



# An advanced lithium-ion battery based on a nanostructured Sn–C anode and an electrochemically stable LiTFSi–Py<sub>24</sub>TFSI ionic liquid electrolyte

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## ABSTRACT

We report here a detailed impedance analysis of the interface between a selected IL electrolyte, i.e. a solution of lithium N,N-bis(trifluoromethane sulfon) imide in N-n-butyl-N-ethyl pyrrolidinium and a N,N-bis(trifluoromethane sulfon) imide, LiTFSi–Py<sub>24</sub>TFSI, and two electrodes, namely a conventional lithium metal and an advanced nanostructured Sn–C alloy, respectively. We show that the Sn–C alloy, in virtue of a specific formation of a surface protecting film, has an interface much more stable than that of the Li electrode. This favourable property is exploited for using Sn–C as a new anode for the development of an advanced lithium-ion battery based on LiTFSi–Py<sub>24</sub>TFSI as the electrolyte and on olivine LiFePO<sub>4</sub> as the cathode. The results demonstrated that this battery has very promising performances in terms of cycle life and rate capability.

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## 1. Introduction

Lithium-ion batteries have triggered the growth of the consumer electronics market and now are the power sources of choice for a series of popular devices, such as mobile phones, lap-top computers, Mp3s and others [1]. Accordingly, lithium-ion batteries are today produced by billions of units per year. In addition, these batteries are now expected to enter in markets which space beyond the consumer electronic sector. There are various parameters which influence the forecast of the lithium-ion battery market evolution. Among the main drivers we may cite: (i) the concern on global warming, which requires with urgency a much greater share than in present times of clean, renewable sources and (ii) the pressing request of moving from gasoline-powered internal combustion engine cars to low-emission, electric or hybrid vehicles (EVs, HEVs or PHEVs).

However, the implementation of lithium-ion batteries for energy storage and vehicle applications is still hindered by safety concerns associated with the use of large-scale cells. Undesired reactions between the battery components and the common liquid organic electrolytes, triggered by unpredictable events, such as short circuit or local overheating, may lead to exothermic events involving the electrolyte and the electrode materials, which in turn reflect on a rapid increase of the battery temperature and, eventually, on fire or explosion.

Therefore, the use of alternative electrolyte media, having more stable features than the conventional LiPF<sub>6</sub>–carbonate solvent mixtures, is mandatory. Very promising candidates are those based on ionic liquids (ILs), i.e. room temperature molten salts. These salts are practically non-flammable and this is indeed an extraordinary safety asset: the replacement of the conventional, flammable and volatile organic solutions with ionic liquid-based, lithium-ion conducting electrolytes may greatly reduce, if not prevent, the risk of thermal runaways. The use of these advanced electrolytes is expected to provide the lithium battery with the level of safety which is required for their large-scale application in important and strategic markets [2–4].

Among the various possible IL types, those based on the imidazolium (Im) or pyrrolidinium (Py) cations and the N,N-bis(trifluoromethane sulfon) imide (TFSI) anion, have been considered to be the most promising for lithium battery application. Extensive work in this direction is in progress and the testing of ILs as novel electrolyte media for future, safe, lithium batteries is underway in many industrial and academic laboratories worldwide [5–9].

However, optimization of the IL electrolytes structure, as well as clear understanding of their electrochemical properties, are still to be fully achieved. One of the unclear aspects is the thermodynamic and kinetic stability towards electrode materials. Common ILs are expected to be only metastable at low potential, e.g., at the potential of lithium reduction: the cations are sensitive to electron injection, with the subsequent formation of a radical and/or proton elimination. For instance, the archetypal IL cation, EMIM (ethylmethylimidazolium) is easily attacked at the acidic C2 proton with a limitation of its stability when polarized below 1.5 V vs. Li.

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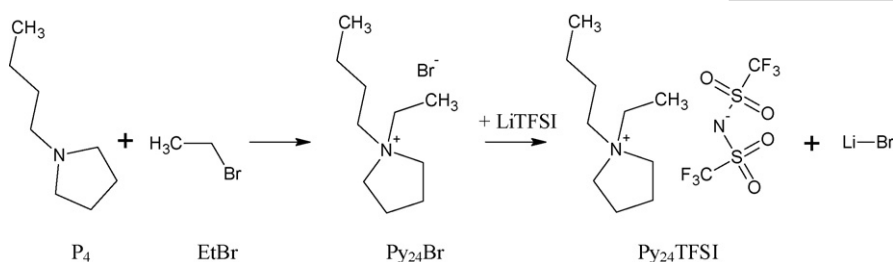
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Thus, the challenge is to widen the cathodic stability without sacrificing the overall IL ionic conductivity. Success has been recently obtained by optimizing the IL cation architecture with the aim of shielding the sites of proton attack. Good examples are systems based on *N-n*-butyl-*N*-ethyl pyrrolidinium (Py<sub>24</sub>) cations having no C-2 acidic protons [6,10,11]. Alternative approaches are directed to the promotion of protective, passivating layers on the electrode surface such as to kinetically widen the IL electrochemical window [12].

The structure of the IL/electrode interfaces is then an aspect which deserves particular attention. In the hope to contribute to its clarification we have undertaken a detailed impedance study of interfacial phenomena in IL-based solutions. In particular, the study reported in this work has been addressed to the interfaces occurring between a selected IL electrolyte (i.e. that formed by a solution of lithium *N,N*-bis(trifluoromethane sulfon) imide in *N-n*-butyl-*N*-ethyl pyrrolidinium cation and a *N,N*-bis(trifluoromethane sulfon) imide anion, LiTFSI-Py<sub>24</sub>TFSI) and two electrodes (i.e. a conventional Li metal and an advanced nanostructured Sn-C alloy, respectively). We show in this paper that the latter, due to the specific formation of a stable surface protecting film, has optimized interfacial properties. These beneficial properties are exploited for the development of a new type of lithium-ion battery.

