

Short communication

Advanced, lithium batteries based on high-performance composite polymer electrolytes

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Received 26 June 2006; received in revised form 14 July 2006; accepted 18 July 2006

Available online 1 September 2006

Abstract

Progress in lithium battery technology may be achieved by passing from a conventional liquid electrolyte structure to a solid-state, polymer configuration. In this prospect, great R&D effort has been devoted to the development of suitable lithium conducting polymer electrolytes. In previous papers [F. Croce, L. Settimi, B. Scrosati, *Electrochem. Commun.* 8 (2006) 364 [1]; F. Croce, S. Sacchetti, B. Scrosati, *J. Power Sources*, in press [2]], we have shown that composite membranes based on blends between poly(ethylene oxide) and lithium salts with the dispersion of functionalized ZrO₂ ceramic filler, have unique transport and interfacial properties. In this paper, we complete the study of these advanced polymer electrolytes by evaluating their use in rechargeable lithium batteries. The results confirm the practical interest of these electrolytes which appear to be suitable for the fabrication of batteries directed to application in emerging technologies, such as those associated to hybrid and electric vehicles. © 2006 Elsevier B.V. All rights reserved.

Keywords: Lithium; Battery; Polymer; Electrolyte; Ceramic filler; Composites

1. Introduction

Lithium batteries are acquiring a leading role in various important markets with particular impact on that of the consumer electronics and, in prospect, on that of electric or hybrid cars. However, considering the evolution of these markets and their associated energy and power demands, new and improved battery configurations are requested. Among the various approaches presently followed to achieve this goal that based on the passage from a conventional liquid electrolyte structure to an advanced polymer electrolyte configuration, is expected to be among the most relevant for the progress of the lithium battery technology [3].

In this evolution, the key component is the polymer electrolyte which must have properties, in terms of lithium conductivity and electrode compatibility, which match those offered by the common liquid electrolytes. Among the many types of lithium conducting membranes developed and characterized to meet this requirement, the most interesting are those based on

blends between poly(ethylene oxide), PEO and a lithium salt, LiX [4].

However, there are still some problems associated with these membranes. The main one is related to the ionic conductivity which remains at high levels only when in the amorphous state, i.e. at temperature exceeding 70 °C. Obviously, this narrows the range of practical applications. Another drawback is associated to the low value of the transference number of the lithium cations, which is generally of the order of 0.2–0.4 [5] and this also may affect the use of these PEO-based electrolytes in practical batteries. In fact, a low cation transference number implies that the current is mainly carried by anions and this in turn, may result in concentration polarization which reflects negatively on the rate of a battery based on lithium-operating electrodes.

As well established, these issues may be partially solved by dispersing selected, low particle size ceramics in the PEO–LiX matrix [6–10]. We have proposed that the favourable action of the ceramic filler is associated to specific Lewis acid–base interactions between its surface states and both the lithium salt X[−] anion and the PEO segments [11,12]. Accordingly, it is expected that the surface states of the ceramic fillers play a key role in improving electrolyte performance.

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This has been confirmed by various experimental results and, in particular, by those related to the effect of a unique ceramic filler, i.e. sulphate-promoted superacid zirconia, S-ZrO₂. This ceramic has a high degree of surface acidity, i.e. an acid strength stronger than 100% H₂SO₄ [13], associated to the coordinated unsaturated Zr⁴⁺ cations which have a high electron accepting ability, the latter being enhanced by the nearness of the charge withdrawing SO₄ groups [14]. This finally results in the presence at the surface of the oxide of a high density of acidic sites both of Lewis and Bronsted form [13].

We have shown that the dispersion in the PEO–LiX matrix of this surface-modified superacid zirconia, S-ZrO₂, promotes an exceptional increase of the value of the lithium transference number of the associated composite polymer electrolytes, NCPEs [1], as well as of the overall ionic conductivity [2]. In addition, these NCPEs have a very stable interface with the lithium metal electrode and an electrochemical stability window which extends to 4.2 V versus Li [2].

