

Characteristics of lithium-ion-conducting composite polymer-glass secondary cell electrolytes

Xiang-Wu Zhang^{a,*}, Chunsheng Wang^a, A. John Appleby^a, Frank E. Little^b

^aCenter for Electrochemical Systems and Hydrogen Research, Texas Engineering Experiment Station,
Texas A&M University, College Station, TX 77843-3402, USA

^bCenter for Space Power, Texas Engineering Experiment Station, Texas A&M University, College Station, TX 77843-3118, USA

Received 11 June 2002; accepted 24 June 2002

Abstract

A family of lithium-ion-conducting composite polymer-glass electrolytes containing the glass composition $14\text{Li}_2\text{O}-9\text{Al}_2\text{O}_3-38\text{TiO}_2-39\text{P}_2\text{O}_5$ (abbreviated as $(\text{LiAlTiP})_x\text{O}_y$) with high ionic conductivity, an excellent electrochemical stability range, and high compatibility with lithium insertion anodes is described. An optimized composition has a room temperature conductivity of $1.7 \times 10^{-4} \text{ S cm}^{-1}$, an Li^+ transference number of 0.39, and an electrochemical stability window to +5.1 V versus Li/Li^+ . It also has good interfacial stability under both open-circuit and lithium metal plating–stripping conditions and provides good shelf-life.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Composite electrolyte; Li^+ -conducting glasses; Conductivity; Stability; Interfacial properties

1. Introduction

Lithium-ion secondary cells are the most effective answer to the increasing requirement for electrochemical power sources with safe and reliable electrochemical power sources with high energy density and long cycle life [1]. Lithium metal anodes would provide higher energy density, but their reactivity with liquid electrolytes to form passivation layers gives poor material utilization, while the formation of lithium dendrites on charge and other uncontrolled phenomena lead to serious safety problems [2]. Work has, therefore, generally focused on the development of true solid-state “dry” electrolytes with both high conductivity and limited reactivity with lithium metal anodes [3–5].

Solid polymer electrolytes based on high molecular weight dielectric polymer hosts, generally polyethylene oxide (PEO), seem the most suitable electrolytes for such applications. Their ether groups solvate lithium-ions in the same manner as crown ethers, and confer low reactivity, increasing safety. However, the room temperature conductivities of PEO-based polymer electrolytes are in the range of 10^{-6} to $10^{-8} \text{ S cm}^{-1}$ because of low effective carrier mobility in the largely crystalline material below the transition

temperature ($\sim 60^\circ\text{C}$) [5,6]. In a recent work, the use of inorganic particle fillers dispersed in host polymer to form a composite solid polymer electrolyte (CSPE) has been examined [3]. Such inorganic fillers as Al_2O_3 , BaTiO_3 and LiAlO_2 increase ionic conductivity by stabilizing the highly conductive amorphous phase, improve the electrode–electrolyte interfacial stability by trapping residual impurities, extend shelf-life by decreasing PEO recrystallization rate and increase the lithium-ion transference number [3,5–7].

These fillers have no lithium-ion conductivity, so the room temperature conductivity of such composite polymer electrolytes is still too low ($< 1 \times 10^{-5} \text{ S cm}^{-1}$) for practical applications. The approach used here to increase their low temperature conductivities is the formulation of new composite solid polymer electrolytes in which the non-conducting particles are replaced by brittle glassy particles with very high lithium-ion conductivity. This approach has been previously explored using the composition $0.56\text{Li}_2\text{S}-0.19\text{B}_2\text{S}_3-0.25\text{LiI}$ and Li_3N , giving electrolytes with conductivities of 3×10^{-4} and $1.4 \times 10^{-4} \text{ S cm}^{-1}$ [8,9]. However, the former is environmentally sensitive, and the latter has poor electrochemical stability ($< 2.5 \text{ V}$ versus Li^+/Li) and is thermally unstable [8,9]. The glass $14\text{Li}_2\text{O}-9\text{Al}_2\text{O}_3-38\text{TiO}_2-39\text{P}_2\text{O}_5$ (abbreviated as $(\text{LiAlTiP})_x\text{O}_y$) has the highest solid-state Li^+ conductivity reported to date ($\sim 10^{-3} \text{ S cm}^{-1}$) [10,11]. It has been used as a filler in polyvinylidene

* Corresponding author. Fax: +1-979-845-9287.
E-mail address: xwzhang@tamu.edu (X.-W. Zhang).

fluoride (PVDF)- and PEG-based gel electrolytes [12,13]. However, high ionic conductivity ($>10^{-4}$ S cm $^{-1}$) was only obtained with a very high filler content (e.g. 66 wt.% with PEG), which resulted in poor processability and mechanical properties. A further disadvantage of such gel compositions is the liquid component, which often results in poor interfacial stability with solid electrolyte interface (SEI) film formation.

