



An advanced lithium-ion battery based on a nanostructured Sn–C anode and an electrochemically stable LiTFSi–Py₂₄TFSI ionic liquid electrolyte

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ARTICLE INFO

Article history:

Received 23 June 2009

Received in revised form 27 July 2009

Accepted 29 July 2009

Available online 5 August 2009

Keywords:

Lithium–tin alloy

Ionic liquid

Lithium-ion

Battery

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 sulfonyl) imide in N-n-butyl-N-ethyl pyrrolidinium and a N,N-bis(trifluoromethane sulfonyl) imide, LiTFSi–Py₂₄TFSI, 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–Py₂₄TFSI as the electrolyte and on olivine LiFePO₄ 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 LiPF₆–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 sulfonyl) 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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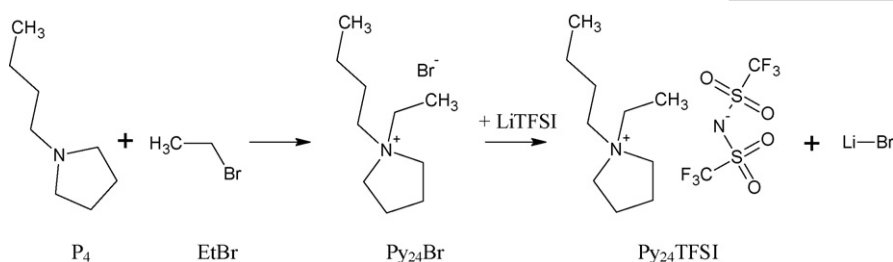
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Thus, the challenge is to widen the cathodic stability without sacrificing the overall IL ionic conductivity. Success has been recently obtained by optimizing the IL cation architecture with the aim of shielding the sites of proton attack. Good examples are systems based on *N-n*-butyl-*N*-ethyl pyrrolidinium (Py₂₄) 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-Py₂₄TFSI) 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 Py₂₄TFSI, was synthesized according to the following scheme [6].



The synthesis was carried out by mixing 1-butylpyrrolidine (P₄) and 1-bromoethane (EtBr) in acetonitrile and stirring at 60 °C for two days. The solvent was then evaporated, leaving a solid product (Py₂₄Br) which was purified by recrystallization in an acetonitrile/ethanol mixture.

The so formed Py₂₄Br was mixed with a TFSI aqueous solution and stirred at room temperature for 2 h to lead to the formation of the Py₂₄TFSI 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 Py₂₄TFSI was finally mixed with the LiTFSI salt, to obtain a homogenous solution at a preferred concentration of 0.2 m LiTFSI-Py₂₄TFSI.

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. LiFePO₄, 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 LiFePO₄ 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⁻² (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-Py₂₄TFSI 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-Py₂₄TFSI and the Sn-C/LiTFSI-Py₂₄TFSI interfaces, an equivalent circuit taking into account the contributions of the electrolyte (R_e), of the surface film (R_1Q_1 in parallel), of the charge transfer (R_2Q_2 in parallel) and, finally of the cell geometric capacitance (Q_c), was used. The experimental and the circuit data matched quite well, with a chi-square factor less than 10⁻⁴ determined by non-linear least 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-Py₂₄TFSI 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 0.01–3.0 V voltage range at a scan rate of 0.2 mV s⁻¹ by using a PAR 362 potentiostat.

The lithium-ion battery was formed by coupling the pre-treated Sn-C anode with a LiFePO₄ cathode in the 0.2 m LiTFSI-Py₂₄TFSI electrolyte solution soaked in a Whatman™ separator. The battery was cycled galvanostatically at various rates (1 C current 0.22 A cm⁻² g⁻¹ respect to the LiFePO₄ 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 Py₂₄TFSI ionic liquid to form a 0.2 mol kg⁻¹ 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 × 10⁻³ S cm⁻¹, i.e. a value suitable for battery applications. Having in mind that the electrochemical stability window (ESW) plays an important role in the practical

