



Preparation and electrochemical properties of glass-polymer composite electrolytes for lithium batteries

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Abstract—Electrochemical behavior of a new class of glass-polymer composites (GPC), consisting of (100-x) vol% (0.56Li₂S·0.19B₂S₃·0.25LiI) glass and x vol% (P(EO)₆·LiN(CF₃SO₂)₂) polymer with x = 7, 13 and 25, has been investigated in cells with different electrodes. Results show that the addition of the polymer to the glass powder increases not only the mechanical flexibility but also the ionic conductivity. The combination of impedance spectroscopy and 4-probe *dc* measurements indicates that the GPC with x = 13 vol% polymer exhibits the highest lithium ion conductivity, varying from $3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ at room temperature to $1.4 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at 80°C. In addition, the GPC electrolytes with x = 13 vol% seem to be relatively stable against Li, Li_xMn₂O₄, and carbon electrodes, since interfacial impedances between the electrolyte and the electrode materials are relatively constant at 70°C for up to 375 hours. © 1997 Elsevier Science Ltd. All rights reserved.

Key words: Glass-polymer composite electrolyte, solid electrolyte, lithium transference number, electrochemical stability, lithium battery.

1. INTRODUCTION

While lithium-ion batteries based on liquid electrolytes have seen significant progress over recent years [1–10], all-solid-state batteries based on solid electrolytes have attracted much attention because of their advantages over batteries based on liquid electrolytes, such as smaller possibility of electrolyte leakage, improved safety, and ease of fabrication. A desired electrolyte for a rechargeable Li battery ought to have high lithium ion conductivities, negligible electronic conductivities, and adequate stability against the two electrodes under operating conditions. In spite of the advantages of a solid electrolyte over a liquid electrolyte, the inherent low mobility of ionic species in solids has been the major limitation of solid electrolytes. This is particularly true for glass electrolytes. For instance, although Li-ion-conducting oxide glasses have shown some potential for battery applications [11], the lithium ion

conductivity has to be enhanced to a level sufficient for practical battery applications. Recently, it was found that much higher conductivities can be achieved by substituting the larger and more polarizable sulfide ion for an oxide ion in the glass structure. With the replacement and the use of dopants, glasses based on B₂S₃, P₂S₅, and SiS₂ [12–17] have shown conductivities of 10^{-3} to $10^{-4} \Omega^{-1} \text{ cm}^{-1}$ at room temperatures.

Another inherent shortcoming of glass electrolytes is the lack of mechanical flexibility, or the brittleness. This can be overcome by forming a glass-polymer composite electrolyte. As recently suggested [18], the addition of a polymer to a glass electrolyte introduces mechanical flexibility to the composite. In addition, when the type and volume fraction of the polymer is properly chosen, the resulting composite electrolytes may exhibit higher ionic conductivity than that of a glass compact electrolyte because (i) the packing density of glass particles may be improved and (ii) the pores between glass particles are filled with a conducting polymer.

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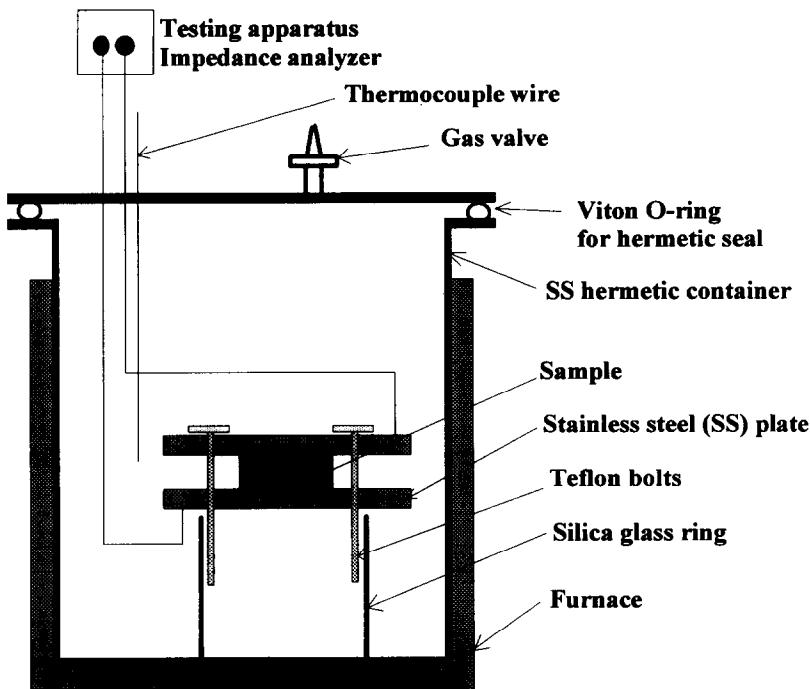
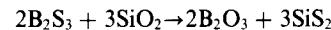


Fig. 1. A schematic view of a hermetic cell for testing the GPC electrolytes or polymer electrolyte.