In this work, a new class of volatile-solvent-free (i.e. plasticizer-free) “dry” solid polymer electrolytes with a dry PEO–lithium salt complex filled with (LiAlTiP) $_x$ O $_y$ glass is reported. Its ionic conductivity, electrochemical stability window, Li $^+$ transference number, shelf-life, and interfacial stability under secondary cell conditions were investigated.

2. Experimental

2.1. Preparation of electrolyte films

The PEO polymer (Aldrich; molecular weight 600,000 Da) was dried under vacuum at 50 °C for 24 h. Lithium bis(perfluoroethanesulfonyl) imide (LiN(SO $_2$ CF $_2$ -CF $_3$) $_2$; 3M Company) and LiClO $_4$ (Aldrich) were dried at 120 °C for 24 h. The glass 14Li $_2$ O–9Al $_2$ O $_3$ –38TiO $_2$ –39P $_2$ O $_5$ was prepared by the method described by Fu from Li $_2$ CO $_3$, Al(OH) $_3$, TiO $_2$, and NH $_4$ H $_2$ PO $_4$ starting materials [10,11]. The product was ball-milled for 24 h and sieved through No. 325 mesh (≤ 45 μ m). Its ionic conductivity was 5×10^{-4} S cm $^{-1}$ at 25 °C.

Weighed quantities of PEO, lithium salt (EO/Li molar ratio 8:1) and glass powder were mixed, ball-milled, and hot-pressed at 110 °C and 50 kg cm $^{-2}$ for 10 min to give homogeneous films of area and thickness 4 cm 2 and 150–250 μ m, respectively. All films were annealed at 180 °C under vacuum for 24 h to ensure homogeneity.

2.2. Property measurements

The ionic conductivity of the films was measured by electrochemical impedance spectroscopy (EIS) using symmetrical two-electrode cells sandwiching a film between two stainless steel plate electrodes. Spectra were obtained by sweeping from 65 kHz to 1 Hz with a Solartron FRA 1250 frequency analyzer and a Solartron model 1286 electrochemical interface. The high-frequency intercept of the Nyquist plot on the real-axis gives the resistance R of the electrolyte, from which the ionic conductivity is calculated.

The Li $^+$ transference number (t_{Li^+}) was obtained in the previously mentioned cells by combining EIS measurement with dc polarization [14,15]. The initial interfacial resistance (R_0) of the cell was first determined by EIS analysis. A 10 mV dc polarization (ΔV) was then applied to the cell, and the initial current (I_0) was measured. The current was measured as a function of time by a EG&G PARC Model 273 potentiostat/galvanostat until a steady-state current (I_s)

was obtained. The steady-state interfacial resistance (R_s) was determined by EIS. From these, t_{Li^+} is given by the expression:

$$t_{Li^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

The electrochemical stability window was determined by 10 mV s $^{-1}$ linear sweep voltammetry on a three-electrode cell with a stainless steel plate working electrode, a lithium disk counter-electrode, and a lithium strip reference-electrode.

The stability of the composite polymer electrolyte–lithium electrode interface was first investigated by monitoring the time dependence of the impedance of symmetrical Li/composite electrolyte/Li cells under open-circuit conditions. This impedance measurement was obtained by sweeping from 65 kHz to 0.01 Hz using the same equipment as that for ionic conductivity measurement. Interfacial stability was also studied by lithium plating–stripping cycle tests on symmetrical Li/composite electrolyte/Li cells using an Arbin (College Station, TX) automatic battery cycler.

3. Results and Discussion

3.1. Ionic conductivity

The most important practical electrolyte property is high ionic conductivity. Fig. 1 shows the temperature dependence of ionic conductivity for PEO–LiClO $_4$ –(LiAlTiP) $_x$ O $_y$ composites. No sharp break is observed at the PEO crystalline–amorphous transition temperature of 60–70 °C, indicating that the glass particle filler enhances amorphous regions within the semicrystalline PEO phase [16]. This enhancement is believed to increase PEO ionic conductivity because Li $^+$ is only transferred in the amorphous phase [17]. In

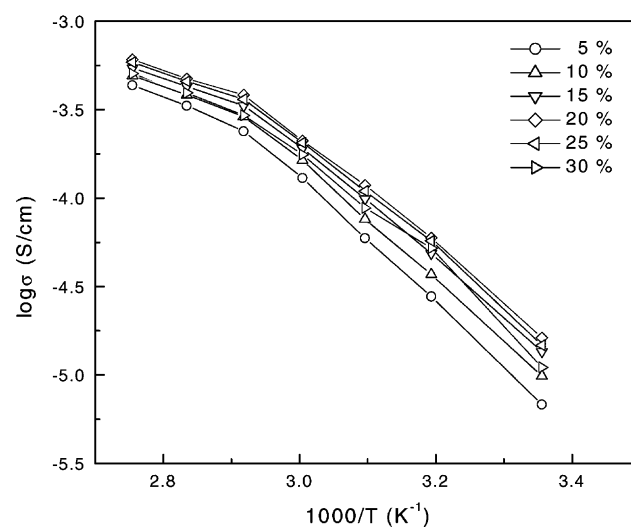


Fig. 1. Arrhenius plots of PEO–LiClO $_4$ –(LiAlTiP) $_x$ O $_y$ composite polymer electrolytes with various (LiAlTiP) $_x$ O $_y$ contents.

