

Xinping Hou · Kok Siong Siow · Zhiqiang Gao

Polymer electrolytes based on acrylonitrile-butadiene-styrene copolymer

Received: 9 December 1998 / Accepted: 9 March 1999

Abstract One of the approaches to improving the ionic conductivity and the mechanical strength of a solid polymer electrolyte is to use polymers in modified forms, such as polymer blends, copolymers and cross-linked polymers. In this study, a new polymer electrolyte based on the acrylonitrile-butadiene-styrene (ABS) copolymer has been prepared. The ionic conductivity, electrochemical stability and interfacial characteristics of the polymer electrolyte in contact with a lithium electrode have been investigated. The temperature dependence of the conductivity below 20 °C can be described by the Arrhenius equation, and above 20 °C by the VTF equation. Lithium passivation appeared to have taken place in the system. The conductivity and electrochemical characteristics of the system are somewhat similar to those of PAN-based polymer electrolytes.

Key words Ion conductivity · Polymer electrolyte · Interface

Introduction

Lithium rechargeable batteries based on solid polymer electrolyte technologies have a wide variety of applications due to an increasing demand for safe, lightweight, high performance batteries such as those used in electric vehicles, portable electronic devices and those used in personal communications. In the past decades, much effort has been involved in trying to improve the ionic conductivity and mechanical properties of solid polymer electrolytes to be used in rechargeable lithium batteries. These have been done through optimizing the combinations of host polymer, plasticizer or solvent and dopant salt [1, 2].

One of the host polymer materials which has been frequently used as a solid polymer electrolyte is the salt-containing poly(ethylene oxide) (PEO) [3–6]. However, PEO is semicrystalline, and the crystalline PEO region is non-conductive and hinders the bulk ionic transfer. There have also been wide discussions on the use of non-conventional polymeric ionic conductors such as composites [2, 7–9], networks [10] and gels [11–13]. In the case of polymeric gel electrolytes, a low molecular weight aprotic plasticizer with a high dielectric constant can certainly improve the ionic conductivity of polymer electrolytes [14–15]. However, the major drawback of such plasticized electrolytes is that they have poor mechanical properties [16]. One approach to overcome this problem is to mix two or three polymers to obtain a blend electrolyte or to use copolymers which provide a trade-off between high ionic conductivity and good mechanical strength. Acrylonitrile-butadiene-styrene (ABS) copolymer is one such copolymer in which acrylonitrile, being polar, will provide an ion path in the electrolyte while butadiene and styrene will give the electrolyte good mechanical strength.

In this paper, we report our studies on a new plasticized polymer electrolyte with ABS as the host polymer, a mixture of ethylene carbonate and propylene carbonate as plasticizer and LiClO₄ as salt.

Experimental

Materials

ABS with an average molecular weight of 1.8×10^5 and a polydispersity of 2.18 was obtained from Polyscience. High purity (>99%) ethylene carbonate (EC) and propylene carbonate (PC) were purchased from Fluka and were used after distillation under reduced pressure. Precaution was taken to control the temperature of the cooling water slightly higher than the melting point of EC (35–38 °C) during its distillation. LiClO₄ (purity >97%) was obtained from Fluka and was dried at 150 °C under vacuum for 24 h before use. Tetrahydrofuran (THF) was purchased from J.T. Baker and distilled from sodium before use.

X. Hou · K.S. Siow (✉) · Z. Gao
Department of Chemistry, The National University of Singapore,
10 Kent Ridge Crescent, Singapore 119260
e-mail: chmsks@nus.edu.sg, Fax: +65-7791691

Preparation of the electrolytes

All the electrolytes were prepared by the solution casting technique. The solutions were prepared by dissolving appropriate amounts of ABS, the plasticizer (EC:PC = 1:1 by volume) and LiClO₄ together in anhydrous THF. The solutions were then poured into Teflon molders and the solvent (THF) was allowed to evaporate at room temperature. After evaporation of the solvent, mechanically stable free-standing films (~120 μm) were obtained. The above operations were carried out in a dry glove box with a nitrogen flow. The films were then further dried in a vacuum oven at 50 °C for 24 h to remove any trace of THF. In this paper, the plasticizer content used is defined as: plasticizer content (%) = (weight of the incorporated plasticizer/total weight of the composite) × 100%; and salt content as: salt content (%) = (weight of the incorporated salt/total weight of the composite) × 100%.

Measurement

AC impedance and conductance analyses were performed over the frequency range 10 mHz–1 MHz on an IM6 Impedance Analyzer (Zahner, Germany) with a DT Hetotherm temperature controller. A specimen for ionic conductivity measurements was prepared in a dry box filled with argon by sandwiching the polymer electrolyte with two stainless steel disc electrodes of diameter 12.86 mm. The conductivity was obtained from the bulk resistance found in the impedance spectra. Each sample was equilibrated at the experimental temperature for 30 min before measurement. The stability of the Li/electrolyte interface was investigated by monitoring the impedance of a Li/polymer electrolyte/Li cell stored at room temperature as a function of storage time.

Cyclic voltammetry of the polymer electrolyte was carried out on a stainless steel current collector using Li both as the counter and the reference electrodes. An EG & G model 273A Potentiostat/Galvanostat was used to perform the voltammetric experiments.

Differential scanning calorimetry (DSC) was carried out under a nitrogen atmosphere with a 2200 Thermal Analyzer (Dupont) at a heating rate of 20 °C min⁻¹. The glass transition temperature (*T_g*) was taken as the temperature of the starting point of the baseline shift observed during the transition from the glassy to the rubbery state.

Results and discussion

Conductivity and thermal analysis

The ionic conductivities as a function of temperature were measured for different plasticizer contents ranging from 24.9% to 62.0% of the total weight of electrolyte. The temperature was varied from –10 °C to 60 °C. As shown in Fig. 1, the conductivity increases with increasing plasticizer content, as is the case in other polymer gel electrolytes [15]. At low temperature (below 20 °C), the conductivity values of the electrolytes obey the Arrhenius equation:

$$\sigma = A \exp[-E_a/RT] \quad (1)$$

where *A* is a pre-exponential factor, *E_a* the activation energy and *T* the temperature in K. However, at temperatures above 20 °C, the conductivities obey the VTF (Vogel-Tamman-Fulcher) equation:

$$\sigma = AT^{-0.5} \exp[-B/(T - T_0)] \quad (2)$$

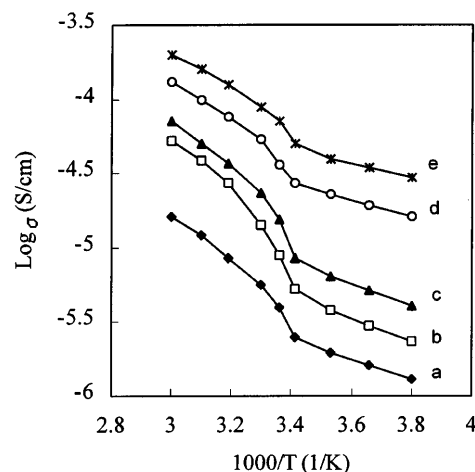


Fig. 1 A comparison of conductivity measured for ABS-LiClO₄-PC-EC electrolytes. Samples of various concentration of plasticizer (PC:EC = 1:1) denoted in wt%: a 24.6%; b 39.5%; c 49.5%; d 56.6%; e 62.0%

where *B* is a pseudo-activation energy for ionic conductivity in K, *A* is a pre-exponential factor that is proportional to the number of charge carriers, and *T₀* (in K) is a quasi-equilibrium glass transition temperature which has been reported to be 30–50 °C lower than *T_g* for many polymer electrolyte systems [2]. The above conduction behaviour can be explained using the DSC results shown in Table 1. The *T_g* values of the electrolyte system composed of LiClO₄ and plasticizer are about 20 °C, which is much lower than the *T_g* of ABS (85 °C). As a result, Li⁺ ions move mainly in plasticizer at temperatures below 20 °C, just like in a liquid electrolyte. Under such conditions, the plasticizer is the main contributor to ionic conduction.

Wang et al. [17] have studied the competition between the plasticizer and polymer on associating with Li⁺ ions in polyacrylonitrile (PAN)-based electrolytes and found that Li⁺ ions moved both in the gel state and along the segmental chain of PAN, especially when the plasticizer was PC. The existence of a lone electron pair on the nitrogen atom of the nitrile group and the empty 2*s* orbital in Li⁺ ion makes it chemically possible for them to form an ion association. Li⁺ ions can, thus, migrate in at least two different ways: (1) move in a gel state which is mainly composed of plasticizers (fast migration), and (2) move along the tunnel provided by the

Table 1 Glass transition temperatures of pure ABS and with the electrolytes

Compound	<i>T_g</i> (°C)
Pure ABS	85.1
ABS (66.5%)-LiClO ₄ (8.91%)-(PC + EC) (24.6%)	21.7
ABS (53.3%)-LiClO ₄ (7.15%)-(PC + EC) (39.5%)	19.6
ABS (44.5%)-LiClO ₄ (5.97%)-(PC + EC) (49.5%)	19.2
ABS (38.2%)-LiClO ₄ (5.13%)-(PC + EC) (56.6%)	19.0
ABS (33.5%)-LiClO ₄ (4.49%)-(PC + EC) (62.0%)	18.9
ABS (29.8%)-LiClO ₄ (3.99%)-(PC + EC) (66.2%)	18.9

PAN molecular chain (slow migration). Thus, in addition to the plasticizer, the acrylonitrile in our ABS system can also contribute to the conductance of the electrolyte at temperatures above 20 °C (T_g of the system). The segmental movement of the polymer matrix increases substantially above the T_g of the electrolyte system. At the same time, ion association decreases with increasing temperature. As a result, the temperature dependence of conductivity obeys the VTF equation above 20 °C.

Figure 2 is a comparison of conductivity-temperature data measured for samples with various concentrations of LiClO_4 , in wt%. The conductivities increase with increasing concentration of LiClO_4 at first and then decrease. Furthermore, there is a somewhat drastic increase in conductivity for samples with 6.53% and 9.25% LiClO_4 at about 40 °C. A high concentration of salt results in ion association in a fixed content of plasticizer, which is the main solvent for Li^+ ion at room temperature. This causes a decrease in conductivity for electrolytes containing 6.53% and 9.25% LiClO_4 from the value of the conductivity for electrolytes containing 4.88% LiClO_4 . When the temperature increases, such ion association decreases and the segmental chain of acrylonitrile can move more rapidly, resulting in a faster increase in conductivity with increasing temperature for the electrolytes containing 6.53% and 9.25% LiClO_4 . For samples with a low salt content there is little ion association and thus they are not affected so much by the change in temperature.

Electrochemical stability

The electrochemical stability of the ABS electrolyte system in cells with a stainless steel working electrode and a lithium counter electrode in the potential range

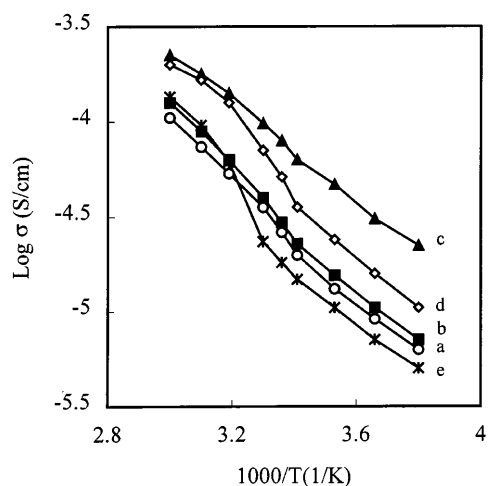


Fig. 2 A comparison of conductivity data measured for ABS- LiClO_4 -PC-EC electrolytes. Samples of various concentrations of LiClO_4 denoted in wt%: a 3.35%; b 3.87%; c 4.88%; d 6.53%; e 9.25%

between 2 V and 6 V was investigated using cyclic voltammetry. The data presented in Fig. 3 did not indicate any electrochemical processes in the potential range between 0 and 5 V. An electrochemical stability window larger than 4.5 V is an important feature for a polymer electrolyte, as this makes it suitable in many lithium-based batteries. Thus, the system has a desirable electrochemical stability for practical uses.

Lithium/polymer electrolyte interface stability

Although high ionic conductivity and a wide electrochemical window are desirable properties, it is insufficient to make an electrolyte completely useful in practical terms. Compatibility with the electrode materials is also an essential parameter to ensure acceptable performance in electrochemical devices. Thus, the lithium/polymer electrolyte interface resistance and its stability over time were investigated by impedance spectroscopy. Figure 4 shows the spectra at progressively longer storage times at 25 °C under open circuit conditions. The right intersection of the arc in the high-frequency range reflects the bulk resistance (R_b) of the polymer electrolyte, while the spur at low frequency can be assigned to ion diffusion in the electrolyte. At the same time, the related cole-cole plots reveal a progressive expansion of the middle frequency semicircle. Since no significant aging process in the polymer electrolyte was observed with stainless steel blocking electrodes, as shown in Fig. 5, where resistivity values as a function of time at 25 °C are reported, this expansion may be typically attributed to interfacial phenomena in lithium cells [18, 19], namely, the formation of a passive layer due to the reactivity of the electrode and the electrolyte. For our system, which was composed of LiClO_4 and PC besides ABS and EC, the passive layer is probably mainly caused by the chemical decomposition of PC in the presence of lithium. This decomposition may result in the following chemical changes:

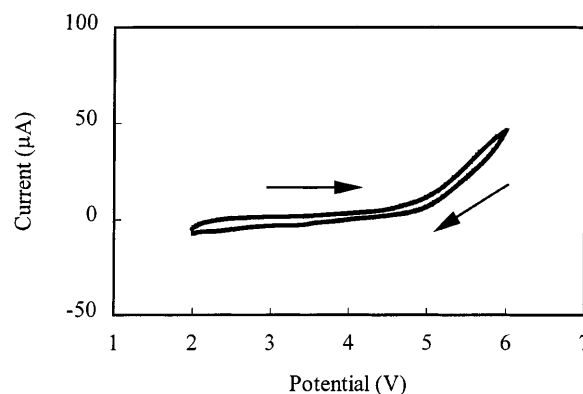


Fig. 3 Cyclic voltammogram for ABS (37.7%)- LiClO_4 (6.5%)-(EC + PC) (55.8%) at 10 mV s^{-1} and 25 °C on a working electrode vs. Li between 2.0 and 6.0 V

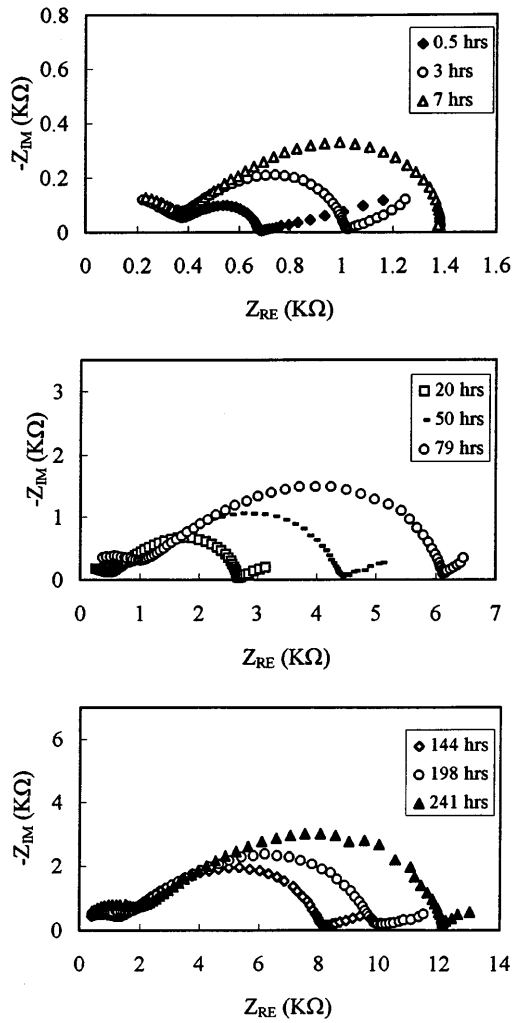


Fig. 4 Impedance spectra of a Li/ABS-LiClO₄-EC-PC/Li cell at increasing storage times at 25 °C under open circuit conditions

1. The formation of propylene and Li₂CO₃ [20, 21].
2. The polymerization of PC to poly(propylene oxide), P(PO), and the formation of P(PO)_xLiClO₄ [19].
3. The formation of Li₂O because of the existence of water in the polymer electrolyte [22].
4. The formation of LiCl by the decomposition of LiClO₄ [19, 23–25].

From the above analysis, the total impedance of the lithium symmetrical cell can be taken as being the combination of the impedance of the electrolyte and that of the interface between the electrolyte and lithium electrode, and accordingly can be simulated using an equivalent circuit as shown in Fig. 6a. The components in the circuit are: R_b (the bulk resistance of the electrolyte), C_g (the geometrical capacitance of the electrolyte), R_i (the resistance of the interface between the electrolyte and the lithium electrode), C_{dl} (the double-layer capacitance of the interface between the electrolyte and the lithium electrode) and Z_w (the Warburg impedance). By using this equivalent circuit, the impedance of the lithium symmetrical cells can be analyzed by superim-

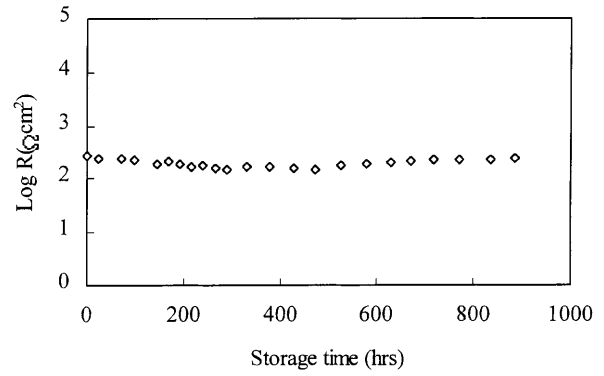


Fig. 5 Resistance data of ABS-LiClO₄-PC-EC electrolyte in a cell with blocking electrodes over time at 25 °C under open circuit conditions

posing the best fit of the dispersion data. A typical impedance response and its fitted dispersion data are shown in Fig. 6b. It is clear that the assumed equivalent circuit fits the experimental impedance data very well.

From this equivalent circuit, it is possible to evaluate the various impedance parameters which contribute to the responses illustrated in Fig. 4. In this way, we can represent the time evolution of the related resistance (R_b and R_i) as shown in Fig. 7. It can be seen clearly that R_i shows a dramatic increase in the initial stage after the assembly of the cell following a gradual growth, while R_b does not increase very rapidly. This indicates that the passivation film grows rapidly immediately after the assembly of the cell and thus contributes greatly to the resistance of charge transfer. At the same time, the formation of the passivation film also affects the morphology of the electrolyte [18, 19] and therefore causes a slight increase in its resistance. As time goes on, the reaction of the polymer electrolyte and the lithium

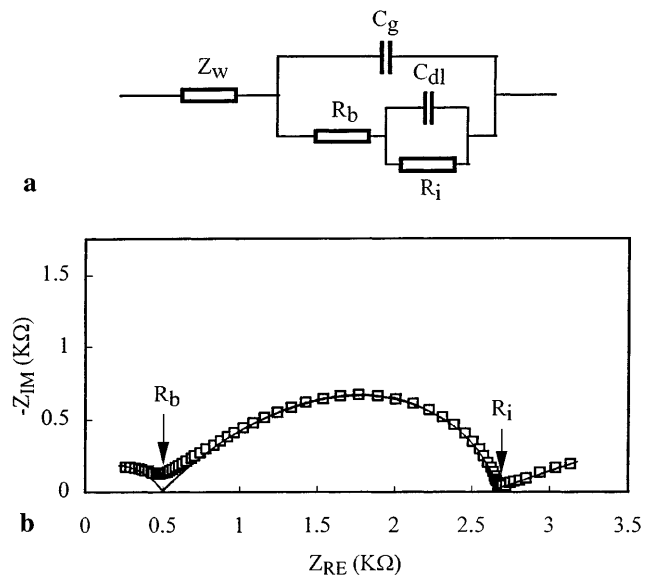


Fig. 6 a Assumed equivalent circuit for the simulation of impedance spectra; b A typical impedance response and its fitted dispersion data

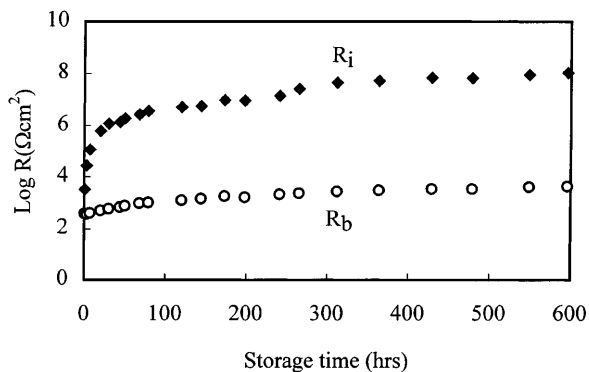


Fig. 7 Time evolution of the bulk resistance (R_b) and the interfacial resistance (R_i) of a Li/ABS-LiClO₄-EC-PC/Li cell at 25 °C under open circuit conditions

electrode slows down with the increase of thickness of the passivation film and the modification of its chemical nature. The continuous growth of the passivation is very similar to that in PAN-based cells but with a lower growth rate here [23, 24]. This suggests that there are some similarities in the kinetics and in the cyclability of the lithium electrode in the two electrolyte media.

Conclusions

Studies on the ABS copolymer-based electrolyte show that the ionic conductivity of the system is about 10^{-5} S cm⁻¹ at ambient temperature. The temperature dependence of the conductivity can be related to the Arrhenius equation below 20 °C and to the VTF equation above 20 °C. The system has a stable electrochemical window between 0 and 5 V. The study of the impedance behaviour of the lithium electrode/polymer electrolyte interface over time shows that lithium passivation takes place and grows rapidly at the initial stage, after the assembly of the cell. The formation of the passivation film also affects the morphology of the electrolyte and causes a slight increase in its bulk resistance.

Acknowledgement The authors are grateful to the National University of Singapore for the research grant for this work.

References

1. MacCallum JR, Vincent CA (1987, 1989) Polymer electrolyte review, vols 1 and 2. Elsevier, New York
2. Gray FM (1991) Solid polymer electrolytes. VCH, