

A search for a single-ion-conducting polymer electrolyte: Combined effect of anion trap and inorganic filler

H. Mazor^a, D. Golodnitsky^{a,b,*}, E. Peled^a, W. Wieczorek^c, B. Scrosati^d

^a School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

^b Wolfson Applied Materials Research Center, Tel Aviv University, Tel Aviv 69978, Israel

^c Faculty of Chemistry, Warsaw University of Technology, Warszawa 00-664, Poland

^d Department of Chemistry, University of Rome “La Sapienza”, Italy

Received 9 August 2007; received in revised form 6 September 2007; accepted 14 September 2007

Available online 2 October 2007

Abstract

Lithium trifluoromethanesulfonate:polyethylene oxide (PEO) polymer electrolytes modified by 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethyl-6-pyrrole (C6P) and nanosize silica filler were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and electrochemical means. An increase in the lithium transference number is observed upon incorporation of even a small amount of C6P. Silica facilitates interchain ion hopping in polymer electrolytes and possibly introduces an additional interfacial ion-conduction path without decreasing t_+ . Stable solid electrolyte interphase resistance (SEI) was achieved in the polymer electrolytes containing calix[6]pyrrole and silica. It was found that lithium single-ion-conductive polymers with good electrochemical stability and ion transport properties have the potential for considerably boosting the performance of lithium/molybdenum oxysulfide all-solid-state thin film batteries.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Polymer electrolyte; Transference number

1. Introduction

Solid polymer electrolytes (PE) have been the subject of numerous studies relating to lithium-ion polymer batteries, capacitors, and electrochromic devices. Most PE research has focused on increasing the conductivity of such systems while maintaining good thermal, electrochemical, and mechanical stability. Long-range ionic transport in PEs is seen to involve a combination of local segmental motion of the polymer host, to which cations are temporarily attached by dative polar bonds, and occasional independent transitions of the ions themselves [1,2]. In semicrystalline polymer electrolytes, ion motion between suitable coordination sites along the PEO helix (denoted as intrachain or bulk conductivity (σ_{bulk})), is accompanied by ion hopping between different polymer strands and grains (termed interchain or grain-boundary conductivity (σ_{gb})).

Ordinary lithium salt-based polymer electrolytes are bi-ionic conductors. The relatively strong coordination of Li^+ within the helical structure of the PEO matrix, is opposed to the relatively weak association of anions with the host polymer. The reported cationic transference number (t_+) for many $\text{LiX}:\text{PEO}$ electrolytes is about 0.2–0.3, i.e., only 30% of the measured conductivity is associated with Li^+ mobility. During constant-current operation of the battery, large concentration gradients develop both across the polymer electrolyte film and in the porous positive electrode. In addition, the mobile anions can take part in undesired surface reactions, reducing the active electrode area. It is clear, therefore, that lithium and lithium-ion batteries comprising single-cation conductive polymers are expected to attain larger energy density and higher power densities [3]. In a typical approach, a number of single-ion-conductive polymers were prepared by immobilization of anions on a polymer chain [4]. However, the decrease in the number of mobile carrier ions due to the immobilization prevents these materials from exhibiting high conductivity. In another effort, single-ion-conductive polymer electrolytes, based on polyethyleneimine, polyphosphazene, and polysiloxane backbones were synthesized [5–7].

* Corresponding author at: School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel. Tel.: +972 36407820; fax: +972 36422649.

E-mail address: golod@post.tau.ac.il (D. Golodnitsky).

Tsutsumi and coworkers reported σ_{bulk} of $7 \times 10^{-7} \text{ S cm}^{-1}$ and t_+ of 0.98 for a single-ion siloxane SPE [7] at room temperature, but σ_{bulk} was $5 \times 10^{-4} \text{ S cm}^{-1}$ for a dual-ion SPE. The t_+ of the dual-ion SPE was reported to be 0.50. Florjanczyk et al. reported significant enhancements by incorporating BF_3 , which is complexed with the bulky, low charge density carboxylate anions of the polymer network [8].

In agreement with [9] we believe that the success of single-ion-conducting polymer electrolytes rests on finding a way to promote dissociation of ion pairs and higher aggregates, thereby enhancing inter- and intrachain mobility of free Li^+ . In our recent

work [10,11], we have shown, by dc–ac techniques, that addition of calix[6]pyrrole (C6P) to polyether-based lithium triflate electrolytes results in a considerable increase in the cation transport number, t_{Li^+} . Contrary to the case of calixarene compounds [12], the increase in the lithium transference number is observed upon incorporation of even a small amount of C6P. The IR spectra revealed that calix[6]pyrrole induces dissociation of triplets to free ions. This, together with structural changes caused by complex receptor–anion and polymer–anion interactions, promotes cation transport and prevents significant lowering of the bulk ionic conductivity at temperatures above the melting point of