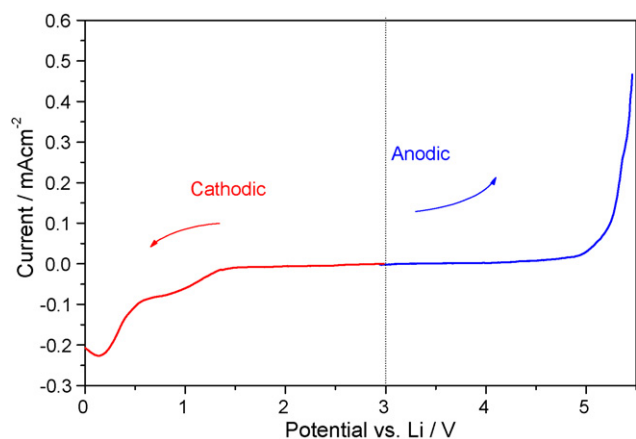


Fig. 1. Current–voltage curve of a Super P electrode in a lithium cell. Electrolyte: 0.2 m LiTFSI-Py₂₄TFSI solution; reference electrode: Li metal. Room temperature.

evaluation of any electrolyte, we have then proceeded to determine this important parameter for the LiTFSI-Py₂₄TFSI solution here under study.

Fig. 1 shows both the anodic and the cathodic stability test in the form of current–voltage plots of a Super P carbon electrode in a cell using the LiTFSI-Py₂₄TFSI solution as the electrolyte and lithium metal as the counter and the reference electrode [18]. We can observe that the value of the voltage at the current onset in the anodic region, which is associated with the anodic decomposition limit of the LiTFSI-Py₂₄TFSI electrolyte, extends to over 4.5 V vs. Li. This wide anodic stability may be accounted for by considering the strong coordination existing between the Li cations and the TFSI anions [19], which results in an high overpotential for the oxidation of the TFSI anions.

More intriguing is the voltammetry response in the cathodic region which reveals the occurrence of various electrochemical events. Based from the trend of the figure, we may assume that the IL electrolyte solution starts to decompose at about 1.5 V vs. Li. Therefore, although stabilized at the Py₂₄ cathode side by the removal of the C2 acidic protons, this solution still suffers by a severe cathodic decomposition, very likely associated with the reduction of the TFSI anion. Data reported in the literature tend to support this interpretation [20].

The broad peaks below 1.5 V vs. Li might be ascribed to a not yet totally clear, additional decomposition processes of the solution, although side processes associated with the lithium insertion in the SP electrode component (see Section 2) cannot be excluded. The multi-step decomposition process results in the precipitation of decomposition products on the electrode surface, to finally form a protecting, SEI film, which in turn may kinetically improve the electrolyte stability. Indeed, the area of the low-voltage peaks significantly decreases in following voltammetry scans (data not reported), this confirming the occurrence of the SEI and its efficiency in kinetically prevent further decomposition of the IL solution [20].

Therefore, due to the occurrence of the SEI formation, we may assume that the cathodic stability of the LiTFSI-Py₂₄TFSI solution may be kinetically extended well below 1,5 V. To further investigate this assumption, we have analyzed the characteristics of the interface establishing in the lithium metal electrode–LiTFSI-Py₂₄TFSI solution system. The study was carried out by determining the time evolution of the impedance response of a symmetrical Li/LiTFSI-Py₂₄TFSI/Li cell kept under open circuit conditions. The impedance response was analyzed by using a common approach based on the definition of an equivalent circuit that takes into account all possible contributions to the impedance of the cell under test [21].

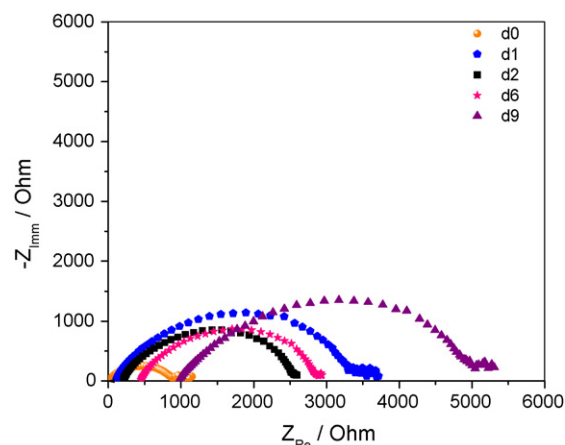


Fig. 2. Time evolution of the impedance response of a Li/LiTFSI-Py₂₄TFSI/Li cell frequency range: 100 kHz to 10 mHz. Applied signal amplitude: 5 mV. Room temperature.