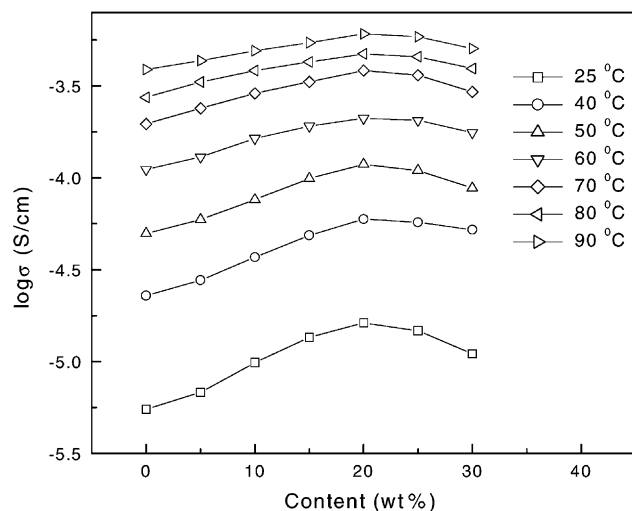


Fig. 2. Ionic conductivities as a function of $(\text{LiAlTiP})_x\text{O}_y$ content for $\text{PEO-LiClO}_4-(\text{LiAlTiP})_x\text{O}_y$ composite polymer electrolytes at various temperatures.

addition, the intrinsic conductivity of the $(\text{LiAlTiP})_x\text{O}_y$ glass ($5 \times 10^{-4} \text{ S cm}^{-1}$) increases the conductivity of the composite, as is discussed later.

Fig. 2 shows the conductivity for $\text{PEO-LiClO}_4-(\text{LiAlTiP})_x\text{O}_y$ composites examined as a function of composition. It is evident that the ionic conductivity increases with the increasing $(\text{LiAlTiP})_x\text{O}_y$ content until a maximum is reached at 20 wt.%. For most non-conducting ceramic fillers, a conductivity enhancement with PEO is only observed below the transition temperature [4]. Above this temperature, the amorphous polymer fraction should be sufficient to assure high ionic conductivity. However, a decrease in conductivity is sometimes observed because non-conducting ceramic fillers often stiffen the host polymer [4]. Hence, the high conductivity of $(\text{LiAlTiP})_x\text{O}_y$ glass filler must play an important role in improving ionic conductivity above the transition temperature (Fig. 2). Thus, $(\text{LiAlTiP})_x\text{O}_y$ glass filler improves composite polymer electrolyte conductivity not only by enhancing the amorphous PEO phase, but also via its intrinsic conductivity.

The nature of the lithium salt also affects the conductivity of the composites electrolytes. Because of their large counter ions, some low solid-state energy lithium salts, e.g. $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$, interfere with PEO crystallization, promoting amorphous regions and increasing ionic conductivity. Fig. 3 shows the temperature dependence of the ionic conductivity for $\text{PEO-LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2-(\text{LiAlTiP})_x\text{O}_y$ composites. Comparing Fig. 3 with Fig. 1 shows that the ionic conductivity of $\text{PEO-LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2-(\text{LiAlTiP})_x\text{O}_y$ is higher than that of the corresponding LiClO_4 -containing material at the same glass content at all temperatures. Fig. 4 shows the dependence of conductivity on composition for $\text{PEO-LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2-(\text{LiAlTiP})_x\text{O}_y$ composites, indicating that the optimum glass content is 30 wt.% at any temperature, with a maximum room temperature

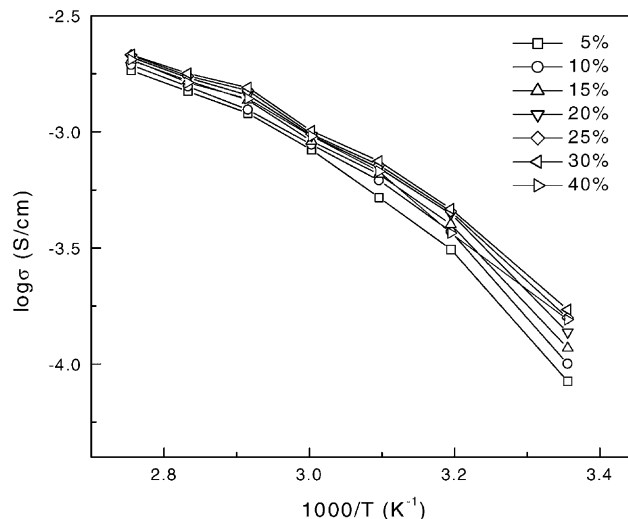


Fig. 3. Arrhenius plots of $\text{PEO-LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2-(\text{LiAlTiP})_x\text{O}_y$ composite polymer electrolytes with various $(\text{LiAlTiP})_x\text{O}_y$ contents.

