Towards safer sodium-ion batteries

via organic solvent/ionic liquid based hybrid electrolytes

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Abstract

Hybrid electrolytes aimed at application in sodium-ion batteries (SIB) consisting of an organic solvent mixture (EC:PC) and different ionic liquids (ILs); EMImTFSI, BMImTFSI, and Pyr₁₃TFSI, and with the NaTFSI salt providing the Na⁺ charge carriers have here been extensively studied. The physicochemical and electrochemical characterisation includes ionic conductivity, viscosity, density, cation coordination and solvation, various safety measures, and electrochemical stability window (ESW). Hybrid electrolytes with 10 to 50% of IL content were found to have ionic conductivities on par with comparable organic solvent based electrolytes, but with highly enhanced safety properties. A systematic Raman spectroscopy study of the cation coordination and solvation before and after electrolyte safety tests by ignition suggest that IL cations and TFSI remain stable when ignited while organic solvents are consumed. Finally, the solid electrolyte interphase (SEI) formed when using hybrid electrolytes has both better mechanical and electrochemical stability than the SEI derived from pure IL based electrolytes. For a half-cell with a hard carbon (HC) electrode and a hybrid electrolyte with a composition of 0.8 m NaTFSI in EC_{0.45}:PC_{0.45}:Pyr₁₃TFSI_{0.10} encouraging results were obtained for IL based electrolytes – *ca*. 182 mAhg⁻¹ at C/10 over 40 cycles.

Keywords: Sodium-ion battery; Ionic liquid; Hybrid electrolytes; Safety; Imidazolium; Pyrrolidinium

1 Introduction

Society is expecting efficient, affordable, safe technologies - and secondary batteries are not an exception to the rule. These are needed in order to take action to meet the increasing energy storage demands for both mobile and stationary applications. Lithium-ion batteries (LIBs) are essential for portable electronics and are starting to play a major role in the development of hybrid electric vehicles (HEV), electric vehicles (EV), and large scale energy storage [1, 2]. However, the world-wide repartition of lithium, where only four countries own more than 90% of the economically exploitable lithium reserves [3], together with the increasing lithium price, makes it advisable to develop complementary technologies. An appealing alternative is to introduce sodium into the next generation batteries, given its abundance and relatively low cost compared to lithium. Na is ranked as the 6th most abundant element on Earth [4], and its derivatives are massively produced around the world for various applications. The interest in sodium for secondary batteries is not new [5-11], but there is currently a revival taking place. At present, the most common sodium based battery technology commercialised is the sodium-sulfur battery [2, 12-18], operational only at medium-high temperatures, ca. 300°C, and therefore mostly used for load-levelling. The sodium-ion battery (SIB) technology, just like the LIB, works at room temperature enabling its use in a larger pool of applications. Armed with the extensive experience and knowledge acquired for LIBs, new materials and electrolyte formulations have now been rapidly developed for SIBs [13, 19-25]. As intercalation electrodes are preferentially used for SIBs just as for LIBs, the difference in energy density using Na instead of Li is not as large as if pure metal electrodes would have been used - recently a SIB reaching 200 Whkg⁻¹ was demonstrated at the laboratory scale [19]. Furthermore, using the BatPaC tool [26] a SIB based on a hard carbon (HC) anode and a $Na_3V_2(PO_4)_2F_3$ cathode was revealed to exhibit a theoretical energy density comparable to graphite//LiFePO₄ based LIBs [27]. As for any other battery technology, the electrolyte choice is utterly important [1, 22, 28-31]. Several basic properties must be taken into account, whereof the ionic conductivity, the ESW, and the thermal stability window are amongst the most studied. Several safety indicators should also be taken into

account; the flash point (FP), the ignition time (IT), and the self-extinguishing time (SET), etc. At present, most commercial battery electrolytes are based on a salt dissolved in organic solvents. These exhibit excellent ionic conductivities, but unfortunately this comes with high flammability and volatility [32, 33]. Packaging and compliance with safety regulations do make the batteries "safe enough", but the risk of battery fires and current legislation activities due to toxicity studies urge us to find alternatives [34-36]. A candidate of choice could be ionic liquid (IL) based electrolytes. LIBs using IL based electrolytes have been extensively studied for over 15 years [28, 37-43] and paved the way to recent work on SIBs [44-50]. Amongst the large diversity of ILs available, pyrrolidinium (Pyr) based ILs have shown large promise in terms of cyclability and large ESWs [45, 46, 51, 52]. Recently, a large-sized (27 Ah) practical SIB using HC and NaCrO₂ as electrodes and a Pyr13FSI IL based electrolyte was successfully cycled >500 cycles [25]. Imidazolium (Im) based ILs have also been studied for SIBs [53, 54], but the presence of an acidic proton on the Im ring [55-57] penalizes the ESW by decomposing the electrolyte. The general promising properties of ILs as electrolyte matrices in terms of safety, such as non-volatility and non-flammability [28, 58], are counteracted by high viscosities and especially by the low ionic conductivities [59] for the charge carrier ions e.q. Na⁺ or Li⁺ as compared to "traditional" organic electrolytes. Therefore, studies of hybrid electrolytes with ILs as additives or (co-)solvents together with organic solvents have been carried out for LIBs [60-64] to balance and improve electrochemical performance as well as safety [59, 63, 65-67].

Here we report a systematic study of safety properties and electrochemical performance of hybrid electrolytes for SIBs using both IL and organic electrolytes as references. The electrolytes were studied both single-handedly and upon cycling vs. negative electrodes. The latter was made to assess the electrochemical stability upon low potential operation and the compatibility for different electrolyte/electrode combinations, including any side-effects on final cell performance. High surface area electrodes representative of real commercial electrodes were used, which is especially important as IL based electrolytes often have problems at low voltages, decomposing at higher potentials than at the potential of the SIB negative electrodes preferentially used *e.g.* HC [29, 39].

