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Ionic liquid and hybrid ionic liquid/organic electrolytes for high temperature lithium-ion battery application

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ABSTRACT

Ionic liquid (IL) and hybrid IL/organic electrolytes with pyrrolidinium cation based ILs have been investigated for application in high temperature lithium-ion batteries (HT-LIBs). The IL based electrolytes show high thermal stabilities, up to 340 °C, ionic conductivities of $>5 \times 10^{-3}$ S cm^{-1} at 80 °C, and broad electrochemical stability windows: 0–5 V *vs.* Li$^+$/Li°. The performance of $LiFePO_4$ based half-cells at 80 °C is promising, delivering *ca.* 160 mAh g^{-1} at 1C, with a rate capability up to 4C and *ca.* 98% coulombic efficiency. The creation of hybrid IL/organic electrolytes by adding different organic cyclic carbonate solvents reduces viscosity of the electrolytes by 28% at 80 °C, thereby improving the ion transport, and further improves the electrochemical performance; higher stability, better rate capability, and $\geq$99% coulombic efficiency. Overall, the electrolytes proposed have a potential to be applied in HT-LIBs, a concept with large advantages at the vehicle system level.

1. Introduction

Lithium-ion batteries (LIBs) have primarily been developed with application in portable devices as a target, but are now prospering also for (hybrid) electric vehicles (XEVs) [1]. For an HEV, the LIB installation is quite more demanding, requiring an additional special cooling circuit, usually working somewhere close to 30 °C, apart from the two cooling circuits of the combustion engine (100–120 °C) and electric motor/power electronics (75–90 °C) [2], in order to ensure expected performance and predictable life-length. In contrast, a high temperature LIB (HT-LIB) with an operating temperature of *ca.* 80–100 °C would in principle allow an overall simplified vehicle cooling system by combining the two lower temperature cooling circuits into one. A preliminary assessment gives at hand that *ca.* 1200-2000 € can be saved on either a passive or an active cooling system, simply by elimination of redundant components *e.g.* fan, water pump, *etc.*, without even considering the additional gains in reduced complexity [3].

Safety and life-length of LIBs at HT is clearly a very critical issue which must be resolved before HT-LIBs can become a commodity [4], whereas the HT lithium metal polymer batteries by Bolloré operating at *ca.* 80 °C employed in the Bluecar (Autolib' *etc.*) is rather much of a special case in terms of design and usage pattern [5,6]. Obviously conventional organic solvent based electrolytes for LIBs, *e.g.* 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) or diethyl carbonate (DEC) (1:1 wt%), are not viable options as they are quite volatile and flammable leading to risks of fires, toxic fumes, and possibly also explosions at HT [7], hence limiting their application to temperatures <60 °C [8,9]. Ionic liquid (IL) based electrolytes, on the other hand, are interesting alternatives owing to negligible vapor pressures, non-flammability, and in addition providing high ionic conductivities [10–12]. Indeed, the properties of ILs can be tailored in detail by the cation and anion combination [13]. The most common IL cations for battery application are imidazolium (XMI), piperidinium (PIP), and pyrrolidinium (Pyr*xy*) derived and these are combined with standard LIB anions such as hexafluorophosphate (PF_6^-), bis(fluorosulfonyl)imide (FSI), or bis(trifluorosulfonyl)imide (TFSI) [14–16], and are doped by the corresponding Li-salts to create IL based electrolytes. The choice of anion is very crucial; some of us recently showed that IL based electrolytes employing the FSI anion possess lower viscosities and higher ionic conductivities, likely owing to the smaller size of the FSI anion as compared to the TFSI anion, but with poorer thermal and electrochemical stabilities [17].

