



# Towards safer sodium-ion batteries via organic solvent/ionic liquid based hybrid electrolytes



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## HIGHLIGHTS

- The ionic liquid of the hybrid electrolytes improves the general safety.
- The cation solvation shell is modified with the composition of the electrolyte.
- The physical properties are relatively unaltered by addition of up to 20% of IL.
- Half-cells using hard carbon electrodes exhibit good capacities and capacity retentions.

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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 Pyr<sub>13</sub>TFSI, and with the NaTFSI salt providing the Na<sup>+</sup> charge carriers have here been extensively studied. The physico-chemical and electrochemical characterisation includes ionic conductivity, viscosity, density, cation coordination and solvation, various safety measures, and electrochemical stability window (ESW). Hybrid electrolytes with 10–50% 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<sub>0.45</sub>:PC<sub>0.45</sub>:Pyr<sub>13</sub>TFSI<sub>0.10</sub> encouraging results were obtained for IL based electrolytes – ca. 182 mAhg<sup>-1</sup> at C/10 over 40 cycles.

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## 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

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[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<sup>-1</sup> 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<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> cathode was revealed to exhibit a theoretical energy density comparable to graphite//LiFePO<sub>4</sub> 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 NaCrO<sub>2</sub> 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.g. Na<sup>+</sup> or Li<sup>+</sup> 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 wt% (wt.%) of various ILs. LP30 and DMC from Merck (battery grade) were used for safety studies while LiPF<sub>6</sub> and NaPF<sub>6</sub> (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 (Pyr<sub>13</sub>TFSI) (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 H<sub>2</sub>O and 0–5 ppm O<sub>2</sub>. The nomenclature used for all electrolytes is based on the molar ratios for the solvents and ILs e.g. EC<sub>0.45</sub>:PC<sub>0.45</sub>:Pyr<sub>13</sub>TFSI<sub>0.10</sub>. 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 Ref. [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 μm thick aluminium foil (Good-fellow) with a 250 μm doctor-blade and dried at 120 °C under vacuum for 2 h. Once dried, 0.8 cm<sup>2</sup> disk electrodes were cut and pressed at 8 tons. Typically the electrode loading was 2 mg, corresponding to ca. 15 μm 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<sub>x</sub>:PC<sub>x</sub>:Pyr<sub>13</sub>TFSI<sub>(1-2x)</sub>, EC<sub>x</sub>:PC<sub>x</sub>:EMImTFSI<sub>(1-2x)</sub>, and EC<sub>x</sub>:PC<sub>x</sub>:BMImTFSI<sub>(1-2x)</sub>, or more generally 0.8 m NaTFSI in EC<sub>x</sub>:PC<sub>x</sub>:CatTFSI<sub>(1-2x)</sub>, 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 broadband dielectric spectrometer in the frequency range 10<sup>-1</sup> – 10<sup>7</sup> Hz between –10 °C and 60 °C with a step of 10 °C. A constant volume (0.14 cm<sup>3</sup>) 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 N<sub>2</sub> 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.

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