2 **Experimental**

2.1 Materials

All hybrid electrolytes were prepared by direct mixing of an organic solvent based electrolyte; 0.8 m NaTFSI in an ethylene carbonate (EC, anhydrous 99.0%, Aldrich) and propylene carbonate (PC, anhydrous 99.7%, Aldrich) mix EC:PC (1:1), with 2, 5, 10, 20, 50, 80, and 100 weight% (wt.%) of various ILs. LP30 and DMC from Merck (battery grade) were used for safety studies while LiPF₆ and NaPF₆ (98.0%, Aldrich) were the salts used for the electrolytes. The ILs 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) (99.9%), 1-butyl-3-methyl-imidazolium TFSI (BMImTFSI) (99.9%), N-Propyl-N-methyl-pyrrolidinium TFSI (Pyr₁₃TFSI) (99.9%), and the corresponding sodium salt (NaTFSI) (99%) were all purchased from Solvionic. Electrolyte preparation and cell assembly were always carried out inside an argon filled glove box with < 1 ppm H₂O and 0-5 ppm O₂. The nomenclature used for all electrolytes is based on the molar ratios for the solvents and ILs e.g. EC_{0.45}:PC_{0.45}:Pyr₁₃TFSI_{0.10}. The NaTFSI concentration was almost always 0.8 m, a salt concentration practical for the hybrid electrolytes and allowing for comparisons with typical organic SIB (and LIB) electrolytes. For the pure IL based electrolytes the 0.8 m NaTFSI concentration however led to saturation, why a molar fraction x=0.15 [54] was chosen as reference. Composite electrodes, mimicking industrial technologies, were prepared from slurries of 85 wt.% HC active material, 5 wt.% of poly(vinylidene fluoride) binder (PVdF, Arkema) and 10 wt.% of Super P carbon (Csp, Timcal) in N-Methyl-pyrrolidone (NMP, Aldrich). The HC was prepared following the procedure described in [68] by pyrolysis of sugar at 1100°C for 6 h under argon flow.

The mixing of electrode components was made using a PM100 Retsch planetary ball miller with a stainless steel container with 3 stainless steel balls of 1 cm diameter at 500 rpm for 2 h with change of rotation direction every 30 min. The obtained slurry was subsequently tape casted on a 20 μ m thick aluminum foil (Goodfellow) with a 250 μ m doctor-blade and dried at 120°C under vacuum for 2

h. Once dried, 0.8 cm^2 disk electrodes were cut and pressed at 8 tons. Typically the electrode loading was 2 mg, corresponding to *ca*. 15 μ m thick deposits.

2.2 Properties

First, the basic physico-chemical properties were determined for all the hybrid electrolytes *i.e.* 0.8 m NaTFSI in $EC_x:PC_x:Pyr_{13}TFSI_{(1-2x)}$, $EC_x:PC_x:EMImTFSI_{(1-2x)}$, and $EC_x:PC_x:BMImTFSI_{(1-2x)}$, or more generally 0.8 m NaTFSI in $EC_x:PC_x:CatTFSI_{(1-2x)}$, and for all reference systems. Second, the safety of the electrolytes was assessed through a combination of three independent measures (FP, IT and SET). Finally, a few electrolytes were selected for electrochemical tests. The layout of the experimental section follows this measurement and assessment scheme.

2.2.1 Ionic conductivity

The ionic conductivity was measured with a Novocontrol broad-band dielectric spectrometer in the frequency range $10^{-1} - 10^7$ Hz between -10° C and 60° C with a step of 10° C. A constant volume (0.14 cm³) cell was used, consisting of two brass (blocking) electrodes separated by a Teflon spacer (to contain the electrolytes and preventing any evaporation), which was sealed inside the argon filled glove-box. During the entire experiment the cell was kept under a flow of dry N₂ gas. The temperature was held constant for at least 20 min before each measurement to allow equilibration of the sample. Finally, the DC conductivities were extracted from the plateaux in the frequency dependent (AC) conductivity plots.

2.2.2 Viscosity

The viscosity analysis between 10°C and 60°C was based on the rolling ball principle (dynamic viscosity) and carried out on a Lovis 2000 M/ME (Anton Paar). A 1.8 mm diameter capillary filled with the sample and a steel ball was used.

2.2.3 Density

The density data between 10°C and 60°C were recorded on a DMA 4500 M (Anton Paar). 1 cm³ of each sample was introduced into a U-shaped borosilicate glass tube excited to vibrate at its characteristic frequency - which depends on the density of the sample.

2.2.4 Raman spectroscopy

A 1 cm³ sample was placed in a cylindrical cuvette of 2 cm³ sealed with paraffin tape inside the argon filled glove-box before being transferred to the Raman set-up. Once the initial measurements were done, the samples were ignited in air and the remaining electrolyte was placed in a different 2 cm³ vial to again be analyzed. All measurements were made at room temperature using a Bruker MultiRAM FT-Raman spectrometer with a nitrogen-cooled germanium detector and a resolution of 2 cm⁻¹. In order to optimize the signal-to-noise ratio and avoid luminescence a Nd-YAG (1064 nm) laser was used as excitation source at an operating power of 500 mW and the spectra were averaged over 1000 scans. For a selection of electrolytes band-fitting and deconvolution were made in order to in detail analyze the Na⁺-coordination. In the analysis stage each band used was fitted using a Voigt function and four models were elaborated upon by considering the position, the width, and the mix of Gaussian and Lorentzian band-shape contributions (successively fixed).

2.2.5 Safety tests

The IT and SET were both determined using a butane torch on *ca*. 0.5 g of electrolyte placed on a watch glass. As the appearance of a flame was not as clear for hybrid electrolytes as for EC:DMC

based electrolytes, a different protocol was chosen for the IT; the time necessary to obtain a sustainable flame. The SET was normalized against the electrolyte mass. Each electrolyte was tested at least six times in order to have some statistics. The FP was determined using a MiniFlash FLP/H TOUCH (Grabner) within which 1 cm³ of sample was placed in a cup with a stirring magnet. The cup is closed during the test and as there thus is no direct flame exposure to the sample possible, the ignition is made by an electric arc. The FP is defined, using a heat sensor, as the lowest temperature at which the electrolyte produces a flammable mixture with air so that a propagating flame is covering at least 75% of the electrolyte surface.

2.2.6 Electrochemical tests

The electrochemical stability of the electrolytes was evaluated by cyclic voltammetry (CV) in threeelectrode Swagelok cells using a sodium metal cube slice (Aldrich, 99.95%) as counter and reference electrodes and an aluminum plunger as the working electrode. The sweep rate was 1 mVs⁻¹ for all tests and a protocol where the voltage window is progressively opened from 0-2 V to 0-5.5 V was used. Battery cycling experiments were carried out in two-electrode Swagelok cells in galvanostatic cycling with potential limitation (GCPL) at different rates ranging from C/10 to 2C (1C being one Na⁺ inserted in one hour, corresponding to 372 mAg⁻¹) to monitor rate capability and capacity evolution upon cycling. All electrochemical tests were performed using a Bio-Logic VMP3 potentiostat.