conductivity of $1.7 \times 10^{-4} \text{ S cm}^{-1}$, a high value for polymer electrolyte lithium secondary cells.

3.2. Shelf-life

Polymer chain thermal motion causes the amorphous PEO phase to slowly recrystallize at room temperature, which results in a loss of ionic conductivity during storage. Conductivity was therefore monitored as a function of time over 80 days at 25 °C with and without the glass filler (Fig. 5). For the compositions studied, conductivity decreased with time until a steady state was reached. However, the decrease was less when an optimum amount of glass filler was present, which is evidence it can hinder recrystallization of the

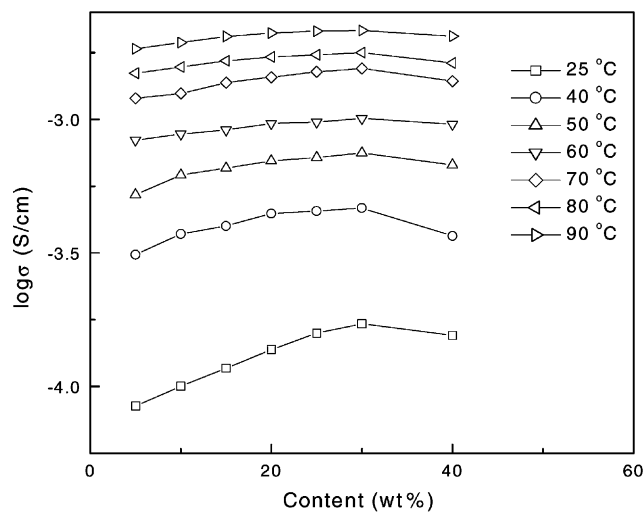


Fig. 4. Ionic conductivities as a function of $(\text{LiAlTiP})_x\text{O}_y$ content for $\text{PEO-LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2-(\text{LiAlTiP})_x\text{O}_y$ polymer electrolytes at various temperatures.

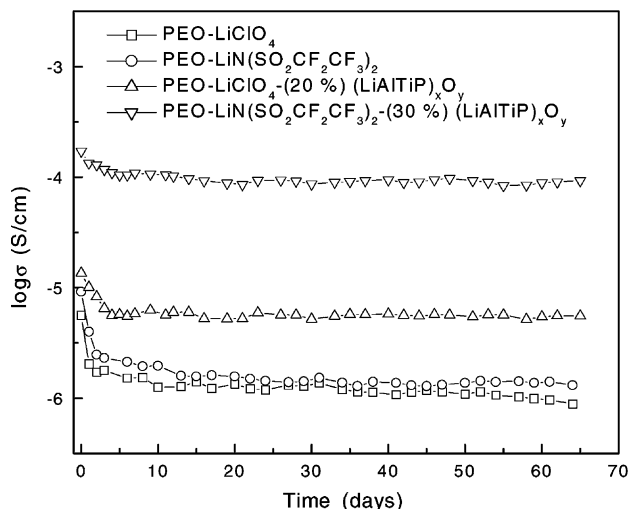


Fig. 5. Ionic conductivities as a function of storage time at 25 °C for the PEO–LiClO₄, PEO–LiN(SO₂CF₂CF₃)₂, PEO–LiClO₄–(20 wt.% (LiAlTiP)_xO_y) and PEO–LiN(SO₂CF₂CF₃)₂–(30 wt.% (LiAlTiP)_xO_y) polymer electrolytes.

amorphous phase by acting as nucleation centers [4]. The influence of the anion on PEO recrystallization of polymer is less clear, but Fig. 5 shows that the decrease for PEO–LiN(SO₂CF₂CF₃)₂–(30 wt.% (LiAlTiP)_xO_y) is less than that of PEO–LiClO₄–(20% (LiAlTiP)_xO_y), which result from its higher glass content.