All these features make the S-ZrO₂-added NCPEs as promising electrolytes for the development of advanced, high-performance lithium polymer rechargeable batteries. In this paper, we confirm this expectation by assembling and testing lithium rechargeable polymer electrolytes batteries using a lithium iron phosphate, LiFePO₄, cathode and a selected NCPE, i.e. that having the P(EO)₂₀LiClO₄ + 5% S-ZrO₂ composition, electrolyte separator.

2. Experimental

The preparation of superacid, sulphated zirconia, S-ZrO₂, as well as that of S-ZrO₂-added PEO–LiX composite polymer electrolytes, NCPEs, have been described in previous works [1,2] to which the reader is referred for details. In this work, we have selected the NCPE having the P(EO)₂₀LiClO₄ + 5% S-ZrO₂ composition as the electrolyte of choice. This has been used as separator in a battery configuration having a lithium metal anode and a lithium iron phosphate, LiFePO₄, cathode. The anode has been prepared by pressing a lithium foil (Chemetal) typically of 250 μm thickness, on a stainless-steel (SS) current collector. The cathode was assembled in a thin foil form (typically of 130–150 μm thickness) by pressing on an Al mould a blend of LiFePO₄ (60%), PEO (25%) and Super P carbon (15%). Lithium iron phosphate was prepared with a procedure developed in our laboratory which yields carbon-coated particles [15].

The battery prototypes were assembled by laminating in sequence the three components, i.e. the lithium foil anode, a layer of the P(EO)₂₀LiClO₄ + 5% S-ZrO₂ NCPE (typically of 300 μm thickness) and the LiFePO₄ composite cathode film. This assembly was housed in a Teflon cell equipped with two SS, current collector electrodes. For comparison purposes also Li/LiFePO₄ batteries based on ceramic-free, P(EO)₂₀(LiClO₄) electrolytes having comparable thickness have been prepared and tested.

The batteries were charged and discharged at various rates and at different temperatures. The cycling conditions were set and controlled by a MACCOR Battery cyler and the temperature by a Buchi oven.

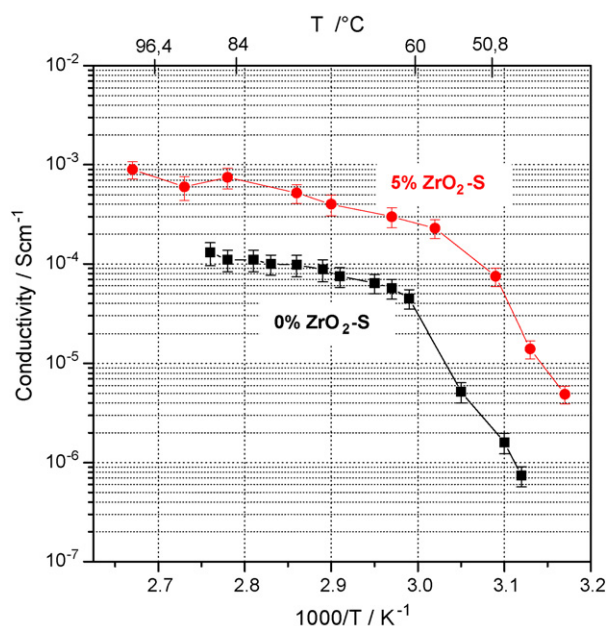


Fig. 1. Arrhenius conductivity plot of a P(EO)₂₀LiClO₄ + 5% S-ZrO₂ NCPE in comparison with that of a ceramic-free P(EO)₂₀LiClO₄ electrolyte.

3. Results and discussion

In this work, the NCPE having the P(EO)₂₀LiClO₄ + 5% S-ZrO₂ composition, was selected as the electrolyte of choice for the fabrication of new types of lithium rechargeable polymer batteries. The choice was motivated by the favourable transport properties of this particular electrolyte material, which, as shown in Fig. 1, has a conductivity almost one order of magnitude higher than the corresponding, ceramic-free electrolyte. In addition, the conductivity of the selected NCPE remains at reasonably high values even at 50–60 °C, i.e. in a temperature range lower than that which conventional, ceramic-free electrolytes can stand. This suggests that the use of the NCPEs may lead to batteries having a wider operational range than those based on conventional PEO-based polymer electrolytes.

