et al* reported that a LiCoPO4/C core-shell structure was readily prepared by a sol-gel approach, where the carbon shell was formed *in situ*. The homogeneous carbon shell increases the kinetics of LiCoPO4 electrode and retards side reactions between electrode and electrolyte. It can deliver a specific capacity of 131 mA h g-1 and exhibit a retention of 78% after 40 cycles at 0.1 C. When discharged at rates of 0.5 and 1 C, the material can deliver capacities of 107 and 95 mA h g-1, respectively.206 Also, Örnek *et al* synthesized nanostructured LiCoPO4/C by a sol-gel method. HR-TEM analysis revealed that a carbon layer of 5 to 10 nm thickness was uniformly distributed on the surface of LiCoPO4.168 Meanwhile, a microwave assisted solvothermal method at temperatures from 140-220 ℃ was applied to synthesized LiCoPO4 cathode with a thin (5-7 nm) and uniform carbon layer distributed on the surface (Figure 3 d).132 This nanostructured LiCoPO4/C cathode exhibited a capacity of 155 mA h g-1 at 0.1 C with a capacity retention of 91% after 80 cycles, and rate capability of 98 mA h g-1 at 5 C (Figure 3 e and f).

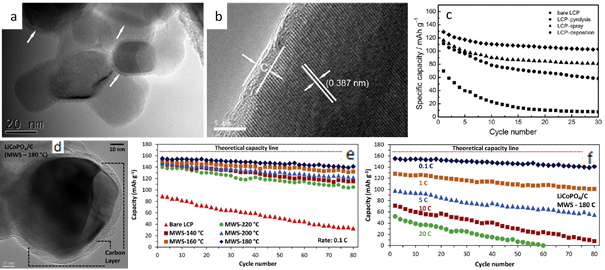


Figure 3 (a) and (b) TEM images of LiCoPO4 showing the carbon coating via vapour deposition technique. The carbon layer is indicated by arrows in (a). (c) Discharge capacity of the bare and LiCoPO4/C electrodes at 0.06 C as a function of cycle number. Reproduced from Ref. 179 with permission from Elsevier 2013. (d) High-resolution TEM image of LiCoPO4/C. (e) and (f) Cycle stability and rate performance of bare and LiCoPO4/C samples prepared by microwave assisted solvothermal synthesis at 180-220 ℃. Reproduced from Ref. 132 with permission from Elsevier 2016.

4.1.4 Surface modification with other materials. Surface modifications of LiCoPO4 with non-carbon materials, such as LiFePO4,52, 93, 113 NiO,26 AlF3,202 VOx,56 Li3V2(PO4)3,196, 216 Al2O3,217 have been reported to improve the cycle stability of LiCoPO4 electrodes by producing a protective film on the LiCoPO4 surface. Lee *et al* prepared LiFePO4 coated LiCoPO4 with a coating layer of about 20 nm in thickness. It was found that the surface modification with LiFePO4 on LiCoPO4 particle mitigated electrolyte degradation, which led to improved cycle stability of high voltage materials.52 As shown in Figure 4, Örnek reported nanoscale NiO-coated LiCoPO4 cathode materials prepared by a newly designed three-step synthesis route, which is a combined technique including advantages of the Stöber, hydrothermal and microwave synthesis methods. LiCoPO4 particles are coated with a continuous NiO layer of 8-10 nm, which can reduce the volumetric stresses and strains that occur during the Li+ insertion and extraction. The 2.5 wt.% NiO-coated cathode had a discharge capacity of 159 mA h g-1 at 0.1 C current rate and showed 85% capacity retention after 80 charge-discharge cycles.26 Qiu *et al* synthesized LiCoPO4 cathode material with a nano-sized uniform AlF3 layer distributed on the surface. 4 mol% AlF3 coated LiCoPO4 material exhibits an initial discharge capacity of 159 mA h g-1 at 0.1 C with 91% capacity retention after 50 cycles, and a discharge capacity of 90 mA h g-1 can be obtained at 1 C rate. The enhanced cycle stability and rate capability are attributed to the fact that the AlF3 layer can suppress the electrolyte decomposition at high voltages.202

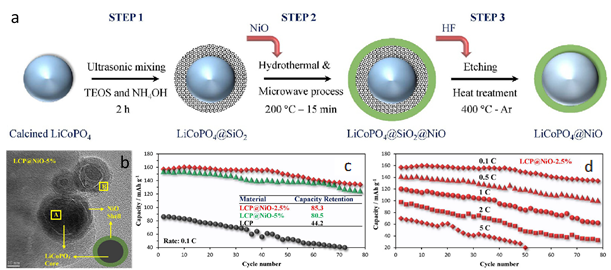


Figure 4 (a) Schematic illustration of NiO-coated LiCoPO4 nanoparticles using stepwise synthesis methodology; (b) high-resolution TEM image of 2.5 wt.% NiO-coated LiCoPO4 sample; (c) cycle stability of bare and NiO-coated LiCoPO4 samples at 0.1 C; (d) rate capability of 2.5 wt.% NiO-coated LiCoPO4 sample at various rates from 0.1 C to 5 C. Reproduced from Ref. 26 with permission from Elsevier 2017.

## 4.2 Carbon network support structures

The use of carbon and other materials to coat LiCoPO4 particles has been discussed in section 4.1. In this section, the use of carbon materials to support and disperse LiCoPO4 particles will be described. Carbon nanofibres,160, 166 carbon nanotubes,218 graphene sheets108, 219 and carbon foams146, 158, 167, 212, 213, 220 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 6. The structural, morphological and electrochemical properties of composites are found to depend on the annealing atmosphere and time.146, 158, 167, 212, 213, 220, 224-226

Carbon nanofibres 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, 221, 222 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 nanofibre composites using electrospun and carbonized nanofibres dipped into a solution containing Li, Co and phosphate ions. The LiCoPO4 crystalline deposits were uniformly distributed on the carbon nanofibre surface. With a discharge capacity of 46 mA h g-1 at 0.1 C, the composites required further optimization.166 Sarapulova *et al* also prepared disordered carbon nanofibre/LiCoPO4 composites (Figure 5 a and b) by a sol-gel method with a discharge capacity of 105 mA h g-1.160

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.223 As shown in Figure 5 c and d, hybrid architectures composed of 3D aligned arrays of MWCNTs and LiCoPO4 nanoparticles have been synthesized by Schneider *et al* *via* tethering lithium phosphoolevins on MWCNTs.218

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 5 e) showed the formation of crystalline “island-like” structures (typically 5-50 μm) supported on carbon.

In recent years, graphene has become an intensively studied material in many fields.227-234 Graphene could be a suitable candidate as an electron conducting additive in the cathodes of LIBs228, 235 due to its extraordinary electronic conductivity higher than 102 S cm-1.236-240 It can build a 3D conductive network for LiCoPO4, which can increase the inter-particle electrical contact and improve the cycle stability and rate capability.219 As shown in Figure 5 g and h, Wang *et al* presented a novel method towards synthesis of two-layer sandwiched [graphene/LiCoPO4](mailto:graphene@(Li0.893Fe0.036)Co(PO4)) nanoparticles. In this approach, the (NH4)2Co8(CO3)6(OH)6·4H2O nanosheets, as the template, and glucose molecules, as the carbon source, are the key factors involved in forming the specific morphology in which both top and bottom graphene sheets tightly envelop the LiCoPO4 nanoparticles, just like a sandwich. This 3D graphene/LiCoPO4 composite displayed promising rate performance (discharge capacity of 85 mA h g-1 at 20 C), stability (capacity retention of 94.6% after 100 cycles) and fast kinetics.219 However, a large amount of graphene can decrease the tap density, thus reducing the volumetric energy density of graphene/LiCoPO4 composites.1

The carbon network support LiCoPO4 3D structures can be combined with methods of carbon coating to further improve the conductivity of LiCoPO4 composites.108 Chen *et al* developed a facile solid-state process for preparing a novel hierarchical LiCoPO4/carbon/graphene composite, consisting of ~3 nm thickness carbon coated LiCoPO4 nanoparticles crosslinked by wrinkled graphene (Figure 5 f). The LiCoPO4/carbon/graphene material delivers a discharge capacity of 146 mA h g-1 at 0.1 C and 93 mA h g-1 at 2 C. This could be attributed to the high electronic conductivity resulted from the synergistic carbon coating and graphene crosslinking.108

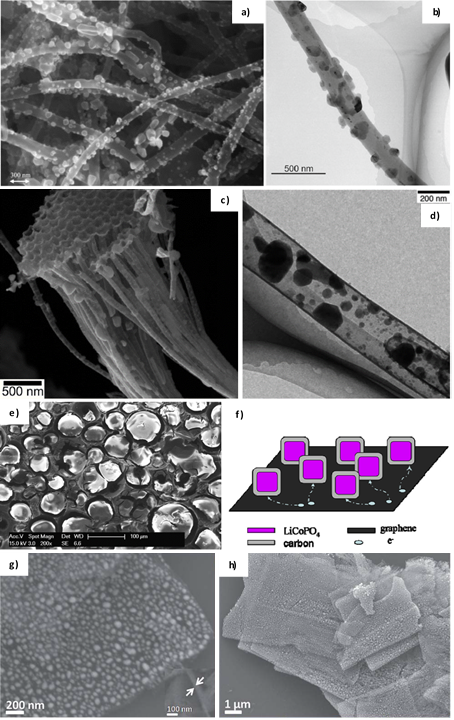


Figure 5 (a) SEM and (b) TEM images of carbon nanofibre/LiCoPO4 composites; Reproduced from Ref. 160 with permission from Springer Nature 2012. (c) SEM and (d) TEM images of ordered 3D carbon nanotube/LiCoPO4 composites; Reproduced from Ref. 218 with permission from John Wiley and Sons 2011. (e) HREM image of carbon foam/LiCoPO4 composites; Reproduced from Ref. 146 with permission from Elsevier 2012. (f) schematic illustration of hierarchical LiCoPO4/carbon/graphene composite; Reproduced from Ref. 108 with permission from Elsevier 2016. (g) SEM and (h) HRSEM images of 3D sandwiched graphene/LiCoPO4 composites. Reproduced from Ref. 219 with permission from the Royal Society of Chemistry 2015.

Table 6 The electrochemical performance of carbon network support LiCoPO4 3D structures.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Synthesis methods | Carbon network | Techniques | Rate performance, mA h g-1 (rate, C) | Cycle stability | Ref. |
| Sol-gel process | Multiwall carbon nanotubes | *Ex situ* | - | 35% capacity retention at 0.1 C after 30 cycles | 218 |
| Pechini-assisted sol-gel process | 3D nonwoven nanofibres | *In situ* | 46 (0.1 C) | 26% capacity retention at 0.1 C after 16 cycles | 166 |
| Pechini-assisted sol-gel process | Graphitic carbon foam | *In situ* | 100 (0.1 C) | 36% capacity retention at 0.1 C after 10 cycles | 213 |
| Hydrothermal synthesis | Graphene sheets | *In situ* | 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 | 219 |
| Solid-state ball mill reaction | Wrinkled graphene | *Ex situ* | 146 (0.1 C), 93 (2 C) | 63% capacity retention at 0.1 C after 40 cycles | 108 |

## 4.3 Size reduction and morphology control

Conductive agents improve the electronic conductivity of LiCoPO4 composites, whereas particle size reduction and morphology control could reduce the time required for Li-ion diffusion within LiCoPO4, thus improving its specific capacity and rate capability. Relevant examples of the electrochemical performance of LiCoPO4 after size reduction or morphology control are shown in Table 7.

4.3.1 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.58, 111, 175 Smaller structures mean shorter diffusion paths for lithium ions, thus better utilization of the LiCoPO4 active materials. Therefore, nanosized LiCoPO4 cathodes are more likely to obtain high discharge capacity and rate capability.175, 183 The effect of carbon coating to improve the electronic conductivity of LiCoPO4 has been discussed in section 4.1. Here, we will describe this approach further, as well as other approaches, in relation to the effect of reducing the particle size of LiCoPO4. Taniguchi *et al* prepared LiCoPO4/C nanocomposites, 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 particles by inhibiting undesirable particle growth during calcination. Due to a much smaller Li-ion diffusion distance in the electrode, and well distributed carbon on the LiCoPO4 agglomerates, it delivered initial discharge capacities of 142 and 109 mA h g-1 at 0.05 and 20 C, respectively.175, 191

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 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.58 Figure 6 g and h show a LiCoPO4/C sample with 500 nm particle size that provides an initial discharge capacity of 124 mA h g-1 at 0.1C, with a retention of 83% after 100 cycles. A discharge capacity of 85 mA h g-1 is still attainable when the rate is up to 2C. Nilges *et al* synthesized particle size-controllable LiCoPO4 platelets by a simple one-step microwave-assisted solvothermal process using an array of water/ethylene glycol solvent mixtures. The particle sizes of the olivine materials were significantly reduced with increasing EG content, which could mainly be attributed to the increased viscosities of the solvent blends.111, 125

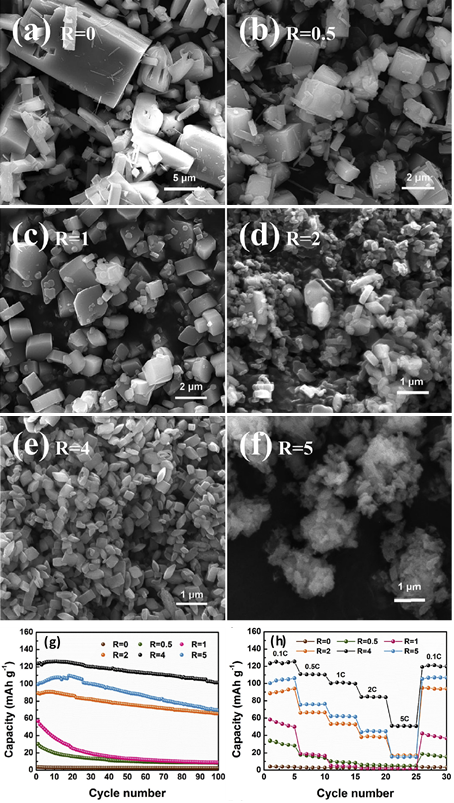


Figure 6 (a-f) SEM images of LiCoPO4 samples prepared via solvothermal synthesis with different water/ethylene glycol ratio R (R = 0, 0.5, 1, 2, 4, and 5); (g) cycle stability at 0.1 C and (h) rate capability at various rates from 0.1 C to 5 C for LiCoPO4 cathodes in LIBs. Reproduced from Ref. 58 with permission from Elsevier 2016.