3 Results and Discussions

3.1 Physical properties

3.1.1 Viscosity and density

The density and viscosity measurements of both pure IL and hybrid electrolytes (Figs. 1 and 2) show the density to increase as a function of IL content and decrease linearly with the temperature. The maximum is *ca.* 1.5 g cm⁻³ for 80% IL and 10°C regardless of the IL used. The difference between the pure IL electrolytes as compared to the 80% IL containing hybrid electrolytes is likely due to the different Na-salt concentrations.



<u>Figure 1:</u> Density of 0.8 m NaTFSI in (a) $EC_x:PC_x:BMImTFSI_{(1-2x)}$ and (b) $EC_x:PC_x:Pyr_{13}TFSI_{(1-2x)}$ as a

function of temperature.



Figure 2: Viscosities and ionic conductivities of 0.8 m NaTFSI in (a, c) $EC_x:PC_x:BMImTFSI_{(1-2x)}$ and (b, d) $EC_x:PC_x:Pyr_{13}TFSI_{(1-2x)}$ as a function of temperature.

The observations are overall, for both concentrations and temperatures, supported by Noor et *al.* [45] and our own previous work [54]. As expected the viscosity (Figs. 2a and 2b) decreases rapidly when the temperature increases, while it increases with IL content. Notable is that the pure IL electrolytes display the highest viscosities, despite having only half the Na-salt concentration as compared to the hybrid electrolytes. The viscosities values all seem, based on the shape of the curves, to follow a Vogel-Tammann-Fulcher [69-72] (VTF) behaviour, as earlier found for other hybrid electrolytes [73].

3.1.2 Ionic conductivity

When any type of IL based electrolyte is analyzed in terms of ionic conductivity, it is important to remember that the transport of Na⁺ (or Li⁺) charge carriers is what primarily matters. In a previous

paper [54] some of us found the total ionic conductivity to be affected only to a minor extent by addition of Na-salt, whereas most of the ionic conductivity was intrinsically due to the IL cations and anions. Admittedly, the sizes of the Na⁺ charge carrying complexes in such electrolytes can be relatively large and also diverse, but the determination of the Na⁺ transport number is outside the scope of the present study due to this complexity. Therefore, the ionic conductivity of IL based electrolytes decreases progressively with the addition of a Li-salt [38, 46, 74-76] or a Na-salt [45, 54]. In contrast, typical ionic conductivity trends for organic solvent (*e.g.* EC, PC, DMC, *etc...*) based electrolytes, with local conductivity maxima at *ca*. 0.5-0.8 M and 1 M for Na and Li-salts, respectively [77, 78]. The measured ionic conductivity (Figs. 2c and 2d) and literature data for both pure Pyr₁₃TFSI [79] and 1 m LiTFSI in BMImTFSI [38] electrolytes reveal similar ionic conductivities, ranging between 2-6 mScm⁻¹ at room temperature – again supporting the large contributions from the IL matrices. Moving to the hybrid electrolytes 0.8 m NaTFSI in EC_x:PC_x:CatTFSI_(1-2x) as compared to an organic 0.8 m NaTFSI in EC_x:PC_x electrolyte, the addition of 10-20% IL slightly increases the ionic conductivity concomitant to an increase in viscosity (Fig. 2).

Again, the contribution of the IL ions must be emphasized. In contrast, at 50% IL and beyond the ionic conductivity decreases, most likely due to the high viscosities. A noticeable difference between the organic based 0.8 m NaTFSI in $EC_{0.50}$:PC_{0.50} and the IL based 0.8 m NaTFSI in $EC_{0.40}$:PC_{0.40}:CatTFSI_{0.20} or $EC_{0.45}$:PC_{0.45}:CatTFSI_{0.10} is the temperature dependence, attributable to varying modifications of the viscosity at low and high temperatures. This is further confirmed by the slightly lower ionic conductivity of 0.8 m NaTFSI in EC_x :PC_x:Pyr₁₃TFSI_(1-2x) as compared to 0.8 m NaTFSI in EC_x :PC_x:BMImTFSI_(1-2x), and its slightly higher viscosity – while they both display similar general trends. High electrolyte viscosity can be connected to non-negligible over-potentials, delaying the potential limits set by the redox reactions, and *e.g.* affect the sodium plating processes in IL based electrolytes.

3.1.3 Raman spectroscopy

Raman spectroscopy measurements were performed in order to determine: *i*) the species consumed after ignition/burning of the electrolytes, but foremost *ii*) the relative stability and amounts of different types of Na⁺-complexes formed in the hybrid electrolytes and details of the competitive cation coordination and solvation. As a common starting point, the Raman scattering cross-sections of the vibrational modes analysed are assumed to not be drastically modified upon cation coordination (Table 1) [80]. Based on this assumption the analysis of the electrolyte spectra 670-1070 cm⁻¹ for different EC:PC *vs.* IL contents, Figures 3a and 3b, can be made rather straight-forward.



Figure 3: Raman spectra of 0.8 m NaTFSI in (a) $EC_x:PC_x:BMImTFSI_{(1-2x)}$ and (b) $EC_x:PC_x:Pyr_{13}TFSI_{(1-2x)}$, between 675-1075 cm⁻¹.

Table 1: Associated vibrational modes to bands used in the analysis of hybrid electrolytes.

Vibrational mode	$ u_{SNS}$		$oldsymbol{ u}_{ring}$ breathing	
Species	TFSI	Na ⁺ -TFSI	EC	Na ⁺ -EC
Experimental Frequency [cm ⁻¹]	741±1	744±1	893±1	901±1
Computed Raman Activity [amu Å ⁻⁴]	20	19.2	13.7	18.3

The band at 714 cm⁻¹ is assigned to the EC ring bending mode [81-84], shifted up 10 cm⁻¹ to 724 cm⁻¹ upon sodium cation coordination. The EC breathing mode is observed at 893 cm⁻¹ [81, 85] and similarly the cation coordinated band is shifted up 7 cm⁻¹ to 900 cm⁻¹. By comparison, the Li⁺ cation coordination up-shift is 11 cm⁻¹, hence the corresponding band is located at 904 cm⁻¹ [80, 86]. All the shifted bands grow as a function of EC content and the spectra are void of any such band for the pure BMImTFSI based electrolyte. For PC the band at 849 cm⁻¹ is ascribed to a complex ring bending style mode [87], while a band from the symmetric ring deformation mode is located at 712 cm⁻¹ (as deconvoluted in our previous work [27]). The solvation contribution by the PC solvent is complex to determine as the effect of the Na⁺ cation interaction with PC is solely visible for this band [84]. As EC and PC share structural similarities it is, however, virtually impossible to unambiguously extract information on the Na⁺ coordination by either EC or PC using the 710- 720 cm⁻¹ range. Thus, we cannot neither exclude nor confirm the participation of PC in the first solvation shell. Between 730 and 765 cm⁻¹ a TFSI anion mode gives rise to a band considered the best probe for studying cation solvation by Raman spectroscopy, with "free" TFSI anions and contact ion-pairs with Li⁺ located at 742 and 746 cm⁻¹, respectively [88-90], and similarly the contact ion-pairs with Na⁺ at 744-745 cm⁻¹ [91].