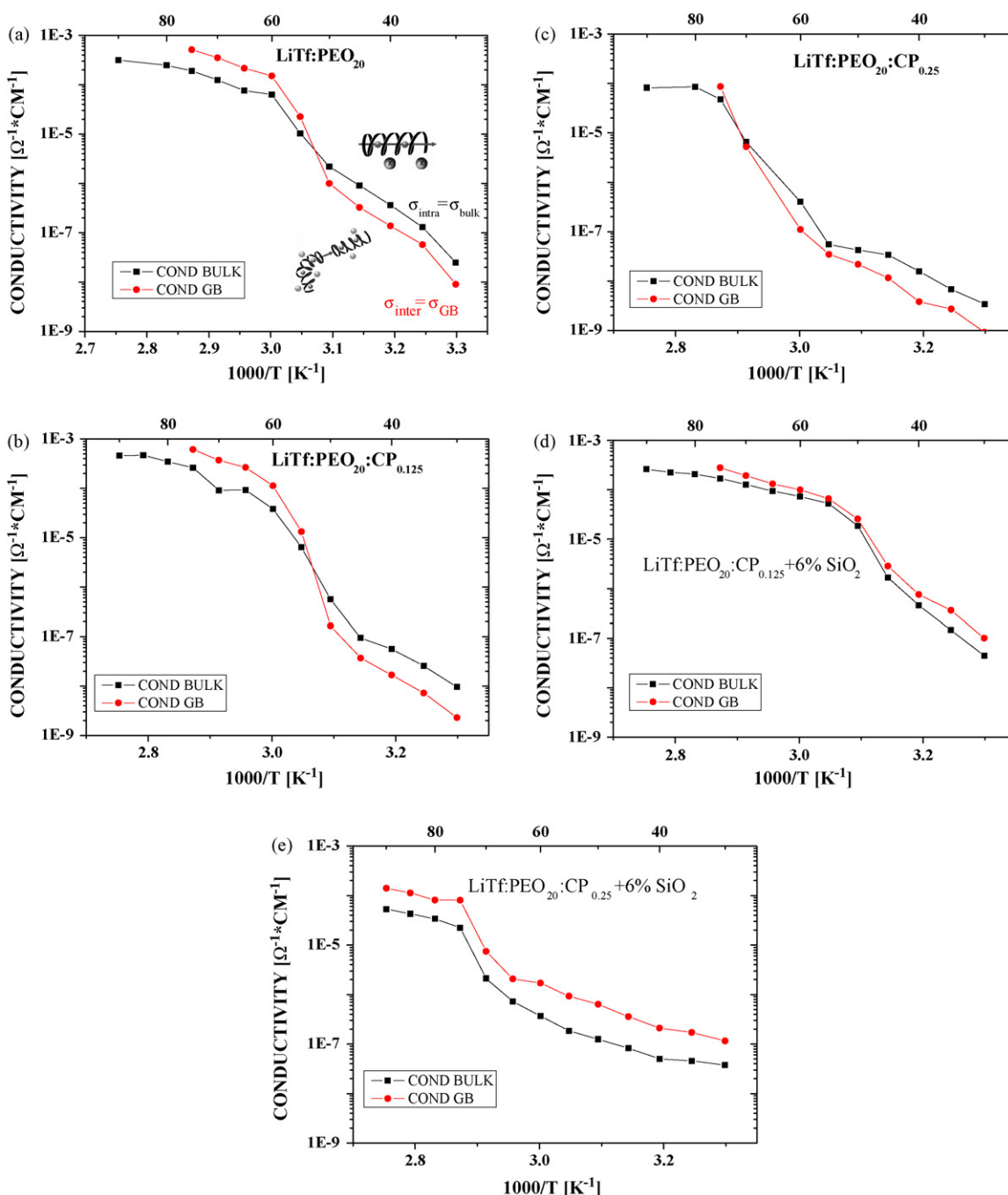


Fig. 1. Arrhenius plots of bulk and grain boundary ionic conductivity of the $\text{LiCF}_3\text{SO}_3:\text{P}(\text{EO})_{20}$ polymer electrolytes with and without C6P and SiO_2 additives.

the host polymer. However, at near ambient temperatures addition of C6P is followed by a dramatic conductivity drop, which may be related to the increased stiffness of the polymer matrix.

In an attempt to assess the tradeoff between high t_+ and hindered ionic transport, in particular low grain boundary conductivity at around 50–60 °C, the PEs containing C6P were modified by nanosize silica. This work is focused on the study of the electrochemical properties and structural changes caused by the combined effect of the anion trap and inorganic filler in lithium trifluoromethanesulfonate (triflate, Tf)–PEO system.

2. Experimental

Calix[6]pyrrole, 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethyl-6-pyrrole, (abbreviated as C6P), was synthesized by the research group of Warsaw University. 100- μ -thick polymer electrolytes were prepared by casting. The preparation of polymer electrolytes has been described in detail elsewhere [11]. 16 nm-size spherical particles SiO₂ 130 (Degussa) was dried at 150 °C under vacuum for about 12 h. All reagents were stored and manipulated under an argon atmosphere in a VAC glove box with water content < 10 ppm. The AC conductivity was measured with the use of a Solartron 1255 frequency-response analyzer controlled by a 586 PC, over the frequency range 1 MHz–1 mHz. The t_+ tests were carried out according to the procedure developed by Bruce et al. and by Scrosati et al [13,14]. A JSM-6300 scanning microscope (Jeol Co.) equipped with a Link elemental analyzer and a silicon detector was used for the study of surface morphology. The polymer–electrolyte samples were vacuum-coated with 0.6 nm of gold. The DSC tests of the vacuum-dried samples were carried out at a scan rate of 10° min⁻¹ in hermetically sealed alodined aluminum pans with a TA Instruments module 2010 and System Controller 2100.

Measurements of the window of electrochemical stability were made with the use of a 263A potentiostat interfaced with power-suite software and a PC. Cyclic-voltammetry measurements were performed at various temperatures with the use of a Li/PE/SS coin type cells over a wide range of potentials at sweep rates of 5–20 mV s⁻¹. The composite polymer electrolyte was tested as a membrane in a battery comprising an electrodeposited MoO_xS_y cathode [15] and a lithium-metal anode. Cycle life and high-power-capability tests were conducted with the use of a Maccor battery cyler at various temperatures. The (coin type) cells were thermally equilibrated for at least 2 h at each operating temperature before beginning measurements.