Furthermore, the particle size and morphology could be controlled by some other experimental conditions.183, 241, 242 For example, Brutti *et al* prepared LiCoPO4 through a solvothermal method, and different Co2+ salts have been used to study the effect of the anion on the crystal growth as well as the effect of solution acidity, reaction temperature and time. A solution with moderate acidity or neutral pH is more likely to form phase pure LiCoPO4; longer reaction time slightly enlarges the crystal size; lower reaction temperatures lead to fewer and larger crystallites; and different cobalt counter-anion in the precursor salts greatly enhance or limit the crystal growth.131 Nallathamby *et al* employed a simple and an easy-to-adopt modified solid state fusion method to achieve morphologically controlled growth of LiCoPO4/C nanorods using H2CO3 + (NH4)2CO3 growth modifiers and heat treatment in an inert (argon) atmosphere. 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 were achieved due to the synergistic effect of controlled growth, formation of conductive Co2P phase under inert atmosphere and presence of amorphous carbon coating.51

As discussed above, reducing the LiCoPO4 particle sizes to nanoscale can improve the rate capability in LIBs due to the shortened 1D Li-ion diffusion channels in LiCoPO4. However, the size reduction decreases the tap density and volumetric energy density. High surface area of nanosized LiCoPO4 particles also increases the electrode/electrolyte interface area, so undesirable electrode/electrolyte by-reactions become more significant,15 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 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 | 191 |
| Spherical nanoporous microparticles (70 nm primary particles agglomerates) with 68 nm pore size | Spray pyrolysis | H2O | Carbon coating | 123 (0.1 C), 82 (5 C) | 95% capacity retention at 0.1 C after 20 cycles | 174 |
| Hedgehog-like, 5-8 μm (compose of nanorods, 40 nm x 1 μm) | Solvothermal synthesis | H2O:BAa =1:1 | Carbon coating | 136 (0.1 C), 85 (5 C) | 91% capacity retention at 0.1 C after 50 cycles | 101 |
| Nanoparticles agglomerates, 87 nm | Spray pyrolysis and wet ball-milling | H2O | 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 | 175 |
| 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 | 114 |
| Nanosheets with 4.6 nm thickness | Liquid-phase exfoliation with solvothermal lithiation process | Ethanol | NH4CoPO4·H2O nanosheets as templates, PVPa 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 | 187 |
| Needle and rod-like nanosized and micronsized particles | Solid-state fusion method | - | Carbonate anion CO32- 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 | 51 |
| Nanoplates, 500 nm x 200 nm x 50 nm; Nanorods, 500-1000 nm length and 50 nm thickness | Supercritical fluid processing | Ethanol | HMDa or HMTa 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 | 188 |
| 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 | 189 |
| Hexagonal/octagonal platelet, sub-micron particles with 50-100 nm thickness | Solvothermal synthesis | H2O:EGa =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 | 115, 116 |
| Flower-like, 5-10 μm (compose of plate-like, 1-2 μm x 200 nm) | Hydrothermal  synthesis | H2O | 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 | 121 |
| Hexagonal platelets, submicron size with thickness ＜ 200 nm | Solvothermal synthesis | H2O:EGa =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 | 131 |
| Hexagonal platelets, 400-600 nm x 700-800 nm x 100-220 nm | Microwave-assisted solvothermal synthesis | H2O:EGa =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 | 137 |
| Badminton-like (compose of nanorods with 200 nm diameters and 3 μm length) | Hydrothermal method | H2O | PEG 200a 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 | 130 |
| Particles, 500 nm-10 μm | Solvothermal synthesis | EGa:H2O =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 | 58 |
| Porous nanoplates with 2-6.6 nm pore size | Modified hydrothermal synthesis | H2O | NH4CoPO4·H2O 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 | 25 |
| Sponge-like, 200 nm-50 μm | Sol-gel process | H2O | Carbon coating | 83 (0.5 C) | 59% capacity retention at 0.5 C after 30 cycles | 169 |
| 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 | H2O:(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 | 53 |
| Hexagonal platelets, 200 x 100 x 50 nm to 1.2 x 1.2 x 0.5 μm | Microwave-assisted solvothermal synthesis | EGa:(H2O+EGa) =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 | 125 |
| Nanoflakes (compose of nanoplates with 10-20 nm in diameter) | solution-phase strategy | H2O:DMSOa =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 | 243 |
| 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. | | | | | | |

4.3.2 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 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.25, 53, 114-116, 125, 131, 188

At the thermodynamic equilibrium state, the surface area of each facet in a crystal usually depends on its free surface energy.244 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.53, 115, 116, 125, 131 Nilges *et al* presented a microwave-assisted solvothermal synthesis route using a 1:1 (v/v) water/ethylene glycol binary solvent mixture. The ethylene glycol co-solvent plays an important role in tailoring the particle size, morphology, and crystal orientation of the LiCoPO4 material. The as-prepared powder consists of single crystalline LiCoPO4 and features a hexagonal platelet-like morphology with dimensions of 700-800 nm x 400-600 nm x 100-220 nm and shows the smallest dimension along [010], which is the direction of the lithium diffusion pathways in the LiCoPO4 olivine crystal structure.137 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 form (010) facet comparing with ethylene glycol, because of the more stable binding geometry.53 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.15 For example, Nilges *et al* synthesized LiCoPO4 by a simple and rapid one-step microwave-assisted solvothermal route, using a variety of water/alcohol 1:1 (v:v) solvent mixtures, including ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol 400 and benzyl alcohol. Figure 7 a-f SEM images reveal a strong influence of these co-solvents on the particle size and morphology of LiCoPO4, resulting in the formation of variations between 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 along the lithium diffusion pathways of the olivine crystal structure. The anisotropic crystal orientations with enhanced Li-ion diffusion properties result in initial discharge capacities of 141 mA h g-1 at 0.1 C, with rate capability of 112 mA h g-1 at 2 C (Figure 7 g and h).53

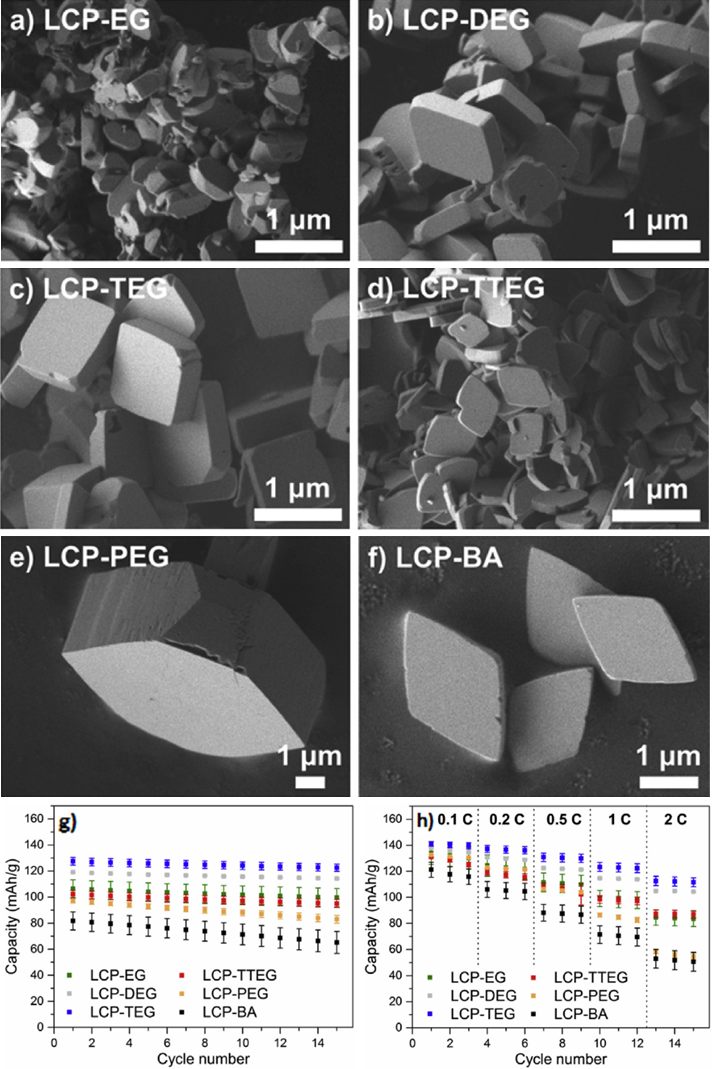


Figure 7 SEM images of the LiCoPO4 samples obtained from microwave assisted solvothermal synthesis using various co-solvents in a 1:1 (v:v) mixture with water: (a) ethylene glycol, (b) diethylene glycol, (c) triethylene glycol, (d) tetraethylene glycol, (e) polyethylene glycol 400 and (f) benzyl alcohol, 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 LiCoPO4 cathodes. Reproduced from Ref. 53 with permission from Elsevier 2017.

In addition, the orientation of LiCoPO4 crystals could be controlled by some other factors like surfactants, templates, etc.25, 114, 188 Devaraju *et al* reported a controlled synthesis of plate-like LiCoPO4 nanoparticles *via* supercritical solvothermal method in presence of oleylamine as a surfactant. The synthesized plate like particles showed 50-200 nm in width, 100-300 nm in length and thickness from 5 to 15 nm.114 Truong *et al* reported that high-voltage LiCoPO4 cathode materials with different shapes and well-developed facets such as nanoplates and nanorods with exposed (010) facets have been synthesized by a one-pot supercritical fluid processing. It was found that amines with long alkyl chains such as hexamethylenediamine played important roles to manipulate the shape of the nanocrystals by selective adsorption on the specific (010) facets. As shown in Figure 8 a-d, the SEM and TEM images show the LiCoPO4 nanoplates with lengths of 500 nm, widths of 200 nm and a mean thickness of 50 nm. The high-resolution TEM image (Figure 8 d) shows the (200) and (020) atomic planes with a lattice spacing of 2.35 Å and 5.1 Å with an interfacial angle of 90°, and the platelike nanocrystals are exposed (010) facets. The results show that the thinnest part of the nanoplates is along the b-axis, which is a favorable direction for the Li-ion diffusion. Thus the nanoplates exhibited better cycle stability and rate capability than nanoparticles.188 Truong *et al* also investigated the benzylamine-directed growth of LiCoPO4 nanoplates with exposed (010) facets by a supercritical ethanol process. The unique structure of the olivine LiCoPO4 nanocrystals, with a shortened Li-ion diffusion pathway, allows fast extraction/ insertion of Li-ion in the structures, thus resulting in an initial discharge capacity of 123 mA h g-1 and capacity retention of 81% after 10 cycles.189 Recently, Chang *et al* prepared highly [010]-oriented self-assembled LiCoPO4/C nanoflakes *via* solution-phase strategies. The formation of 5-hydroxylmethylfurfural and levoglucosan *via* the dehydration of glucose during the reaction played a key role in mediating the morphology and structure of the products. The resulting LiCoPO4/C nanoflakes as cathode materials provide a capacity of 155 mA h g-1 at 0.1 C and stable cycling with 93% capacity retention after 100 cycles.243

Yan *et al* fabricated ultrathin LiCoPO4 nanosheets (thickness: 4.6 nm) with exposed (010) surface facets by using NH4CoPO4·H2O nanosheets as templates. The as-synthesized LiCoPO4 nanosheets have high contact area with the electrolyte and fast lithium transport, 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.187 Also, with NH4CoPO4·H2O nanosheets as templates, Wang *et al* fabricated LiCoPO4 nano-plates with porous structure (Figure 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.25, 245

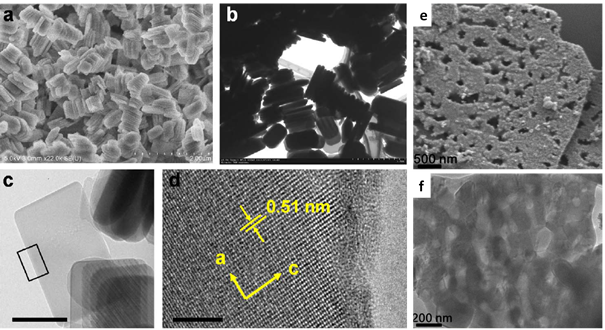


Figure 8 Nanoplate particles synthesized with hexamethylenediamine. (a) SEM image (scale bar = 2 μm); (b) low-magnification TEM image (scale bar = 1 μm); (c) high-magnification TEM image (scale bar = 200 nm); (d) HRTEM image of a portion of the particle shown in (c) (scale bar = 5 nm). Reproduced from Ref. 188 with permission from Nature Publishing Group 2014. (e) SEM and (f) TEM images for LiCoPO4 nano-plates with porous structure prepared with NH4CoPO4·H2O nanosheets as templates. Reproduced from Ref. 25 with permission from Elsevier 2016.