In this paper, the effect of volume fraction of a polymer phase on the electrochemical properties of glass-polymer composite (GPC) electrolytes is investigated. The lithium ion transference number and ionic conductivity are correlated with the volume fractions of polymer in the GPC. The chemical stabilities of the GPC electrolytes are also studied using Li, Li_xC_6 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ as electrodes. Further, preliminary performance of a $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell based on the GPC electrolyte will be discussed.

2. EXPERIMENTAL

All chemicals handling, preparation of the GPC electrolytes, and cell assembly were performed in a glove box (Vacuum Atmosphere) with the residual O_2 and H_2O less than 5 ppm. Since the commercially available B_2S_3 has low purity and contains considerable amounts of water [19, 20], high purity B_2S_3 was prepared as follows. Appropriate amounts of amorphous boron powder (99.9%, Alfa) and crystalline sulfur (99.999%, Aldrich) were mixed in a mortar and pestle and the powder mixture was then transferred to a previously flame-dried, carbon-coated, and re-flame-dried silica tube. The carbon coating was formed by the pyrolytic decomposition of acetone on the inside of the tube at about 850°C. This carbon coating is necessary because uncoated silica tubes react with B_2S_3 at elevated temperatures according to [19]



The tube was sealed under vacuum using a gas-oxygen torch, and was then heated in a rotating furnace to 850°C and held for 8 h. Then, the tube was quenched in air to room temperature and the obtained glassy B_2S_3 (ν - B_2S_3) was homogenous and dark green in color. The IR spectral analysis indicated that the prepared ν - B_2S_3 contained no observable amount of water. Also, total sulfur

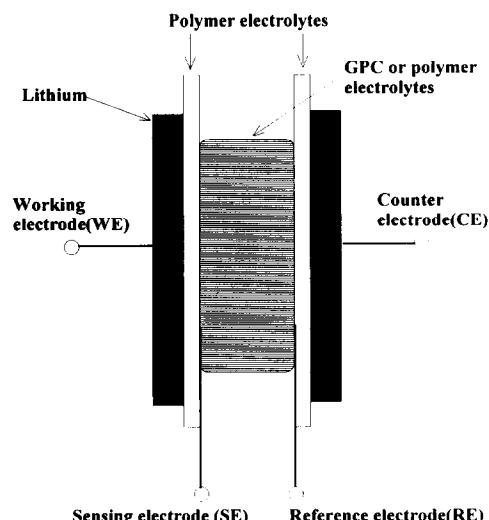


Fig. 2. A schematic view of a cell for 4-probe measurements. Two $\text{P}(\text{EO})_8\text{-LiN}(\text{CF}_3\text{SO}_2)_2$ layers are used to block electronic transport through the cell and for isolation of re from ce and se from we .

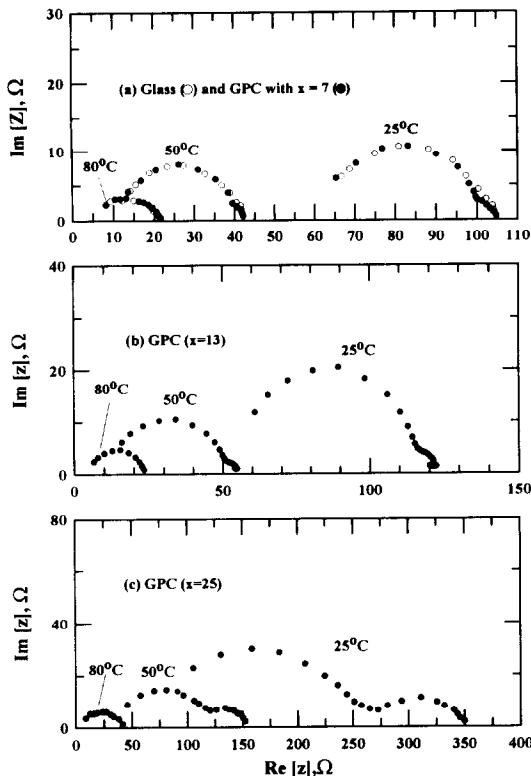


Fig. 3. Typical impedance spectra of $(100-x)$ vol% $(0.55\text{Li}_2\text{S} \cdot 0.19\text{B}_2\text{S}_3 \cdot 0.25\text{LiI})$ and x vol% $((\text{P}(\text{EO})_6 \cdot \text{LiN}(\text{CF}_3\text{SO}_2)_2)$, where $x = 0, 7, 13$, and 25 as measured in a 4-probe cell (the thicknesses of $x = 0$ and 7 were 0.6 mm and the thicknesses of $x = 13$ and 25 were 0.9 mm, the electrode area was 2.85 cm^2).

analyses indicated that the prepared B_2S_3 contained 99% B_2S_3 and about 1% oxides [19, 20].