The polarization curve tests of the Li/PE/MoO_xS_y battery with LiTf:PEO₂₀-based membranes with and without C6P and SiO₂ additives, were conducted at various temperatures. These measurements were made by applying an ascending-step current for 30 s in the range of 10 μ A–2 mA. The batteries were allowed to rest for 1 min between steps.

3. Results and discussion

Fig. 1 shows a series of Arrhenius plots, which compare the bulk and grain-boundary conductivity in pure and modi-

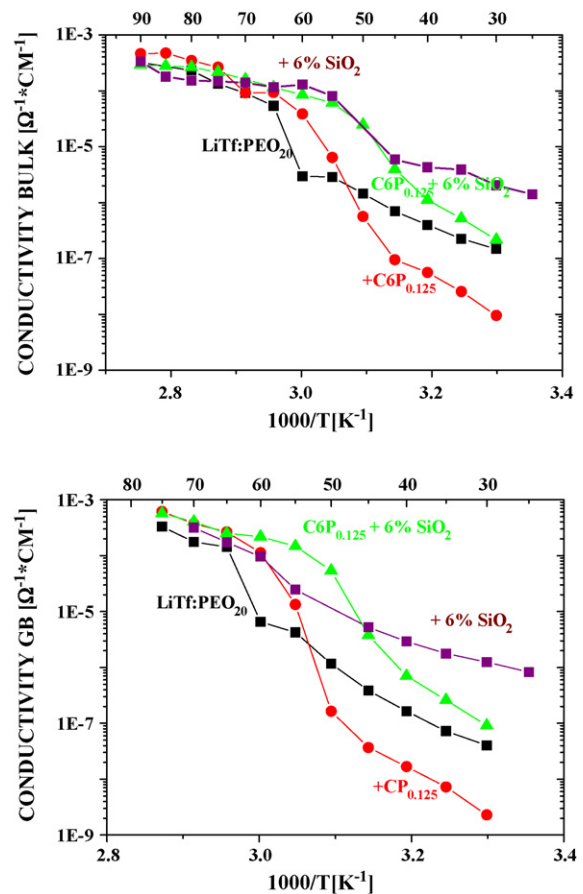


Fig. 2. Arrhenius plots of ionic conductivity of the LiCF₃SO₃:P(EO)₂₀ polymer electrolytes with and without C6P and SiO₂ additives.

fied composite PEs. As can be seen from Fig. 1a–c, σ_{gb} in semicrystalline pure 1:20 PE and polymer electrolytes containing calix[6]pyrrole is lower than σ_{bulk} at near-ambient temperatures. This indicates that interchain and intergrain ion

Table 1

Comparison of t_+ values of various PE compositions investigated in this study

Composition of polymer	T (°C)	Transference number (t_+)
LiCF ₃ SO ₃ :P(EO) ₂₀	60	0.26
LiCF ₃ SO ₃ :P(EO) ₂₀	75	0.34
LiCF ₃ SO ₃ :P(EO) ₂₀ :(CP) _{0.125}	60	0.74
LiCF ₃ SO ₃ :P(EO) ₂₀ :(CP) _{0.125}	75	0.68
LiCF ₃ SO ₃ :P(EO) ₂₀ :(CP) _{0.25}	60	0.79
LiCF ₃ SO ₃ :P(EO) ₂₀ :(CP) _{0.25}	75	0.78
LiCF ₃ SO ₃ :P(EO) ₂₀ :(CP) _{0.125} + 6%(wt.) SiO ₂	60	0.75
LiCF ₃ SO ₃ :P(EO) ₂₀ :(CP) _{0.125} + 6%(wt.) SiO ₂	75	0.74
LiCF ₃ SO ₃ :P(EO) ₂₀ :(CP) _{0.25} + 6%(wt.) SiO ₂	60	0.78
LiCF ₃ SO ₃ :P(EO) ₂₀ :(CP) _{0.25} + 6%(wt.) SiO ₂	75	0.70
LiCF ₃ SO ₃ :P(EO) ₉	60	0.50
LiCF ₃ SO ₃ :P(EO) ₉	90	0.54
LiCF ₃ SO ₃ :P(EO) ₉ :(CP) _{0.125}	55	0.62
LiCF ₃ SO ₃ :P(EO) ₉ :(CP) _{0.125}	75	0.71
LiCF ₃ SO ₃ :P(EO) ₉ :(CP) _{0.125}	90	0.81
LiCF ₃ SO ₃ :P(EO) ₉ :(CP) _{0.125} + 6%(wt.) SiO ₂	60	0.64
LiCF ₃ SO ₃ :P(EO) ₉ :(CP) _{0.125} + 6%(wt.) SiO ₂	70	0.65
LiCF ₃ SO ₃ :P(EO) ₉ :(CP) _{0.125} + 6%(wt.) SiO ₂	90	0.82

hopping is the rate-determining step in long-range ion transport. The inflection point shifts from 50 to 70 °C as the C6P concentration increases, making interchain ion motion even more difficult. Silica promotes ion transport and has the strongest effect on σ_{gb} (Fig. 1d and e). In the presence of SiO₂ the bulk conductivity increases by a factor of 2–8, while the enhancement of grain-boundary conductivity induced by silica is more than an order of magnitude at near-ambient temperatures (Fig. 2). This is true for the C6P-free pure PE, as well. Notwithstanding the fact that the dispersion of fine ceramic particles in a polymer matrix is the subject of considerable literature, the mechanism of ion conduction in composite polymer electrolytes, to our knowledge, is not clearly understood yet. In agreement with [16,17], we suggest that the conductivity enhancement may be due to the appearance of additional, parallel to current flow interfacial ion conduction path with a high charge carrier concentration. In [18], the nanoceramic additive effect is associated to specific Lewis acid–base interactions between the ceramic surface states and both the lithium salt anion and the PEO segments.