4.3.3 3D porous architectures with hierarchical structures. Hierarchical structures of LiCoPO4 facilitate the fast transport of lithium ions through the LiCoPO4 material, similarly to nanoparticles or planar structures. As shown in Figure 9 a-d, Richardson *et al* synthesized spherical nanoporous LiCoPO4/C composite microparticles by spray pyrolysis. The porous micron-size particles consisted of an agglomeration of ~70 nm primary particles with 3-5 nm thick conformal carbon coating. The material delivered a reversible capacity of 123 mA h g-1 at 0.1 C, and exhibited a capacity retention of 95% over 20 cycles.174

Hierarchical LiCoPO4 with hedgehog-like (Figure 9 e),101 flower-like,121 dumbbell-like,124 straw-like (Figure 9 f),128 shuttlecock-like (consisting of many thin nanorods which are about 200 nm in diameters and 3 μm in length),130 and spongy54, 156, 169, 212, 220 architectures have also been developed.38, 110 The hedgehog-like LiCoPO4/C hierarchical microstructures were first synthesized by Yang *et al* *via* a simple solvothermal process in water-benzyl alcohol mixed solvent at 200 ℃. The hedgehog-like LiCoPO4/C microstructures in the size of 5-8 μm are composed of large numbers of nanorods in diameter of ~40 nm and length of ~1 μm, which are coated with a carbon layer of ~ 8 nm in thickness. It delivers an initial discharge capacity of 136 mA h g-1 at 0.1 C and capacity retention of 91% after 50 cycles.101

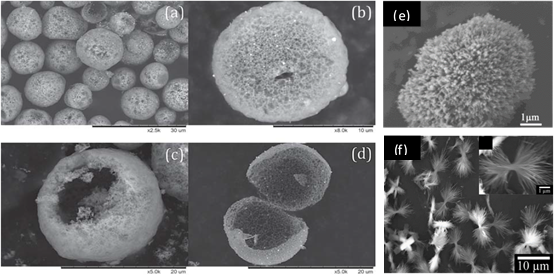


Figure 9 SEM images of (a) the nanoporous LiCoPO4/C composite particles synthesized by spray pyrolysis; (b) the surface of a single particle; (c, d) broken particles, showing the 3D interconnected pores; Reproduced from Ref. 174 with permission from the Royal Society of Chemistry 2011. (e) hedgehog-like LiCoPO4/C synthesized via a solvothermal process in water-benzyl alcohol mixed solvent at 200 ℃; Reproduced from Ref. 101 with permission from Elsevier 2011. and (f) straw-like LiCoPO4/C composite prepared by solvothermal process with poly(vinylpyrrolidone) as the carbon source and template. Reproduced from Ref. 128 with permission from Elsevier 2011.

## 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 LiCoPO4.246 Ion doping is expected to improve the discharge capacity of LiCoPO4 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 LiCoPO4, but the role of ion doping in LiCoPO4 is still controversial. The metal ions could be doped on both Li sites and Co sites.34, 201, 247 The control of proper doping at preferable sites is important for the overall LiCoPO4 performance improvement. Relevant examples of the electrochemical performance of LiCoPO4 after ion doping are shown in Table 8.

4.4.1 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.247, 248 Wang *et al* doped Fe into Li-site of LiCoPO4 structure and found that the lattice parameter a slightly increases and b diminishes after Fe doping, resulting in a shorter and wider Li+ diffusion pathway in LiCoPO4 crystals.219 Although the rate performance of LiCoPO4 has been improved by Li site doping in some reports,34, 201, 219, 249 the role of Li site doping in LiCoPO4 is still unclear and under debate.

4.4.2 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, LiCoPO4 indeed has exhibited improved cycle stability and rate capability after aliovalent doping, using V3+,113, 117 V5+,196, 250, 251 Fe3+,36, 57, 157, 201, 208, 249, 252 Y3+,162 Cr3+,209, 253 Si4+253 or Cu+.34 Yang *et al* improved the initial discharge capacity of LiCoPO4/C cathode material from 112 to 135 mA h g-1 at 0.1 C after doping with V5+. The Li1.025Co0.95V0.05(PO4)1.025/C displays a narrower distribution of smaller particles (300-500 nm) when compared with pristine LiCoPO4/C with particle size ranging from 400 to 800 nm.250 Similar phenomena were observed by Wang162 and Karthikeyan *et al*251 with Y3+ and V5+ doping at Co site in LiCoPO4, respectively. Manthiram *et al* reported a low-temperature microwave-assisted solvothermal synthesis of aliovalently substituted LiCo1−3x/2Vxx/2PO4 (x = 0-0.08), and it was found that V3+ substitution produced a systematic decrease in the unit cell dimensions. The specific capacity and cycling stability were greatly improved compared to the unsubstituted LiCoPO4 which was attributed to an improved conductivity of the vanadium doped sample.113, 117 Kosova *et al* achieved a better cycle stability of LiCoPO4 by vanadium modification *via* mechanochemically assisted carbothermal reduction. It has been found that only a small amount of V ions incorporated into the LiCoPO4 structure. The other V ions formed monoclinic Li3V2(PO4)3. Incorporated V ions are in a mixed oxidation state (3+, 4+ or 5+) and predominantly substitute for Co2+. The compensation mechanism for supervalent V ion substitution in LiCoPO4 involves lithium vacancy formation. The as-prepared 0.95LiCoPO4·0.05Li3V2(PO4)3 shows enhanced cycle stability compared to pure LiCoPO4, due to a suitable amount of structural defects, which improve ionic and electronic conductivity, and to the presence of the Li-conductive Li3V2(PO4)3 on the surface of the LiCoPO4 particles promoting the transport of the Li-ion from the electrolyte to the (010) facet.196

In comparison to aliovalent doping, isovalent substitution has attracted more attention for LiCoPO4, and many divalent cations, such as Fe2+,25, 36, 52, 57, 81, 84, 99, 165, 178, 192, 195, 201, 208, 214, 249, 252-255 Mn2+,90, 118, 129, 141, 168 Ca2+,54, 158, 213 Mg2+,54, 90, 156, 167, 213 Zn2+,98 Ni2+41, 90, 163 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. Fe2+ doping at Co sites can enhance the discharge capacity and rate capability for LiCoPO4,25, 253 which could be attributed to the enhanced Li+ diffusivity induced by the enlargement of 1D Li+ diffusion channel in polyanion structure of LiCoPO4.99, 192 Furthermore, Kang *et al* have shown using *ab initio* calculations and absorption spectroscopy that preferential Fe2+ occupation of the 4c sites suppresses 4a-4c antisite mixing of Li and Co, thereby stabilizing the olivine structure by compensating for the Co-encapsulating oxygen octahedron shrinkage due to Co2+ oxidation during Li+ extraction (Figure 10).84 This reduces the cell volume change in the material during the Li extraction/insertion process.195 Fe substituted LiCoPO4 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.66, 81, 254, 256 It has been reported that isovalent ion doping in Co site with Mn2+,118, 168 Fe2+,208, 257 Ni2+,163 Ca2+54, 158 or Mg2+54, 156 can affect the size and morphology of products. For example, Örnek *et al* reduced the LiCoPO4 particles size with homogenous particle distribution and well-defined grain boundaries after doping with Mn2+.168 Mn2+ can occupy the Co2+ site *via* doping, which induces the lattice distortion of LiCoPO4 crystal. This lattice distortion could reduce the surface energy of LiCoPO4 particles and then impede the growth of LiCoPO4 crystal.258 Similar observation was reported by Ni *et al* who found that Mn2+ doping can remarkably reduce the particles size of LiCoPO4 from 1 µm to 100 nm as Mn2+ substitution can facilitate the formation of the olivine structure under hydrothermal condition.118

The electrochemical performance of LiCoPO4 could also be improved by a combination of Li site and Co site (aliovalent and isovalent) doping. Allen *et al* reported that Fe-substituted LiCoPO4 exhibited improved cycling stability, with 80% capacity retention after 500 cycles, while pure LiCoPO4 loses more than half capacity after 10 cycles. This could be attributed to the partial substitution of Li+ by Fe3+ and Co2+ by Fe2+ and Fe3+ which appears to stabilize the structure.201, 249 Further investigation showed that Fe2+/Fe3+ substituted LiCoPO4 exhibits both higher bulk ionic and electronic conductivity.36 This result is inconsistent with the first principles investigation on LiMPO4 (M = Fe, Mn, 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 LiFePO4, thus Fe2+ substitution into LiCoPO4 will improve the electronic conductivity.259 Brutti *et al* also confirmed that the partial substitution of Co2+ in the olivine lattice with Fe2+/Fe3+ strongly affects the long range crystal structure as well as the short range atomic coordination. These structural changes alter the concentration of anti-site defects, the natural concentration of lithium vacancies, and the size of the lithium diffusion channels along the [010] direction as well as their local distortion. The balancing between these competitive effects modulate the lithium transport properties in the lattice.57, 208 Besides, Fe, Cr and Si substituted-LiCoPO4 (Cr,Si-LiCo0.9Fe0.1PO4) was investigated by Allen *et al* as an improved LiCoPO4-based cathode material. Fe substitution greatly improves the cycle life and increases the energy density. Cr substitution further increases the energy density, cycle life and rate capability. Si substitution reduces the reactivity of the cathode with electrolyte thereby increasing cycle life. In combination, the substituents lead to a LiCoPO4-based cathode material in Li/Cr,Si-LiCo0.9Fe0.1PO4 half cells, with a discharge capacity of 140 mA h g-1 at C/3 rate, and no capacity fading over 250 cycles.253 Further investigation reveals that substituting ions to generate Li1.025Co0.84Fe0.10Cr0.05Si0.01(PO4)1.025 can stabilize both the electronic structure and crystal structure and, therefore, substantially improve the ability to fully utilize the redox capacity of the material.27, 260

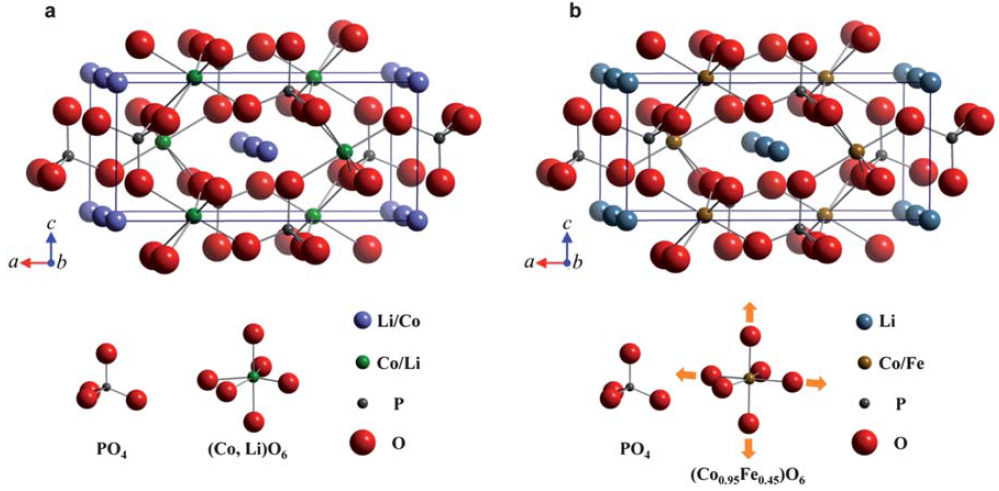


Figure 10 The [010] projections of the local structures of the pristine and Fe-doped LiCoPO4. Configuration of atoms (a) with antisite-mixing in LiCoPO4 and (b) without antisite-mixing in LiCo0.95Fe0.05PO4. Note that the latter configuration provides larger channels for Li+ transport due to the expanded oxygen octahedron (indicated by arrows). Reproduced from Ref. 84 with permission from the Royal Society of Chemistry 2011.

