

Short communication

Dual-composite polymer electrolytes with enhanced transport properties

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Received 22 January 2007; received in revised form 12 February 2007; accepted 13 February 2007

Available online 24 February 2007

Abstract

New types of composite, solvent-free lithium ion conducting polymer electrolytes have been prepared by dispersing two complementary additives to a PEO–LiX (LiX = LiCF₃SO₃) matrix. The additives have been chosen in such a way that one of them (calix(6)pyrrole) enhances the lithium ion transference number while the other (super-acid zirconia) enhances the conductivity of the electrolyte. The results demonstrate that these dual-composite polymer electrolytes have a high conductivity with significantly high lithium transference number. This rare combination makes the new polymer electrolytes of interest for the development of advanced, solid-state, lithium polymer batteries.

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Keywords: PEO-based composite electrolytes; Calixpyrrole; Super-acid zirconia; Conductivity; Lithium ion transference number; Lithium batteries

1. Introduction

Lithium polymer electrolytes have attracted great interest due to their potential application in batteries designed for powering hybrid vehicles. Among others, the systems based on the combination between poly(ethylene oxide) (PEO) and a lithium salt, LiX, are the most popular examples of polymer electrolytes of practical relevance [1]. However, these electrolytes have still some unsolved drawbacks which mainly are: (i) a conductivity which remains at practical levels only at medium-high temperature, i.e. above 70 °C and (ii) a low lithium ion transference number, i.e. of the order of 0.25 [1]. The conductivity problem may be tolerated since batteries powering a vehicle are anyhow expected to operate at high temperatures. Much more serious is the second issue since it reflects in concentration polarizations which in turn depress the value of the limiting current and thus, of the power density of the lithium battery.

Accordingly, various attempts to enhance the lithium ion transference number of PEO-based polymer electrolytes have been reported. A promising one is the addition of anionic recep-

tors, such as boron [2–4], to the polymer matrix; however, this generally resulted in a serious reduction of the electrolyte ionic conductivity.

In previous works, we have shown that the addition of 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6]pyrrole, see Fig. 1, which reports the structural formula, hereby simply indicated as calixpyrrole (CP), to PEO–LiX-based electrolytes greatly enhances the lithium ion transference number, this being associated to the X[−] anion-blocking-action of this macromolecule [5,6]. Also in this case, however, the ionic conductivity is in part depressed by the addition of CP as a result of its action in lowering the anion mobility [5].

In this work, we have further refined the composition of CP-added electrolytes with the aim of keeping the significantly high value of the lithium transference number, however, combined with high conductivity levels. In particular, we have dispersed into the electrolyte a second additive, namely a highly surface functionalized, super-acid zirconia ceramic, hereby simply indicated as S-ZrO₂. In previous work, we have shown that this ceramic greatly improves the transport properties of standard PEO–LiX-based polymer electrolytes [7] due to specific Lewis acid–base interactions between its surface states and both the lithium salt X[−] anion and the PEO segments [8,9]. It is then expected that S-ZrO₂ may carry out its promoting action also in the case of CP-added electrolytes and thus, contrast the conductivity depression induced by CP, so as to obtain a new family of

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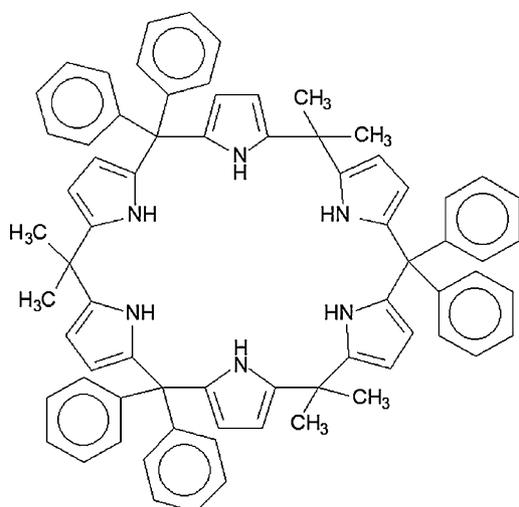


Fig. 1. Structural formula of 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6]pyrrole.

dual-composite PEO-based, solvent-free polymer electrolytes where a high value of lithium ion transference number is combined with high conductivity. The results reported in this work, confirm the validity of this approach.