The $0.56\text{Li}_2\text{S} \cdot 0.19\text{B}_2\text{S}_3 \cdot 0.25\text{LiI}$ glasses were prepared by crushing the B_2S_3 in a mortar and pestle into a fine powder and then mixing with appropriate amount of Li_2S (99.9%, Cerac) and LiI (99.999%, Aldrich) powder in a mortar and pestle. The powder mixture was then transferred to a carbon-coated silica tube and vacuum-sealed using a gas–oxygen torch. Subsequently, the tube was heated to 830°C and kept for 20 min before quenching in liquid N_2 to form glasses.

The GPC electrolytes were prepared by mixing and grinding $(100-x)$ vol% $[0.56\text{Li}_2\text{S} \cdot 0.19\text{B}_2\text{S}_3 \cdot 0.25\text{LiI}]$ glass powder and x vol% $[(\text{P}(\text{EO})_6 \cdot \text{LiN}(\text{CF}_3\text{SO}_2)_2)]$ ($x = 7, 13$, and 25) powder mixture in a mortar and pestle. Polyethylene oxide (Aldrich) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (3 M) were dried under vacuum at 50 and 110°C , respectively, for 10 h before use. The powder mixtures were pressed into pellets in a glove box and then kept at 80°C for 2 h to ensure the polymer flow into the voids between glass particles.

MnO_2 and Li_2CO_3 were reagent grade chemicals obtained from Aldrich and were used as received. Positive electrode material, $\text{Li}_x\text{Mn}_2\text{O}_4$, was prepared in air by solid state reaction of Li_2CO_3 and MnO_2 in

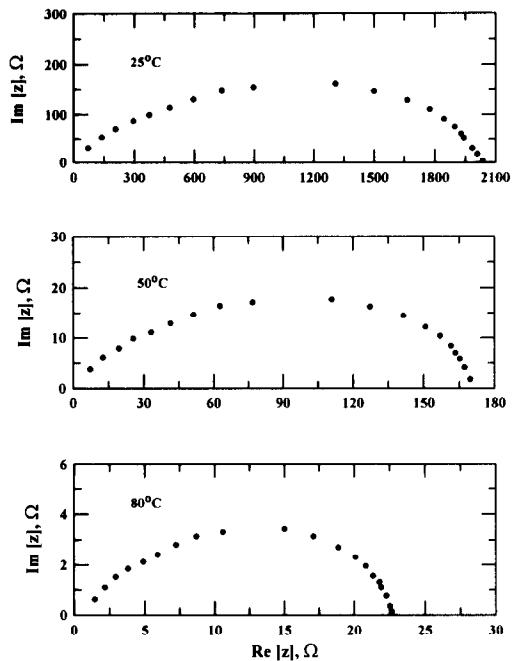


Fig. 4. Typical impedance spectra of a $\text{P}(\text{EO})_6 \cdot \text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte as measured in a 4-probe cell (the electrolyte thickness was $100 \mu\text{m}$ and the electrode area was 4.9 cm^2).

a molar ratio 1:4. The mixture was calcined first at 650°C for 12 h and then at 800°C for 24 h to form the spinel phase, followed by slow cooling to room temperature. A composite positive electrode was prepared by mixing $\text{Li}_x\text{Mn}_2\text{O}_4$, carbon blacks, and GPC electrolyte powder in a weight ratio of 40:10:50. Carbon (Alfa, 99.99%) and GPC electrolyte in a weight ratio of 50:50 were used as the negative

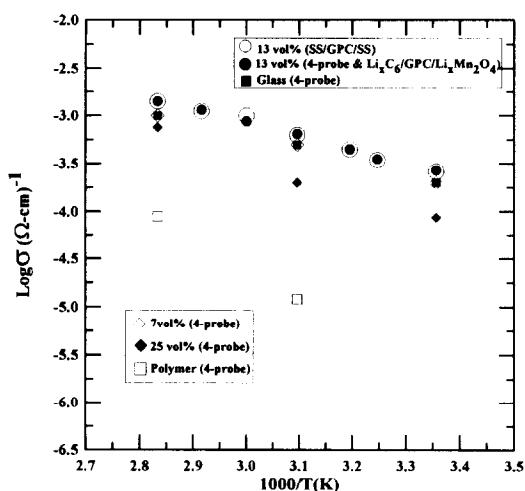


Fig. 5. Total conductivities of glass $(0.55\text{Li}_2\text{S} \cdot 0.19\text{B}_2\text{S}_3 \cdot 0.25\text{LiI})$, polymer $((\text{P}(\text{EO})_6 \cdot \text{LiN}(\text{CF}_3\text{SO}_2)_2)$, and the GPC electrolytes with $7, 13$, and 25 vol% polymer as determined from impedance spectra measured in different cells, SS/GPC/SS, $\text{Li}_x\text{C}_6/\text{GPC}/\text{LiMn}_2\text{O}_4$, and $\text{Li}/\text{PEO}/\text{GPC}/\text{PEO}/\text{Li}$ (4-probe cell).