With decreasing EC:PC concentration in the electrolytes the relative amount of Na⁺-TFSI contact ionpairs increases, as expected, shifting the centre of the envelope to higher wavenumbers (Figs. 4a and 4b). This shift is not only due to the modification of the EC:PC concentration, but also to the modification of the electrolyte permittivity [92], why the addition of IL also shift all TFSI bands to slightly higher wavenumbers. The areal ratio [Na⁺-EC/Total] increases with the addition of IL, while the areal ratio associated to TFSI coordination [Na⁺-TFSI/Total] remains constant, possibly due to a maximum TFSI coordinated being *ca*. 1/3 of the total TFSI available, while EC is relatively more active in coordinating Na⁺ as its concentration is reduced. The solvation numbers (SNs) show the addition of IL to: i) increase the SN of TFSI, ii) decrease the SN of EC, and iii) to decrease the total SN (Table 2.). The latter is likely due to steric effects hindering both EC and TFSI to coordinate Na⁺ simultaneously.

As a second part of the Raman analysis a selection of spectra of post-burnt electrolytes, 0.8 m NaTFSI in $EC_xPC_xBMImTFSI_{(1-2x)}$ and $EC_xPC_xPyr_{13}TFSI_{(1-2x)}$ are presented (Fig. 4). The differences in the relative intensities of the EC and PC bands in the region 830-920 cm⁻¹ (Figs. 4c and 4d) reveal the organic solvents to be partially and preferentially consumed.



Figure 4: Raman spectra of 0.8 m NaTFSI in EC:PC:IL before and after ignition (a, b) between 700-760 cm⁻¹, (c, d) 830-920 cm⁻¹, and Raman bands associated to the cations (e) Pyr₁₃ and (f) BMIm before and after ignition

For the ILs the corresponding bands (Figs. 4e and 4f) relatively increase and their global shapes are conserved - interpreted as due to the IL cations being stable upon ignition of the electrolyte and not consumed. In addition, the EC solvents coordinated by Na⁺ (the feature at *ca.* 900 cm⁻¹) are less ignitable/more stable than un-coordinated EC (the feature at *ca.* 893 cm⁻¹) and/or the equilibrium

shifting accordingly. The area ratios of post-burnt electrolytes are always larger than for the original electrolytes for similar total SNs (Table 2).

Table 2: Solvation number analysis of hybrid electrolytes for two different types of ILs before and after burning.

	$\frac{A_{Na^+-EC}}{A_{Total}}$	$\frac{A_{Na^+-TFSI}}{A_{Total}}$	SN _{EC}	SN _{TFSI}	SN _{Total}
Original					
0.8 m NaTFSI in:					
EC _{0.45} PC _{0.45} BMImTFSI _{0.10}	0.41	0.27	2.16	0.35	2.52
EC _{0.25} PC _{0.25} BMImTFSI _{0.50}	0.47	0.31	1.42	0.79	2.21
EC _{0.10} PC _{0.10} BMImTFSI _{0.80}	0.54	0.31	0.67	1.07	1.73
				<u>.</u>	
EC _{0.45} PC _{0.45} Pyr ₁₃ TFSI _{0.10}	0.37	0.30	1.98	0.40	2.38
$EC_{0.25}PC_{0.25}Pyr_{13}TFSI_{0.50}$	0.55	0.27	1.71	0.70	2.41
$EC_{0.10}PC_{0.10}Pyr_{13}TFSI_{0.80}$	0.58	0.34	0.72	1.20	1.92
				•	-
Post-burnt					_
0.8 m NaTFSI in:					
EC _{0.45} PC _{0.45} BMImTFSI _{0.10}	0.72	0.48	1.56	0.64	2.21
EC _{0.25} PC _{0.25} BMImTFSI _{0.50}	0.61	0.59	0.58	1.49	2.07
EC _{0.10} PC _{0.10} BMImTFSI _{0.80}	0.62	0.58	0.17	2.00	2.16
				•	
EC _{0.45} PC _{0.45} Pyr ₁₃ TFSI _{0.10}	0.58	0.43	1.91	0.57	2.48
EC _{0.25} PC _{0.25} Pyr ₁₃ TFSI _{0.50}	0.82	0.66	1.31	1.69	3.00
EC _{0.10} PC _{0.10} Pyr ₁₃ TFSI _{0.80}	0.88	0.58	0.39	2.05	2.43

3.2 Electrochemical tests

3.2.1 Cyclic voltammetry

Cyclic voltammetry was performed both to determine the useful ESW and to assess the feasibility of sodium metal plating/stripping. The CVs of the pure IL based electrolytes (Fig. 5) display low currents at low potentials, indicative of good stabilities upon reduction, with values that diminish upon successive cycles. This is ascribed to a surface passivation related to formation of a solid electrolyte interphase (SEI) as already reported for imidazolium IL based electrolytes containing TFSI [93-96]. At high potentials the behaviour is somewhat different for the three electrolytes. For the 0-5.5 V vs. Na⁺/Na⁰ CV, some waves are observed upon reduction which are not present in the 0-4.5 V vs. Na⁺/Na⁰ CV. These are ascribed to reduction of products previously produced by oxidation. In agreement with the larger oxidative stability of the Pyr₁₃TFSI based electrolyte, the magnitude of the waves is smaller.



Figure 5: CVs of Pyr₁₃TFSI, EMImTFSI, and BMImTFSI based electrolytes (0.8 m NaTFSI) between (a) 0-4.5 V vs. Na^+/Na^0 and (b) 0-5.5 V vs. Na^+/Na^0 .