2. Experimental

Calix[6]pyrrole was synthesized according to the procedure originally proposed by Eichen and coworkers [10] and adopted by us [11] for the preparation of anionic receptors used as additives to polymeric electrolytes. Details of the preparation procedure are described in our previous work [11]. In the first step of the proposed procedure, diphenyldi(pyrrol-2-yl)methane was obtained in condensation of benzophenone with pyrrole. This was followed by the condensation of di(phenyl)di(pyrrol-2-

Table 1

Composition of the polymer electrolyte samples investigated in this work

Electrolyte sample composition	Percentage of dispersed zirconia	Acronym
$\text{P}(\text{EO})_{20}\text{LiCF}_3\text{SO}_3(\text{CP})_{0.125}$	0	PEO-CP-SZ-0
$\text{P}(\text{EO})_{20}\text{LiCF}_3\text{SO}_3(\text{CP})_{0.125} + \text{S-ZrO}_2$	5	PEO-CP-SZ-5
$\text{P}(\text{EO})_{20}\text{LiCF}_3\text{SO}_3(\text{CP})_{0.125} + \text{S-ZrO}_2$	10	PEO-CP-SZ-10
$\text{P}(\text{EO})_{20}\text{LiCF}_3\text{SO}_3(\text{CP})_{0.125} + \text{S-ZrO}_2$	15	PEO-CP-SZ-15
$\text{P}(\text{EO})_{20}\text{LiCF}_3\text{SO}_3(\text{CP})_{0.125} + \text{S-ZrO}_2$	20	PEO-CP-SZ-20

yl)methane with acetone (catalyst: trifluoroacetic acid) leading to the preparation of 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6]pyrrole. The structure of the final product, reported in Fig. 1, was confirmed by NMR and MS spectra analyses. Prior to application as additives to polymeric electrolytes, the anion receptor was dried for about 200 h under high vacuum.

LiCF_3SO_3 (Aldrich) and PEO (600,000 MW, Aldrich reagent grade) were dried under vacuum at 100 °C and 45 °C, respectively, for at least 36 h before use. Zirconia, obtained by Mell Chemical in the form of $\text{S-Zr}(\text{OH})_2$ was heat treated at 500 °C for 2 h to turn it into the desired super-acid version, S-ZrO_2 and vacuum dried at 150 °C for 6 h prior to use.

Five samples having constant $\text{P}(\text{EO})_{20}\text{LiCF}_3\text{SO}_3(\text{CP})_{0.125}$ composition but varying by the amount of dispersed S-ZrO_2 , were considered. Their total compositions and the corresponding acronyms are reported in Table 1. All the samples were prepared by a hot-pressing, solvent-free synthesis originally developed in our laboratory [12]. Fig. 2 illustrates in scheme the basic steps of the synthesis procedure.

The electrolyte components were carefully sieved and then introduced in their correct proportion inside sealed polyethylene bottles and thoroughly mixed by ball-milling for at least

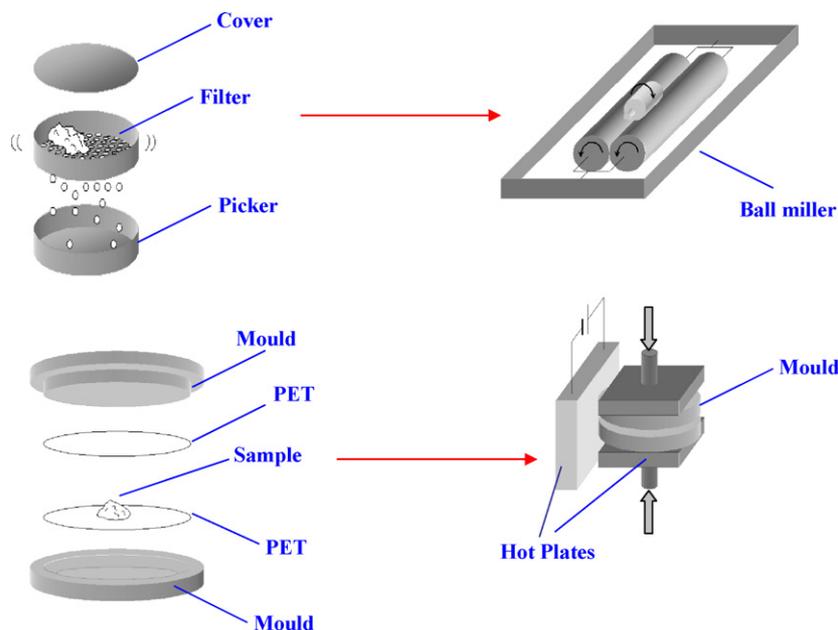


Fig. 2. Scheme of the synthesis procedure of the solvent-free polymer electrolyte samples listed in Table 1.