Table 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 | Fe2+ | (Li0.893Fe0.036)CoPO4 | 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 | 219 |
| Co site aliovalent doping | V5+ | Li1+0.5xCo1−xVx(PO4)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 | 196, 250, 251 |
| Y3+ | LiCo1-xYxPO4 (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 | 162 |
| Fe3+ | Li1-xCo1-xFexPO4 (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 | 157 |
| V3+ | LiCo1−3x/2Vx□x/2PO4 (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 | 113, 117 |
| Cr3+ | LiCo1-1.5xCrxPO4/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 | 209 |
| Co site isovalent doping | Fe2+ | LiCo0.95Fe0.05PO4 | 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 Co2+ 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 | 81, 84, 192, 254 |
| Li1+x(Co1−yFey)1−xPO4 (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 | 52, 99, 165 |
| LiCo1-xFexPO4 (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 | 195 |
| LiCo0.8Fe0.2PO4 | 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 | 25 |
| Mg2+ | LiCo1-xMgxPO4 (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 | 54, 156, 167, 213 |
| Ca2+ | LiCo1-xCaxPO4 (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 | 54, 158, 213 |
| Ni2+ | LiCo1-xNixPO4 (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 | 163 |
| Mn2+ | LiCo1−xMnxPO4/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 | 141, 168 |
| Combination doping | Fe3+ (Li site) and Fe2+/Fe3+ (Co site) | Li0.92Co0.8Fe2+  0.12Fe3+  0.08PO4 | Extra Li vacancies and more mobile hole polarons after Fe2+/Fe3+ substitution, resulting in increased ionic conductivity and electronic conductivity, Fe3+ substitution stabilize the structure | Citrate complexation  route | 121 (0.1 C), 86 (2 C) | 80% capacity retention at 0.1 C after 500 cycles | 36, 201, 249 |
| Fe2+/Fe3+ (Co site) | Li0.973(Fe0.1Co0.9)1.014PO4 | 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 | 57, 208 |
| Fe2+, Cr3+ and Si4+ (Co site) | LiCo(0.9-y-z)/(1+0.5y)Fe0.1/(1+0.5y)Cry/(1+0.5y)SizPO4 (y = 0.025, 0.05, 0.1, z = 0, 0.01, 0.02) | Charge compensation for Cr3+ and Si4+ substitution of Co2+ 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 | 27, 253, 260 |

## 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 LiCoPO4 are summarised in Table 9. Surface modification (e.g. carbon coating) on LiCoPO4 particles improves the electronic conductivity of composites. Furthermore, carbon coating not only reduces the particle size and alleviates the aggregation of LiCoPO4 particles by inhibiting undesirable particle growth during heat treatment, but also protects LiCoPO4 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.14 Also, it could reduce the tap density of LiCoPO4 cathodes thus decrease the volumetric energy density of LIBs. Carbon network structures to support LiCoPO4 particles provide good electrical conductivity, but it is hard to achieve uniform distribution. Decreasing the particle size of LiCoPO4 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 LiCoPO4 although the mechanism is still in controversy.59, 261-263

The combination of the advantages of various approaches is promising for high performance LiCoPO4 cathodes in LIBs. For example, Örnek *et al* synthesized a nanostructured LiCo0.95Mn0.05PO4/C composite by sol-gel assisted carbothermal reduction method. The particle size of the LiCo0.95Mn0.05PO4/C nanocomposite was between 40 and 80 nm with a uniform carbon layer of 5-10 nm thickness distributed on the surface. The LiCo0.95Mn0.05PO4/C cathode exhibited a specific capacity of 140 mA h g-1 with a capacity retention of 91.8% after 60 cycles at 0.1 C rate. This was mainly ascribed to the combination of the advantages of size reduction, carbon coating and Mn doping.168

Table 9 Comparison of various approaches to improve the electrochemical performance of LiCoPO4.

|  |  |  |  |
| --- | --- | --- | --- |
| 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 LiCoPO4 | High ion conductivity, rapid electrochemical kinetics | Low tap density and volumetric power density |
| LiCoPO4 plates | High ion conductivity | - |
| 3D hierarchical LiCoPO4 | - | Complex synthesis |
| Ion doping | Li site doping | - | Low Li-ion conductivity |
| Co site doping | High ion conductivity | Controversial doping site and mechanism |

# 5 Optimization of other components in high-voltage LIBs

The cycle stability and rate capability of LiCoPO4 cathode is not only limited by the material itself but is also affected by the battery components, such as electrolytes,199, 264-266 separators44, 47, 267 and conductive additives,69, 105, 159, 268 as illustrated in Table 10.

## 5.1 Electrolyte optimisation

LiCoPO4 high voltage cathodes with LiPF6-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 LiPF6, especially at elevated temperatures and in water-containing environments.46, 69, 113, 269-273 Various efforts have been made to optimize conventional electrolytes i.e. LiPF6 in ethylene carbonate / dimethyl carbonate / ethyl methyl carbonate (LiPF6-EC/DMC/EMC) for LiCoPO4 high voltage cathodes, such as developing electrolyte additives, investigating alternatives to LiPF6 salt or EC/DMC/EMC co-solvent, and introducing ionic liquids or solid-state electrolytes.

The electrolyte additives to optimise the conventional electrolyte LiPF6-EC/DMC/EMC mainly include thiophene (TPN),153 lithium difluoro(oxalate)borate (LiDFOB),274 tris(trimethylsilyl) borate (TMSB),275 lithium bis(oxalato)borate (LiBOB),102 trimethylboroxine (TMB)45, 276 and tris(hexafluoroisopropyl) phosphate (HFiP).65, 201, 249 Wei *et al* introduced TPN as an electrolyte additive to LiCoPO4/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 11 a and b).153 It was also found that the LiDFOB electrolyte additive decomposed at 4.35 V *vs* Li/Li+ and assisted in forming a stable interphase film, which passivated the cathode surface and inhibited the catalytic decomposition of the electrolyte.274 In addition, TMSB is used by Qiu *et al* as electrolyte additive to overcome the severe capacity fading of LiCoPO4 cathode at high voltage. The presence of 1 wt.% TMSB effectively improves the cycle stability of LiCoPO4 cathode in EC-based electrolyte. LiCoPO4 cathode delivers an initial discharge capacity of 144 mA h g-1 at 0.1C and with a capacity retention of 76% after 50 cycles, while only 132 mA h g-1 and 45% is found for that electrolyte without TMSB. The enhancement of specific capacity and cycle stability is attributed to the thin protective SEI film that originates from TMSB, which stabilizes the interface of the cathode and electrolyte, and suppresses the continuous decomposition of conventional electrolyte at 5 V high voltage.275

LiBF4 has been used as an alternative to LiPF6 salt.217, 277-279 Eftekhari investigated the electrochemical performance of LiCoPO4 electrodes protected with a thin layer of Al2O3 in LiBF4-based electrolytes. It was found that both approaches significantly improved 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.217 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 1:4.277

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.280-282 Markevich *et al* reported that FEC-based electrolyte solutions result in dramatically improved cycling behavior of LiCoPO4 cathodes in LIBs compared to that with standard EC-based electrolyte solutions (Figure 11 c). It was found that FEC participates in the formation of protective surface films on the high-voltage cathodes, which are much more effective than the surface films formed in EC-based electrolyte solutions, thus resulting in an improved cycling stability with 76% capacity retention at 0.2 C after 100 cycles.45, 50, 283

By replacing both the salt and co-solvent in conventional electrolytes,279 Fukutsuka *et al* examined the compatibility of LiF combined with anion receptors in propylene carbonate (PC) electrolyte solution with high potential positive electrodes. As anion receptors, tripropyl borate (TPB), tris(pentafluorophenyl) borane (TPFPB), and tris(hexafluoroisopropyl) borate (THFIPB) were used. LiCoPO4 thin-film electrodes were prepared by sol-gel method and used as carbon- and binder-free model electrodes. LiCoPO4 showed better cycle stability in 0.1 M LiF + 0.1 M THFIPB/PC electrolyte, which was ascribed to the formation of a surface protecting layer from the reaction of F--THFIPB complex.55

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.284, 285 For example, Chou *et al* reported that LiCoPO4 showed better cycling 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) indicating that the former is more stable at a high working voltage cell system.207 Hassoun *et al* reported LIBs formed by the combination of a Fe-substituted, C-coated 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).214

Apart from liquid-based electrolytes, some solid-state electrolytes such as Li1.3Al0.3Ti1.7(PO4)3,91, 286 Li1+x+yAlxTi2-xSiyP3-yO12,39 Li3.3PO3.8N0.22,287 Li2O-Al2O3-TiO2-P2O5288 and LiTi2(PO4)3289 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 Li1.3Al0.3Ti1.7(PO4)3 *via* heat treatment. It was found that both the solid electrolyte layer and the active material layers could be co-sintered without significant formation of new materials, and the resultant interfaces were electrochemically active.91 Also, Kunshina *et al* used a peroxide solution of a Li1.3Al0.3Ti1.7(PO4)3 precursor to create a composite consisting of an electrochemically active substance and an electrically conductive additive distributed uniformly between LiCoPO4 particles. After annealing at 700 ℃, the two-phase LiCoPO4/Li1.3Al0.3Ti1.7(PO4)3 composite was obtained, the conductivity of which was two orders of magnitude higher than that of LiCoPO4 at room temperature.286

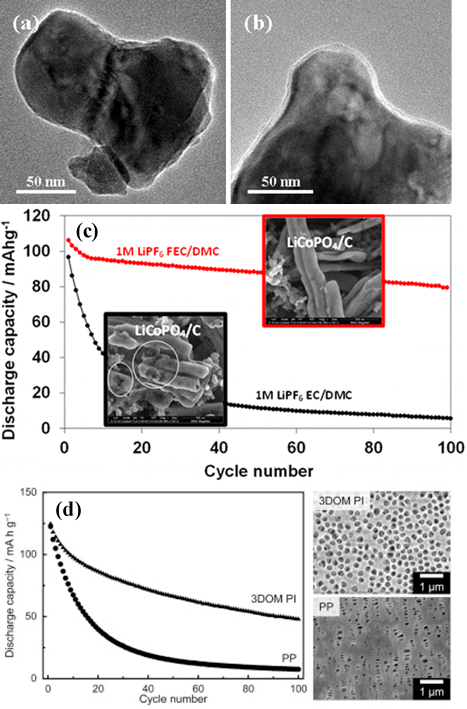


Figure 11 TEM images of LiCoPO4/C particles in the cells (a) without and (b) with 0.1 wt.% TPN as electrolyte additive after 5 cycles. Reproduced from Ref. 153 with permission from Elsevier 2012. (c) Specific capacity versus cycle number of LiCoPO4/Li half cells with 1M LiPF6 in FEC/DMC or EC/DMC as 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. 50 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. 267 with permission from Elsevier 2017.

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

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Materials | Synthesis methods | Electrolytesa (v/v) | Electrolyte additivesa | Separators / conductive additives | Rate performance, mA h g-1 (rate, C) | Cycle stability | Ref. |
| Li0.92Co0.8Fe0.2PO4 | Citrate complexation route | 1 M LiPF6 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 | 201 |
| LiCoPO4/C | Sol-gel Process | 1 M LiPF6 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 | 153 |
| LiCoPO4 | Solid-state reaction | 1 M LiPF6 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 | 102 |
| LiCoPO4 | Sol-gel Process | 1 M LiPF6 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 | 274 |
| LiCoPO4/C | Hydrothermal synthesis | 1 M LiPF6 in FEC/DMC 1:4, 1 M LiPF6 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 | 45 |
| LiCoPO4 | Solid-state reaction | 1 M LiPF6 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 | 276 |
| LiCoPO4 | Solid-state reaction | 1 M LiPF6 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 | 65 |
| LiCoPO4 | Sol-gel Process | 1 M LiPF6 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 | 275 |
| LiCoPO4/Al2O3 | Solid-state reaction | 1 M LiBF4 in EC/DMC 1:1 | - | - | 127 (0.1 C) | 83% capacity retention at 0.1 C after 50 cycles | 217 |
| LixCoPO4 (x = 0.90, 0.95, 1, 1.05) | Sol-gel Process | 1 M LiTFSI in Pyr13TFSI ionic liquid, 1 M LiPF6 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 | 207 |
| LiCoPO4/C | Hydrothermal synthesis | 1 M LiPF6 in EC/DMC 1:1, 1 M LiPF6 in FEC/DMC 1:4 (wt.%) | - | - | 105 (0.2 C) | 80 mA h g-1 at 0.2 C after 100 cycles | 50, 283 |
| LiFe0.1Co0.9PO4/C | Solvothermal synthesis | 0.2 mol kg-1 LiTFSI in Pyr14TFSI ionic liquid | - | - | 90 (0.05 C) | 75 mA h g-1 at 0.05 C after 7 cycles | 214 |
| LiCoPO4/C | Solvothermal synthesis | LiBF4 in PC 1:12, 1:6, 1:4, molar ratio | - | - | 137 (0.1 C) | 79% capacity retention at 0.1 C after 10 cycles | 277 |
| LiCoPO4/C | Hydrothermal synthesis | 1 M LiPF6 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 | 47 |
| LiCoPO4/C | Hydrothermal synthesis | 1 M LiPF6 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 | 44 |
| LiCoPO4/C | Hydrothermal synthesis | 1 M LiPF6 in EC/DEC 1:2 | - | Separators: 3D ordered macroporous polyimide | 125 (0.1 C) | 39% capacity retention at 0.1 C after 100 cycles | 267 |
| LiCoPO4 | Solid-state reaction with high-energy ball-milling process | 1 M LiPF6 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 | 105 |
| LiCoPO4 | Sol-gel Process | 1 M LiPF6 in EC/DEC 1:1 | - | Conductive additives: Ketjen black | 145 (0.1 mA cm-2) | - | 159 |
| LiCoPO4/C | Hydrothermal synthesis | 1 M LiPF6 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 | 268 |
| 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(oxalate)borate; TMSB: tris(trimethylsilyl) borate; LiBOB: lithium bis(oxalato)borate; TMB: trimethylboroxine; HFiP: tris(hexafluoroisopropyl) phosphate. | | | | | | | |