In addition to conductivity, also the compatibility with electrode materials and the electrochemical stability window are key requisites for an electrolyte proposed for battery application. The compatibility of the selected NCPE with a lithium metal anode is demonstrated by the value of the related interfacial impedance, which has been shown to be low, i.e. of the order of 15 Ω cm⁻², and stable upon long contact times [2]. The anodic stability has been evaluated by running a sweeping voltammetry of a lithium blocking electrode, e.g. a MCMB graphite electrode, in a cell using a lithium counter electrode and the selected P(EO)₂₀LiClO₄ + 5% S-ZrO₂ electrolyte. Under these conditions, the onset of the current in the anodic scan may be assumed as the decomposition of the electrolyte. The results of a typical sweep run at 100 °C is shown in Fig. 2. Clearly, the electrolyte is stable up to 4.2 V versus Li. The high electrochemical stability and the intrinsic purity of this electrolyte are further confirmed by the low value of the residual current prior to the decomposition voltage.

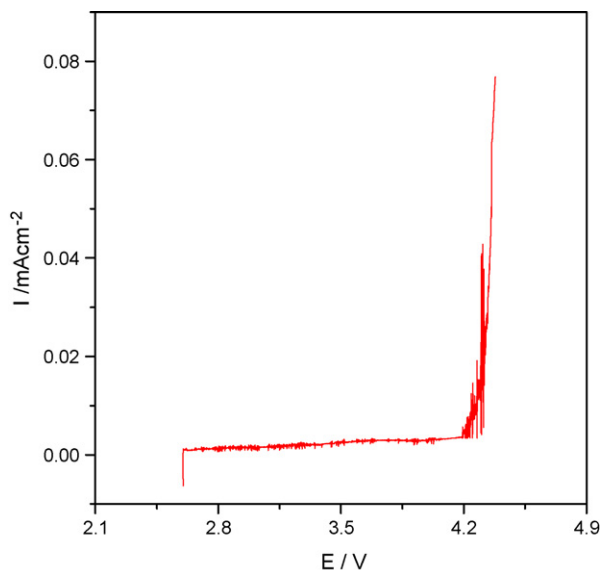


Fig. 2. Current–voltage curve of a graphite MCMB electrode in a cell using a lithium counter electrode and the $\text{P}(\text{EO})_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2$ electrolyte. Temperature, 100°C ; voltage scan, 0.1 mV s^{-1} .

These experimental evidences demonstrate that the selected $\text{P}(\text{EO})_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2$ NCPE is suitable for application in lithium batteries using a lithium metal anode coupled with cathode materials operating within the 0–4 V range. Accordingly, we have selected lithium iron phosphate, LiFePO_4 as the preferred cathode material. The charge–discharge process of the $\text{Li}/\text{LiFePO}_4$ battery is the removal–uptake of lithium from and out the lithium iron phosphate:



to which is associated a maximum, theoretical capacity of 170 mAh g^{-1} . The two-phase process (1) evolves with a flat voltage plateau centered on 3.4 V versus Li, i.e. quite within the stability window of the electrolyte, compare Fig. 2.

However, the full capacity of the LiFePO_4 is difficult to achieve under normal conditions, due to the low kinetics of process (1) which are limited by the intrinsic low electronic conductivity of the two phases, which in turn reflects into slow Li diffusion within the electrode bulk [16]. Various approaches have been used to overcome this issue. They include dispersion [17] or coating [18] of or by conducting additives. Accordingly, the LiFePO_4 used in this work has been prepared by a special synthesis route which leads to kinetically improved electrode material [15].