24 h to obtain homogeneous mixture of powders. Contamination with external ambient was carefully avoided by performing all the preparation steps in a controlled argon atmosphere having a humidity content below 10 ppm. The samples were removed from the dry box for any desired characterization test only after having been housed in sealed coffee bag envelopes. Homogeneous rigid membrane samples, having thickness ranging from 50 to 300 μm were obtained after hot-pressing. They were stored under argon filled dry box for subsequent measurements.

The conductivity of the various electrolyte samples was measured by impedance spectroscopy analysis of cells formed by sandwiching the given electrolyte sample between two stainless-steel blocking electrodes. The samples were cut in pellets having 8 mm and accommodated in a Teflon O-ring, which, by circling the pellet, assured to maintain a fixed sample thickness throughout the measurement. The cells were heated to about 100 °C and kept at this temperature for 24 h to assure thermal equilibrium. The measurements were made in the 100–40 °C temperature range on both cooling and heating scans. A Solartron Impedance Response Analyzer was used for the measurement which were extended over a 10 Hz–100 kHz frequency range.

The lithium ion transference number was determined by the technique introduced by Bruce et al. [13]. A constant dc voltage was applied across a symmetrical Li/sample/Li cell and the current was monitored through the cell until it reached a steady state, constant value. An impedance analysis was carried out immediately before and after the application of the dc voltage to estimate the effect of changes of the passive layer resistance at the Li electrode interface. The cell was left to thermally equilibrate for at least 1 day before each measurement.

The transference number T_{Li^+} was calculated by the following equation:

$$T_{\text{Li}^+} = \frac{I_{\text{ss}}(\Delta V - R_0 I_0)}{I_0(\Delta V - R_{\text{ss}} I_{\text{ss}})} \quad (1)$$

where I_0 is the initial current, I_{ss} the steady state current, ΔV the applied voltage and R_0 and R_{ss} are the initial and final resistances, respectively, of the passive layer onto lithium metal electrodes.

3. Results and discussion

Fig. 3 shows in comparison the Arrhenius plots of the conductivity of a ceramic-free PEO-CP-SZ-0 polymer electrolyte with that of the various S-ZrO₂-added, dual-composite polymer electrolytes. The measurements were extended in a temperature range varying from 40 to 100 °C. The addition of S-ZrO₂ into the polymer electrolyte significantly enhances the conductivity of the dual-composite electrolytes, which is higher than that of the S-ZrO₂-free electrolyte in the entire high temperature range: in particular, the conductivity of the PEO-CP-SZ-15 sample shows an almost six fold increase over the measured temperature region. This conductivity value is not yet at the same level of the of the CP- and S-ZrO₂-free, P(EO)₂₀LiCF₃SO₃ electrolyte. The difference, however, is very limited and certainly much lower than that generally observed for electrolytes modified for T_{Li^+} improvement [2–4]. This confirms the validity of our approach.

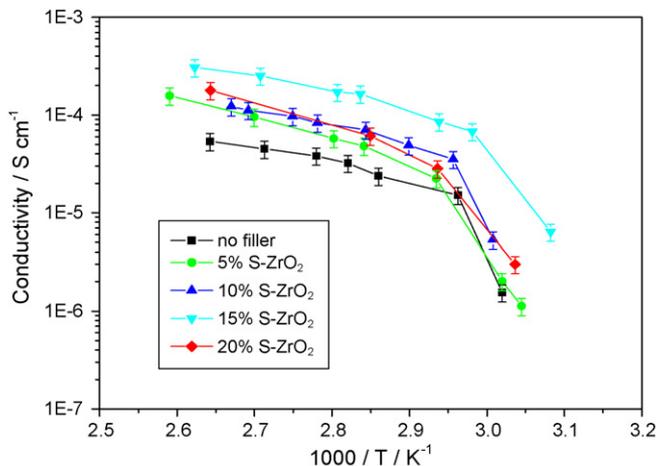


Fig. 3. Arrhenius plots ionic conductivity for P(EO)₂₀LiCF₃SO₃(CP)_{0.125} electrolytes with and without S-ZrO₂ ceramic filler. Data obtained by impedance spectroscopy.