Fig. 2 shows the results. The impedance evolves with the expected semicircle trend, where, in accordance with the circuit analysis, the intercept of the high-frequency semicircle with the real axis gives the value of the bulk electrolyte resistance, R_e , while its amplitude provides the resistance of the interface with the lithium electrode. Clearly, the interfacial resistance, which is mainly associated with the combination of surface film resistance (R_1) and charge transfer resistance (R_2), increases consistently by time, reaching values of the order of several ohms in the round of few days of storage. This behavior suggests a continuous decomposition of the electrolyte and thus, the results of Fig. 2 demonstrate that the LiTFSI-Py₂₄TFSI electrolyte, although modified with respect to standard, imidazolium-based IL systems, is still not suitable to be used in connection with a Li metal electrode.

In view of battery application, a different, more stable, anode material has to be used. We focused our attention on a Sn–C nanocomposite electrode which, as originally demonstrated in our laboratory [13,14], offers a series of important properties, which include: (i) a high specific capacity, i.e. of the order of 400–500 mAh g⁻¹; (ii) a high rate capability, i.e. exceeding 5 C; (iii) a long cycle life, i.e. of several hundred cycles and (iv) an excellent chemical stability.

The operational voltage of Sn–C in a lithium cell is centered around 0.4 V vs. Li [13,14] and thus, apparently, also this electrode is outside the stability domain of the electrolyte. However, one has to keep in mind that the electrochemical decomposition of the electrolyte depends upon the type of the testing electrode and in addition, that the decomposition may be influenced by the occurrence of interface phenomena, such as surface passivating film formation. These conditions apply to the case of the Sn–C electrode which, beside been different than carbon, is also supplied by a stable SEI [16].

Fig. 3 shows the cathodic scan response of a cell formed by using pre-treated Sn–C as the working electrode, LiTFSI-Py₂₄TFSI solution as the electrolyte and lithium metal as the counter and reference electrode. We notice only a broad peak in the 0.7–0.1 V region (quite likely associated with the Sn–Li alloying, see (1)) while there is no evidence of the 1.5 V peak observed in the case of the scan run with a Super P working electrode, compare Fig. 1. This evidence supports the assumption that the Sn–C electrode, in virtue of its pre-formed SEI, may indeed prevent early decomposition of the LiTFSI-Py₂₄TFSI solution and thus, that it behaves as a quite stable electrode in this IL-based media.

To further investigate the Sn–C/LiTFSI-Py₂₄TFSI interfacial properties, an impedance spectroscopy was run on a symmetrical

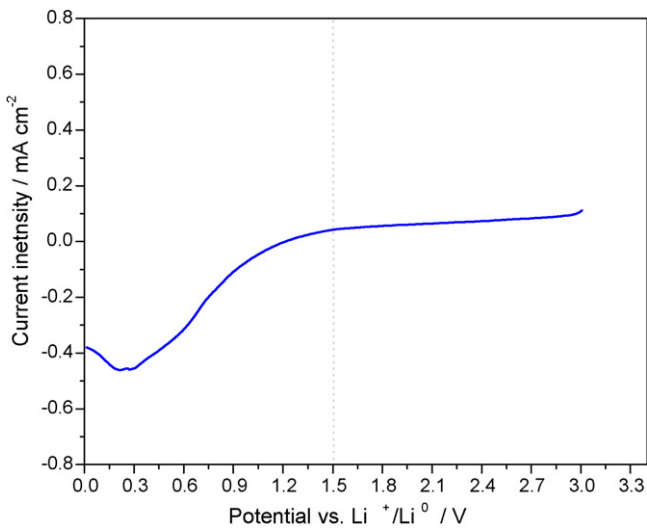


Fig. 3. Cathodic scan of a pre-treated Sn–C electrode in a lithium cell. Electrolyte: 0.2 m LiTFSI-Py₂₄TFSI solution; reference electrode: Li metal. Room temperature.

Sn–C/LiTFSI-Py₂₄TFSI/Sn–C cell kept under open circuit conditions. Fig. 4A and B shows the time evolution of the impedance response measured in the course of the first hour and of the initial nine days of contact, respectively. We may describe the overall response as formed by a small, high-frequency semicircle extending over about 10 Ω. Quite likely, this semicircle reflects the resistance R_1 of the SEI formed by the pre-treatment on the Sn–C surface, although an additional contribution from an initial, modest decomposition of the ionic liquid solution, cannot be excluded. This high-frequency, small semicircle is followed by another one evolving in the medium-low frequency range with an initial amplitude of about 20 Ω. This second semicircle may be associated with the charge transfer resistance, R_2 related to the electrode process, i.e.:



Fig. 4C shows the time evolution of the values of the electrolyte resistance, R_e , of the charge transfer resistance R_2 and of the interfacial resistance R_1 , respectively, extracted by fitting the response with a program based on the quoted equivalent circuit (see Section 2). The surface of the electrode is modified by the evolving formation of the passivating film and this explains the increase of the charge transfer resistance. Particularly interesting is the trend of the interfacial resistance R_1 , which remains almost unchanged for over nine days. This in turn strongly suggests that the pre-induced SEI on the electrode surface is thin and does not consistently grow by time and thus, that it kinetically prevents the electrolyte decomposition.