3.3. Li⁺ transference number

The Li⁺ transference number is another important practical parameter, since in operating cells all the current must be carried by this ion, but electroneutrality must be maintained against any anion concentration gradient. A value lower than unity may result in a low anion concentration at the anode on charge, and at the cathode on discharge, resulting in limiting lithium-ion currents [18]. Thus, the ionic conductivity cannot give a complete knowledge of practical cell resistance. The t_{Li^+} values for optimized chlorate–(20 wt.% glass) and imide–(30 wt.% glass) anion–glass composites and of the corresponding glass-free electrolytes were determined at 25 and 80 °C. The results in Table 1 show that the t_{Li^+} values for all the electrolytes

Table 1

Li⁺ transference number of PEO–LiClO₄, PEO–LiN(SO₂CF₂CF₃)₂, PEO–LiClO₄–(20 wt.% (LiAlTiP)_xO_y) and PEO–LiN(SO₂CF₂CF₃)₂–(30 wt.% (LiAlTiP)_xO_y) polymer electrolytes

	t_{Li^+}	
	25 °C	80 °C
PEO–LiClO ₄	0.27	0.19
PEO–LiClO ₄ –(20 wt.% (LiAlTiP) _x O _y)	0.31	0.24
PEO–LiN(SO ₂ CF ₂ CF ₃) ₂	0.34	0.20
PEO–LiN(SO ₂ CF ₂ CF ₃) ₂ –(30 wt.% (LiAlTiP) _x O _y)	0.39	0.23

studied are lower at 80 °C than at 25 °C, which may be due to the higher mobility of the anions compared to Li⁺ at evaluated temperature.

(LiAlTiP)_xO_y is believed to be exclusively a Li⁺ conductor with $t_{Li^+} = 1$ [13]. Therefore, the introduction of conducting glass into the polymer electrolyte increases the overall t_{Li^+} value. As shown in Table 1, the imide anion increases the t_{Li^+} value by a larger amount than chloride, and the composition optimized for conductivity has a value of 0.39 at 25 °C, which is sufficient to meet the requirements of lithium secondary cells [19]. One striking aspect of the results is the large increase in total conductivity at 25 °C (a factor of 18; Fig. 5) when the glass is added to the imide electrolyte. In this case, the lithium cation conductivity rises by a factor of 21, whereas the imide anion conductivity increases by a factor of 17. In the chlorate case, the corresponding figure for the increase in total conductivity is only a factor of 2.1, corresponding to an increase in lithium cation conductivity by a factor of 2.4, and an increase in anion conductivity by 2.0. In both cases, the increase in cation to anion conductivity is a factor of 1.25. The most probable explanation of the results is the “plasticizing” nature of the imide anion, which results in a much more amorphous PEO phase, especially in the presence of the glass. It is also clear that the addition of approximately 10–15 vol.% of lithium-conducting glass with a conductivity 50–100 times higher than that of the polymer matrix has relatively little effect in the chlorate anion mixture. The glass is certainly not being effectively used for conduction in the chlorate anion case. The problem may be due to interfacial polarization at the PEO–glass interface.

3.4. Electrochemical stability window

A third parameter for the practical electrolytes is its kinetic electrochemical stability window. This was determined by linear sweep voltammetry on a cell containing polymer electrolytes sandwiched between stainless steel working- and a lithium counter-electrode, with a lithium reference-electrode. The potential of current onset may be regarded as the breakdown voltage of the electrolyte. Fig. 6 shows the results for chlorate anion composites with and without 20 wt.% glass, and Fig. 7 shows those for the corresponding imide materials with and without 30 wt.% glass. It is clear that the glass acts as a stabilizer, enhancing the electrochemical stability of the PEO phase. The stability window of the 20 wt.% chlorate anion composite is about 4.6 V versus Li/Li⁺, while that of the 30 wt.% imide composite is 5.1 V. The imide anion therefore also contributes to overall electrochemical stability.

The experimental windows are kinetic, and may depend on processes occurring at the electrode [20], so the composite electrolytes may possibly break down at somewhat lower voltages under differing conditions. However, the chlorate and imide anion–glass composites should be safe to about 4.0 and 4.5 V versus Li/Li⁺, respectively.

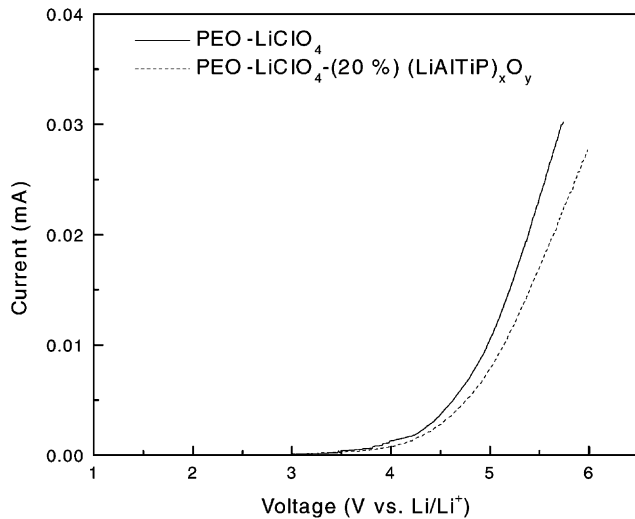


Fig. 6. Linear sweep voltammetry for PEO-LiClO₄ and PEO-LiClO₄-(20 wt.% (LiAlTiP)_xO_y) polymer electrolytes. Scan rate: 10 mV s⁻¹.

