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Review on high temperature secondary Li-ion batteries

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Abstract

Lithium-ion batteries have revolutionised the energy storage market; applications for batteries are rapidly expanding with demands for high performance batteries required in many technological fields. In applications such as portable devices or electric vehicles, lithium-ion batteries have currently no contender in terms of energy density or durability. However, the restricted temperature range of -25 °C to 60 °C is a problem for a number of applications that require high energy rechargeable batteries that operate at a high temperature (>100 °C). This review discusses the work that has been done on the side of electrodes and electrolytes for use in high temperature Li-ion batteries.

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1. Introduction

Lithium-ion batteries have revolutionised the energy storage market and applications for batteries are rapidly expanding, with demands for high performance batteries required in many technological fields. In applications such as portable devices or electric vehicles, lithium-ion batteries have currently no contender in terms of energy density or durability. However, the restricted temperature range of -25 °C to 60 °C is a problem for a number of applications that require high energy rechargeable batteries that operate at a high temperature (>100 °C). One such application is the oil and gas industry which requires batteries to operate at temperatures of up to 150 °C. Going above the maximum operating temperature risks degradation and irrecoverable damage often resulting in reduced cell capacity, reduced cell lifetime, cell failure and in some cases fires and explosions. High temperature batteries used in the oil and gas industry are typically Li-ion primary batteries, however there is a drive to replace this with secondary lithium ion technology. Currently the options for high temperature lithium-ion secondary batteries are limited due to the instability of the interface between the lithiated carbon negative electrode and the organic electrolyte. Development of lithium-ion batteries suitable for high temperature applications requires a holistic approach to battery design because degradation of some of the battery components can produce a serious deterioration of the other components, and the products of degradation are often more reactive than the starting materials. Therefore a careful selection and systematic characterisation of the components of lithium ion batteries is required in order to identify a number of materials and protocols for battery assembly that give promising performance at high temperatures.

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2. Electrodes

Materials research has focused on finding new materials for lithium ion batteries in order to increase the specific energy (Wh kg⁻¹), energy density (Wh L⁻¹) and operating voltage of lithium ion batteries. However a lot of these materials e.g. NMC and LNMO shown to be unstable at elevated temperatures producing gases such as O₂, CO₂ and CO and have large capacity fading on cycling.[1,2] This has meant such materials have only been investigated as high as 60 °C, as can be seen in table 1. However, good performance has been observed at 60 °C with these materials, it has been reported that a 90% capacity retention after 400 cycles at 60 °C for NMC 442 vs Li using an electrolyte of 0.6M LiTFSI + 0.4M LiBOB + 0.05M LiPF₆ in EC/EMC (4:6 w/w). [3] However not all studies show such good performance for example a study of LiMn₂O₄ (PVDF) vs graphite with a 1M LiPF₆ + 0.5 wt% FSE in EC/DMC (3:7 v/v) shows a poor performance at 60 °C retaining only 62% of the capacity after 20 cycles.[4] The performance of electrode materials, is dependent on the electrolyte formulation since the electrode/electrolyte interface is a large source of degradation. [5,6] Research has therefore focused on using more stable materials for studies >100 °C. Lithium iron phosphate (LFP) was introduced by Goodenough [7] in 1997 as a safer, non-toxic, more stable positive electrode material. This is due to structural stability from the covalent bonded PO₄ units and the chemical stability of having Fe^{2+/3+} rather than M^{3+/4+} in LiMO₂ materials. Lithium iron phosphate is a well-established positive electrode material which has been shown in the literature to possess high thermal stability, electrochemical stability and good cycle life.[8,9] The majority of high temperature studies >100 °C utilise LiFePO₄ as the electrode choice, due to its higher thermal stability than other positive electrode materials. The performance of lithium iron phosphate is improved at higher temperatures with the increase in rate capability and increase in capacity.[10,11] LFP has shown to be effective as a stable positive electrode material up to 250 °C, as can be seen in table 1. As discussed above the performance of the LFP is dependent on electrolyte formulation also seen in table 1.