Table 1 summarizes transference-number data of all the polymer electrolytes studied. The data demonstrate that incorporation of calix[6]pyrrole in the LiCF₃SO₃:P(EO)₂₀ sample enhances the transference number substantially at various temperatures. As can be seen, the transference number for the polymer electrolyte without C6P at 60 °C is 0.26. This is much

lower than the t_+ values of PEs with C6P-to-salt ratios of 0.125 and 0.25 at the same temperature, which are 0.74 and 0.79, respectively. Of special note is the retaining of high values of the transference number in the composite 1:20 PEs with incorporated ceramic filler. A similar tendency was observed upon the addition of C6P and silica to the LiCF₃SO₃:P(EO)₉ membrane. At 90 °C, the transference number for pure 1:9 polymer electrolyte is 0.54, while combined modification substantially enhances the transference number to 0.82. It should be mentioned that the positive effect of nanosize fillers on the ionic conductivity and cation transference number was detected by several researchers [18,19]; however, when an anion trap is not used, t_+ does not exceed 0.5.

Fig. 3 shows effect of silica additive on the Li/PE interfacial resistance (R_{SEI}). It is obvious that SiO₂ significantly decreases R_{SEI} in both 1:20 and 1:9 lithium triflate single-cation-conducting polymer electrolytes. This positive effect is especially strong at temperatures below the melting point of the PEO matrix.

An important parameter in the characterization of polymer electrolytes is the window of electrochemical stability, especially in view of applications for lithium and lithium-ion all-solid-state batteries. A wide range of electrochemical-stability window allows a large choice of redox couples as electrode materials for the lithium battery. Given that ether-based electrolytes are known to oxidatively degrade at relatively low voltages

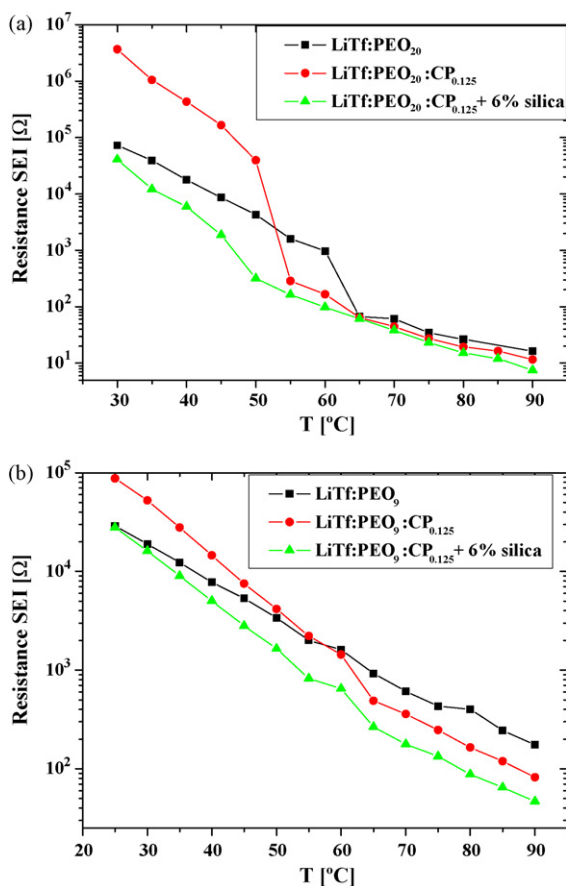


Fig. 3. Plots of the interfacial resistance (R_{SEI}) vs. temperature of the Li/LiCF₃SO₃:P(EO)₂₀:C6P_n:SiO₂/Li cells.

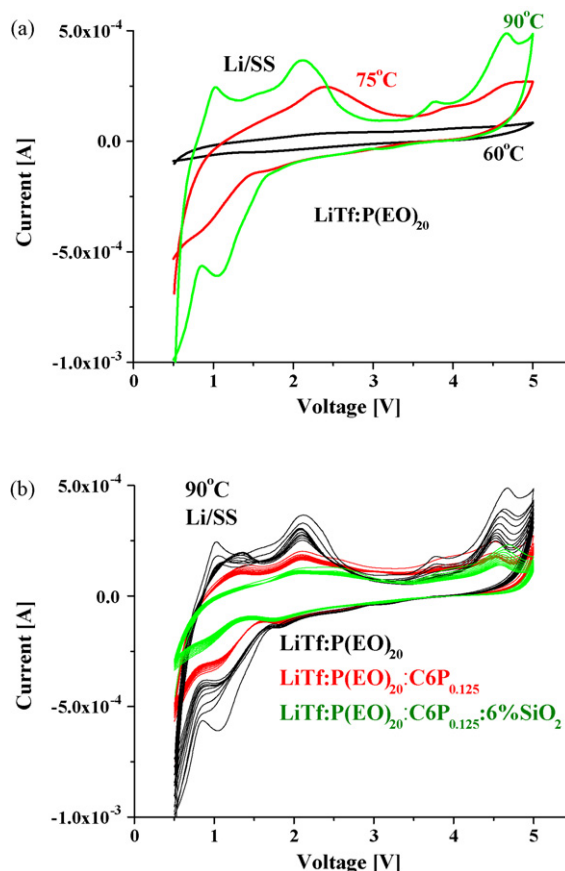


Fig. 4. Cyclic voltammograms of Li/LiCF₃SO₃:P(EO)₂₀:C6P_n:SiO₂/ss cells.