## 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.267 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.267 Some advanced porous membranes have been developed for LIBs.290, 291 Kanamura *et al* reported improved coulombic efficiency and capacity retention of LiCoPO4 by using a three-dimensionally ordered macroporous polyimide separator, compared with a conventional polypropylene separator with heterogeneous pore structure (Figure 11 d). The enhanced cycle stability of the cell using this separator is attributed to its ordered macroporous structure and high anodic stability.267 Markevich *et al* achieved significantly improved capacity retention of LiCoPO4 cathodes in a 1 M LiPF6 EC/DMC electrolyte with SiO2-containing separators (quartz, glassy paper), compared to that obtained for the cells with ordinary polyethylene separators.47 Markevich *et al* also showed that using glass fibre separators decreases the extent of structural degradation of LiCoPO4 electrodes.44

## 5.3 Conductive additive optimisation

Conductive additives in the cathode are also subject to undesirable degradation reactions at high potentials.292-294 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.295, 296 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.268 High surface area materials are required to produce a conductive network, but high surface area also leads to enhanced degradation. Kanamura *et al* investigated the effect of conductive carbon additives (acetylene black with various specific surface areas and ketjen black) on the electrochemical performance of LiCoPO4. By using acetylene black with a moderate surface area as a conductive additive for LiCoPO4 electrode, a better cycle performance was achieved.268 Jin *et al* investigated the effect of different conductive additives including acetylene black and carbon black (SP270) on charge/discharge properties of LiCoPO4 cathodes, showing that acetylene black showed better electrochemical properties with an initial discharge capacity of 110 mA h g-1 at a discharge current density of 0.05 mA cm-2.105 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-1.159 Wohlfahrt-Mehrens *et al* investigated the electrochemical and thermal behaviour of LiCoPO4-based cathode. In the charging process of LiCoPO4 cathodes, while the partially delithiated cathode shows a high thermal stability, the fully delithiated cathode decomposes between 160 and 260 ℃. The highest thermal stability was obtained by using carbon black (super-P) and graphite (KS6) as conductive additives without carbon coating.69

## 5.4 Summary of optimising other components in high-voltage LIBs

The electrolyte additives to optimise LiPF6-EC/DMC/EMC conventional electrolytes for LiCoPO4 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 LiPF6 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.

# 6 Conclusions and outlook

Olivine LiCoPO4 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 LiCoPO4. 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 sol-gel process provide better control of the morphology and particle size of LiCoPO4, 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 LiCoPO4 cathodes for LIBs with high specific capacity, good cycle stability and rate capability.

Tremendous efforts have been made to improve the electrochemical performance of LiCoPO4, 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 LiCoPO4 improves the electronic conductivity of composites effectively but reduces the tap density and volumetric power density of LIBs. Carbon network structures to support LiCoPO4 particles provides good electrical conductivity, but it’s hard to achieve uniform distribution. Decreasing the particle size of LiCoPO4 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 LiCoPO4 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 LiCoPO4 cathodes in LIBs. For instance, optimization of the electrolyte components coupled to the use of tailored surface coatings and/or ion doping can be an effective approach to improve the chemical stability of LiCoPO4 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 LiCoPO4 in the future, further improvement of the electrochemical performance of LiCoPO4 is highly desirable, since despite major advances, the cycle stability and rate performance is still unsatisfactory.

# Acknowledgements

MZ thanks the China Scholarship Council (CSC) and the University of Southampton for support. NGA thanks the EPSRC for an early career fellowship (EP/N024303/1).

# References

1.C. Gong, Z. Xue, S. Wen, Y. Ye and X. Xie, *J. Power Sources*, 2016, **318**, 93-112.

2.H. Wu, Q. Liu and S. Guo, *Nano-Micro Lett.*, 2014, **6**, 316-326.

3.T. Yi, X. Li, H. Liu, J. Shu, Y. Zhu and R. Zhu, *Ionics*, 2012, **18**, 529-539.

4.T. V. S. L. Satyavani, A. Srinivas Kumar and P. S. V. Subba Rao, *Eng. Sci. Technol. Int J.*, 2016, **19**, 178-188.

5.N. Dupre, M. Cuisinier, J. F. Martin and D. Guyomard, *ChemPhysChem*, 2014, **15**, 1922-1938.

6.F. Yu, L. Zhang, Y. Li, Y. An, M. Zhu and B. Dai, *RSC Adv.*, 2014, **4**, 54576-54602.

7.S. Deng, H. Wang, H. Liu, J. Liu and H. Yan, *Nano-Micro Lett.*, 2014, **6**, 209-226.

8.L.-X. Yuan, Z.-H. Wang, W.-X. Zhang, X.-L. Hu, J.-T. Chen, Y.-H. Huang and J. B. Goodenough, *Energy Environ. Sci.*, 2011, **4**, 269-284.

9.Y. Zhang, Q. Huo, P. Du, L. Wang, A. Zhang, Y. Song, Y. Lv and G. Li, *Synth. Met.*, 2012, **162**, 1315-1326.

10.C. Jin, X. Zhang, W. He, Y. Wang, H. Li, Z. Wang and Z. Bi, *RSC Adv.*, 2014, **4**, 15332-15339.

11.J. Wang and X. Sun, *Energy Environ. Sci.*, 2012, **5**, 5163-5185.

12.Y. Wang, P. He and H. Zhou, *Energy Environ. Sci.*, 2011, **4**, 805-817.

13.A. Eftekhari, *J. Power Sources*, 2017, **343**, 395-411.

14.Z. Yang, Y. Dai, S. Wang and J. Yu, *J. Mater. Chem. A*, 2016, **4**, 18210-18222.

15.J. Wang and X. Sun, *Energy Environ. Sci.*, 2015, **8**, 1110-1138.

16.Z. Bi, X. Zhang, W. He, D. Min and W. Zhang, *RSC Adv.*, 2013, **3**, 19744-19751.

17.W.-J. Zhang, *J. Power Sources*, 2011, **196**, 2962-2970.

18.D. Jugović and D. Uskoković, *J. Power Sources*, 2009, **190**, 538-544.

19.G. K. Singh, G. Ceder and M. Z. Bazant, *Electrochim. Acta*, 2008, **53**, 7599-7613.

20.Z. L. Gong and Y. Yang, *Energy Environ. Sci.*, 2011, **4**, 3223-3242.

21.Z. Li, D. Zhang and F. Yang, *J. Mater. Sci.*, 2009, **44**, 2435-2443.

22.S. Kraas, A. Vijn, M. Falk, B. Ufer, B. Luerßen, J. Janek and M. Fröba, *Prog. Solid State Chem.*, 2014, **42**, 218-241.

23.K. Amine, H. Yasuda and M. Yamachi, *Electrochem. Solid-State Lett.*, 2000, **3**, 178-179.

24.M. Hu, X. L. Pang and Z. Zhou, *J. Power Sources*, 2013, **237**, 229-242.

25.L. Fang, H. J. Zhang, Y. Zhang, L. Liu and Y. Wang, *J. Power Sources*, 2016, **312**, 101-108.

26.A. Örnek, *J. Power Sources*, 2017, **356**, 1-11.

27.D. Liu, W. Zhu, C. Kim, M. Cho, A. Guerfi, S. Delp, J. Allen, T. Jow and K. Zaghib, *J. Power Sources*, 2018, **388**, 52-56.

28.J. L. Allen, J. L. Allen, S. A. Delp and T. R. Jow, *ECS Trans.*, 2014, **61**, 63-68.

29.W. F. Howard and R. M. Spotnitz, *‎J. Power Sources*, 2007, **165**, 887-891.

30.Y. H. Hu, U. Burghaus and S. Qiao, *Nanotechnology for sustainable energy*, ACS Publications, Washington, 2013.

31.Y. Maeyoshi, S. Miyamoto, Y. Noda, H. Munakata and K. Kanamura, *J. Power Sources*, 2017, **337**, 92-99.

32.J. Wolfenstine, U. Lee, B. Poese and J. L. Allen, *J. Power Sources*, 2005, **144**, 226-230.

33.K. Tadanaga, F. Mizuno, A. Hayashi, T. Minami and M. Tatsumisago, *Electrochemistry*, 2003, **71**, 1192-1195.

34.J. Wolfenstine, *J. Power Sources*, 2006, **158**, 1431-1435.

35.J. Wolfenstine, J. Read and J. L. Allen, *J. Power Sources*, 2007, **163**, 1070-1073.

36.J. L. Allen, T. Thompson, J. Sakamoto, C. R. Becker, T. R. Jow and J. Wolfenstine, *J. Power Sources*, 2014, **254**, 204-208.

37.K. Rissouli, K. Benkhouja, J. Ramos-Barrado and C. Julien, *Mater. Sci. Eng. B*, 2003, **98**, 185-189.

38.M. Prabu, S. Selvasekarapandian, M. V. Reddy and B. V. R. Chowdari, *J. Solid State Electrochem.*, 2012, **16**, 1833-1839.

39.J. Xie, N. Imanishi, T. Zhang, A. Hirano, Y. Takeda and Y. Yamamoto, *J. Power Sources*, 2009, **192**, 689-692.

40.M. Prabu, S. Selvasekarapandian, A. R. Kulkarni, S. Karthikeyan, G. Hirankumar and C. Sanjeeviraja, *Solid State Sci.*, 2011, **13**, 1714-1718.

41.D. Shanmukaraj and R. Murugan, *Ionics*, 2004, **10**, 88-92.

42.D. Morgan, A. Van der Ven and G. Ceder, *Electrochem. Solid-State Lett.*, 2004, **7**, A30-A32.

43.Y. H. Ikuhara, X. Gao, C. A. J. Fisher, A. Kuwabara, H. Moriwake, K. Kohama, H. Iba and Y. Ikuhara, *J. Mater. Chem. A*, 2017, **5**, 9329-9338.

44.R. Sharabi, E. Markevich, V. Borgel, G. Salitra, G. Gershinsky, D. Aurbach, G. Semrau, M. A. Schmidt, N. Schall and C. Stinner, *J. Power Sources*, 2012, **203**, 109-114.

45.R. Sharabi, E. Markevich, K. Fridman, G. Gershinsky, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Schall and C. Bruenig, *Electrochem. Commun.*, 2013, **28**, 20-23.

46.E. Markevich, R. Sharabi, H. Gottlieb, V. Borgel, K. Fridman, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Schall and C. Bruenig, *Electrochem. Commun.*, 2012, **15**, 22-25.

47.R. Sharabi, E. Markevich, V. Borgel, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Schall and C. Stinner, *Electrochem. Commun.*, 2011, **13**, 800-802.

48.E. Markevich, R. Sharabi, O. Haik, V. Borgel, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Schall and C. Stinner, *J. Power Sources*, 2011, **196**, 6433-6439.

49.N. N. Bramnik, K. Nikolowski, C. Baehtz, K. G. Bramnik and H. Ehrenberg, *Chem. Mater.*, 2007, **19**, 908-915.

50.E. Markevich, G. Salitra, K. Fridman, R. Sharabi, G. Gershinsky, A. Garsuch, G. Semrau, M. A. Schmidt and D. Aurbach, *Langmuir*, 2014, **30**, 7414-7424.

51.Gangulibabu, K. Nallathamby, D. Meyrick and M. Minakshi, *Electrochim. Acta*, 2013, **101**, 18-26.

52.I. C. Jang, C. G. Son, S. M. G. Yang, J. W. Lee, A. R. Cho, V. Aravindan, G. J. Park, K. S. Kang, W. S. Kim, W. I. Cho and Y. S. Lee, *J. Mater. Chem.*, 2011, **21**, 6510-6514.

53.J. Ludwig, C. Marino, D. Haering, C. Stinner, H. A. Gasteiger and T. Nilges, *J. Power Sources*, 2017, **342**, 214-223.

54.L. Dimesso, C. Spanheimer and W. Jaegermann, *J. Power Sources*, 2013, **243**, 668-675.

55.T. Fukutsuka, T. Nakagawa, K. Miyazaki and T. Abe, *J. Power Sources*, 2016, **306**, 753-757.

56.N. Laszczynski, A. Birrozzi, K. Maranski, M. Copley, M. E. Schuster and S. Passerini, *J. Mater. Chem. A*, 2016, **4**, 17121-17128.

57.S. Brutti, J. Manzi, D. Meggiolaro, F. M. Vitucci, F. Trequattrini, A. Paolone and O. Palumbo, *J. Mater. Chem. A*, 2017, **5**, 14020-14030.

58.B. R. Wu, H. L. Xu, D. B. Mu, L. L. Shi, B. Jiang, L. Gai, L. Wang, Q. Liu, L. B. Ben and F. Wu, *J. Power Sources*, 2016, **304**, 181-188.

59.J. Ludwig and T. Nilges, *J. Power Sources*, 2018, **382**, 101-115.

60.S. Okada, S. Sawa, M. Egashira, J. Yamaki, M. Tabuchi, H. Kageyama, T. Konishi and A. Yoshino, *J. Power Sources*, 2001, **97**, 430-432.

61.T. Kimura, C. K. Chang, F. Kimura and M. Maeyama, *J. Appl. Crystallogr.*, 2009, **42**, 535-537.