For HT applications Pyr*xy*TFSI is an appealing IL candidate due to its high ionic conductivity, $>10^{-3}$ S cm^{-1} at room temperature (RT), excellent thermal stability, >300 °C, and broad electrochemical stability window (ESW): 0 – > 5 V *vs.* Li$^+$/Li° [18–23]. Previously, Gao et al. used 1 M LiTFSI in Pyr14TFSI as electrolyte *vs.* the 5 V

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$LiNi_{0.5}Mn_{1.5}O_4$ cathode material at RT and found it more stable at high potentials than a conventional organic electrolyte [24]. Additionally, a high cathodic stability allows the use of low potential anode materials such as graphite with a working potential of *ca.* 0.2 V *vs.* Li^+/Li° [23,25].

The main disadvantage of IL electrolytes is that they are rather viscous compared to the conventional organic electrolytes, leading to slow ion transport and the impregnation of porous electrodes cumbersome. Addition of organic solvents such as cyclic carbonates to IL electrolytes, thereby creating hybrid IL/organic electrolytes, improves the electrochemical performance primarily by reducing the viscosity and definitively improving the ion transport [26–31]. However, there is a compromise needed to be made between performance enhancements and HT-LIB safety, but the flammability and volatility of the hybrid electrolytes can indeed be controlled and suppressed by careful adjustment of the concentration of organic solvent [32–35]. For example, Montanino et al. showed a LiTFSI:Pyr13TFSI:(EC/DEC 1:1 mol%) (10:60:30 mol %) electrolyte to be non-flammable at RT and perform close to commercial organic electrolytes in both Li||$LiFePO_4$ (LFP) and Li||$Li_4Ti_5O_{12}$ (LTO) half-cells [32].

Indeed, some few elevated temperature studies employing hybrid IL/organic electrolytes have been made: Yang et al. cycled a Li||LFP half-cell at 75 °C using a 0.3 M LiTFSI in Pyr13TFSI:(EC/DMC 1:1 wt%):vinylene carbonate (VC) (65:30:5 vol%) electrolyte, delivering capacities of 150 and 140 mAh g^{-1} at 1C and 2C, respectively, and being stable for 60 cycles [33]. Likewise, Kühnel et al. cycled a Li||LFP half-cell at 60 °C using a 0.3 M LiTFSI in Pyr14TFSI:propylene carbonate (PC) (1:1 wt%) electrolyte for up to 700 cycles delivering capacities of 145 mAh g^{-1} at 3 C, 135 mAh g^{-1} at 5 C, and 85 mAh g^{-1} at 10 C [26].

Besides EC, PC, DMC, and DEC, both VC and fluoroethylene carbonate (FEC) are popular solvents most often used at an additive level ($<\sim 5$ wt%) for battery applications, primarily due to their ability to form stable solid electrolyte interphases (SEIs) on anodes [25,36–40]. Additionally, VC and FEC, as well as PC, possess high dielectric constants, $\varepsilon = 65–125$, meaning a large ability to dissociate Li-salts, and are much less viscous, $\eta = 2.5–4.0$ mPa s at 25 °C [41,42], than ILs, $\eta = 71$ mPa s for Pyr13TFSI at 25 °C, and thus they should lower the viscosity of the electrolytes and improve the ion transport.

While physical and electrochemical properties of IL and hybrid IL/organic electrolytes have been reported in the open literature before, almost all studies were made at RT or up to maximum 75 °C. Thus, the electrochemical properties such as ESW, stability, and rate capability above 75 °C are hitherto largely unknown. In this work we investigate $Li_xPyr13_{1-x}TFSI$; x = 0.1, 0.2 & 0.3 IL electrolytes and hybrid IL/organic electrolytes aiming at application in HT-LIBs. For the latter, the organic solvents PC, VC, and FEC are all used at a co-solvent level. As a first assessment, the thermal stabilities and ionic conductivities as functions of temperature are studied, followed by the ESWs. The latter are determined at 80 °C to ensure stability at the desired operating temperature and are followed by cycling performance tests *vs.* standard LFP electrodes in half-cells to probe their viability in HT-LIBs.