3. Electrolytes

As detailed in section 2 the high temperature performance of the electrodes is dependent on the electrolyte formulation, due to instability of the electrode/ electrolyte interface. Typically the electrolyte used in lithium ion cells is lithium hexafluorophosphate (LiPF₆) in a combination of organic carbonate solvents. LiPF₆ is used because it improves the corrosion resistance of the aluminium current collector, has good solubility in a range of solvents, has a good conductivity at room temperature.[12–17] LiPF₆ is a thermally stable salt with a melting temperature of 200°C and a decomposition temperature of >175°C. [18] However LiPF₆ reacts with water even at room temperature, as shown in equations 1-2 [19,20]. Electrochemically initiated reactions of LiPF₆ with solvents have also been demonstrated, as shown in equations 1, 3-5. The rate of these reactions is accelerated at higher temperatures, the products of which react with the cell components [21]. Literature has shown that LiPF₆ is unstable at elevated temperatures [5,19,29–31,20,22–28].

LiBOB has received much attention in the research of lithium ion battery salts, due to having good thermal stability, with a decomposition temperature above 290 °C [55]. The major advantage of LiBOB is that it doesn't undergo the degradation reactions shown in equations 1-5. It has also been demonstrated that LiBOB facilitates the passivation of the aluminium current collector. [35,55–59] However LiBOB has some drawbacks [55] firstly it has issues with solubility in solvents such as EC and PC, which limits the concentration of LiBOB that can be used (typically < 1 M depending on solvents used). However it has been reported that γ -butyrolactone can be used as a co-solvent to allow higher concentrations.[60] It has been shown that LiBOB is less conductive than LiPF₆ when dissolved in the same carbonate solvents. Many of these disadvantages can be overcome when LiBOB is used at higher temperatures since solubility and conductivity are increased with higher temperatures. LiBOB has been shown to operate in cells at temperatures between 60-115°C. Kurita *et al* prepared cells using an electrolyte of 1M LiBOB in EC, with an LFP electrode vs lithium metal using a glass fibre separator and cycled them using galvanostatic cycling for 50 cycles at a range of c-rates (0.5C-200C) and a range of temperatures (60-115°C). They observed that capacity is not temperature dependent at low c-rates, which they ascribed to the fact that Li is not diffusion limited for slow cycling. At high c-rates however they observed that capacity is temperature dependent, which they ascribed to the fact that a high c-rate is lithium diffusion limited, and so temperature increase improves the diffusion kinetics. At 115 °C the capacity observed was 160 mAh g⁻¹ showing an 86% capacity retention after 50 cycles. [35]

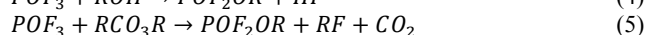
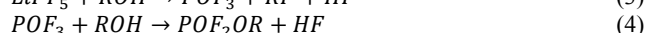
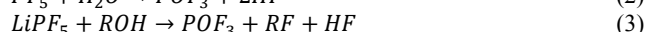