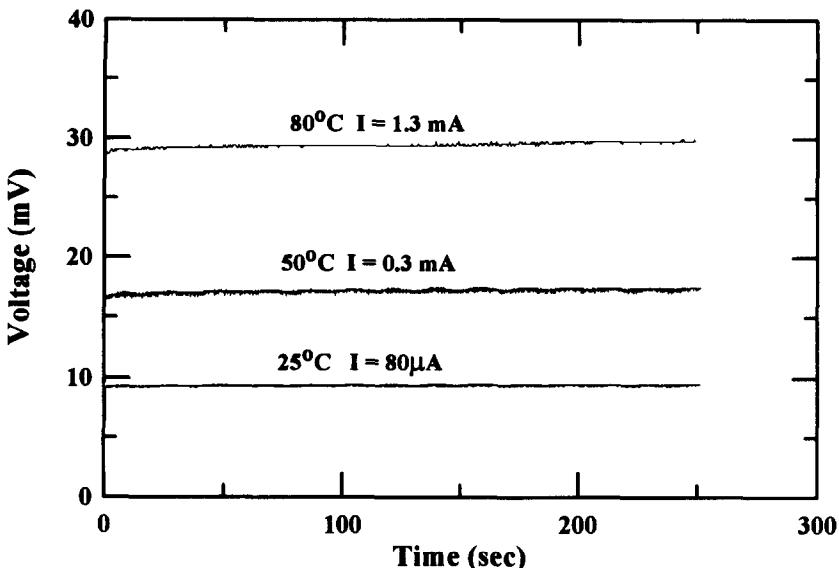


Fig. 6. The observed voltages between *se* and *re* when a constant current is applied through *ce* and *we* in 4-probe *dc* measurements at 25, 50 and 80°C (the thickness of the GPC ($x = 13$) was 0.9 mm and the electrode area was 2.85 cm^2).

electrode. A C/GPC/Li_xMn₂O₄ cell was constructed by pressing a composite Li_xMn₂O₄ electrode, a GPC electrolyte, and a composite carbon electrode into a three-layered pellet and then sandwiched between two stainless steel blocks, which are connected to testing apparatus. The cell was charged and discharged at a current density of 0.1 mA cm^{-2} at 70°C.

A Potentiostat/Galvanostat (EG & E 273A) and a lock-in amplifier (M5120), interfaced with a computer, were used for the electrochemical characterization of the electrolytes and the cells. A Schlumberger frequency response analyzer (1255) and an electrochemical interface (1286), interfaced with a computer, were used to measure the impedance of the GPC or polymer electrolytes in a hermetic cell as shown in Fig. 1. The stability of the GPC electrolytes against Li, Li_xC₆, and Li_xMn₂O₄ electrodes was determined from the impedance spectra of the interfaces. The lithium ion transference number was determined from the combination of impedance spectroscopy and 4-probe *dc* measurements. In Fig. 2 is shown a schematic view of an electrochemical cell with a single layer of the electrolyte to be studied (GPC electrolytes or P(EO)₆·LiN(CF₃SO₂)₂ polymer electrolyte), two layers of PEO electrolytes, and four electrodes: counter electrode (*ce*), reference electrode (*re*), sensing electrode (*se*), and working electrode (*we*) [21].

3. RESULTS AND DISCUSSION

3.1. Preparation of 0.56Li₂S·0.19B₂S₃·0.25LiI glass

It was found that a direct quenching the melt of 0.56Li₂S·0.19B₂S₃·0.25LiI in liquid nitrogen was

sufficiently rapid to obtain glasses. However, partially crystallized glasses or polycrystals were observed when the amount of LiI and Li₂S was more than 25 mol% and 56 mol%, respectively. This is because the continuous addition of glass dopants (LiI and Li₂S) increased the break-down of the long range order of the glass network (*viz.*, the increasing formation of the non-bridging short order structure) and, therefore, the limit of glass formation was eventually reached.

3.2. Total conductivity

Figures 3 and 4 show some typical impedance spectra of the GPC and polymer electrolytes measured in a 4-probe cell, Li/PEO/GPC (or polymer)/PEO/Li, with two reference electrodes. Since the voltages were acquired from the sensing electrode and the reference electrode while a current was applied through the counter and working electrodes, the impedance spectra shown in Figs 3 and 4 are the impedances of the electrolytes. Accordingly, the total resistance or total conductivity of the electrolytes can be readily determined from these impedance spectra.

In Fig. 5 is shown the temperature dependence of conductivities of [P(EO)₆·LiN(CF₃SO₂)₂] polymer, glass, and GPC electrolytes with different volume fractions of polymer measured in cells with different electrodes. The addition of 13 vol% [P(EO)₆·LiN(CF₃SO₂)₂] into 87 vol% [0.56Li₂S·0.19B₂S₃·0.25LiI] glass powder showed the highest conductivity and good mechanical integrity. The ionic conductivity of the GPC electrolyte with $x = 13$ increased from about $3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ at room temperature to $1.4 \times 10^{-3} \text{ W}^{-1} \text{ cm}^{-1}$ at 80°C.

As expected, the ionic conductivities of the GPC electrolyte measured in cells with different electrodes (Li, stainless steel, and $\text{Li}_x\text{C}_6/\text{Li}_x\text{Mn}_2\text{O}_4$) are in a good agreement. It is clear that the conductivities of the GPC electrolyte are greater than those of a pellet consisting of the pure glassy electrolyte powder. We believe that this is because the added polymer fills up the pores among the glass particles.

The conductivities of the GPC with $x = 7$ were similar to those of the glass without polymer, indicating that 7 vol% polymer added to glass powder is not enough to fill up the voids among the glass particles. The conductivities of the GPC with $x = 25$, however, were much smaller than those of GPC with $x = 13$, suggesting that $\text{P}(\text{EO})_6\text{-LiN}(\text{CF}_3\text{SO}_2)_2$ polymer added was too much and influenced the total conductivity of the

composite. As seen in Fig. 5, the conductivities of the polymer electrolyte are much smaller than those of the glass, ranging from $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at room temperature to $9 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 80°C.

3.3. Lithium ion transference number (t_{Li})

Figure 6 shows the observed voltage between the sensing and the reference electrode as a function of time when a constant current was applied through the working and counter electrodes. In a steady state, only lithium cations are allowed to transport through the cell and all other charged species, if there are any, are blocked. Thus, the resistance to the motion of lithium ions in the GPC electrolyte, *i.e.*, the resistance of the electrolyte when used in a lithium battery, is

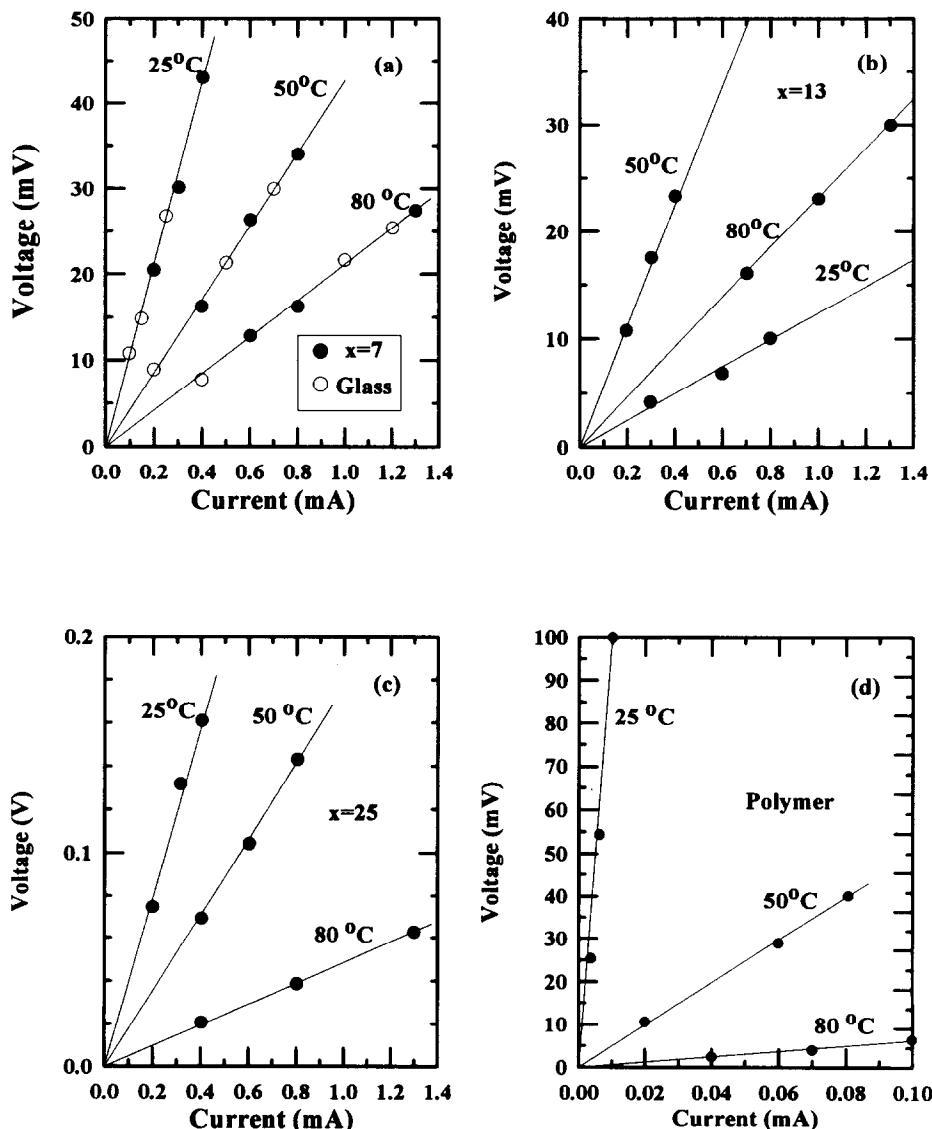


Fig. 7. Current-voltage plots for 4-probe measurements at different temperatures for GPC electrolytes with $x = 0$ (glass), 7, 13, 25, and 100 (polymer).