No evidence of corrosion of the aluminum plunger working electrode is observed for any of the pure IL electrolytes, in agreement with Peng *et al.* and Garcia *et al.* [97-99]. For the high potential limit, it is known that ILs containing TFSI have a positive effect on reducing the aluminium corrosion [38, 99-103]. The presence of ILs in the electrolyte composition shifts the corrosion potential of Al to a higher voltage; from 3.5 to 4.0 V vs. Na^+/Na^0 (Fig S1, Supplementary Information), as already observed by Kuhnel et *al.* [103] for Pyr-based ILs. In order to ascertain whether the SEI formed enables Na^+ diffusion and sodium deposition/plating, CVs with an even lower cut-off potential (-0.5 V vs. Na^+/Na^0) were performed (Fig. 6). For a 1 M NaTFSI in PC electrolyte, already studied by Ponrouch *et al.* [104], the oxidation starts at *ca.* 3.5 V vs. Na^+/Na^0 . However, no evidence whatsoever for sodium plating was found, possibly due to the formation of a film not permeable for sodium ions or decomposition of organic cations and/or TFSI anions.



Figure 6: CVs for (a) the pure ILs $Pyr_{13}TFSI$, EMImTFSI, and BMImTFSI, and (b) 0.8 m NaTFSI hybrid electrolytes, for -0.5-3 V vs. Na^{+}/Na^{0} .

The CVs for hybrid electrolytes rich in IL (Fig. S2, Supplementary Information) showed the same trends as for pure IL both in terms of ESW and absence of sodium plating/stripping. The absence of reversible sodium deposition could be due to the TFSI anion as FSI based IL electrolytes have been shown to reversibly deposit Li⁺ and Na⁺ upon cycling [105]. In addition, corrosion of the aluminum plunger working electrode was observed coupled to the introduction of the organic solvents. In contrast, the CVs for hybrid electrolytes rich in organic solvents indicate that Na plating/stripping takes place, *i.e.* for 0.8 m NaTFSI in EC_{0.40}:PC_{0.40}:BMImTFSI_{0.20}, EC_{0.40}:PC_{0.40}:EMImTFSI_{0.20}, and EC_{0.45}:PC_{0.45}:Pyr₁₃TFSI_{0.10} in the -0.5-3 V vs. Na⁺/Na⁰ window (Fig. 6b). Ideally the process should have an onset potential as close as possible to 0 V vs. Na⁺/Na⁰ and 100% Coulombic efficiency (CE), and

the best hybrid electrolyte, 0.8 m NaTFSI in EC_{0.45}:PC_{0.45}:Pyr₁₃TFSI_{0.10}, has an onset potential of *ca*. - 0.27 V *vs*. Na⁺/Na⁰ and a CE >84%. Overall, the better Na plating/stripping performance for electrolytes richer in organic solvents is most likely related to the SEIs formed having different compositions, enabling sodium ion permeation – supported by previous reports on the effect of organic solvent addition to IL based electrolytes [95, 106, 107]. In view of these results, the 0.8 m NaTFSI in EC_{0.45}:PC_{0.45}:Pyr₁₃TFSI_{0.10} hybrid electrolyte was selected for further studies involving active electrode materials.

3.2.2 Galvanostatic cycling with potential limitation (GCPL)

The GCPL potential *vs*. capacity profiles, at C-rates ranging from C/10 to 2C using the 0.8 m NaTFSI in $EC_{0.45}$:PC_{0.45}:Pyr₁₃TFSI_{0.10} hybrid electrolyte and the HC based electrode, are presented in Fig. 7. In both the C/10 and C/5 cases a linear potential decay is observed followed by a low potential pseudo-plateau at *ca*. 50 mV *vs*. Na⁺/Na⁰. According to Stevens and Dahn [68], the first step corresponds to the insertion of Na⁺ between graphene layers of HC, while the plateau can be associated to the adsorption of Na⁺ within the HC pores.

In Fig. 7a, the capacities as a function of cycle number at various C-rates are displayed together with the CEs. The 1st cycle – shown – exhibits a large irreversible capacity leading to a CE of 40%, while for the subsequent seven cycles the capacity was found to only slightly decrease with concomitant increase in the CE, indicative of continuous SEI formation. After these few cycles the capacity stabilizes at 182 mAhg⁻¹ at C/10 with a CE of *ca.* 96%. The CE is low for the hybrid electrolytes suggesting that the passivation of HC in the presence of an IL is not as efficient as in pure organic solvent based electrolytes, urging for further in depth analysis of the SEI formed. For higher C-rates lower capacities are obtained; *ca.* 132 and 92 mAhg⁻¹ for 1C and 2C, respectively. This trend has been rationalized by some of us as being directly related to the IR drop of the cell; *ca.* 90 and 130 mV for 1C and 2C, respectively, which is very detrimental for the performance for a low working voltage electrode active material such as HC [108, 109]. Overall a significant capacity retention and a specific capacity of 182 mAhg⁻¹ at C/10 after 40 cycles was achieved. This is almost on par with the 200

mAhg⁻¹ found in the literature for using organic electrolytes such as 1 M NaTFSI in EC:PC [104], while Komaba et *al.* reported an as high value as 240 mAhg⁻¹ over 100 cycles using a 1 M NaClO₄ in PC electrolyte [110].



Figure 7: (a) Potential vs. capacity profiles at different rates for HC of 0.8 m NaTFSI in $EC_{0.45}$: $PVr_{13}TFSI_{0.10}$ and (b) coulombic efficiency and discharge capacity vs. cycle numbers for HC electrodes tested at C/10, C/5, 1C, and 2C vs. 0.8 m NaTFSI in $EC_{0.45}$: $PC_{0.45}$: $Pyr_{13}TFSI_{0.10}$.

3.3 Safety tests

In Fig. 8 the FP, IT, and SET are reported for all hybrid electrolytes and for some of the references. When carrying out an FP test aimed at describing battery application safety an analysis of an open system is less suited (as batteries usually are sealed). There is thus a trade-of between simplicity of set-up – direct contact of a flame on the sample – and the usefulness and interpretation of the results. Indeed, the mixture of dispersed gaseous materials can be ignited in air only if the fuel concentration is within flammability limits. For pure ILs the upper flammability limit can readily be passed in a closed system, why these will not ignite, as already described by Shimizu et *al.* [111], but in an open system it indeed would. Therefore, a closed system has been used to better mimic a sealed battery.

For a fixed IL content similar FPs are obtained for both the Li and Na based electrolytes. As expected, significantly higher FPs were obtained for the EC:PC as compared to the EC:DMC based electrolytes, most probably due to the high volatility of DMC. Indeed, the EC:PC based electrolytes have FPs of *ca*. 140°C for IL contents of 20% or below (regardless of the nature of the IL cation) and the FP increases with the IL content, reaching 180°C for 80% IL. The FPs for the pure BMImTFSI and Pyr₁₃TFSI IL based electrolytes could not be recorded as the apparatus is limited to 200°C. The increase in FP as function of IL content indicates that the IL inhibits the vaporization and decomposition of organic solvents, reducing the ignitable content in the vapor.