(2.5–3.5 V vs. Li^+/Li) [20] it was of interest to determine the electrochemical stability of the $\text{LiCF}_3\text{SO}_3:\text{P}(\text{EO})_n$ electrolytes in the presence of C6P and ceramic filler. Some concerns were raised by the possible electropolymerization of calix[6]pyrrole,

particularly at high temperatures [21]. Electrochemical stability was tested by linear-sweep voltammetry on a coin cell containing pure and composite electrolytes sandwiched between a stainless-steel working electrode and a lithium counter electrode. As

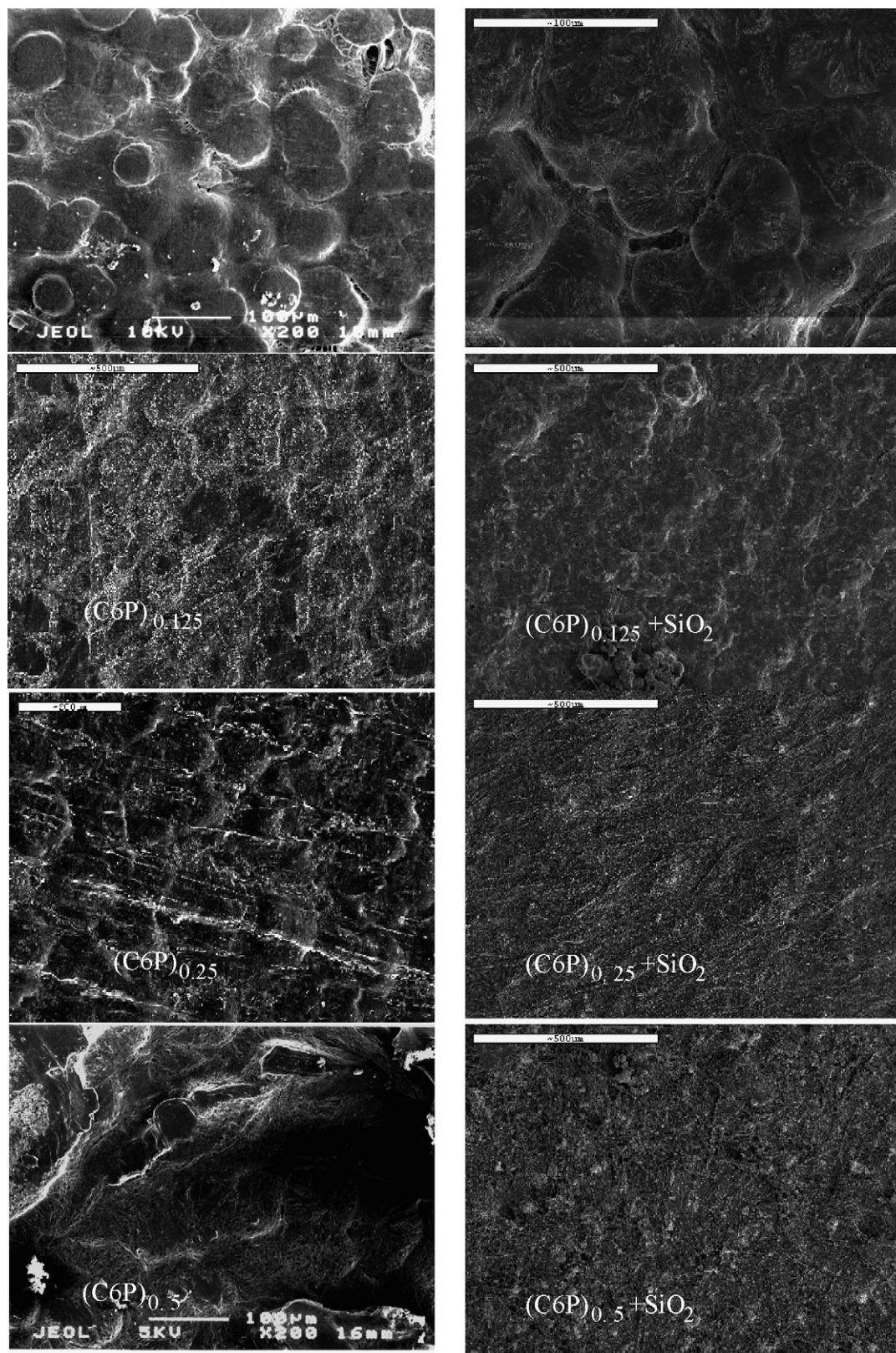


Fig. 5. SEM images of the $\text{LiCF}_3\text{SO}_3:\text{P}(\text{EO})_{20}$ polymer electrolytes with and without C6P and SiO_2 additives.

shown in Fig. 4a, when cyclic-voltammetry tests are performed at different temperatures on a pure 1:20 lithium triflate polymer electrolyte, good electrochemical stability below 60 °C is observed over a voltage range of 0.5–5.0 V vs. Li⁺/Li. However, at higher temperatures (75 and 90 °C), significantly poorer stability is detected, in agreement with [22]. Although heating does not significantly affect the stability limit, it seems to promote the breakdown-reaction rate. In the cathodic region, i.e. at low voltages, reduction reactions of the salt, impurities and PEO form soluble products as well as SEI. The assignment of the irreversible anodic peak at 4.5 V is not yet clear and deserves further investigation. It may be associated with the oxidation of PEO, the anion and maybe the SS electrode. Incorporation of C6P is followed by a decrease in the oxidative and reductive instability of the PE (Fig. 4b). The combined positive impact of the anion trap and inorganic filler is even more pronounced. As shown in Fig. 4b, the single-cation-conducting composite polymer electrolyte shows significantly enhanced electrochemical stability. It is obvious that the additives influence the reaction rate rather than the stability window of the electrolytes studied. We explain this by the formation of a strong bidentate calix[6]pyrrole-triflate complex [9], followed by suppressed anion reduction. Silica, in addition, can serve as a scavenger and adsorb the possible PE impurities, thus eliminating undesired reactions.