Table 1. Summary of high temperature studies

Temp. °C	Electrolyte	Electrode(s) and binder	Separator	Capacity and retention	Reference
60	0.6M LiTFSI + 0.4M LiBOB in EC/EMC (4:6 w/w)	LiFePO ₄ (PVDF 5130) vs Li	Not stated	155 mAh g ⁻¹ 94 % after 1000 cycles	[32]
65	1M LiODFB EC/PC/DMC (1:1:3, v/v)	LiFePO ₄ (PVDF) vs graphite (PVDF)	Celgard 2400	375 mAh 88% after 100 cycles	[33]
80	polymeric lithium tartaric acid borate poly(vinylidene fluoride-co-hexafluoropropene (PLTB@PVDF-HFP) swollen with PC	LiFePO ₄ (PVDF) vs Li	Electrolyte is separator	159.6 mAh g ⁻¹ 89.8% after 60 cycles	[34]
115	1M LiBOB in EC	LiFePO ₄ PVDF vs Li	Glass Fibre	160 mAh g ⁻¹ 86% after 50 cycles	[35]
120	poly(oxyethylene) methacrylate-g-poly(dimethyl siloxane) (POEM-g-PDMS) doped with lithium triflate (1:20)	LiFePO ₄ (electrolyte is binder) vs Li	Electrolyte is separator	160 mAh g ⁻¹ 63% after 30 cycles	[36]
120	1M LiBOB in PC	LiFePO ₄ (PVDF) vs Li	FCCN- flame retardant thermal resistant cellulose based composite nonwoven separator (cellulose, sodium alginate, flame retardant, silica 2:1:1:0.5)	160 mAh g ⁻¹ 90% after 20 cycles	[37]
250 + 230	Molten LiTFSI	LiFePO ₄ vs Li	No separator	84% after 5 cycles at 250 °C 69% after 3 cycles at 230 °C	[38]
40	1M LiPF ₆ in FEC:TFEC + 2% PES and 0.5% MMDS	NMC 442 (PVDF) vs Graphite (CMC/ SBR)	Not specified	240 mAh g ⁻¹ 75% after 800 cycles	[39]
60	0.6M LiTFSI + 0.4M LiBOB + 0.05M LiPF ₆ in EC/EMC (4:6 w/w)	NMC 442 vs Li	Celgard 2500	163 mAh g ⁻¹ 90% after 400 cycles	[3]
55	1M LiPF ₆ in FEC/ F-EMC/ E-EPE (3:5:2)	LMNO (PVDF 5130) vs Graphite (PVDF 9300)	Celgard 2325	130 mAh g ⁻¹ 50% after 250 cycles	[40]
55	1M LiPF ₆ + 0.25 wt% SDM in EC/EMC/DEC (3:5:2 wt%)	LiNi _{0.5} Mn _{1.5} O ₄ (PVDF) vs Li	Celgard 2400	120 mAh g ⁻¹ 96% after 100 cycles	[41]
55	1.2M LiPF ₆ in F-AEC/F-EMC/F-EPE (2:6:2)	LiNi _{0.5} Mn _{1.5} O ₄ vs Li ₄ Ti ₅ O ₁₂	Celgard 3501	125 mAh g ⁻¹ 96% after 80 cycles	[42]
55	0.4M Li ₂ B ₁₂ F ₉ H ₃ + 2% LiODFB in EC/EMC (3:7, w/w)	Graphite / Li _{1.1} [Ni _{1/3} Mn _{1/3} Co _{1/3}] _{0.9} O ₂ pouch cells	Not Stated	250 mAh g ⁻¹ 70% after 1200 cycles	[43]
55	1M LiPF ₆ + 5 wt% di-(2,2,2 trifluoroethyl)carbonate (DFDEC) alone and 3 wt% VC in EC/EMC (3:7 v/v)	Li _{1.13} Mn _{0.463} Ni _{0.203} Co _{0.203} O ₂ (PVDF) vs graphite (PVDF)	Celgard C210	227 mAh g ⁻¹ 77% after 50 cycles	[44]
55	1.2M LiPF ₆ + 1 wt% LTFOP in EC/EMC (3:7 w/w)	LiNi _{0.33} Co _{0.33} Mn _{0.33} O ₂ (PVDF) vs MCMB (PVDF)	Celgard 3501	120 mAh g ⁻¹ 88% after 200 cycles	[45]
60	1.15M LiPF ₆ in EC/EMC (3:7 v/v) Plus the following additives: 2% vinylene carbonate (VC) 2% succinonitrile (SN)	Li[Ni _x Co _y Mn _z]O ₂ (NCM) (PVDF) vs graphite (CMC/SBR)	Not stated	VC = 90% after 50 cycles SN = 95% after 50 cycles PST = 97% after 50 cycles	[46]