3.5. Interfacial stability

A final condition for practical lithium metal secondary cells is compatibility with a lithium anode [21], which often involve a continuously-growing surface electrolyte interface film or passivation layer, which is a reaction product of lithium with electrolyte components [22]. This layer not only impedes charge transfer, but also introduces a heterogeneous potential gradient, which in turn may initiate dendrite growth because of its heterogeneity structure, which leads to serious safety problem. Hence, interfacial stability was studied under both open-circuit and lithium plating-stripping conditions.

The EIS of a symmetrical Li/composite electrolyte/Li cell was first obtained at open-circuit at 80 °C (Fig. 8). The

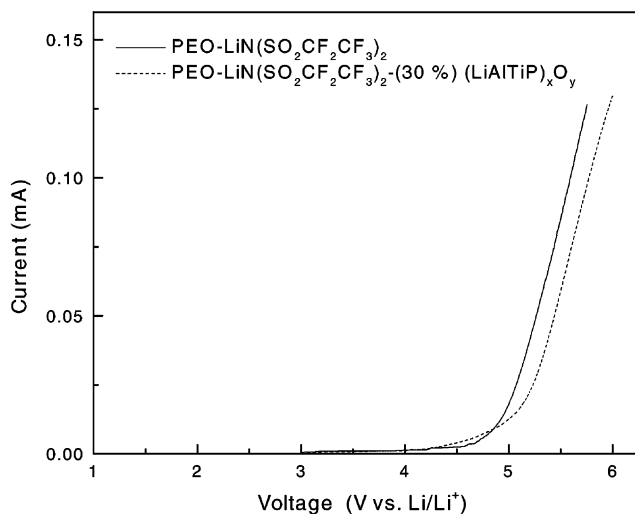


Fig. 7. Linear sweep voltammetry for the PEO-LiN(SO₂CF₂CF₃)₂ and PEO-LiN(SO₂CF₂CF₃)₂-(30 wt.% (LiAlTiP)_xO_y) polymer electrolytes. Scan rate: 10 mV s⁻¹.

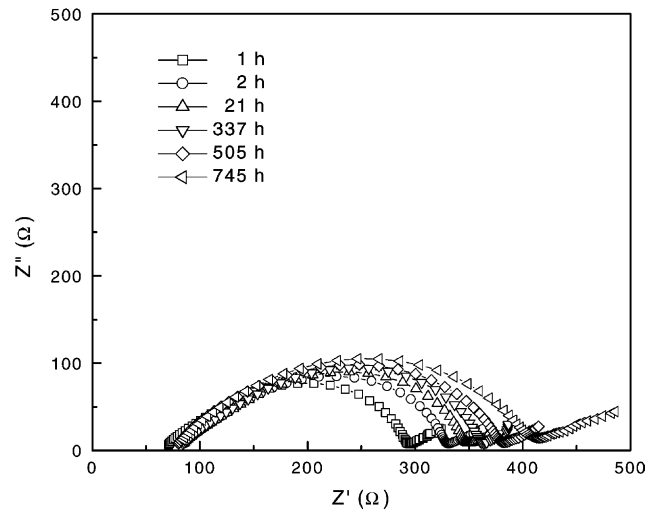


Fig. 8. Time dependence of the impedance response of a Li/PEO-LiN(SO₂CF₂CF₃)₂-(30 wt.% (LiAlTiP)_xO_y)/Li cell at 80 °C. Electrode area: 0.5 cm².

Nyquist plots show an extension of the intermediate-frequency semicircle, indicating the growth of a SEI-like film. Fig. 9 shows the interfacial resistance calculated from the semicircle diameter as a function of time. For all the electrolytes studied, this resistance first increases in a distinct manner indicating film formation, and then shows a further irregular increase indicating structural instability of the film [23]. The passivation reactions usually result from the presence of plasticizing organic solvents and unstable anions in polymer electrolytes [18]. For electrolytes without such solvents containing stable anions, they mainly result from trace impurities from the raw materials or preparation procedure. The results in Fig. 9 show that the glass additive must trap such impurities, stabilizing the anode interface. The anion also influences the interfacial stability, but to a