Moving to the IT as a function of IL content (Fig. 8b) there is almost no influence of the salt nature (Li *vs.* Na) for electrolytes with >10% IL. In contrast, for electrolytes with <10% IL the IT changes from 10 to 18 s for Li and Na, respectively. Again, the EC:PC based electrolytes are safer as compared to the EC:DMC based electrolytes such as LP30; only 2 s are needed to ignite the latter as compared to a minimum of 10 s for the former electrolytes. It was impossible to at all ignite the electrolytes with 80% IL content or more. Finally, the choice of IL cation does not seem to have an impact on the IT.



Figure 8: (a) FP, (b) IT, and (c) SET for 0.8 m NaTFSI and LiTFSI – all as a function of IL content. Reference data for 1 M MPF₆ in EC:DMC (M=Na, Li) represented by horizontal lines.

The SET measurements have large systematic errors and uncertainties (Fig. 8c), but still the data obtained are consistent, exemplified by our results for LP30 being comparable to those reported by Xu and Lombardo [58, 62, 67]. Again, comparing first Na and Li based electrolytes, for low IL contents the Na based electrolytes exhibit shorter SETs, while for higher IL contents there is no significant difference obtained. This could be related to differences in the stabilities and/or the nature of the complexes formed with Na⁺ as compared to Li⁺, delaying and/or reducing the flammable compounds/radicals transported to the vapor phase. The general trend is that the SET decreases more or less linearly with the addition of IL, but initially, when going from a fully organic electrolyte to a hybrid electrolyte with only 2% IL the SET is reduced by 50%. No significant differences were observed based on the IL nature. Additionally, the final mass loss after ignition of all samples correspond to 50-60% of the EC:PC, assuming the ILs are not consumed.

Conclusions

The addition of the ILs BMImTFSI, EMImTFSI, and Pyr₁₃TFSI to organic EC:PC SIB electrolytes all show positive trends in several properties of interest; the improved safety and the electrochemical properties being the most significant features. The total ion conductivities of the hybrid electrolytes are similar to organic electrolytes as long as the IL content is kept below 20%, but as more IL is added, the ion conductivity decreases due to an increased viscosity. Based on the IT, SET and FP results, the presence of an IL in the electrolytes improves their safety. With 80% of IL the FP has increased by 40°C, while the IT analysis shows that the ILs behave as retardants. In addition, the SET is reduced by half by the introduction of only 2% of IL. The solvation and coordination analysis show that the IL cations and TFSI anions remain stable upon ignition, while the organic solvents are consumed. Moreover, the sodium cation first solvation shell is modified depending on the electrolyte composition. Finally, good capacity retention was obtained for HC with hybrid electrolytes showing a specific capacity of 182 mAhg⁻¹ at C/10 after 40 cycles.

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References

[1] J.B. Goodenough, Y. Kim, Chem Mater, 22 (2010) 587-603.

[2] B. Dunn, H. Kamath, J.M. Tarascon, Science, 334 (2011) 928-935.

[3] Mineral Commodity Summaries 2013, Lithium, U.S. Geological Survey, (2013).

[4] Mineral Commodity Summaries 2013, Sodium, U.S. Geological Survey, (2013).

[5] C. Delmas, J.J. Braconnier, C. Fouassier, P. Hagenmuller, Solid State Ionics, 3-4 (1981) 165-169.

[6] K.M. Abraham, Solid State Ionics, 7 (1982) 199-212.

[7] J. Molenda, C. Delmas, P. Hagenmuller, Solid State Ionics, 9-10 (1983) 431-435.

[8] J.M. Tarascon, G.W. Hull, Solid State Ionics, 22 (1986) 85-96.

[9] K. West, B. Zachau-Christiansen, T. Jacobsen, S. Skaarup, Solid State Ionics, 28 (1988) 1128-1131.

[10] M.M. Doeff, Y.P. Ma, S.J. Visco, L.C. Dejonghe, J Electrochem Soc, 140 (1993) L169-L170.

[11] M.M. Doeff, S.J. Visco, Y.P. Ma, M. Peng, L. Ding, L.C. Dejonghe, Electrochim Acta, 40 (1995) 2205-2210.

[12] W. Fischer, Solid State Ionics, 3-4 (1981) 413-424.

[13] B.L. Ellis, L.F. Nazar, Curr Opin Solid St M, 16 (2012) 168-177.

[14] T. Oshima, M. Kajita, A. Okuno, Int J Appl Ceram Tec, 1 (2004) 269-276.

[15] A. Kita, K. Takashima, E. Nomura, K. Matsui, H. Kagawa, S. Iijima, J Electrochem Soc, 134 (1987) C409-C409.

[16] Y.F.Y. Yao, J.T. Kummer, J Inorg Nucl Chem, 29 (1967) 2453-2475.

[17] K.M. Abraham, R.D. Rauh, S.B. Brummer, Electrochim Acta, 23 (1978) 501-507.

[18] P.G. Bruce, L.J. Hardwick, K.M. Abraham, Mrs Bull, 36 (2011) 506-512.

[19] H.L. Pan, Y.S. Hu, L.Q. Chen, Energ Environ Sci, 6 (2013) 2338-2360.

[20] M.D. Slater, D. Kim, E. Lee, C.S. Johnson, Adv Funct Mater, 23 (2013) 947-958.

[21] D. Kundu, E. Talaie, V. Duffort, L.F. Nazar, Angewandte Chemie, 54 (2015) 3431-3448.

[22] A. Ponrouch, D. Monti, A. Boschin, B. Steen, P. Johansson, M.R. Palacin, J Mater Chem A, 3 (2015) 22-42.

[23] M. Sawicki, L.L. Shaw, Rsc Adv, 5 (2015) 53129-53154.

[24] L.P. Wang, L.H. Yu, X. Wang, M. Srinivasan, Z.C.J. Xu, J Mater Chem A, 3 (2015) 9353-9378.

[25] A. Fukunaga, T. Nohira, R. Hagiwara, K. Numata, E. Itani, S. Sakai, K. Nitta, J Appl Electrochem, 46 (2016) 487-496.