	2% propene sulfone (PST)			PS = 99% after 50 cycles	
	2% propane sulfone (PS)				
60	1M LiPF ₆ in EC/DEC (1:1 w/w)	LiNi _{0.33} Co _{0.33} Mn _{0.33} (PVDF) vs Li ₄ Ti ₅ O ₁₂ (LTO) (PVDF)	Celgard 2325	175 mAh g ⁻¹ 95% after 100 cycles	[47]
55	1M LiPF ₆ + 0.1 wt% TPSPA in EC/DEC (1:1 v/v)	LiMn ₂ O ₄ (PVDF) vs graphite (PVDF)	Not stated	120 mAh g ⁻¹ 75% after 100 cycles	[48]
60	1M LiPF ₆ + 2 wt% FEC in EC/DEC/PC (30:65:5 wt%)	LiMn ₂ O ₄ vs graphite	Not stated	116 mAh g ⁻¹ 88% after 130 cycles	[49]
60	1M LiPF ₆ + 0.5 wt% FSE in EC/DMC (3:7 v/v)	LiMn ₂ O ₄ (PVDF) vs graphite (SBR/CMC)	Polyolefin porous membrane (layered Polypropylene-polyethylene)	90 mAh g ⁻¹ 62% after 20 cycles	[4]
60	1M LiPF ₆ in (EC/DMC/DEC) (1:1:1 v/v/v)	LTO-coated LiMn ₂ O ₄ (PVDF) vs Li	Celgard 2400	132 mAh g ⁻¹ 97% after 100 cycles	[50]
60	1M LiFNFSI in EC / EMC (3:7 v/v)	LiCoO ₂ vs Graphite	Celgard 2325	120 mAh g ⁻¹ 63% after 100 cycles	[51]
60	1.05M LiPF ₆ in EC/DMC (1:1 v%)	AlPO ₄ coated LiCoO ₂ (PVDF) vs Li	15 μm microporous polyethylene separator	180 mAh g ⁻¹ 79% after 30 cycles	[52]
100	1.6 M LiTFSI mono-(C ₆) ₃ PC ₁₀ -TFSI	LiCoO ₂ vs Li	Celgard 480	135 mAh g ⁻¹ 52% after 70 cycles	[53]
100		LiCoO ₂ vs Sn _x N _y		193 μAh 5 cycles	
200	LiPON	No Binder sputtered onto glass substrate with Pt currently collectors	LiPON	140 μAh 1 Cycle	[54]

Another lithium salt receiving much attention[18,33,61,62] is lithium oxalyldifluoroborate (LiODFB) The structure is a variation on LiBOB, by where one of oxalato groups has been replaced with two fluorine groups, and has found to possess the properties of both LiBOB and LiBF₄. It has been shown that LiODFB has a much improved solubility compared to LiBOB which means higher concentrations of the salt are possible. The conductivity of LiODFB is improved compared to LiBOB, and it is comparable to that of LiPF₆. It has been effectively demonstrated that LiODFB retains much more capacity (88% after 100 cycles) compared to LiPF₆ (50% after 100 cycles) when cycled at 65 °C in LiFePO₄/ graphite full cells, literature hasn't investigated above this temperature.[33]

Regarding the selection of the solvent, for high temperature operation out of all the carbonate solvents used in Li-ion cells only EC and PC are suitable. However it has been reported in the literature that PC causes graphite exfoliation.[5] EC has been well documented to form a very stable SEI on graphite, thus protecting from further electrolyte breakdown. It has been shown in the literature that EC can be used successfully as the electrolyte solvent in high temperature batteries up to a temperature of 115 °C.[5,35]

Another class of promising carbonate solvents is that of fluorinated carbonate solvents, these have a higher thermal and voltage stability than conventional carbonate solvents. Hu *et al* demonstrated the use of a fluorinated solvent combination of Fluoroethylene carbonate (FEC), Methyl 2,2,2-trifluoroethyl carbonate (F-EMC) and 1,1,2,2-tetrafluoroethyl 2,2,2,2-tetrafluoropropyl ether (F-EPE) 3:5:2 V:V with 1M Lithium hexafluorophosphate (LiPF₆). This type of electrolyte has shown to achieve better capacities and coulombic efficiencies than LiPF₆ in EC/EMC electrolytes in LiNi_{0.5}Mn_{1.5}O₄/graphite cells cycled between 3.9 V and 4.9 V at 55 °C.[40] Dahn *et al* have also investigated fluorinated solvents and have showed that fluoroethylene carbonate (FEC) and di-2,2,2-trifluoroethyl carbonate (TFEC) (3:7) show better performance than EC:EMC at 40 °C up to 4.6 V.[39]

For higher temperature batteries ionic liquids have been researched. Lin *et al* has shown that a phosphonium ionic liquid with LiTFSI that was shown to operate at 100 °C with capacity dropping to 50% after 70 cycles.[53] Marczewski *et al* proposed an ionic liquids-in-salt electrolyte (where the salt content is higher than the ionic liquid content) reporting high ionic conductivities; however this work was a proof of concept study and did not test the electrolytes in a working cell.[63] Ionic liquids have also been used in combination with carbonate solvents to give both the advantages of an ionic liquid (high temperature stability) and carbonate solvents (good conductivity). Ababtain *et al* showed that a mixture of 80% 1-methyl-1-propylpiperidinium bis(trifluoromethanesulfonyl)-imide (pip) ionic liquid to 20% propylene carbonate (PC) was capable of operation between 25 °C to 100 °C using a 3D nano silicon negative electrode.[64]