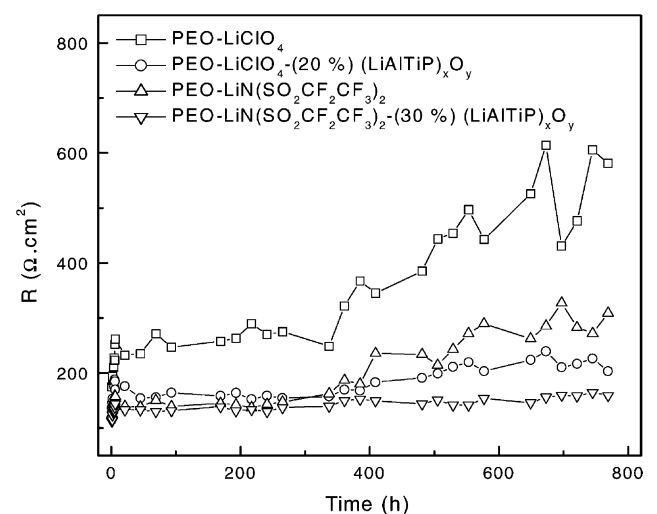


Fig. 9. Interfacial resistances as a function of time at 80 °C for the PEO-LiClO₄, PEO-LiN(SO₂CF₂CF₃)₂, PEO-LiClO₄-(20 wt.% (LiAlTiP)_xO_y) and PEO-LiN(SO₂CF₂CF₃)₂-(30 wt.% (LiAlTiP)_xO_y) polymer electrolytes.

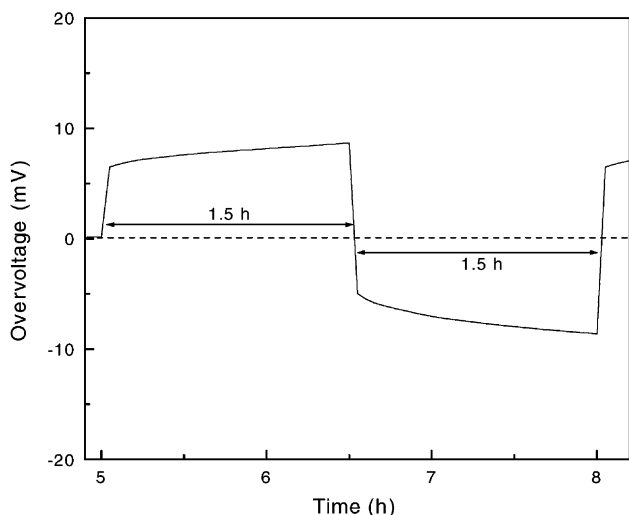


Fig. 10. Typical voltage behavior of a Li/PEO-LiN(SO₂CF₂CF₃)₂-(30 wt.% (LiAlTiP)_xO_y)/Li cell at 25 °C during lithium plating-stripping test at 0.15 mA cm⁻² reversed every 1.5 h. Electrode area: 1.0 cm².

much less extent than that of the glass. Overall, the PEO-LiN(SO₂CF₂CF₃)₂-(30 wt.% (LiAlTiP)_xO_y) composite shows the highest open-circuit interfacial stability of the electrolytes tested.

Stability during lithium plating-stripping cycling, i.e. under operating conditions, is examined in Fig. 10 for a symmetrical Li/imide anion-30 wt.% glass/Li cell. A constant current of 0.15 mA cm⁻² was applied whose direction was reversed every 1.5 h. A passivation film continuously formed at the cathodic electrode during lithium deposition, whereas the pre-existing film formed on the dissolving electrode tended to break down [7,23]. The cell voltage at the end of each plating-stripping half-cycle corresponds to the overall cell impedance, i.e. the electrolyte and the two

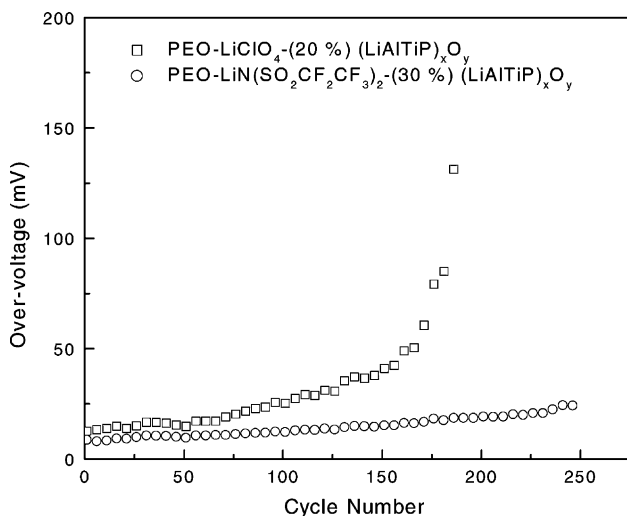


Fig. 11. End of half-cycle voltages as a function of cycle number for the Li/PEO-LiClO₄-(20 wt.% (LiAlTiP)_xO_y)/Li and Li/PEO-LiN(SO₂CF₂CF₃)₂-(30 wt.% (LiAlTiP)_xO_y)/Li cells.

electrolyte-electrode interfacial impedances. Since this cell voltage is very sensitive to any changes in the passivation layer, this is a good test of interfacial stability under cycling conditions [23].