The improvement in conductivity obtained with our dual-composite electrolytes (see Fig. 3) may be explained on the basis of interactions between the ceramic surface states and both the PEO chains and the lithium salts. These interactions weaken the attraction force between the lithium ions and the oxygen atoms, thus, favoring lithium ion motion and ultimately the ionic conductivity of the electrolyte [8,9]. This increase in conductivity is a stable effect, as demonstrated by Fig. 4 which shows the Arrhenius plot of the composite PEO-CP-SZ-5 sample determined during heating and cooling scans. The two scans overlap, thus, confirming that the transport properties are not affected by thermal excursions.

Fig. 5 shows the conductivity at 70 °C versus the S-ZrO₂ content of the various samples examined in this work. The conductivity increases with increasing ceramic content; however, the trend inverts at 15% S-ZrO₂, probably due to a percolating blockage. Thus, the PEO-CP-SZ-15 appears to be the sample of choice on which to concentrate further characterization.

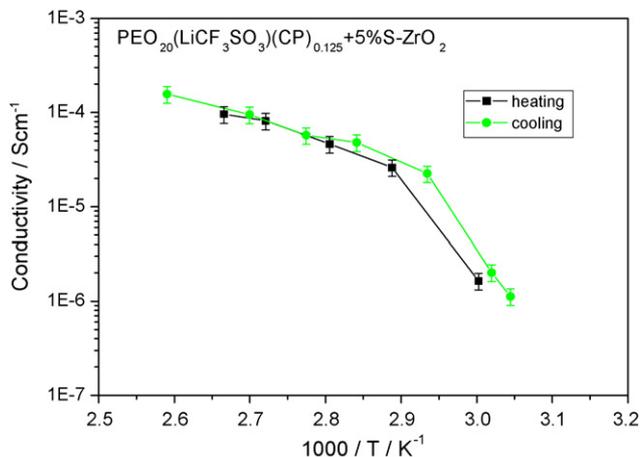


Fig. 4. Conductivity Arrhenius plots of the composite P(EO)₂₀LiCF₃SO₃(CP)_{0.125} + 5% S-ZrO₂ polymer electrolyte determined in heating and cooling scans. Data obtained by impedance spectroscopy.

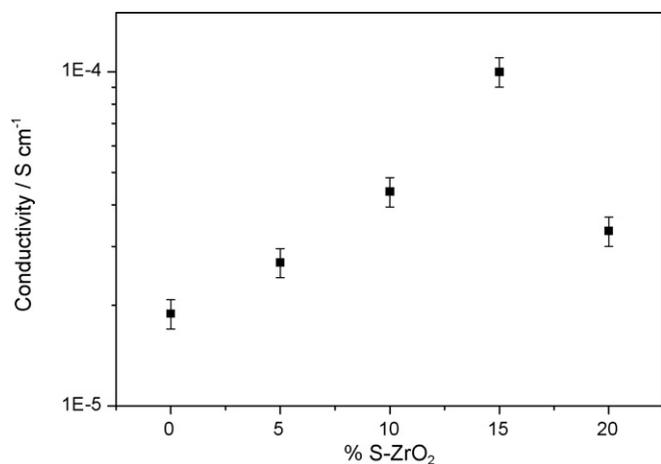


Fig. 5. Conductivity vs. S-ZrO₂ content for the polymer electrolyte samples investigated in this work at 70 °C. Data obtained by impedance spectroscopy.