Polymer electrolytes have also been researched for higher temperature batteries since they have a much higher thermal stability than liquid electrolytes and have been shown to be suitable above 100°C. Poly ethylene oxide (PEO) is an ion-conducting polymer and has been shown to operate at temperatures as high as 120 °C. The poor cycle life and low voltage operation however are major

drawbacks.[65,66]

There have been recent advances in PEO electrolytes. Yan-Hua Li *et al* have showed that a PEO based electrolyte can be operated up to 170 °C. This is achieved by making an electrolyte of lithium(oxalato)borate-succinonitrile-polyethylene oxide (LiBOB-SN-PEO) and casting this onto a porous polyimide (PI) film (made by electrospinning techniques). The resulting polymer electrolyte (LiBOB-SN-PEO-PI) was characterised using XRD, DSC, SEM, linear sweep voltammetry and impedance spectroscopy and shown to be stable up to 170 °C. It was shown that the PI provides a stable network that allows the electrolyte to maintain mechanical stability during use at high temperatures.[67] Another similar system using PTFE instead of PI was shown by Xing-Long Wu *et al* who prepared two different polymer electrolytes (LiBOB-SN-PEO-PTFE) and (LiCF₃SO₃-SN-PEO-PTFE), where LiCF₃SO₃ is lithium trifluoromethanesulfonate. Both polymers show stability up to 160 °C, due to the PTFE being heat resistant and maintaining the mechanical stability of the electrolyte.[68] Recent work has found a polymer electrolyte that has the ionic conductivity close to that of liquid electrolytes. This has been achieved through the synthesis of a graft copolymer electrolyte. Poly(oxyethylene) methacrylate-poly(dimethyl siloxane) (POEM-PDMS) doped with lithium triflate which has been shown to effectively operate to 120°C.[36]

Gel polymer electrolytes, which contain solvents, have the advantage that their room temperature conductivity is improved, however they are limited to operate below 90°C. This is due to limitation of the solvents used to make the gel. Work by Wang *et al* has shown a novel gel polymer electrolyte PLTB@PVDF-HFB to work to a temperature of 80 °C, the polymer itself is stable up to 330 °C[34]. Ionic liquids have also been used in gel polymer electrolytes with Kelly *et al* showing that performance decreases at higher temperatures due to phase separation and PEO blocking the pores of the electrode surfaces. This type of cell is to allow thermal cut-off of the cell once it reaches a set temperature, acting as a chemical safety “switch”.[69]

Solid state lithium batteries for use at high temperatures have been researched since their conductivity and electrode kinetics are much improved at higher temperatures. They also have the potential to be used with lithium metal since they are believed to avoid lithium dendrite formation which has plagued the use of metal lithium in lithium ion batteries. Dezhao Li *et al* have claimed to have made a thin film solid state lithium battery. The cell is composed of Pt/LiCoO₂/LiPON/Sn_xN_y/Pt and it has been claimed that this type of battery is capable of operation from 20 °C to 200 °C, with a capacity of 142 μAh at 20 °C and 152 μAh at 200 °C. The cell is capable of a maximum of 163 μAh at 150 °C, which is its peak operating temperature.[54]

4. Conclusions

Much research has been done to extend and improve the thermal tolerance of Li-ion batteries operating at higher temperatures, ultimately high temperature lithium ion batteries will require much more research particularly because a majority of studies don't investigate temperatures exceeding 60 °C. The design of a high temperature electrolyte is ultimately one of the largest key issues to high temperature operation since it's the electrode/ electrolyte interface that is responsible for capacity fade at high temperatures. It has been shown that the thermally reactive LiPF₆ can be replaced with alternative lithium salt chemistries which do not breakdown at high temperatures. Many studies have shown that alternative electrolyte systems exist that can perform better than carbonate based systems such as polymers and solid state systems. However, these still need further research in order to become contenders to carbonate based electrolytes.

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