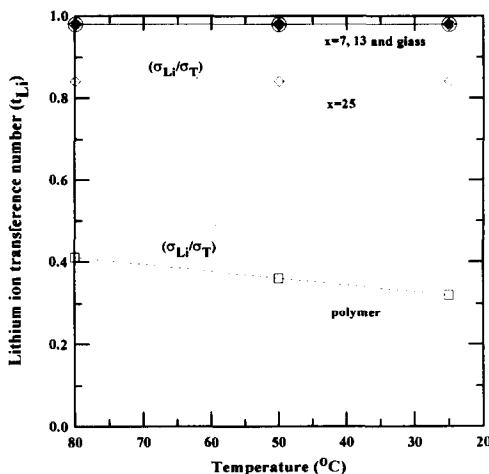


Fig. 8. Ratios of $\sigma_{Li}/\sigma_{total}$ for glass ($0.55Li_2S \cdot 0.19B_2S_3 \cdot 0.25LiI$), polymer ($(P(EO)_6 \cdot LiN(CF_3SO_2)_2$), and for the GPC electrolytes with 7, 13, and 25 vol% polymer.

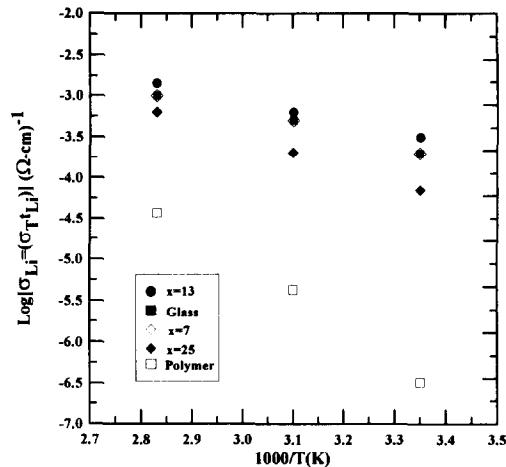


Fig. 9. Lithium ion conductivities of glass ($0.55Li_2S \cdot 0.19B_2S_3 \cdot 0.25LiI$), polymer ($(P(EO)_6 \cdot LiN(CF_3SO_2)_2$), and the GPC electrolytes with 7, 13, and 25 vol% polymer.

given by

$$R_{Li} = V_{\text{steady state}}/I_{\text{applied}}. \quad (1)$$

Figure 7 shows the dependence of the observed voltages between se and re on the applied currents through we and ce at 25, 50 and 80°C. The slopes of these plots give directly the values of R_{Li} . Thus, the lithium ion transference number of the electrolytes can be approximated by

$$t_{Li} = \sigma_{Li}/\sigma_{total} = R_{total}/R_{Li}, \quad (2)$$

where R_{total} is the total resistance of the GPC or $[P(EO)_6 \cdot LiN(CF_3SO_2)_2]$ electrolyte as determined from an impedance measurement.

The calculated values of R_{total}/R_{Li} for the glass and for the GPC electrolytes with 7 and 13 vol%

polymers are around 0.98 at various temperatures, which are in good agreement with those reported in the literature for similar glass systems [14, 17]. This suggests that the glass is a single ion (Li^+) conductor. However, the calculated ratio of R_{total}/R_{Li} is about 0.84 for the GPC with $x = 25$ and varied from 0.32 to 0.41 for the polymer electrolyte at various temperatures, as summarized in Fig. 8 and Table 1. Although the ratio of R_{total}/R_{Li} may be different from the lithium ion transference number for polymer electrolytes due to deviations from ideality [22] (*i.e.*, interactions between cations and anions in polymers), the measurement of R_{total}/R_{Li} is adequate for the GPC electrolytes for the purpose of this study.

Large deviations of R_{total}/R_{Li} ratio from unity clearly indicate that the addition of 25 vol% polymer to the GPC is excessive; the polymer phase disrupts the continuity of glass phase and, hence, reduces the conductivity and lithium ion transference number of the composite. The lithium ion conductivities, *i.e.*, the useful conductivities when used as an electrolyte for a lithium battery, of various electrolytes with different volume fraction of PEO are summarized in Fig. 9. Clearly, the GPC with $x = 13$ exhibited the highest lithium conductivities among all electrolytes investigated in this study. Thus, this electrolyte was further studied in terms of stability against various electrode materials.