62.S. Okada, M. Ueno, Y. Uebou and J. Yamaki, *Ieice/Ieee Intelec.*, 2003, **19-23**, 66-71.

63.Y. N. Xu, W. Y. Ching and Y. M. Chiang, *J. Appl. Phys.*, 2004, **95**, 6583-6585.

64.H. Ehrenberg, N. N. Bramnik, A. Senyshyn and H. Fuess, *Solid State Sci.*, 2009, **11**, 18-23.

65.M. Kaus, I. Issac, R. Heinzmann, S. Doyle, S. Mangold, H. Hahn, V. S. K. Chakravadhanula, C. Kubel, H. Ehrenberg and S. Indris, *J. Phys. Chem. C*, 2014, **118**, 17279-17290.

66.F. C. Strobridge, R. J. Clement, M. Leskes, D. S. Middlemiss, O. J. Borkiewicz, K. M. Wiaderek, K. W. Chapman, P. J. Chupas and C. P. Grey, *Chem. Mater.*, 2014, **26**, 6193-6205.

67.C. A. Fisher, V. M. Hart Prieto and M. S. Islam, *Chem. Mater.*, 2008, **20**, 5907-5915.

68.N. N. Bramnik, K. Nikolowski, D. M. Trots and H. Ehrenberg, *Electrochem. Solid-State Lett.*, 2008, **11**, A89-A93.

69.S. Theil, M. Fleischhammer, P. Axmann and M. Wohlfahrt-Mehrens, *J. Power Sources*, 2013, **222**, 72-78.

70.M. Nakayama, S. Goto, Y. Uchimoto, M. Wakihara and Y. Kitajima, *Chem. Mater.*, 2004, **16**, 3399-3401.

71.M. Nakayama, S. Goto, Y. Uchimoto, M. Wakihara, Y. Kitajima, T. Miyanaga and I. Watanabe, *J. Phys. Chem. B*, 2005, **109**, 11197-11203.

72.M. Minakshi, P. Singh, N. Sharma, M. Backford and M. Ionescu, *Ind. Eng. Chem. Res.*, 2011, **50**, 1899-1905.

73.Q. D. Truong, M. K. Deyaraju, Y. Sasaki, H. Hyodo, T. Tomai and I. Honma, *Chem. Mater.*, 2014, **26**, 2770-2773.

74.A. Boulineau and T. Gutel, *Chem. Mater.*, 2015, **27**, 802-807.

75.D. Dal, M. H. Whangbo, H. J. Koo, X. Rocquefelte, S. Jobic and A. Villesuzanne, *Inorg. Chem.*, 2005, **44**, 2407-2413.

76.M. S. Islam and C. A. Fisher, *Chem. Soc. Rev.*, 2014, **43**, 185-204.

77.J. E. Sansom, J. R. Tolchard, M. S. Islam, D. Apperley and P. R. Slater, *J. Mater. Chem.*, 2006, **16**, 1410-1413.

78.F. Sauvage, J.-M. Tarascon and E. Baudrin, *J. Phys. Chem. C*, 2007, **111**, 9624-9630.

79.Y. Shimakawa, T. Numata and J. Tabuchi, *J. Solid State Chem.*, 1997, **131**, 138-143.

80.M. G. Palmer, J. T. Frith, A. L. Hector, A. W. Lodge, J. R. Owen, C. Nicklin and J. Rawle, *Chem. Commun.*, 2016, **52**, 14169-14172.

81.F. C. Strobridge, H. Liu, M. Leskes, O. J. Borkiewicz, K. M. Wiaderek, P. J. Chupas, K. W. Chapman and C. P. Grey, *Chem. Mater.*, 2016, **28**, 3676-3690.

82.J. Manzi, F. M. Vitucci, A. Paolone, F. Trequattrini, D. Di Lecce, S. Panero and S. Brutti, *Electrochim. Acta*, 2015, **179**, 604-610.

83.L. Dimesso, C. Forster, W. Jaegermann, J. P. Khanderi, H. Tempel, A. Popp, J. Engstler, J. J. Schneider, A. Sarapulova, D. Mikhailova, L. A. Schmitt, S. Oswald and H. Ehrenberg, *Chem. Soc. Rev.*, 2012, **41**, 5068-5080.

84.Y. M. Kang, Y. I. Kim, M. W. Oh, R. Z. Yin, Y. Lee, D. W. Han, H. S. Kwon, J. H. Kim and G. Ramanath, *Energy Environ. Sci.*, 2011, **4**, 4978-4983.

85.O. Le Bacq, A. Pasturel and O. Bengone, *Phys. Rev. B*, 2004, **69**, 245107.

86.F. Zhou, M. Cococcioni, K. Kang and G. Ceder, *Electrochem. Commun.*, 2004, **6**, 1144-1148.

87.H. B. Gu, B. Jin, D. K. Jun and Z. Han, *J. Nanosci. Nanotechnol.*, 2007, **7**, 4037-4040.

88.C. H. Rhee, S. J. Kim and C. S. Kim, *J. Korean Phys. Soc.*, 2010, **56**, 611-614.

89.J. Wu, Z. H. Li, L. Ju, D. C. Li, J. W. Zheng and Y. H. Xu, *Rare Metal Mater. Eng.*, 2013, **42**, 684-687.

90.M. Kishore and U. V. Varadaraju, *Mater. Res. Bull.*, 2005, **40**, 1705-1712.

91.K. Nagata and T. Nanno, *J. Power Sources*, 2007, **174**, 832-837.

92.C. Sronsri, C. Danvirutai and P. Noisong, *React. Kinet. Mech. Catal.*, 2017, **121**, 555-577.

93.I. C. Jang, H. H. Lim, S. B. Lee, K. Karthikeyan, V. Aravindan, K. S. Kang, W. S. Yoon, W. I. Cho and Y. S. Lee, *J. Alloys Compd.*, 2010, **497**, 321-324.

94.A. Goni, L. Lezama, G. E. Barberis, J. L. Pizarro, M. I. Arriortua and T. Rojo, *J. Magn. Magn. Mater.*, 1996, **164**, 251-255.

95.N. N. Bramnik, K. G. Bramnik, T. Buhrmester, C. Baehtz, H. Ehrenberg and H. Fuess, *J. Solid State Electrochem.*, 2004, **8**, 558-564.

96.Y. He, S. Liao, Z. P. Chen, Y. Li, Y. Xia, W. W. Wu and B. Li, *Ind. Eng. Chem. Res.*, 2013, **52**, 1870-1876.

97.C. H. Rhee, S. J. Kim and C. S. Kim, *IEEE Trans. Magn.*, 2011, **47**, 2697-2700.

98.S. Karthickprabhu, G. Hirankumar, A. Maheswaran, R. S. D. Bella and C. Sanjeeviraja, *J. Electrostat.*, 2014, **72**, 181-186.

99.S. M. G. Yang, V. Aravindan, W. I. Cho, D. R. Chang, H. S. Kim and Y. S. Lee, *J. Electrochem. Soc.*, 2012, **159**, A1013-A1018.

100.Y. H. Huang, Z. F. Tong, T. Y. Wei and B. Li, *Acta Phys.-Chim. Sin.*, 2011, **27**, 1325-1334.

101.F. Wang, J. Yang, Y. N. NuLi and J. L. Wang, *J. Power Sources*, 2011, **196**, 4806-4810.

102.V. Aravindan, Y. L. Cheah, W. C. Ling and S. Madhavi, *J. Electrochem. Soc.*, 2012, **159**, A1435-A1439.

103.L. Tan, Z. M. Luo, H. W. Liu and Y. Yu, *J. Alloys Compd.*, 2010, **502**, 407-410.

104.X. M. Lin, Y. W. Ma, J. Q. Wan and Y. Wang, *Chem. Eng. J.*, 2017, **315**, 304-314.

105.B. Jin, H. B. Gu and K. W. Kim, *J. Solid State Electrochem.*, 2008, **12**, 105-111.

106.J. M. Lloris, C. P. Vicente and J. L. Tirado, *Electrochem. Solid-State Lett.*, 2002, **5**, A234-A237.

107.Q. Sun, J. Y. Luo and Z. W. Fu, *Electrochem. Solid-State Lett.*, 2011, **14**, A151-A153.

108.H. Y. Chen, M. Chen, C. Y. Du, Y. Z. Cui, P. J. Zuo, X. Q. Cheng and G. P. Yin, *Mater. Chem. Phys.*, 2016, **171**, 6-10.

109.S. Konishi, D. Murayama, A. Itadani, K. Uematsu, K. Toda, M. Sato, N. Arimitsu, T. Aoki and T. Yamaguchi, *Electrochemistry*, 2017, **85**, 643-646.

110.Y. J. Zhao, S. J. Wang, C. S. Zhao and D. G. Xia, *Rare Metals*, 2009, **28**, 117-121.

111.J. Ludwig, D. Nordlund, M. M. Doeff and T. Nilges, *J. Solid State Chem.*, 2017, **248**, 9-17.

112.A. V. Murugan, T. Muraliganth and A. Manthiram, *J. Electrochem. Soc.*, 2009, **156**, A79-A83.

113.K. J. Kreder and A. Manthiram, *ACS Energy Lett.*, 2017, **2**, 64-69.

114.M. K. Devaraju, D. Rangappa and I. Honma, *Electrochim. Acta*, 2012, **85**, 548-553.

115.S. Brutti, J. Manzi, A. De Bonis, D. Di Lecce, F. Vitucci, A. Paolone, F. Trequattrini and S. Panero, *Mater. Lett.*, 2015, **145**, 324-327.

116.S. Brutti, J. Manzi, A. De Bonis, D. Di Lecce, F. Vitucci, A. Paolone, F. Trequattrini and S. Panero, *Mater. Lett.*, 2016, **172**, 98-98.

117.K. J. Kreder, G. Assat and A. Manthiram, *Chem. Mater.*, 2016, **28**, 1847-1853.

118.J. F. Ni, Y. H. Han, J. Z. Liu, H. B. Wang and L. J. Gao, *ECS Electrochem. Lett.*, 2013, **2**, A3-A5.

119.M. Zhang, N. Garcia-Araez, A. L. Hector and J. R. Owen, *J. Mater. Chem. A*, 2017, **5**, 2251-2260.

120.Y. Liu, M. Zhang, Y. Li, Y. Hu, M. Zhu, H. Jin and W. Li, *Electrochim. Acta*, 2015, **176**, 689-693.

121.C. Neef, H. P. Meyer and R. Klingeler, *Solid State Sci.*, 2015, **48**, 270-277.

122.X. A. Huang, J. F. Ma, P. W. Wu, Y. M. Hu, J. H. Dai, Z. B. Zhu, H. Y. Chen and H. F. Wang, *Mater. Lett.*, 2005, **59**, 578-582.

123.G. Assat and A. Manthiram, *Inorg. Chem.*, 2015, **54**, 10015-10022.

124.C. Alarcon-Suesca, J. Ludwig, V. Hlukhyy, C. Stinner and T. Nilges, *Inorganics*, 2016, **4**, 35-49.

125.J. Ludwig, D. Haering, M. M. Doeff and T. Nilges, *Solid State Sci.*, 2017, **65**, 100-109.

126.C. Neef, C. Jahne and R. Klingeler, *Microwave-assisted synthesis and properties of nanosized LiMPO4 (M = Mn, Co)*, Crc Press-Taylor & Francis Group, Boca Raton, 2012.

127.C. Jahne, C. Neef, C. Koo, H. P. Meyer and R. Klingeler, *J. Mater. Chem. A*, 2013, **1**, 2856-2862.

128.J. Su, B. Q. Wei, J. P. Rong, W. Y. Yin, Z. X. Ye, X. Q. Tian, L. Ren, M. H. Cao and C. W. Hu, *J. Solid State Chem.*, 2011, **184**, 2909-2919.

129.Y. H. Han, J. F. Ni, J. Z. Liu, H. B. Wang and L. J. Gao, *Mater. Technol.*, 2013, **28**, 265-269.

130.S. X. Lin, X. G. Wen and W. Qin, in *Proceedings of the 2nd Annual International Conference on Advanced Material Engineering*, eds. A. K. Bhatnagar, R. Dahai, K. M. Pandey, H. Haeri, R. A. Andrievskiy, M. Ziara and G. Feng, Atlantis Press, Paris, 2016, vol. 85, pp. 565-570.

131.J. Manzi, M. Curcio and S. Brutti, *Nanomaterials*, 2015, **5**, 2212-2230.

132.A. Örnek, A. Yesildag, M. Can and S. Akturk, *Mater. Res. Bull.*, 2016, **83**, 1-11.

133.N. Recham, J. Oro-Sole, K. Djellab, M. R. Palacin, C. Masquelier and J. M. Tarascon, *Solid State Ionics*, 2012, **220**, 47-52.

134.A. Örnek, *J. Alloys Compd.*, 2017, **710**, 809-818.

135.A. Örnek, *Chem. Eng. J.*, 2018, **331**, 501-509.

136.K. J. Kreder, G. Assat and A. Manthiram, *Chem. Mater.*, 2015, **27**, 5543-5549.

137.J. Ludwig, C. Marino, D. Haering, C. Stinner, D. Nordlund, M. M. Doeff, H. A. Gasteiger and T. Nilges, *RSC Adv.*, 2016, **6**, 82984-82994.

138.Q. D. Truong, M. K. Devaraju, T. Tomai and I. Honma, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9926-9932.