A confirmation of the stability of the pre-treated Sn–C electrode is provided by Fig. 5, which shows the photographic images of a Sn–C sample immersed in the LiTFSI-Py₂₄TFSI ionic liquid solution. The figure compares the appearance of the sample, as well as of the over floating IL solution, at the initial time of contact and after 1 month of continuous immersion. No sign of deterioration and/or attack of the sample is detected and the ionic liquid remains clear for all the duration of the test. A similar visual experiment, carried out under the same conditions, but using as testing material a Li metal sample, evidenced massive deterioration after only few days of contact in the same IL electrolyte solution [6]. The evolution of the impedance response and the visual test concur to evidence that Sn–C is a much more stable electrode than Li metal in this solution.

Indeed, the difference in stability between the two electrode materials is clearly demonstrated by comparing the time evolution

of their respective impedance responses, see Fig. 6. The difference is dramatic: while the overall interfacial resistance of Sn–C remains stable at the low value of about 300 Ω (compare also Fig. 4B), that of Li metal is two orders of magnitude higher (compare also Fig. 2).

All the above results demonstrate that the pre-treated Sn–C electrode is a very promising candidate for IL-based, lithium battery application. To confirm this assumption, we have assembled and tested a new type of lithium-ion battery using Sn–C as the anode, LiTFSI-Py₂₄TFSI ionic liquid solution as the electrolytes and LiFePO₄ as the cathode. The expected electrochemical process of this battery is the lithium transfer from the cathode (evolving on a flat 3.45 V profile [22]) to the anode (evolving on a sloping voltage