Fig. 3 shows a typical charge–discharge cycle of the $\text{Li}/\text{P}(\text{EO})_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery developed in this work. The flat 3.4 V voltage plateau, expected on the basis of process (1), is clearly visible. A capacity exceeding 140 mAh g^{-1} , i.e. 82% of the theoretical value, is easily achieved, this demonstrating that the LiFePO_4 produced in this work has indeed good kinetics and that it can effectively operate in a battery having a polymer configuration. Fig. 3 also shows, for comparison purpose, the charge–discharge cycle obtained under the same temperature and rate conditions

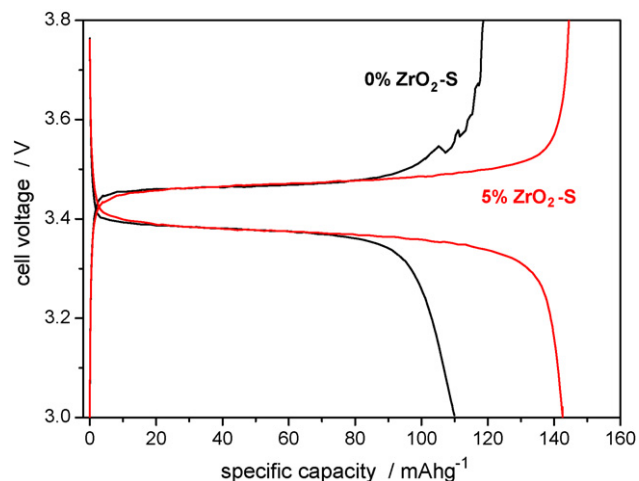


Fig. 3. Typical charge–discharge cycle of the $\text{Li}/\text{P}(\text{EO})_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery and of the $\text{Li}/\text{P}(\text{EO})_{20}\text{LiClO}_4/\text{LiFePO}_4$ battery. Temperature, 90°C ; rate, $C/7$. The capacity is referred to the cathode.

of a $\text{Li}/\text{P}(\text{EO})_{20}\text{LiClO}_4/\text{LiFePO}_4$ battery using a comparable, ceramic-free electrolyte. The much lower value of capacity achieved in this case confirms that the composite electrolyte has indeed improved transport properties which results in an optimization of the electrochemical process, especially in terms of a decrease of the ohmic and concentration polarizations.

This is further confirmed by Fig. 4, which compares the current–voltage polarization curve of the two batteries. The resistance of the composite electrolyte battery, as determined by the linear part of the curve in the middle current range, is lower than of the battery using a standard, ceramic-free electrolyte. More significant is the difference in the value of the limiting current which is consistently higher for the battery based on the composite electrolyte.

The high rate capability of the battery is further demonstrated by Fig. 5, which reports the discharge curves at various rates. A good fraction of the capacity is delivered at $C/5$ and the battery is still able to operate even at $2C$.

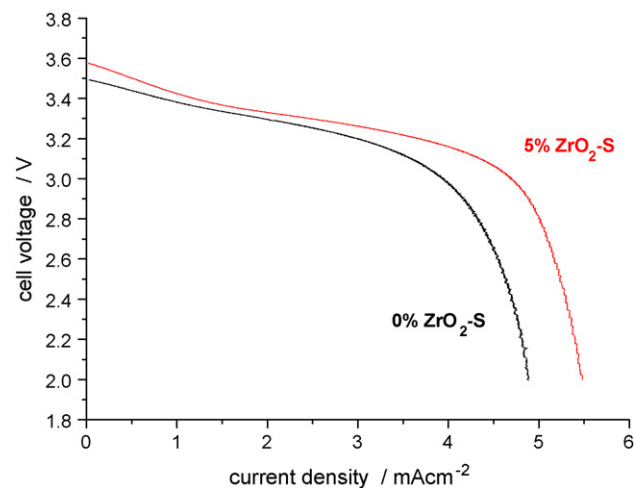


Fig. 4. Typical current–voltage polarization curves of the $\text{Li}/\text{P}(\text{EO})_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery and of the $\text{Li}/\text{P}(\text{EO})_{20}\text{LiClO}_4/\text{LiFePO}_4$ battery. Temperature, 90°C .

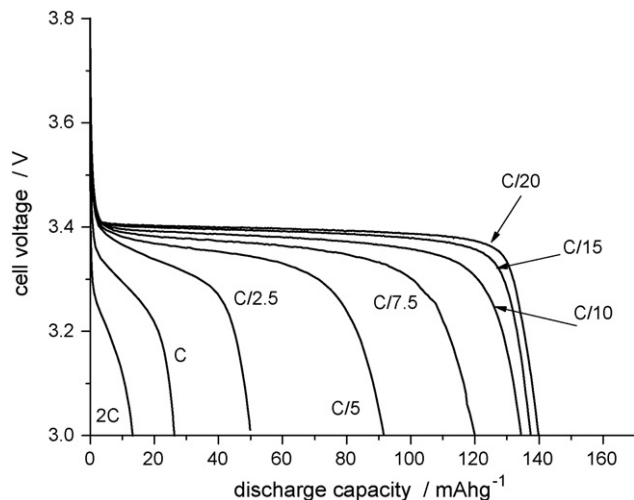


Fig. 5. Discharge voltage profiles of the $\text{Li/P(EO)}_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery at various rates. Room temperature. The capacity values are referred to the cathode.

The cycling capabilities of the $\text{Li/P(EO)}_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery are shown by Fig. 6, which reports the capacity versus cycle number. The battery operates over 100 cycles with a very good capacity retention thus confirming its long life expectancy. Important is also the observed high charge–discharge efficiency (ratio between charge and discharge capacity), a value which confirms the good interfacial stability between the lithium metal electrode and the NCPE. In the same Fig. 6 is shown, for comparison purpose, the cycling response of a comparable Li/LiFePO_4 battery using a conventional, ceramic-free electrolyte. In addition to the already discussed lower value of cycling capacity, this battery, although cycled at a lower rate ($C/7$ versus $C/5$), shows a more consistent capacity decay upon cycling and, particularly, a lower, more scattered value of the charge–discharge coulombic efficiency, this being a clear evidence of a more reactive $\text{Li}/\text{electrolyte}$ interface.

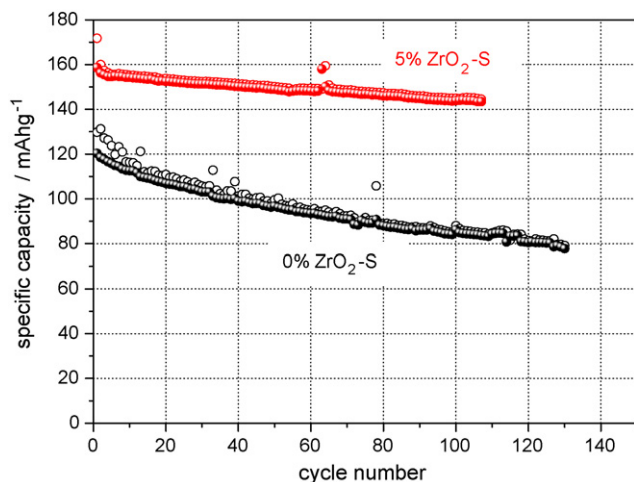


Fig. 6. Capacity vs. charge–discharge cycles of the $\text{Li/P(EO)}_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery and of the $\text{Li/P(EO)}_{20}\text{LiClO}_4/\text{LiFePO}_4$ battery. Temperature, 90°C ; rate, $C/5$, corresponding to a current density of 0.20 mA cm^{-2} for the NCPE battery and of $C/7$ (0.16 mA cm^{-2}) for the ceramic-free electrolyte battery. The capacity values are referred to the cathode.

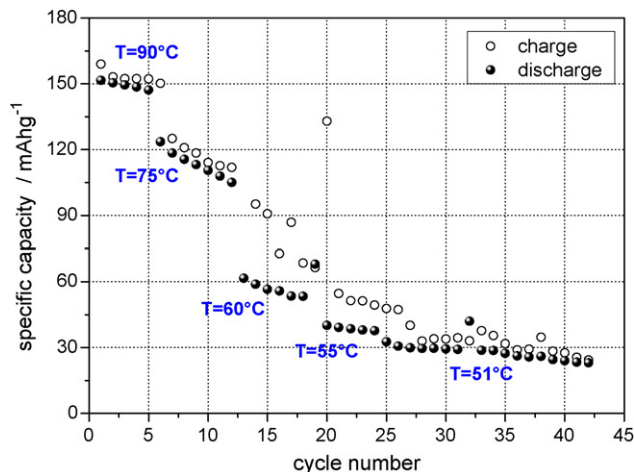


Fig. 7. Capacity vs. charge–discharge cycles of the $\text{Li/P(EO)}_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery at various temperatures. Rate, $C/7$, corresponding to a current density of 0.21 mA cm^{-2} . The capacity values are referred to the cathode.

As already pointed out, the dispersion of the ceramic filler in addition to enhance value of the ionic conductivity of the resulting NCPE, it also widens its useful temperature range, see Fig. 1. Accordingly, batteries based on this NCPE are expected to operate at temperature values which are normally excluded for polymer batteries using conventional electrolytes. This is indeed confirmed by Fig. 7 which shows the cycling response of the $\text{Li/P(EO)}_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery developed in this work. The battery operates well at temperatures of the order 75°C and it is still capable to deliver a fraction of its capacity even around 50°C , i.e. at a temperature level at which, to our knowledge, conventional solvent-free, solid-state polymer lithium batteries fail.

From Fig. 8, which illustrates some typical discharge voltage profiles, one can clearly evidence a certain irregularities in the response at low temperature, especially in the charge curves (not reported). These are probably associated to ionic transport limitations in a temperature range which is just at the limit of the

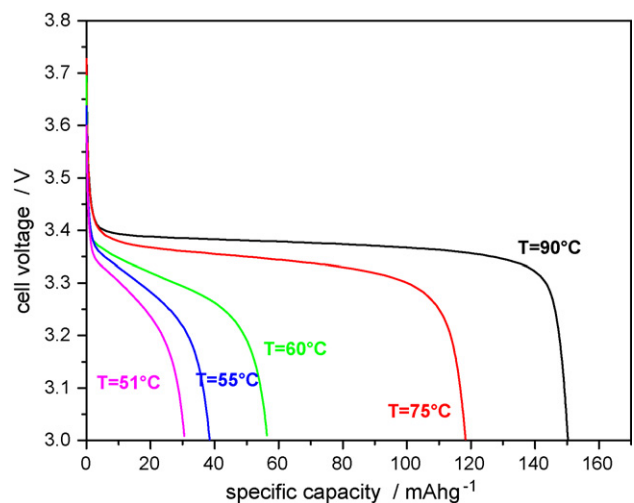


Fig. 8. Discharge voltage profiles of the $\text{Li/P(EO)}_{20}\text{LiClO}_4 + 5\% \text{ S-ZrO}_2/\text{LiFePO}_4$ battery at various temperatures. Rate, $C/7$, corresponding to a current density of 0.21 mA cm^{-2} . The capacity values are referred to the cathode.

amorphous to crystalline transition phase of the polymer electrolyte chains. However, it is expected that by a proper control of the cell geometry and, especially of its thermal management, the response of the battery may be further improved even in the low temperature range.

4. Conclusion

The data reported in this work demonstrate the relevance of nanocomposite polymer electrolytes for the progress of the lithium battery technology. This is associated to the improved transport and interfacial properties of these electrolytes. Indeed, here, we show that lithium batteries based on a PEO-LiClO₄ electrolyte containing a dispersed S-ZrO₂ filler have capacity and charge–discharge features which largely exceed those offered by similar batteries using conventional, ceramic-free polymer electrolytes. The battery described in this work is in a complete solid-state configuration and it is based on a low price, environmentally compatible cathode material. Due to these characteristics we believe that this battery and, more generally, lithium batteries using solvent-free nanocomposite polymer electrolytes with compatible electrode couples, may be of relevance as new, advanced types of power sources for hybrid and electric vehicles.

Acknowledgements

This work has been carried out with the support of the European Network of Excellence “ALISTORE” and of the Italian

Ministry of Research and University, MIUR, under a PRIN 2005 project. The authors thank Mel Chemicals, UK for kindly providing samples of superacid zirconia.

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