139.M. K. Devaraju, Q. D. Truong, T. Tomai, H. Hyodo, Y. Sasaki and I. Honma, *RSC Adv.*, 2014, **4**, 52410-52414.

140.J. Chen, S. Wang and M. S. Whittingham, *J. Power Sources*, 2007, **174**, 442-448.

141.M. Li, *Ionics*, 2012, **18**, 507-512.

142.L. Vijayan, R. Cheruku and G. Govindaraj, in *Solid State Physics*, eds. A. K. Chauhan, C. Murli and S. C. Gadkari, Amer Inst Physics, Melville, 2013, vol. 1512, pp. 428-429.

143.Gangulibabu, D. Bhuvaneswari, N. Kalaiselvi, N. Jayaprakash and P. Periasamy, *J. Sol-Gel Sci. Technol.*, 2009, **49**, 137-144.

144.A. L. Hector, *Chem. Soc. Rev.*, 2007, **36**, 1745-1753.

145.B. Mazumder and A. L. Hector, *J. Mater. Chem.*, 2009, **19**, 4673-4686.

146.L. Dimesso, G. Cherkashinin, C. Spanheimer and W. Jaegermann, *J. Alloys Compd.*, 2012, **516**, 119-125.

147.A. L. Hector, *Coord. Chem. Rev.*, 2016, **323**, 120-137.

148.M. S. Bhuwaneswari, L. Dimesso and W. Jaegermann, *J. Sol-Gel Sci. Technol.*, 2010, **56**, 320-326.

149.A. W. Jackson and A. L. Hector, *J. Mater. Chem.*, 2007, **17**, 1016-1022.

150.M. Minakshi and S. Kandhasamy, *J. Sol-Gel Sci. Technol.*, 2012, **64**, 47-53.

151.B. M. Gray, S. Hassan, A. L. Hector, A. Kalaji and B. Mazumder, *Chem. Mater.*, 2009, **21**, 4210-4215.

152.S. Hassan, A. L. Hector, J. R. Hyde, A. Kalaji and D. C. Smith, *Chem. Commun.*, 2008, **42**, 5304-5306.

153.L. Y. Xing, M. Hu, Q. Tang, J. P. Wei, X. Qin and Z. Zhou, *Electrochim. Acta*, 2012, **59**, 172-178.

154.J. S. Yang and J. J. Xu, *J. Electrochem. Soc.*, 2006, **153**, A716-A723.

155.P. N. Poovizhi and S. Selladurai, *Ionics*, 2011, **17**, 13-19.

156.L. Dimesso, C. Spanheimer and W. Jaegermann, *J. Alloys Compd.*, 2014, **582**, 69-74.

157.R. Hanafusa, Y. Oka and T. Nakamura, *J. Electrochem. Soc.*, 2015, **162**, A3045-A3051.

158.L. Dimesso, C. Spanheimer, M. M. Mueller, H. J. Kleebe and W. Jaegermann, *Ionics*, 2015, **21**, 2101-2107.

159.E. J. Kim, H. Y. Xu, J. S. Lim, J. W. Kang, J. H. Gim, V. Mathew and J. Kim, *J. Solid State Electrochem.*, 2012, **16**, 149-155.

160.A. Sarapulova, D. Mikhailova, L. A. Schmitt, S. Oswald, N. Bramnik and H. Ehrenberg, *J. Sol-Gel Sci. Technol.*, 2012, **62**, 98-110.

161.L. Dimesso, S. Jacke, C. Spanheimer and W. Jaegermann, *J. Solid State Electrochem.*, 2012, **16**, 911-919.

162.H. H. Li, Y. P. Wang, X. L. Yang, L. Liu, L. Chen and J. P. Wei, *Solid State Ionics*, 2014, **255**, 84-88.

163.S. M. Rommel, J. Rothballer, N. Schall, C. Brunig and R. Weihrich, *Ionics*, 2015, **21**, 325-333.

164.S. L. Wang, Z. Y. Tang, O. Sha, J. Yan and L. Ma, in *Future Material Research and Industry Application*, ed. K. S. Thaung, Trans Tech Publications Ltd, Durnten-Zurich, 2012, vol. 455-456, pp. 726-729.

165.V. Singh, Y. Gershinsky, M. Kosa, M. Dixit, D. Zitoun and D. T. Major, *Phys. Chem. Chem. Phys.*, 2015, **17**, 31202-31215.

166.L. Dimesso, C. Spanheimer, W. Jaegermann, Y. Zhang and A. L. Yarin, *Electrochim. Acta*, 2013, **95**, 38-42.

167.L. Dimesso, C. Spanheimer and W. Jaegermann, *Solid State Sci.*, 2014, **30**, 89-93.

168.A. Örnek, M. Can and A. Yesildag, *Mater. Charact.*, 2016, **116**, 76-83.

169.K. Kim and J. K. Kim, *Mater. Lett.*, 2016, **176**, 244-247.

170.S. L. Wang, Z. Y. Tang, O. Sha, J. Yan and L. Ma, *Preparation and Electrochemical Investigation of LiCoPO4 Cathode Material for Lithium Ion Batteries*, Ieee, New York, 2011.

171.R. Tussupbayev and I. Taniguchi, *J. Power Sources*, 2013, **236**, 276-284.

172.J. L. Shui, Y. Yu, X. F. Yang and C. H. Chen, *Electrochem. Commun.*, 2006, **8**, 1087-1091.

173.V. D. Nithya, K. Pandi, Y. S. Lee and R. K. Selvan, *Electrochim. Acta*, 2015, **167**, 97-104.

174.J. Liu, T. E. Conry, X. Y. Song, L. Yang, M. M. Doeff and T. J. Richardson, *J. Mater. Chem.*, 2011, **21**, 9984-9987.

175.T. N. L. Doan and I. Taniguchi, *J. Power Sources*, 2011, **196**, 5679-5684.

176.I. Taniguchi, N. L. D. The and B. Shao, *Electrochim. Acta*, 2011, **56**, 7680-7685.

177.N. L. D. The and I. Taniguchi, *Powder Technol.*, 2012, **217**, 574-580.

178.L. Deng, D. Y. Zhang, Y. Liu and C. K. Chang, *Mater. Res. Innovations*, 2014, **18**, 462-466.

179.J. F. Ni, L. J. Gao and L. Lu, *J. Power Sources*, 2013, **221**, 35-41.

180.C. Delacourt, C. Wurm, P. Reale, M. Morcrette and C. Masquelier, *Solid State Ionics*, 2004, **173**, 113-118.

181.D. Choi, X. Li, W. A. Henderson, Q. Huang, S. K. Nune, J. P. Lemmon and V. L. Sprenkle, *Heliyon*, 2016, **2**, e00081.

182.R. Vasanthi, D. Kalpana and N. G. Renganathan, *J. Solid State Electrochem.*, 2008, **12**, 961-969.

183.P. R. Kumar, M. Venkateswarlu, M. Misra, A. K. Mohanty and N. Satyanayana, *J. Nanosci. Nanotechnol.*, 2011, **11**, 3314-3322.

184.L. Dimesso, C. Spanheimer, T. T. D. Nguyen, R. Hausbrand and W. Jaegermann, *EPJ web conf.*, 2012, **33**, 02008.

185.P. R. Kumar, V. Madhusudhanrao, B. Nageswararao, M. Venkateswarlu and N. Satyanarayana, *J. Solid State Electrochem.*, 2016, **20**, 1855-1863.

186.N. Padmanathan and S. Selladurai, *Asian J. Chem.*, 2013, **25**, 9605.

187.X. H. Rui, X. X. Zhao, Z. Y. Lu, H. T. Tan, D. H. Sim, H. H. Hng, R. Yazami, T. M. Lim and Q. Y. Yan, *ACS nano*, 2013, **7**, 5637-5646.

188.Q. D. Truong, M. K. Devaraju, Y. Ganbe, T. Tomai and I. Honma, *Sci. Rep.*, 2014, **4**, 3975.

189.Q. D. Truong, M. K. Devaraju and I. Honma, *J. Mater. Chem. A*, 2014, **2**, 17400-17407.

190.M. K. Devaraju, Q. D. Truong, H. Hyodo, T. Tomai and I. Honma, *Inorganics*, 2014, **2**, 233-247.

191.H. H. Li, J. Jin, J. P. Wei, Z. Zhou and J. Yan, *Electrochem. Commun.*, 2009, **11**, 95-98.

192.D. W. Han, Y. M. Kang, R. Z. Yin, M. S. Song and H. S. Kwon, *Electrochem. Commun.*, 2009, **11**, 137-140.

193.R. E. Rogers, G. M. Clarke, O. N. Matthew, M. J. Ganter, R. A. DiLeo, J. W. Staub, M. W. Forney and B. J. Landi, *J. Appl. Electrochem.*, 2013, **43**, 271-278.

194.S. Rosenberg and A. Hintennach, *Russ. J. Electrochem.*, 2015, **51**, 305-309.

195.N. V. Kosova, O. A. Podgornova, E. T. Devyatkina, V. R. Podugolnikov and S. A. Petrov, *J. Mater. Chem. A*, 2014, **2**, 20697-20705.

196.N. V. Kosova, O. A. Podgornova, I. A. Bobrikov, V. V. Kaichev and A. V. Bukhtiyarov, *Mater. Sci. Eng. B Adv. Funct. Solid State Mater.*, 2016, **213**, 105-113.

197.A. Osnis, M. Kosa, D. Aurbach and D. T. Major, *J. Phys. Chem. C*, 2013, **117**, 17919-17926.

198.S. M. Oh, S. T. Myung and Y. K. Sun, *J. Mater. Chem.*, 2012, **22**, 14932-14937.

199.J. Manzi and S. Brutti, *Electrochim. Acta*, 2016, **222**, 1839-1846.

200.J. Wolfenstine, J. L. Allen, T. R. Jow, T. Thompson, J. Sakamoto, H. Jo and H. Choe, *Ceram. Int.*, 2014, **40**, 13673-13677.

201.J. L. Allen, T. R. Jow and J. Wolfenstine, *J. Power Sources*, 2011, **196**, 8656-8661.

202.Y. Wang, J. Y. Qiu, Z. Yu, H. B. Ming, M. Li, S. T. Zhang and Y. S. Yang, *Ceram. Int.*, 2018, **44**, 1312-1320.

203.M. Matsuoka, A. Kondo, T. Kozawa, M. Naito, H. Koga, T. Saito and H. Iba, *Ceram. Int.*, 2017, **43**, 938-943.

204.L. T. Yang, Y. G. Xia, X. Fan, L. F. Qin, B. Qiu and Z. P. Liu, *Electrochim. Acta*, 2016, **191**, 200-206.

205.J. J. Wang, J. L. Yang, Y. J. Tang, R. Y. Li, G. X. Liang, T. K. Sham and X. L. Sun, *J. Mater. Chem. A*, 2013, **1**, 1579-1586.

206.J. F. Ni, H. B. Wang, L. J. Gao and L. Lu, *Electrochim. Acta*, 2012, **70**, 349-354.

207.J. T. Xu, S. L. Chou, M. Avdeev, M. Sale, H. K. Liu and S. X. Dou, *Electrochim. Acta*, 2013, **88**, 865-870.

208.D. Di Lecce, J. Manzi, F. M. Vitucci, A. De Bonis, S. Panero and S. Brutti, *Electrochim. Acta*, 2015, **185**, 17-27.

209.Y. Wang, J. H. Chen, J. Y. Qiu, Z. B. Yu, H. Ming, M. Li, S. T. Zhang and Y. S. Yang, *J. Solid State Chem.*, 2018, **258**, 32-41.

210.T. K. Kim, C. S. Rustomji, H. M. Cho, D. Chun, J. Y. Jung, E. Caldwel, Y. Kim, J. H. Han and S. Jin, *Electron. Mater. Lett.*, 2016, **12**, 147-155.

211.M. E. Rabanal, M. C. Gutierrez, F. Garcia-Alvarado, E. C. Gonzalo and M. E. Arroyo-de Dompablo, *J. Power Sources*, 2006, **160**, 523-528.

212.L. Dimesso, C. Spanheimer and W. Jaegermann, *Ionics*, 2014, **20**, 621-628.

213.L. Dimesso, D. Becker, C. Spanheimer and W. Jaegermann, *Prog. Solid State Chem.*, 2014, **42**, 184-190.

214.D. Di Lecce, S. Brutti, S. Panero and J. Hassoun, *Mater. Lett.*, 2015, **139**, 329-332.

215.T. Liu, Q. B. Xia, W. Lu, J. J. Xu and X. D. Wu, *Electrochim. Acta*, 2015, **174**, 120-126.

216.L. Wu, S. N. Shi, X. P. Zhang, J. Q. Liu, D. Chen, H. Ding and S. K. Zhong, *Mater. Lett.*, 2015, **152**, 228-231.

217.A. Eftekhari, *J. Electrochem. Soc.*, 2004, **151**, A1456-A1460.

218.J. J. Schneider, J. Khanderi, A. Popp, J. Engstler, H. Tempel, A. Sarapulova, N. N. Bramnik, D. Mikhailova, H. Ehrenberg, L. A. Schmitt, L. Dimesso, C. Forster and W. Jaegermann, *Eur. J. Inorg. Chem.*, 2011, **2011**, 4349-4359.