## 2. Experimental

*N-n*-butyl-*N*-ethyl pyrrolidinium *N,N*-bis(trifluoromethane sulfon) imide, here simply noted as Py<sub>24</sub>TFSI, was synthesized according to the following scheme [6].



The synthesis was carried out by mixing 1-butylpyrrolidine (P<sub>4</sub>) and 1-bromoethane (EtBr) in acetonitrile and stirring at 60 °C for two days. The solvent was then evaporated, leaving a solid product (Py<sub>24</sub>Br) which was purified by recrystallization in an acetonitrile/ethanol mixture.

The so formed Py<sub>24</sub>Br was mixed with a TFSI aqueous solution and stirred at room temperature for 2 h to lead to the formation of the Py<sub>24</sub>TFSI IL. The IL phase was spontaneously separated from the aqueous phase and repeatedly rinsed with fresh water to remove residual traces of LiBr. The complete removal of the bromides was ascertained by silver nitrate test. Organic and water residues were then removed by consecutive treatments with activated carbon and active acidic alumina. The final product was dried by two consecutive, under vacuum, heat treatments, i.e. at 80 °C for 12 h and then at 120 °C for 24 h. The so-obtained TFSI IL solution had a very low water content, i.e. few tenths of ppm, as determined by Karl Fischer analysis. The Py<sub>24</sub>TFSI was finally mixed with the LiTFSI salt, to obtain a homogenous solution at a preferred concentration of 0.2 m LiTFSI-Py<sub>24</sub>TFSI.

The synthesis of the Sn-C nanostructured composite material was described in details in previous works [13,14]. Basically, the synthesis involved the infiltration of an organometallic tin precursor in an organic Resorcinol (benzene-1,3-diol)-formaldehyde (methanal) gel, followed by calcination under argon. LiFePO<sub>4</sub>, kindly provided by Dr. Margret Wohlfahrt-Mehrens of ZSW, Ulm, Germany, was previously tested in our laboratory [15].

The electrodes were prepared as 10 mm diameter thin films by doctor-blade deposition of Sn-C on a copper substrate (anode) and of LiFePO<sub>4</sub> on an aluminium substrate (cathode). The depositing slurries were formed of 80% active material, 10% PVdF 6020, Solvay Solef (binder) and 10% SP carbon (electronic support). The average loading of the active materials was 2 and 4 mg cm<sup>-2</sup> (versus geometric area) for the anode and for the cathode, respectively. Prior testing, the Sn-C anode was pre-treated by using a procedure originally set in our laboratory that basically involves a direct contact with an electrolyte-wetted metallic lithium foil, this producing *in situ* the formation of a stable solid electrolyte interface (SEI) on the electrode surface [16].

The electrochemical spectroscopy analysis (EIS) was carried out using cells based on: (i) Li electrodes in a 0.2 m LiTFSI-Py<sub>24</sub>TFSI electrolyte solution soaked in a Whatman™ separator and (ii) Sn-C in the same electrolyte solution. The EIS was performed by submitting the cell to a 10 mV signal in the 100 kHz to 10 mHz frequency range using a Frequency Response Analyzer (FRA) Schlumberger Solartron model 1260 coupled with EG&G Princeton Applied Research model 362 potentiostat. The impedance response was evaluated by using the Non-Linear Least-Square (NLLSQ) fit software developed by Boukamp [17]. To adequately represent both the Li/LiTFSI-Py<sub>24</sub>TFSI and the Sn-C/LiTFSI-Py<sub>24</sub>TFSI interfaces, an equivalent circuit taking into account the contributions of the electrolyte (*R<sub>e</sub>*), of the surface film (*R<sub>1</sub>Q<sub>1</sub>* in parallel), of the charge transfer (*R<sub>2</sub>Q<sub>2</sub>* in parallel) and, finally of the cell geometric capacitance (*Q<sub>c</sub>*), was used. The experimental and the circuit data matched quite well, with a chi-square factor less than 10<sup>-4</sup> determined by non-linear last square analysis using Boukamp's program [17]. Such a low value of the chi factor is considered an

acceptable prerequisite to the validity of the proposed circuit model.

The stability domain of the 0.2 m LiTFSI-Py<sub>24</sub>TFSI electrolyte solution was determined in cells using both SP carbon and pre-treated Sn-C as working electrodes and a lithium foil as reference electrode. Each cell was scanned in a 0.1–3.0 V voltage range at a scan rate of 0.2 mV s<sup>-1</sup> by using a PAR 362 potentiostat.

The lithium-ion battery was formed by coupling the pre-treated Sn-C anode with a LiFePO<sub>4</sub> cathode in the 0.2 m LiTFSI-Py<sub>24</sub>TFSI electrolyte solution soaked in a Whatman™ separator. The battery was cycled galvanostatically at various rates (1 C current 0.22 A cm<sup>-2</sup> g<sup>-1</sup> respect to the LiFePO<sub>4</sub> active mass), using a Maccor Series 4000 Battery Test System as the driving and controlling instrument.

## 3. Results and discussion

The electrolyte used in this work was obtained by dissolving LiTFSI in the Py<sub>24</sub>TFSI ionic liquid to form a 0.2 mol kg<sup>-1</sup> solution. Previous work in our laboratory [6] has shown that this is the concentration which gives the best conductivity value. Increasing the concentration results in an increase in viscosity and thus, in a drop in conductivity. Indeed, this solution has at room temperature a lithium-ion conductivity of 1.3 × 10<sup>-3</sup> S cm<sup>-1</sup>, i.e. a value suitable for battery applications. Having in mind that the electrochemical stability window (ESW) plays an important role in the practical

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