[26] P.A. Nelson, K.G. Gallagher, I. Bloom, D.W. Dees, *Modeling the Performance and Cost of Lithiumion Batteries for Electric Vehicles Chemical Sciences and Engineering Division*, Argonne National Laboratory, ANL-11/32, Argonne, IL USA, (2011). [27] A. Ponrouch, R. Dedryvere, D. Monti, A.E. Demet, J.M.A. Mba, L. Croguennec, C. Masquelier, P. Johansson, M.R. Palacin, Energ Environ Sci, 6 (2013) 2361-2369.

[28] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Nat Mater, 8 (2009) 621-629.

[29] B. Scrosati, J. Garche, J Power Sources, 195 (2010) 2419-2430.

[30] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.M. Tarascon, Nat Mater, 11 (2012) 19-29.

[31] K. Xu, Chem Rev, 114 (2014) 11503-11618.

[32] S.G. Cull, J.D. Holbrey, V. Vargas-Mora, K.R. Seddon, G.J. Lye, Biotechnol Bioeng, 69 (2000) 227-233.

[33] G. Nagasubramanian, K. Fenton, Electrochim Acta, 101 (2013) 3-10.

[34] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, Energ Environ Sci, 4 (2011) 3243-3262.

[35] S.W. Kim, D.H. Seo, X.H. Ma, G. Ceder, K. Kang, Adv Energy Mater, 2 (2012) 710-721.

[36] M.R. Palacin, Chem Soc Rev, 38 (2009) 2565-2575.

[37] H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, Y. Miyazaki, Chem Lett, 29 (2000) 922-923.

[38] B. Garcia, S. Lavallee, G. Perron, C. Michot, M. Armand, Electrochim Acta, 49 (2004) 4583-4588.

[39] M. Galinski, A. Lewandowski, I. Stepniak, Electrochim Acta, 51 (2006) 5567-5580.

[40] A. Lewandowski, A. Swiderska-Mocek, J Power Sources, 194 (2009) 601-609.

[41] H. Matsumoto, H. Sakaebe, K. Tatsumi, J Power Sources, 146 (2005) 45-50.

[42] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, A. Usami, Y. Mita, N. Kihira, M. Watanabe, N. Terada, J Phys Chem B, 110 (2006) 10228-10230.

[43] G.B. Appetecchi, M. Montanino, A. Balducci, S.F. Lux, M. Winter, S. Passerini, J Power Sources, 192 (2009) 599-605.

[44] C.S. Ding, T. Nohira, K. Kuroda, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, S. Inazawa, J Power Sources, 238 (2013) 296-300.

[45] S.A.M. Noor, P.C. Howlett, D.R. MacFarlane, M. Forsyth, Electrochim Acta, 114 (2013) 766-771.

[46] J.S. Moreno, G. Maresca, S. Panero, B. Scrosati, G.B. Appetecchi, Electrochem Commun, 43 (2014) 1-4.

[47] M. Forsyth, H. Yoon, F.F. Chen, H.J. Zhu, D.R. MacFarlane, M. Armand, P.C. Howlett, J Phys Chem C, 120 (2016) 4276-4286.

[48] K. Matsumoto, Y. Okamoto, T. Nohira, R. Hagiwara, J Phys Chem C, 119 (2015) 7648-7655.

[49] K. Matsumoto, T. Hosokawa, T. Nohira, R. Hagiwara, A. Fukunaga, K. Numata, E. Itani, S. Sakai, K. Nitta, S. Inazawa, J Power Sources, 265 (2014) 36-39.

[50] C. Ding, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, Electrochim Acta, 176 (2015) 344-349.

[51] H. Yoon, H.J. Zhu, A. Hervault, M. Armand, D.R. MacFarlane, M. Forsyth, Phys Chem Chem Phys, 16 (2014) 12350-12355.

[52] L.G. Chagas, D. Buchholz, L.M. Wu, B. Vortmann, S. Passerini, J Power Sources, 247 (2014) 377-383.

[53] D. Kumar, S.A. Hashmi, Solid State Ionics, 181 (2010) 416-423.

[54] D. Monti, E. Jónsson, M.R. Palacin, P. Johansson, J Power Sources, 245 (2014) 630-636.

[55] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem, 3 (2001) 156-164.

[56] K.D. Kreuer, A. Fuchs, M. Ise, M. Spaeth, J. Maier, Electrochim Acta, 43 (1998) 1281-1288.

[57] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Inorg Chem, 35 (1996) 1168-1178.

[58] K. Xu, M.S. Ding, S.S. Zhang, J.L. Allen, T.R. Jow, J Electrochem Soc, 150 (2003) A161-A169.

[59] A. Guerfi, M. Dontigny, P. Charest, M. Petitclerc, M. Lagace, A. Vijh, K. Zaghib, J Power Sources, 195 (2010) 845-852.

[60] R.S. Kuhnel, A. Balducci, J Phys Chem C, 118 (2014) 5742-5748.

[61] S. Menne, R.S. Kuhnel, A. Balducci, Electrochim Acta, 90 (2013) 641-648.

[62] S. Wilken, S.Z. Xiong, J. Scheers, P. Jacobsson, P. Johansson, J Power Sources, 275 (2015) 935-942.

[63] M. Montanino, M. Moreno, M. Carewska, G. Maresca, E. Simonetti, R. Lo Presti, F. Alessandrini, G.B. Appetecchi, J Power Sources, 269 (2014) 608-615.

[64] T. Vogl, S. Menne, A. Balducci, Phys Chem Chem Phys, 16 (2014) 25014-25023.

[65] B.B. Yang, C.H. Li, J.H. Zhou, J.H. Liu, Q.L. Zhang, Electrochim Acta, 148 (2014) 39-45.

[66] T. Sato, T. Maruo, S. Marukane, K. Takagi, J Power Sources, 138 (2004) 253-261.

[67] L. Lombardo, S. Brutti, M.A. Navarra, S. Panero, P. Reale, J Power Sources, 227 (2013) 8-14.

[68] D.A. Stevens, J.R. Dahn, J Electrochem Soc, 147 (2000) 1271-1273.

- [69] G.S. Fulcher, J Am Ceram Soc, 8 (1925) 339-355.
- [70] G.S. Fulcher, J Am Ceram Soc, 8 (1925) 789-794.

[71] G. Tammann, W. Hesse, Z Anorg Allg Chem, 156 (1926) 245-257.

[72] H. Vogel, Phys Z, 22 (1921) 645-646.

[73] M. Kerner, N. Plylahan, J. Scheers, P. Johansson, Phys Chem Chem Phys, 17 (2015) 19569-19581.