Fig. 5 shows SEM micrographs of the LiTf:P(EO)₂₀ polymer electrolytes with and without C6P and silica additives. The polymer electrolytes that do not contain additives have clear, crystalline grain structure with about 50–100 μm grain size. From Fig. 5 it is seen that the morphology of membranes containing a small amount of C6P resembles that of the pure polymer electrolyte. However, the grains of PEs with C6P additive are larger than those of the additive-free PE. Incorporation of silica into the LiTf:P(EO)₂₀:C6P_n-based membranes decreases the grain size and smoothes the surface.

The results of the DSC tests are consistent with SEM observations. As can be seen from Fig. 6, the DSC thermograms of LiTf:P(EO)₂₀ PEs with C6P additive are characterized by a strong endotherm at about 60 °C. This peak represents two

overlapped melting transitions of the eutectic and uncomplexed PEO. The endotherm with onset at 125 °C is the liquidus point, which is related to the temperature of dissolution of the 1:3 Li:P(EO) complex in the melt mixture. With increase in the C6P concentration to above one-fourth of the salt content, an additional endothermic peak is detected at 249 °C. This peak is attributed either to the dissolution of some bidentate anion–C6P complex that is not fully dissolved at lower temperature, or to the dissolution of Calix[6]pyrrole in the molten mixture following decomposition of the C6P-anion complex. Addition of silica suppresses the liquidus phase transition (Fig. 6a) or shifts its onset towards lower temperatures (Fig. 6b and c). The main endotherm broadens and shifts to lower temperatures as well. The enthalpy of the peak decreases by 16% in the LiTf:P(EO)₂₀:CP_{0.5} 6%SiO₂ sample. Three well-pronounced peaks were easily distinguished in the DSC thermogram of the LiTf:P(EO)₉ polymer electrolyte (not shown here). The first one with the onset point at 49 °C is assigned to the melting of the eutectic. The second peak at 89 °C can possibly be associated with the dissolution of the intermediate 1:6 complex in molten eutectic and PEO, and the third is the liquidus point. As in the case of 1:20 PE, the addition of silica is followed by broadening of the melting peaks of the 1:9 polymer electrolyte and a 30% decrease in the total enthalpy value of the phase transitions occurring up to 150 °C. The enthalpy of the C6P high-temperature transition decreases by 9%. This indicates a decrease in the amount of the crystalline phase in the sample as well as improved interaction between anion and anion trap. Increased flexibility of the PEO chains may facilitate interchain ion-hopping, as shown above.

Li/MoO_xS_y thin-film batteries with pure and modified polymer electrolytes were assembled and tested. Batteries were run over 100 reversible cycles in the temperature range of 75 and 90 °C at a low discharge rate of about 0.5C (Fig. 7a). The capacity loss of the batteries with the double modified polymer electrolytes is lower than those with pure PE and does not exceed 0.4%/cycle at 90 °C. At 75 °C the capacity is very stable at the first 20 cycles. Charge/discharge profiles of the cells

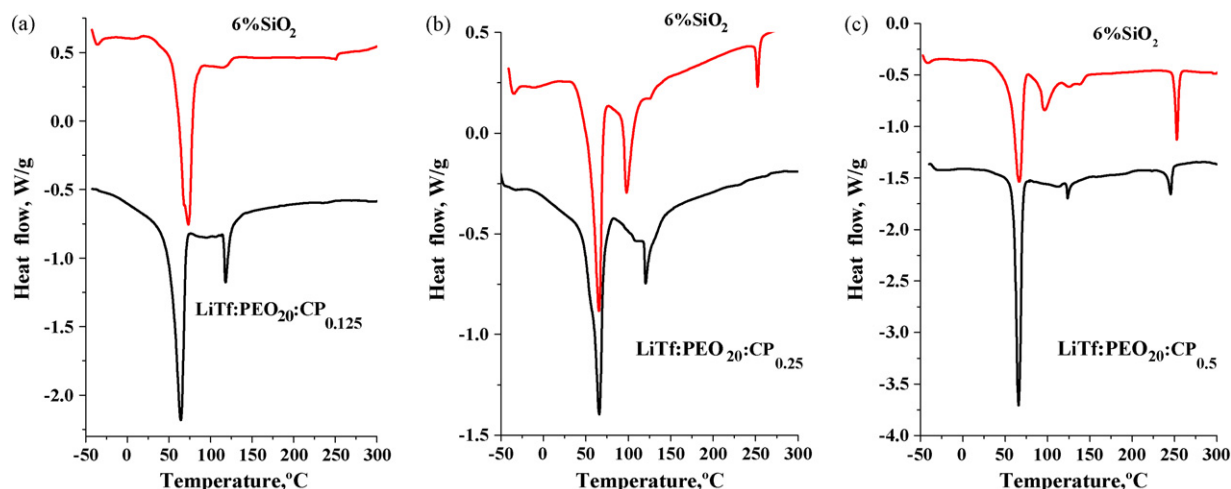


Fig. 6. DSC thermograms of LiCF₃SO₃:P(EO)₂₀ polymer electrolyte with calix[6]pyrrole and silica additives.