Table 1.
Total conductivities and ratios of σ_{Li}/σ_T for glass, GPC (with $x = 7, 13$, and 25), and polymer electrolytes.

Vol% polymer	Temperature (°C)	σ_T ($\Omega^{-1} cm^{-1}$)	σ_{Li}/σ_T
0 (glass)	25	2×10^{-4}	0.98
	50	5×10^{-4}	0.98
	80	1×10^{-4}	0.98
7	25	2×10^{-4}	0.98
	50	5×10^{-4}	0.98
	80	1×10^{-4}	0.98
13	25	3×10^{-4}	0.98
	50	5.5×10^{-4}	0.98
	80	1.4×10^{-3}	0.98
25	25	8.6×10^{-6}	0.84
	50	2×10^{-4}	0.84
	80	7.5×10^{-4}	0.84
100 (polymer)	25	1×10^{-6}	0.32
	50	1.2×10^{-5}	0.36
	80	9×10^{-5}	0.41

3.4. Electrolyte/electrode interfacial resistances

To determine the stabilities of the GPC electrolytes with 13 vol% polymer against Li , Li_xC_6 , and $Li_xMn_2O_4$, the impedance spectra of three symmetric cells, $Li/GPC/Li$, $Li_xC_6/GPC/Li_xC_6$, and $Li_xMn_2O_4/GPC/Li_xMn_2O_4$, were measured at 70°C in a sealed cell (Fig. 10) as a function of time. Figure 10 shows the

evolution of the impedance spectra of these cells. The interfacial resistance between lithium and the GPC, as shown in Fig. 11(a), increased from the initial value of $586\ \Omega$ to $631\ \Omega$ after 150 hours operation at 70°C , and then stayed relatively constant, suggesting that the interface is relatively stable during storage at 70°C . The initial increase in the interfacial resistance is believed to be due to the formation of a passivation layer at the interface. Likewise, it has been reported that the B_2S_3 — Li_2S — LiI glasses have excellent stability against Li metal at 50°C for a long storage time [12].

Further, the trend of the interfacial resistance of the Li_xC_6 /GPC/ Li_xC_6 cell was similar to that of the $\text{Li}/\text{GPC}/\text{Li}$ cell. However, the interfacial resistance of the $\text{Li}_x\text{Mn}_2\text{O}_4$ /GPC/ $\text{Li}_x\text{Mn}_2\text{O}_4$ cell remained

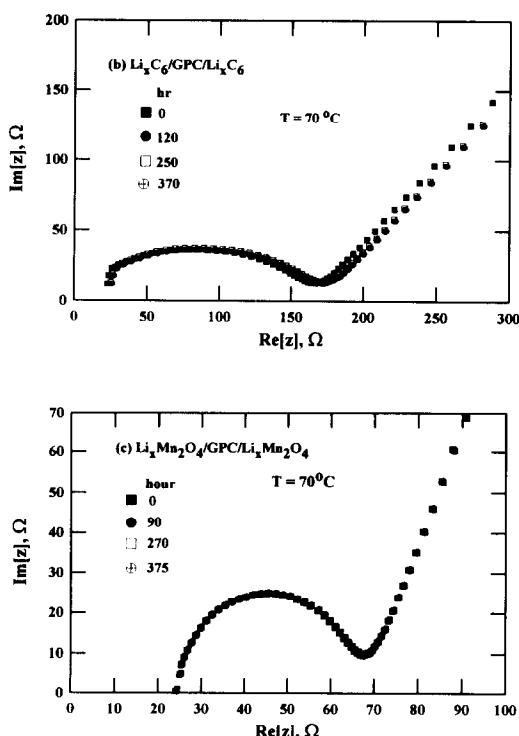
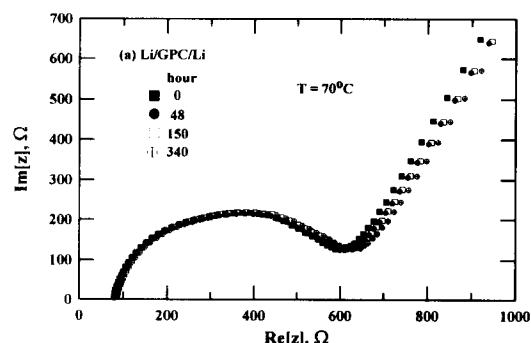


Fig. 10. Evolution of the impedance spectra of symmetrical cells based on the GPC electrolyte with $x = 13$ at 70°C : (a) $\text{Li}/\text{GPC}/\text{Li}$, (b) $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{C}_6$, and (c) $\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$.