Fig. 11 shows the end of the half-cycle voltage during lithium plating-stripping cycling for the symmetrical cells studied. Although the chlorate anion-(20 wt.% glass) electrolyte showed good interfacial stability at open-circuit, it showed a rapid increase in half-cycle voltage after about 150 cycles. The imide anion-(30 wt.% glass) electrolyte showed an initially lower half-cycle voltage, which remained very stable over 250 cycles. The poor interfacial stability of the chlorate anion-(20 wt.% glass) electrolyte on cycling may be associated with the nature of the anion and its lower ceramic content. In contrast, the imide anion-(30 wt.% glass) electrolyte has satisfactory interfacial stability at both open-circuit and under lithium plating-stripping cycling.

4. Conclusions

The addition of Li⁺-conducting (LiAlTiP)_xO_y glass into PEO-based polymer electrolyte improves ionic conductivity, with some increase in Li⁺ transference number, and extends the PEO electrolyte stability window. The use of the large bis(perfluoroethanesulfonyl) imide anion-N(SO₂CF₂CF₃)₂⁻ with 30 wt.% glass in the composite significantly increases conductivity, Li⁺ ion charge transfer, and interfacial stability under open-circuit and cycling conditions.

Acknowledgements

We gratefully acknowledge NASA-Glenn Research Center, Cleveland OH, for support of this work.

References

- [1] P. Mustarelli, E. Quartarone, C. Tomasi, A. Magistris, *Solid State Ionics* 135 (2000) 81.
- [2] G.B. Appetecchi, W. Henderson, P. Villano, M. Berretoni, S. Passerini, *J. Electrochem. Soc.* 148 (2001) A1171.
- [3] B. Scrosati, F. Croce, L. Persi, *J. Electrochem. Soc.* 147 (2000) 1718.
- [4] H.Y. Sun, H.-J. Sohn, O. Yamamoto, Y. Takeda, N. Imanishi, *J. Electrochem. Soc.* 146 (1999) 1672.
- [5] L. Persi, F. Croce, B. Scrosati, E. Plichta, M.A. Hendrickson, *J. Electrochem. Soc.* 149 (2002) A212.
- [6] G.B. Appetecchi, F. Croce, G. Dautzenberg, M. Mastragostino, F. Ronci, B. Scrosati, F. Soavi, A. Zaneli, F. Alessandrini, P.P. Prosini, *J. Electrochem. Soc.* 145 (1998) 4126.
- [7] G.B. Appetecchi, S. Passerini, *Electrochim. Acta* 45 (2000) 2139.
- [8] E. Quataarone, P. Mustarelli, A. Magistris, *Solid State Ionics* 110 (1998) 1.
- [9] J. Cho, M. Liu, *Electrochim. Acta* 42 (1997) 1481.
- [10] J. Fu, *J. Mater. Sci.* 33 (1998) 1549.
- [11] J. Fu, *Solid State Ionics* 96 (1997) 195.
- [12] K.M. Abraham, V.R. Koch, T.J. Blakley, *J. Electrochem. Soc.* 147 (2000) 1251.

- [13] K. Nairn, M. Forsyth, H. Every, M. Greville, D.R. MacFarlane, *Solid State Ionics* 86–88 (1996) 589.
- [14] Y. Kato, M. Watanabe, K. Sanui, N. Ogata, *Solid State Ionics* 40 (1990) 632.
- [15] J. Cho, M. Liu, *Electrochim. Acta* 42 (1997) 1481.
- [16] B. Scrosati, F. Croce, *Pol. Adv. Technol.* 4 (1993) 198.
- [17] F. Capuano, F. Croce, B. Scrosati, *J. Electrochem. Soc.* 138 (1991) 1918.
- [18] F.B. Dias, L. Plomp, J.B.J. Veldhuis, *J. Power Sources* 88 (2000) 169.
- [19] K.L. Heitner, *J. Power Sources* 89 (2000) 128.
- [20] Y. Xia, T. Fujieda, K. Tatsumi, P.P. Prosini, T. Sakai, *J. Power Sources* 92 (2000) 234.
- [21] G.B. Appetecchi, G. Dautzenberg, B. Scrosati, *J. Electrochem. Soc.* 143 (1996) 6.
- [22] Q. Li, H.Y. Sun, Y. Takeda, N. Imanishi, J. Yang, O. Yamamoto, *J. Power Sources* 94 (2001) 201.
- [23] G.B. Appetecchi, S. Scaccia, S. Passerini, *J. Electrochem. Soc.* 147 (2000) 4448.