2. Experimental

2.1. Electrolyte preparation

Pyr13TFSI (99.9%) and LiTFSI (99%) were both purchased from Solvionic. The organic solvents PC (99.7%) and VC (97%) were purchased from Sigma-Aldrich, while FEC was kindly provided by Solvay. The commercial organic electrolyte "LP30" *i.e.* 1 M $LiPF_6$ in EC:DMC (1:1 wt%) was purchased from Merck. The ILs and the organic solvents were used as received. Prior to electrolyte preparation, the LiTFSI salt was dried at 120 °C under vacuum (<7 Pa) for 48 h. The IL electrolytes were prepared by adding the appropriate amount of LiTFSI directly into Pyr13TFSI and stirring at RT for 24 h to create electrolytes with mole fractions of salt; x = 0.1, 0.2, and 0.3 (Table 1). All hybrid IL/organic electrolytes were made by mixing LiTFSI, Pyr13TFSI, and the co-solvent chosen *i.e.* PC, VC, or FEC in 0.2:0.6:0.2 mole fractions, and these were likewise stirred at RT for 24 h to render the final compositions: $Li_{0.2}Pyr13_{0.6}TFSI_{0.8}PC_{0.2}$, $Li_{0.2}Pyr13_{0.6}TFSI_{0.8}VC_{0.2}$, and $Li_{0.2}Pyr13_{0.6}TFSI_{0.8}FEC_{0.2}$. All materials were stored and all sample preparation was carried out in an argon filled glovebox (H_2O <1 ppm & O_2 <10 ppm). The water content in all the resulting electrolytes were <40 ppm as measured by Karl-Fischer titration (Metrohm).

2.2. Thermal stability

The thermal stabilities of the electrolytes were studied by thermo gravimetric analysis (TGA) using a TG 209 F1 Iris from Netzsch. All experiments were performed using Al pans with a sample loading of *ca.* 10 mg and under a 100 ml min^{-1} N_2 flow. The decomposition temperatures (T_d:s) of the IL-based electrolytes and the hybrid electrolytes were determined by dynamic TGA using a heating rate of 5 °C min^{-1} in the range of 25 to 500 °C. For the hybrid electrolytes including the neat IL and IL x = 0.2, isothermal TGA for 10 h at 100 and 10 h at 125 °C was performed to study "long-term" stability and finally the temperature was increased to 500 °C to obtain the T_d:s. The heating rate for each ramp was 5 °C min^{-1}.

2.3. Ionic conductivity

The ionic conductivities (σ) of the electrolytes were measured using a Concept 80 (Novocontrol GmbH) broadband dielectric spectrometer. The dielectric cell was composed of two identical stainless steel (SS) circular plates separated by a Teflon ring of 1.5 mm thickness and 12.4 mm inner diameter and the empty space filled with electrolyte. The cell was prepared inside the glovebox and then placed in the sample holder in the N_2 flowed temperature-controlled chamber of the spectrometer. The conductivities were measured as functions of temperature using a sequence 0 °C–120 °C in the frequency range of 10^7 to 10^{-1} Hz. The conductivities were recorded every 10 °C and the equilibration time at each temperature was 30 min. The DC conductivities were at each temperature determined by the plateaux from the frequency dependent (AC) conductivity plots.

2.4. Viscosity

Viscosity (η) measurements were performed with a Lovis 2000 M micro-viscometer module from Anton Paar connected to a

Table 1
Electrolyte compositions.

	Concentration[*]	
	LiTFSI mol dm^3	Solvent wt%
IL based		
$Li_{0.1}Pyr13_{0.9}TFSI$	0.37	–
$Li_{0.2}Pyr13_{0.8}TFSI$	0.78	–
$Li_{0.3}Pyr13_{0.7}TFSI$	1.23	–
Hybrids		
$Li_{0.2}Pyr13_{0.6}TFSI_{0.8}PC_{0.2}$	0.92	6.32
$Li_{0.2}Pyr13_{0.6}TFSI_{0.8}VC_{0.2}$	0.94	5.38
$Li_{0.2}Pyr13_{0.6}TFSI_{0.8}FEC_{0.2}$	0.93	6.55

[*] Calculated based on the density of the electrolytes measured at 20 °C.