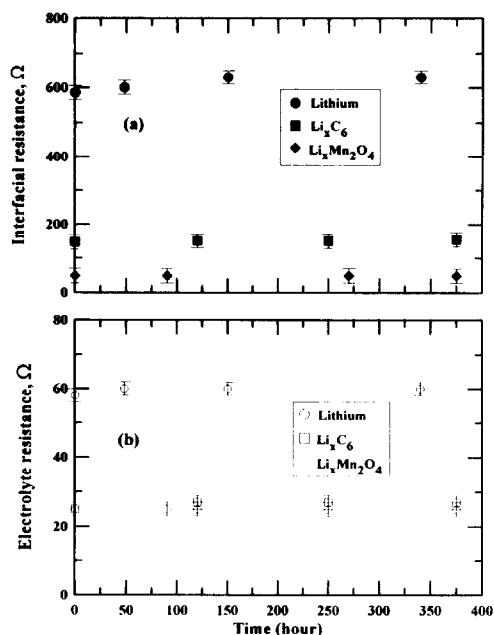


Fig. 11. Stability of electrolytes during storage at 70°C : (a) changes in interfacial resistance of symmetric cells based on the GPC ($x = 13$) electrolytes with different electrodes (Li, Li_xC_6 and $\text{Li}_x\text{Mn}_2\text{O}_4$) and (b) changes in the resistance of the GPC ($x = 13$) electrolytes as measured in cells with different electrodes (Li, Li_xC_6 and $\text{Li}_x\text{Mn}_2\text{O}_4$).

unchanged during storage, suggesting that there is no interfacial reaction between the two materials. As expected, the bulk resistances of the GPC electrolytes in the cells with different electrodes remained relatively unchanged as shown in Fig. 11(b).

3.5. Cell performance

A cell with a capacity of 2 C was assembled in the fully discharged state and the OCV of the cell was 4.5 V after being charged. The $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell using GPC electrolyte with 13 vol% polymer was initially cycled between 4.5 and 3 V at 70°C with a charge and discharge current density of $0.1\ \text{mA cm}^{-2}$ (Fig. 12). The capacity loss during cycling was relatively small and the cell exhibited good reversibility over 10 cycles and the utilization of the positive electrode was about 62% for the discharge.

4. CONCLUSIONS

Li^+ -ion-conducting glass-polymer composite (GPC) electrolytes with conductivities ranging from 3×10^{-4} to $1.4 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$ has been developed. Results indicate that the addition of 13 vol% polymer electrolyte ($\text{P}(\text{EO})_6\cdot\text{LiN}(\text{CF}_3\text{SO}_2)_2$) to 87 vol% glass powder

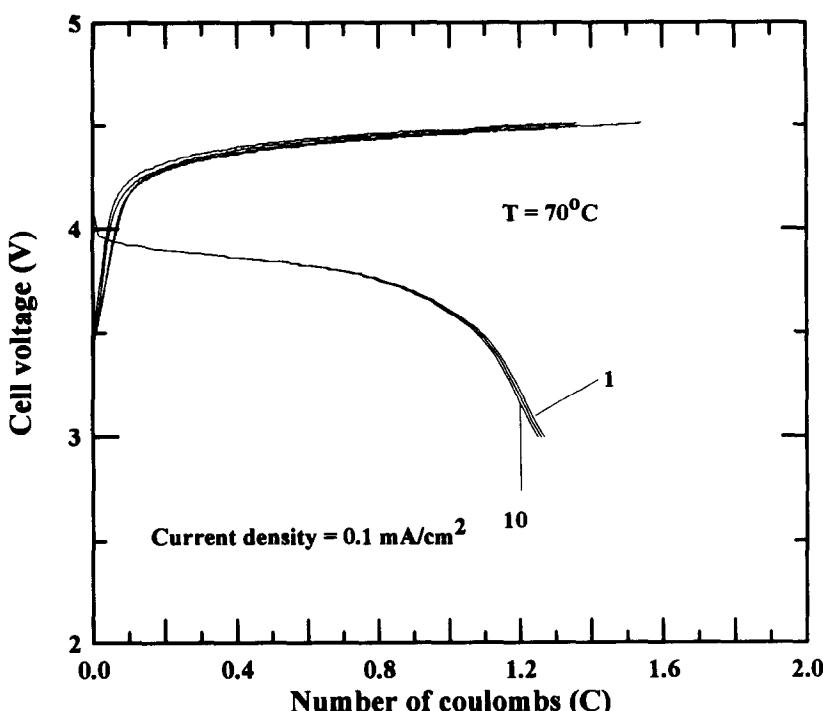


Fig. 12. Cycling curves of a $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell at 70°C with a charge and discharge rate of 0.1 mA cm^{-2} .

($0.55\text{Li}_2\text{S}\cdot0.19\text{B}_2\text{S}_3\cdot0.25\text{LiI}$) increases mechanical flexibility and ionic conductivity. The lithium ion transference number of the GPC electrolyte with 13 vol% polymer is about 0.98. The GPC electrolytes with $x = 13$ have also shown sufficient stabilities with respect to Li , Li_xC_6 and $\text{Li}_x\text{Mn}_2\text{O}_4$ electrode materials. The cycling of a solid state $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell has demonstrated good stability and reversibility of the system.

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