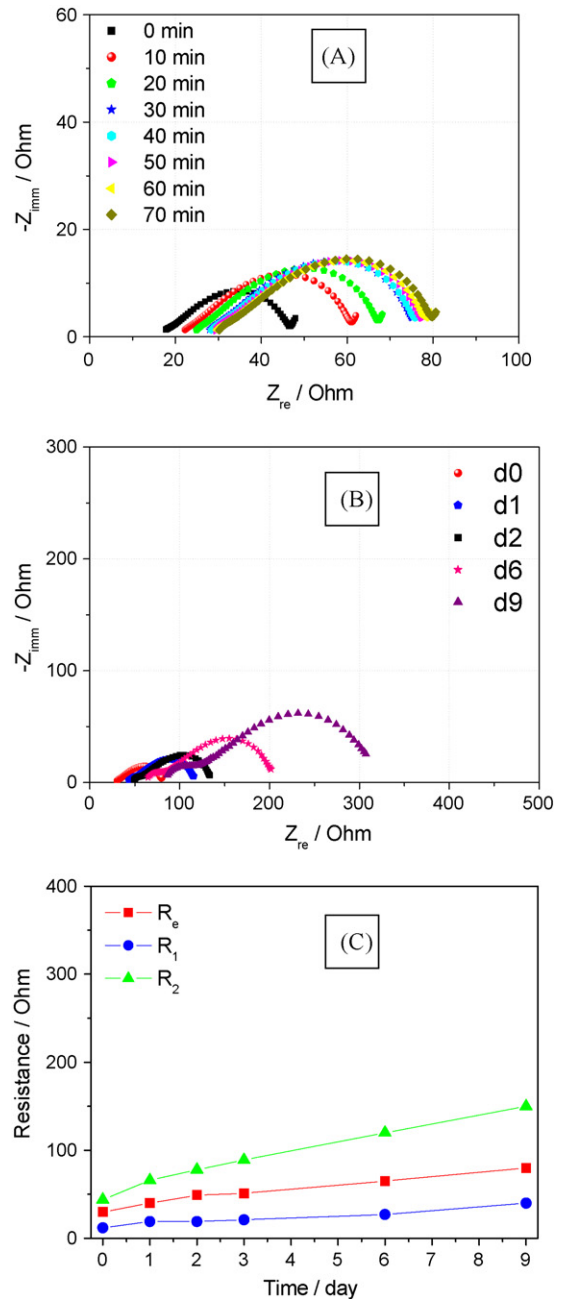


Fig. 4. Time evolution of the impedance spectra of a symmetrical SnC/0.2mLiTFSI-Py₂₄TFSI/SnC cell under open circuit conditions. The figure shows overall impedance responses in the course of the first hour (A) and of nine days (B) after cell assembling and related dependence of the resistances with time. R_e = electrolyte resistance; R_1 = interfacial resistance and R_2 = charge transfer resistance. Frequency range: 75 kHz to 1 Hz. d = day. Applied signal amplitude: 5 mV. Room temperature.

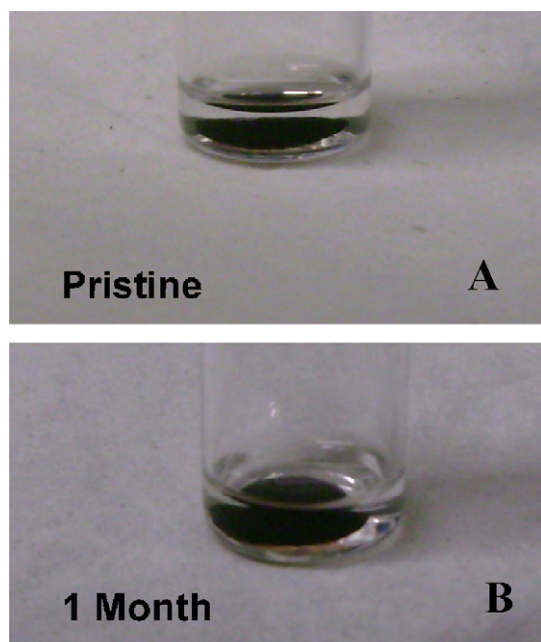
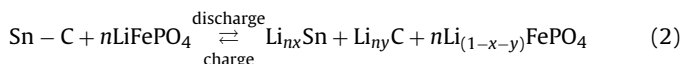


Fig. 5. Photographic images of a pre-treated Sn-C sample immersed in the 0.2mLiTFSI-Py₂₄TFSI ionic liquid solution at the initial time of contact (A) and after 1 month of continuous immersion (B).

profile centred on 0.5 V) and vice versa:



Since cathode-limited, the maximum capacity of the battery is 170 mAh g^{-1} . The battery was tested by galvanostatic charge–discharge cycles and Fig. 7 shows the results in terms of voltage profiles (A) and of cycle life under different charge–discharge rates, i.e. C/10, C/7 and C/5 rates (B). The voltage profiles, which evolve within an operating voltage centred around 3 V, match those expected by the combination of the Sn-C and LiFePO₄ voltage evolutions.

The capacity delivery, however, is lower than the theoretical 170 mAh g^{-1} , reaching stable values of the order of 140 mAh g^{-1} (i.e. 82% of theoretical) at C/10 and 112 mAh g^{-1} (i.e. 66% of theoretical) at C/5, see Fig. 7B. The difficulty in achieving full capacity may be due to a series of factors, which mainly include: (i) a relatively high viscosity of the ionic liquid solution that affects the ionic

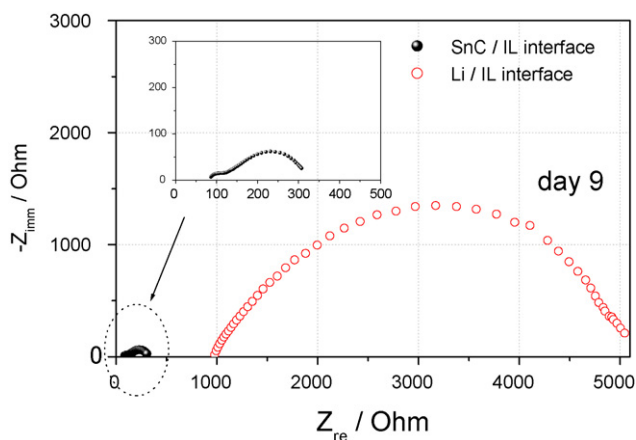


Fig. 6. Comparison between the impedance spectra of SnC/0.2mLiTFSI-Py₂₄TFSI/SnC and of Li/0.2mLiTFSI-Py₂₄TFSI/Li cells after nine days of storage under open circuit conditions.