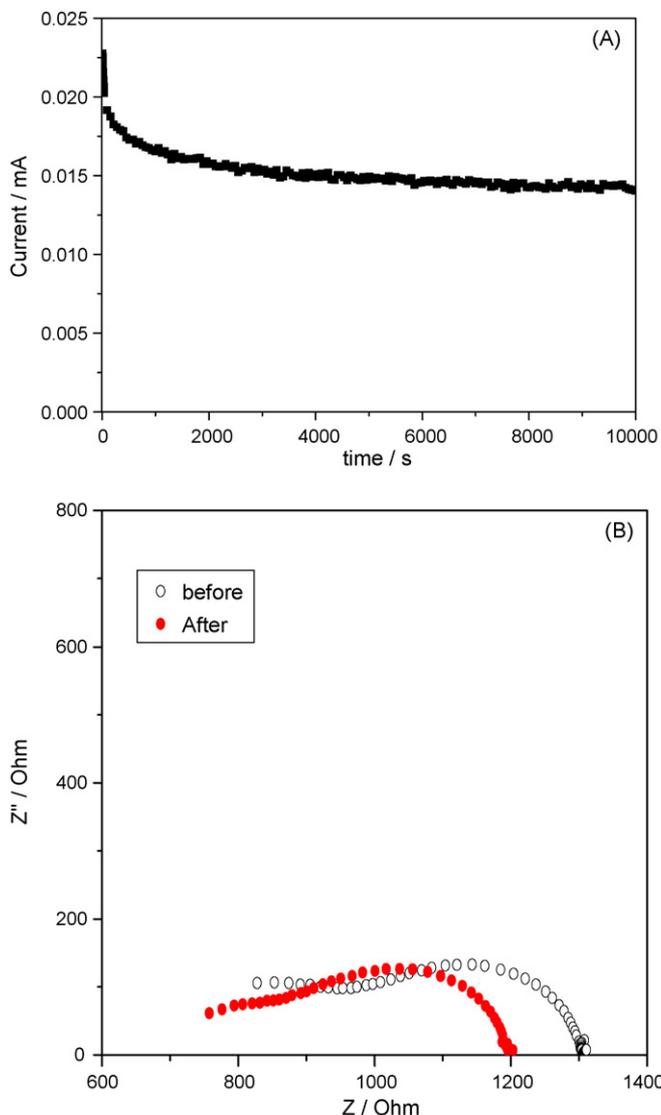


Fig. 6. (A) Current time curve at 70 °C of a cell Li/PEO-CP-SZ-15/Li cell and (B) impedance response of the same cell before and after dc polarization test.

Accordingly, the lithium ion transference number, T_{Li^+} , of this electrolyte was measured using the procedure suggested by Bruce et al. [13], which implies a combination of dc and ac polarizations. Fig. 6(A) illustrates the chronoamperometric curve obtained at 70 °C by applying a 30 mV dc pulse across a Li/PEO-CP-SZ-15/Li cell. This curve shows the value of the initial current I_0 and that of the steady state I_{ss} current that flow through the cell. It can be seen that the I_{ss}/I_0 ratio is about 0.6, this being a preliminary but firm suggestion that the value of T_{Li^+} is indeed high in this PEO-CP-SZ-15 electrolyte.

Fig. 6(B) shows the impedance plots of the cell before and after the dc polarization test. The spectra evolve along two convoluted semicircles, associated to the passive layer resistance and to the interface charge transfer resistance, respectively. The de-convolution of the spectra was made using the nonlinear squares fit software developed by Boukamp [14,15] which allowed to extract the the initial R_0 and the final R_{ss} passive layer resistance values. The T_{Li^+} of the PEO-CP-SZ-15 electrolyte sample was then determined by using Eq. (1) to be 0.54 at 70 °C. This value is indeed much greater than that of standard PEO-based electrolytes which is generally of the order of 0.25 [1], as well as than that of the CP- and S-ZrO₂-free, P(EO)₂₀LiCF₃SO₃ electrolyte, evaluated with the same technique as 0.31.

4. Conclusion

The results reported in this work demonstrate that the addition of a surface functionalized ceramic, such as acid zirconia, S-ZrO₂, to P(EO)₂₀LiCF₃SO₃(CP)_{0.125} electrolytes, results in a consistent enhancement of the ionic conductivity. In our opinion, this is an interesting result, which opens the path for developing a new class of PEO-based, dual-composite, solvent-free polymer electrolytes which combine high lithium ion transference number (as induced by the CP component) with high ionic conductivity (as promoted by the S-ZrO₂ ceramic component).

For instance, a selected example of this class, i.e. the P(EO)₂₀LiCF₃SO₃(CP)_{0.125} + 15% S-ZrO₂ electrolyte, has at 70 °C, a conductivity of 1×10^{-4} S cm⁻¹ and a lithium ion transference number of 0.54. These results appear of practical relevance, since to our knowledge polymer electrolytes having the above properties were never reported before. Work is in progress in our laboratories to test these new electrolytes as separators in advanced, rechargeable lithium polymer batteries.

Acknowledgements

This work has been carried out with the financial support of the European Office of Aerospace Research and Development, London, UK. One of us (H.H.S.) wishes to acknowledge the TRIL Fellowship offered by the International Centre for Theoretical Physics (ICTP) Trieste.

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