219.L. Liu, H. J. Zhang, X. Chen, L. Fang, Y. J. Bai, R. C. Liu and Y. Wang, *J. Mater. Chem. A*, 2015, **3**, 12320-12327.

220.L. Dimesso, C. Spanheimer, D. Becker and W. Jaegermann, *J. Eur. Ceram. Soc.*, 2014, **34**, 933-941.

221.J. Zhang, M. Terrones, C. R. Park, R. Mukherjee, M. Monthioux, N. Koratkar, Y. S. Kim, R. Hurt, E. Frackowiak, T. Enoki, Y. Chen, Y. S. Chen and A. Bianco, *Carbon*, 2016, **98**, 708-732.

222.X. M. Liu, Z. D. Huang, S. W. Oh, B. Zhang, P. C. Ma, M. M. F. Yuen and J. K. Kim, *Compos. Sci. Technol.*, 2012, **72**, 121-144.

223.P. Kim, L. Shi, A. Majumdar and P. L. McEuen, *Phys. Rev. Lett.*, 2001, **87**, 215502.

224.L. Dimesso, C. Spanheimer, S. Jacke and W. Jaegermann, *J. Power Sources*, 2011, **196**, 6729-6734.

225.L. Dimesso, S. Jacke, C. Spanheimer and W. Jaegermann, *J. Alloys Compd.*, 2011, **509**, 3777-3782.

226.L. Dimesso, D. Becker, C. Spanheimer and W. Jaegermann, *J. Solid State Electrochem.*, 2012, **16**, 3791-3798.

227.V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chem. Rev.*, 2012, **112**, 6156-6214.

228.G. Kucinskis, G. Bajars and J. Kleperis, *J. Power Sources*, 2013, **240**, 66-79.

229.V. Chabot, D. Higgins, A. P. Yu, X. C. Xiao, Z. W. Chen and J. J. Zhang, *Energy Environ. Sci.*, 2014, **7**, 1564-1596.

230.X. J. Zhou, J. L. Qiao, L. Yang and J. J. Zhang, *Adv. Energy Mater.*, 2014, **4**, 25.

231.A. Aghigh, V. Alizadeh, H. Y. Wong, M. S. Islam, N. Amin and M. Zaman, *Desalination*, 2015, **365**, 389-397.

232.K. Toda, R. Furue and S. Hayami, *Anal. Chim. Acta*, 2015, **878**, 43-53.

233.Y. Zhao, X. F. Li, B. Yan, D. J. Li, S. Lawes and X. L. Sun, *J. Power Sources*, 2015, **274**, 869-884.

234.K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666-669.

235.H. X. Wu, Q. J. Liu and S. W. Guo, *Nano-Micro Lett.*, 2014, **6**, 316-326.

236.Y. Si and E. T. Samulski, *Nano Lett.*, 2008, **8**, 1679-1682.

237.M. D. Stoller, S. J. Park, Y. W. Zhu, J. H. An and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 3498-3502.

238.B. Marinho, M. Ghislandi, E. Tkalya and C. E. Koning, *Powder Technol.*, 2012, **221**, 351-358.

239.K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim and H. L. Stormer, *Solid State Commun.*, 2008, **146**, 351-355.

240.A. A. Balandin, S. Ghosh, W. Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, *Nano Lett.*, 2008, **8**, 902-907.

241.V. Koleva, E. Zhecheva and R. Stoyanova, *Eur. J. Inorg. Chem.*, 2010, **26**, 4091-4099.

242.S. L. Wang, Z. Y. Tang, O. Sha and J. Yan, *Acta Phys.-Chim. Sin.*, 2012, **28**, 343-348.

243.Y. Hou, K. Chang, B. Li, H. Tang, Z. Wang, J. Zou, H. Yuan, Z. Lu and Z. Chang, *Nano Res.*, 2018, **11**, 2424-2435.

244.K. A. Persson, B. Waldwick, P. Lazic and G. Ceder, *Phys. Rev. B*, 2012, **85**, 235438.

245.V. A. Alyoshin, E. A. Pleshakov, H. Ehrenberg and D. Mikhailova, *J. Phys. Chem. C*, 2014, **118**, 17426-17435.

246.S. Brutti and S. Panero, in *Nanotechnology for Sustainable Energy*, eds. Y. H. Hu, U. Burghaus and S. Qiao, Amer Chemical Soc, Washington, 2013, vol. 1140, pp. 67-99.

247.Z. P. Lin, Y. J. Zhao and Y. M. Zhao, *Chin. Phys. Lett.*, 2009, **26**, 4.

248.Z. P. Lin, Y. M. Zhao and Y. J. Zhao, *Chin. Phys. B*, 2011, **20**, 6.

249.J. L. Allen, T. R. Jow and J. Wolfenstine, in *Intercalation Compounds for Rechargea Ble Batteries*, eds. C. M. Julien, S. Meng, K. Zaghib and R. Kanno, Electrochemical Soc Inc, Pennington, 2012, vol. 41, pp. 15-20.

250.F. Wang, J. Yang, Y. N. NuLi and J. L. Wang, *J. Power Sources*, 2010, **195**, 6884-6887.

251.A. Rajalakshmi, V. D. Nithya, K. Karthikeyan, C. Sanjeeviraja, Y. S. Lee and R. K. Selvan, *J. Sol-Gel Sci. Technol.*, 2013, **65**, 399-410.

252.D. Zhang, J. Zhou, J. Chen, B. Xu, W. Qin and C. Chang, *Int. J. Electrochem. Sci.*, 2018, **13**, 2544-2555.

253.J. L. Allen, J. L. Allen, T. Thompson, S. A. Delp, J. Wolfenstine and T. R. Jow, *J. Power Sources*, 2016, **327**, 229-234.

254.F. C. Strobridge, D. S. Middlemiss, A. J. Pell, M. Leskes, R. J. Clement, F. Pourpoint, Z. G. Lu, J. V. Hanna, G. Pintacuda, L. Emsley, A. Samoson and C. P. Grey, *J. Mater. Chem. A*, 2014, **2**, 11948-11957.

255.A. Smaldone, S. Brutti, A. De Bonis, N. Ciarfaglia, A. Santagata and R. Teghil, *Appl. Surf. Sci.*, 2018, **445**, 56-64.

256.H. Liu, F. C. Strobridge, O. J. Borkiewicz, K. M. Wiaderek, K. W. Chapman, P. J. Chupas and C. P. Grey, *Science*, 2014, **344**, 1252817.

257.R.-r. Zhao, I.-M. Hung, Y.-T. Li, H.-y. Chen and C.-P. Lin, *J. Alloys Compd.*, 2012, **513**, 282-288.

258.W. Zhang, Y. Hu, X. Tao, H. Huang, Y. Gan and C. Wang, *J. Phys. Chem. Solids*, 2010, **71**, 1196-1200.

259.M. D. Johannes, K. Hoang, J. L. Allen and K. Gaskell, *Phys. Rev. B*, 2012, **85**, 115106.

260.J. G. Lapping, S. A. Delp, J. L. Allen, J. L. Allen, J. W. Freeland, M. D. Johannes, L. Hu, D. T. Tran, T. R. Jow and J. Cabana, *Chem. Mater.*, 2018, **30**, 1898-1906.

261.A. Mauger, C. M. Julien, M. Armand, J. B. Goodenough and K. Zaghib, *Curr. Opin. Electrochem.*, 2017, **6**, 63-69.

262.C. M. Julien and A. Mauger, *Ionics*, 2013, **19**, 951-988.

263.V. Aravindan, J. Gnanaraj, Y. S. Lee and S. Madhavi, *Chem. Rev.*, 2014, **114**, 11619-11635.

264.E. Nanini-Maury, J. Swiatowska, A. Chagnes, S. Zanna, T. V. Pierre, P. Marcus and M. Cassir, *Electrochim. Acta*, 2014, **115**, 223-233.

265.T. R. Jow, J. L. Allen, O. A. Borodin, S. A. Delp, J. L. Allen and Tms, *Challenges in Developing High Energy Density Li-Ion Batteries with High Voltage Cathodes*, John Wiley & Sons Inc, Hoboken, 2014.

266.M. Metzger, J. Sicklinger, D. Haering, C. Kavakli, C. Stinner, C. Marino and H. A. Gasteiger, *J. Electrochem. Soc.*, 2015, **162**, A1227-A1235.

267.Y. Maeyoshi, S. Miyamoto, H. Munakata and K. Kanamura, *J. Power Sources*, 2017, **350**, 103-108.

268.Y. Maeyoshi, S. Miyamoto, H. Munakata and K. Kanamura, *J. Power Sources*, 2018, **376**, 18-25.

269.A. M. Haregewoin, A. S. Wotango and B.-J. Hwang, *Energy Environ. Sci.*, 2016, **9**, 1955-1988.

270.Y.-R. Zhu and T.-F. Yi, *Ionics*, 2016, **22**, 1759-1774.

271.T.-F. Yi, J. Mei and Y.-R. Zhu, *J. Power Sources*, 2016, **316**, 85-105.

272.S. W. Lee, C. Carlton, M. Risch, Y. Surendranath, S. Chen, S. Furutsuki, A. Yamada, D. G. Nocera and Y. Shao-Horn, *J. Am. Chem. Soc.*, 2012, **134**, 16959-16962.

273.O. Fromm, P. Meister, X. Qi, S. Rothermel, J. Huesker, H. W. Meyer, M. Winter and T. Placke, in *Intercalation Compounds for Rechargeable Batteries*, ed. M. M. Doeff, Electrochemical Soc Inc, Pennington, 2014, vol. 58, pp. 55-65.

274.M. Hu, J. P. Wei, L. Y. Xing and Z. Zhou, *J. Appl. Electrochem.*, 2012, **42**, 291-296.

275.Y. Wang, H. Ming, J. Y. Qiu, Z. Yu, M. Li, S. T. Zhang and Y. S. Yang, *J. Electroanal. Chem.*, 2017, **802**, 8-14.

276.A. Freiberg, M. Metzger, D. Haering, S. Bretzke, S. Puravankara, T. Nilges, C. Stinner, C. Marino and H. A. Gasteiger, *J. Electrochem. Soc.*, 2014, **161**, A2255-A2261.

277.O. A. Drozhzhin, V. A. Shevchenko, M. V. Zakharkin, P. I. Gamzyukov, L. V. Yashina, A. M. Abakumov, K. J. Stevenson and E. V. Antipov, *Electrochim. Acta*, 2018, **263**, 127-133.

278.S. S. Zhang, K. Xu and T. R. Jow, *J. Electrochem. Soc.*, 2002, **149**, A586-A590.

279.P. Deniard, A. M. Dulac, X. Rocquefelte, V. Grigorova, O. Lebacq, A. Pasturel and S. Jobic, *J. Phys. Chem. Solids*, 2004, **65**, 229-233.

280.Z. Zhang, L. Hu, H. Wu, W. Weng, M. Koh, P. C. Redfern, L. A. Curtiss and K. Amine, *Energy Environ. Sci.*, 2013, **6**, 1806-1810.

281.J. Xia, R. Petibon, A. Xiao, W. Lamanna and J. Dahn, *J. Power Sources*, 2016, **330**, 175-185.

282.I. A. Shkrob, K. Z. Pupek and D. P. Abraham, *J. Phys. Chem. C*, 2016, **120**, 18435-18444.

283.E. Markevich, G. Salitra and D. Aurbach, *ACS Energy Lett.*, 2017, **2**, 1337-1345.

284.M. Galiński, A. Lewandowski and I. Stępniak, *Electrochim. Acta*, 2006, **51**, 5567-5580.

285.M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621.

286.G. B. Kunshina, V. I. Ivanenko, O. G. Gromov and E. P. Lokshin, *Russ. J. Inorg. Chem.*, 2014, **59**, 1175-1179.

287.W. C. West, J. F. Whitacre and B. V. Ratnakumar, *J. Electrochem. Soc.*, 2003, **150**, A1660-A1666.

288.T. Okumura, T. Takeuchi and H. Kobayashi, *Electrochemistry*, 2014, **82**, 906-908.

289.R. Harada, K. Aso, A. Hayashi and M. Tatsumisago, *Electrochemistry*, 2015, **83**, 898-901.

290.S. S. Zhang, *J. Power Sources*, 2007, **164**, 351-364.

291.H. Lee, M. Yanilmaz, O. Toprakci, K. Fu and X. Zhang, *Energy Environ. Sci.*, 2014, **7**, 3857-3886.

292.F. La Mantia, R. A. Huggins and Y. Cui, *J. Appl. Electrochem.*, 2013, **43**, 1-7.

293.A. Kajiyama, R. Masaki, T. Wakiyama, K. Matsumoto, A. Yoda, T. Inada, H. Yokota and R. Kanno, *J. Electrochem. Soc.*, 2015, **162**, A1516-A1522.

294.J. Zheng, J. Xiao, W. Xu, X. Chen, M. Gu, X. Li and J.-G. Zhang, *J. Power Sources*, 2013, **227**, 211-217.

295.M. E. Spahr, D. Goers, A. Leone, S. Stallone and E. Grivei, *J. Power Sources*, 2011, **196**, 3404-3413.

296.J. Xiao, D. Wang, W. Xu, D. Wang, R. E. Williford, J. Liu and J.-G. Zhang, *J. Electrochem. Soc.*, 2010, **157**, A487-A492.