[74] S. Seki, Y. Ohno, Y. Kobayashi, H. Miyashiro, A. Usami, Y. Mita, H. Tokuda, M. Watanabe, K. Hayamizu, S. Tsuzuki, M. Hattori, N. Terada, J Electrochem Soc, 154 (2007) A173-A177.

[75] J.K. Kim, A. Matic, J.H. Ahn, P. Jacobsson, J Power Sources, 195 (2010) 7639-7643.

[76] H. Yoon, A.S. Best, M. Forsyth, D.R. MacFarlane, P.C. Howlett, Phys Chem Chem Phys, 17 (2015) 4656-4663.

[77] M.S. Ding, T.R. Jow, J Electrochem Soc, 151 (2004) A2007-A2015.

[78] A. Bhide, J. Hofmann, A.K. Durr, J. Janek, P. Adelhelm, Phys Chem Chem Phys, 16 (2014) 1987-1998.

[79] P. Johansson, L.E. Fast, A. Matic, G.B. Appetecchi, S. Passerini, J Power Sources, 195 (2010) 2074-2076.

[80] P. Johansson, M. Edvardsson, J. Adebahr, P. Jacobsson, J Phys Chem B, 107 (2003) 12622-12627.

[81] B. Fortunat, P. Mirone, G. Fini, Spectrochimica Acta, A 27 (1971) 1917-1927.

[82] K.L. Dorris, J.E. Boggs, A. Danti, L.L. Altpeter, J Chem Phys, 46 (1967) 1191-1193.

[83] J.R. Durig, G.L. Coulter, D.W. Wertz, J Mol Spectrosc, 27 (1968) 285-295.

[84] J.L. Allen, O. Borodin, D.M. Seo, W.A. Henderson, J Power Sources, 267 (2014) 821-830.

[85] B. Klassen, R. Aroca, M. Nazri, G.A. Nazri, J Phys Chem B, 102 (1998) 4795-4801.

[86] S.A. Hyodo, K. Okabayashi, Electrochim Acta, 34 (1989) 1557-1561.

[87] D. Battisti, G.A. Nazri, B. Klassen, R. Aroca, J Chem Phys, 97 (1993) 5826-5830.

[88] J.C. Lassegues, J. Grondin, C. Aupetit, P. Johansson, J Phys Chem A, 113 (2009) 305-314.

[89] M. Herstedt, M. Smirnov, P. Johansson, M. Chami, J. Grondin, L. Servant, J.C. Lassegues, J Raman Spectrosc, 36 (2005) 762-770.

[90] J.C. Lassegues, J. Grondin, D. Talaga, Phys Chem Chem Phys, 8 (2006) 5629-5632.

[91] A. Boschin, P. Johansson, Electrochim Acta, 175 (2015) 124-133.

[92] P.M. Wang, A. Anderko, Fluid Phase Equilibr, 186 (2001) 103-122.

[93] C.X. Peng, L. Yang, S.H. Fang, J.X. Wang, Z.X. Zhang, K. Tachibana, Y. Yang, S.Y. Zhao, J Appl Electrochem, 40 (2010) 653-662.

[94] M. Holzapfel, C. Jost, A. Prodi-Schwab, F. Krumeich, A. Wursig, H. Buqa, P. Novak, Carbon, 43 (2005) 1488-1498.

[95] L. Zhao, J.I. Yamaki, M. Egashira, J Power Sources, 174 (2007) 352-358.

[96] H. Srour, H. Rouault, C. Santini, J Electrochem Soc, 160 (2013) A66-A69.

[97] W. Garcia, M. Armand, J Power Sources, 132 (2004) 206-208.

[98] C.X. Peng, L. Yang, Z.X. Zhang, K. Tachibana, Y. Yang, S.Y. Zhao, Electrochim Acta, 53 (2008) 4764-4772.

[99] C.X. Peng, L. Yang, Z.X. Zhang, K.H. Tachibana, Y. Yang, J Power Sources, 173 (2007) 510-517.

[100] M. Nadherna, R. Dominko, D. Hanzel, J. Reiter, M. Gaberscek, J Electrochem Soc, 156 (2009) A619-A626.

[101] J. Mun, T. Yim, C.Y. Choi, J.H. Ryu, Y.G. Kim, S.M. Oh, Electrochem Solid St, 13 (2010) A109-A111.

[102] E. Cho, J. Mun, O.B. Chae, O.M. Kwon, H.T. Kim, J.H. Ryu, Y.G. Kim, S.M. Oh, Electrochem Commun, 22 (2012) 1-3.

[103] R.S. Kuhnel, M. Lubke, M. Winter, S. Passerini, A. Balducci, J Power Sources, 214 (2012) 178-184.

[104] A. Ponrouch, E. Marchante, M. Courty, J.M. Tarascon, M.R. Palacin, Energ Environ Sci, 5 (2012) 8572-8583.

[105] I.A. Shkrob, T.W. Marin, Y. Zhu, D.P. Abraham, J Phys Chem C, 118 (2014) 19661-19671.

[106] Y. Katayama, M. Yukumoto, T. Miura, Electrochem Solid St, 6 (2003) A96-A97.

[107] M. Egashira, T. Kiyabu, I. Watanabe, S. Okada, J. Yamaki, Electrochemistry, 71 (2003) 1114-1116.

[108] A. Ponrouch, M.R. Palacin, Electrochem Commun, 54 (2015) 51-54.

[109] A. Ponrouch, A.R. Goni, M.R. Palacin, Electrochem Commun, 27 (2013) 85-88.

[110] S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, K. Fujiwara, Adv Funct Mater, 21 (2011) 3859-3867.

[111] M. Shimizu, H. Usui, K. Yamane, T. Sakata, T. Nokami, T. Itoh, H. Sakaguchi, Int J Electrochem Sc, 10 (2015) 10132-10144.

<u>Glossary:</u>

BMImTFSI	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
CV	Cyclic voltammetry
DMC	Dimethyl carbonate
DSC	Differential scanning calorimetry
EC	Ethylene carbonate
EMImTFSI	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
EV	Electric vehicle
FP	Flash point
GCPL	Galvanostatic cycling with potential limitation
НС	Hard carbon
HEV	Hybrid electric vehicle
IL	Ionic liquid
Im	Imidazolium
ІТ	Ignition time

LIB	Lithium-ion battery
РС	Propylene carbonate
Pyr	Pyrrolidinium
Pyr ₁₃ TFSI	N-propyl-N-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide
SET	Self-extinguishing time
SIB	Sodium-ion battery
SN	Solvation number
T _g	Glass transition temperature