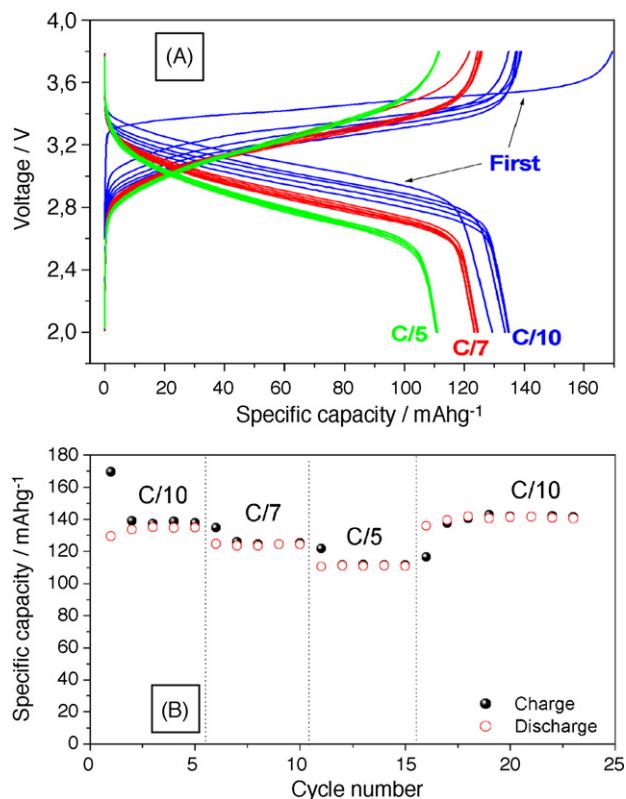


Fig. 7. Typical cell voltage profiles vs. specific capacity (A) and specific capacity vs. cycle number (B) of the SnC/0.2mLiTFSI-Py₂₄TFSI/LiFePO₄ lithium-ion battery at room temperature and at C/10, C/7 and C/5 rates.

conductivity, thus ultimately enhancing the ohmic drops, and (ii) a low wettability of the electrodes that in turn prevents full utilization of the active materials, thus ultimately limiting the overall exchanged charge. These drawbacks are expected to be mitigated by rising the temperature of operation and, effectively, by testing the battery at temperatures of the order of $50\text{--}60^\circ\text{C}$, a net increase in the reversible capacity was observed (data not shown).

4. Conclusion

Ionic liquid solutions are very appealing electrolyte media for the development of advanced, safe lithium batteries. However, their application may be somewhat limited by the poor cathode stability limit of the electrolyte that in principle prevents the use of electrodes with operating voltages lower than 1.5 V vs. Li. We show in this work that even modification of the IL architecture, such as the elimination of the easily attacked acidic C2 protons, apparently is not sufficient to assure stable operation of low-voltage electrodes. The cathodic limit issue may be circumvented by inducing kinetic stability with the formation of protective films on the electrode surface. We report here a valid example as provided by a Sn-C electrode modified by coating its surface by a stable SEI. The operational voltage this electrode in a lithium cell is around 0.4 V vs. and thus, in principle it should not be suitable for operation in IL-based media. However, we show that the SEI confers a practical stable behavior. This approach, here exemplified with the case of the Sn-C electrode, may of course be extended to other low-voltage electrodes, which then can be used as valid anodes for the development of advanced, IL-based, lithium-ion batteries. We report here an example based on the combination of the Sn-C anode with a LiFePO₄ cathode in the LiTFSI-Py₂₄TFSI ionic liquid electrolyte solution. Among other advantages, this battery benefits also by the use of a cathode material which is very appealing in virtue of its favourable characteristics

in terms of cost, specific capacity and environmental compatibility [23]. Although still not totally optimized in terms of structures and temperature of operation, this battery shows very promising performances and may be regarded as a first, valid demonstration of the feasibility of using ionic liquid electrolytes for the progress of the lithium-ion battery technology.

Acknowledgments

This work has been carried out with the financial support of the Italian Ministry of University and Research under a PRIN 2007 project. The authors wish to thank Dr. Margret Wohlfahrt-Mehrens of Zentrum für Sonnenenergie- und Wasserstoff-Forschung, in Ulm, Germany for kindly providing the LiFePO_4 cathode samples.

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