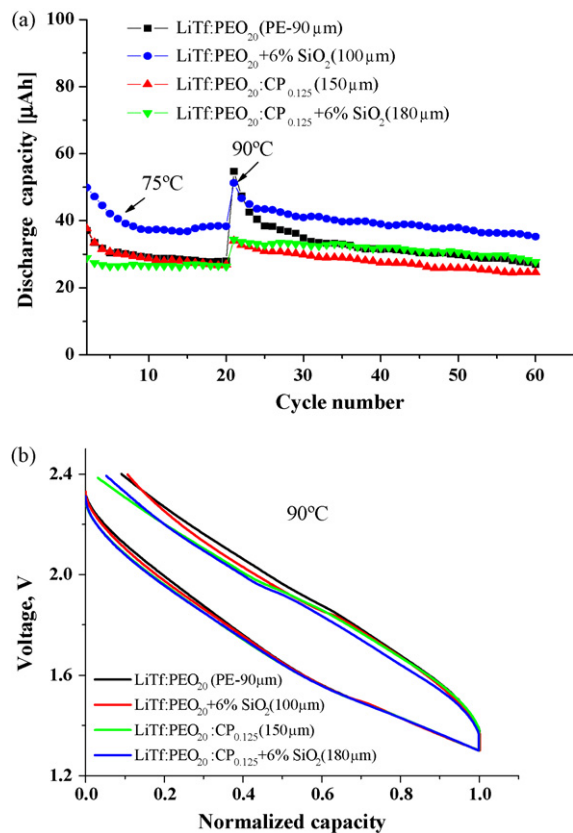


Fig. 7. Cycle life (a) and normalized charge/discharge curves (b) of thin-film Li/LiCF₃SO₃:P(EO)₂₀:C6P_n:SiO₂/MoO_xS_y cells.

are almost identical and do not change upon prolonged cycling (Fig. 7b). The sloping character of the curves is typical of an insertion/de-insertion process into a single-phase cathode host material according to the reaction (1).



While the charge/discharge overpotential of the cell with single-cation-conducting PE is lower by few tens of mV, Faradaic efficiency is close to 100% in all the cells. The 10% difference in the absolute value of the discharge capacity between the pure membrane and the C6P:SiO₂-containing polymer electrolyte is apparently caused by the difference in the membrane thickness, which is 90 and 180 μm, respectively. Another possible explanation is the 8% reproducibility of the capacity of electrodeposited home-made MoO_yS_z cathodes

A comparison of the polarization curves of the pure polymer electrolyte and the additive-incorporated membrane is shown in Fig. 8. As can be seen from the graph that shows the power as a function of the applied current at 90 °C, the peak power of the Li/MoO_xS_y thin-film cell with the pure LiTf:P(EO)₂₀ membrane and that containing C6P is about 1.6 mW cm⁻² (at 50C) and 2.1 mW cm⁻² (at 75C), respectively. While adding both C6P and silica the highest power was achieved (about 2.6 mW cm⁻², Fig. 8a) and this was the only cell that delivered 2.0 mA cm⁻² (100C) without losing power. Even at 150C the cell with dual composite polymer electrolyte exhibited power higher than 2 mW cm⁻². At low rates the power vs. current density plots

of the two cells containing silica one with and one without the C6P are overlapping (Fig. 8). This is in spite of the difference in the thickness of the polymer membranes, (a fact that causes higher internal resistance). In [23] the high polarization of the intercalation/deintercalation cells with single-cation-conducting PE is ascribed to poor kinetics or ion transport across the cathode/electrolyte interface. High peak power capability was measured for the cell with modified polymer electrolyte operating at 110 °C as well (Fig. 8b), which indicates high mechanical strength of the C6P-SiO₂-containing membrane.

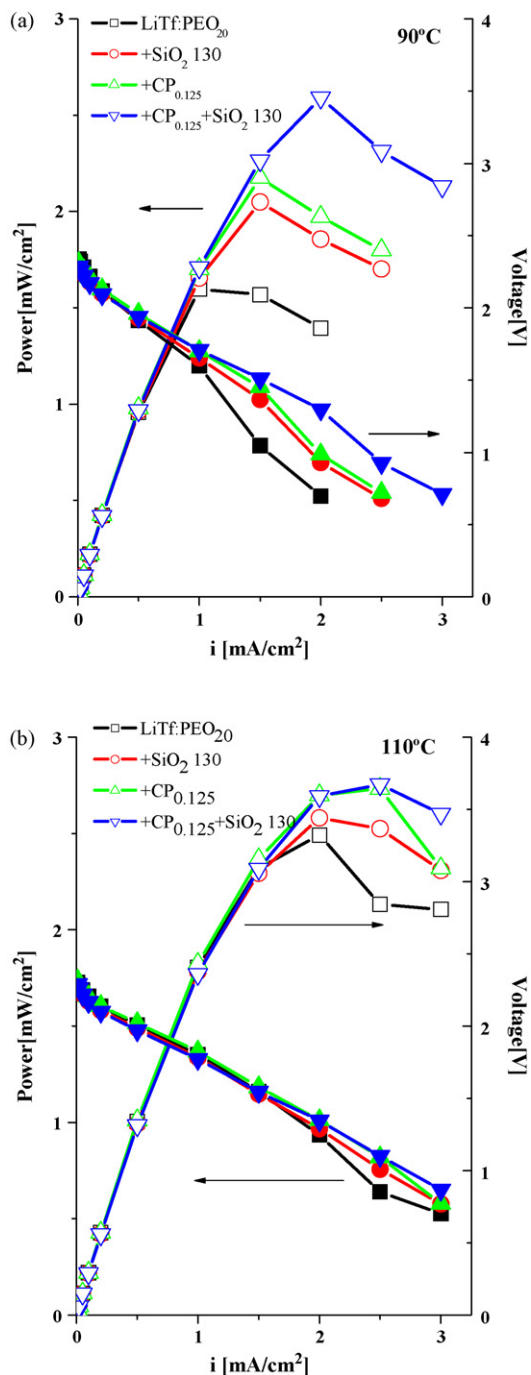


Fig. 8. Polarization curves of thin-film Li/LiCF₃SO₃:P(EO)₂₀:C6P_n:SiO₂/MoO_xS_y cells at 90 °C (a) and 110 °C (b).

4. Conclusions

Modification of lithium triflate:PEO-based polymer electrolyte by calix[6]pyrrole and silica was carried out. Effect of these additives on the lithium transference number, ionic conductivity and electrochemical stability has been studied. Single cation conducting composite polymer electrolyte with good electrochemical properties has been demonstrated. It is shown that addition of calix[6]pyrrole to polyether-based lithium triflate electrolyte results in a considerable increase in the cation transport number, t_{Li^+} even at small amount of additive. Additional incorporation of silica results in enhancement of ionic conductivity and electrochemical stability window. At low current density Li/MoO_xS_y thin film batteries with modified PE show stable reversible behavior with charge-discharge curves almost identical to the cells comprising pure membrane. However, the batteries, which consist of composite polymer electrolyte with both silica and the anion trap (C6P), seem to be promising for high-power applications.

Acknowledgement

This work has been carried out with the financial support of the European Office of Aerospace Research and Development, London, U.K.

References

- [1] M.B. Armand, J.M. Chabagno, M. Duclot, in: P. Vashishta, J.N. Mundy, G.K. Shenoy (Eds.), *Fast Ion Transport in Solids*, North Holland, New York, 1979, p. 131.
- [2] M.A. Ratner, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Review 1*, Elsevier, New York, 1987, p. 173.
- [3] M. Doyle, T.F. Fuller, J. Newman, *Electrochim. Acta* 39 (13) (1994) 2073.
- [4] B. Scrosati, in: B. Scrosati (Ed.), *Applications of Electroactive Polymers*, Chapman and Hall, London, 1993.
- [5] H.R. Allcock, D.T. Welna, A.E. Maher, *Solid State Ionics* 177 (2006) 741.
- [6] D.P. Siska, D.F. Shriver, *Chem. Mater.* 13 (2001) 4698.
- [7] Y. Matsuda, M. Morita, H. Tsutsumi, *Polymers for Advanced Technologies* 4 (2–3) (2003) 209.
- [8] Z. Florjanczyk, W. Bzducha, N. Langwald, J.R. Dugas, F. Krok, B. Misztal-Faraj, *Electrochim. Acta* 45 (2000) 3563.
- [9] P.E. Trapa, M.H. Acar, D.R. Sadoway, A.M. Mayes, *J. Electrochem. Soc.* 152 (12) (2005) A2281.
- [10] M. Kalita, M. Bukat, M. Ciosek, S.H. Chung, T. Rodríguez, S.G. Greenbaum, R. Kovarsky, D. Golodnitsky, E. Peled, D. Zane, B. Scrosati, W. Wieczorek, *Electrochim. Acta* 50 (19) (2005) 3942.
- [11] D. Golodnitsky, R. Kovarsky, H. Mazar, Yu. Rosenberg, I. Lapidés, E. Peled, W. Wieczorek, A. Plewa, M. Siekierski, M. Kalita, L. Settini, B. Scrosati, L.G. Scanlon, *J. Electrochem. Soc.* 154 (6) (2007) A547.
- [12] A. Błażejczyk, M. Szczupak, W. Wieczorek, P. Cmoch, G.B. Appetecchi, B. Scrosati, R. Kovarsky, D. Golodnitsky, E. Peled, *Chem. Mater.* 17 (2005) 1535.
- [13] P.G. Bruce, J. Evans, C.A. Vincent, *Solid State Ionics* 28–30 (1988) 918.
- [14] G.B. Appetecchi, G. Dautzenberg, B. Scrosati, *J. Electrochem. Soc.* 143 (1996) 6.
- [15] V. Yufit, M. Nathan, D. Golodnitsky, E. Peled, *J. Power Sources* (2003) 169.
- [16] J. Maier, *Solid State Ionics* 175 (2004) 7.
- [17] D. Golodnitsky, G. Ardel, E. Peled, *Solid State Ionics* 147 (2002) 141.
- [18] S. Panero, B. Scrosati, H.H. Sumathipala, W. Wieczorek, *J. Power Sources* 167 (2007) 510–514.
- [19] D. Golodnitsky, G. Ardel, E. Strauss, E. Peled, Y. Lareah, Yu. Rosenberg, *J. Electrochem. Soc.* 144 (10) (1997) 3484.
- [20] L.A. Dominey, in: G. Pistoia (Ed.), *Lithium Batteries: New Materials, Developments and Perspectives*, Elsevier, 1994, p. 137 [Chapter 4].
- [21] S. Sadki, P. Schottland, G. Sabouraud, N. Brodie, *Chem. Soc. Rev.* 29 (2000) 283.
- [22] I.W. Cheung, K.B. Chin, E.R. Greene, M.C. Smart, S. Abbrent, S.G. Greenbaum, G.K.S. Prakash, S. Surampudi, *Electrochim. Acta* 48 (14–16) (2003) 2149.
- [23] P.E. Trapa, A.B. Reyes, R.S.D. Gupta, A.M. Mayes, D.R. Sadoway, *J. Electrochem. Soc.* 153 (2006) A1098.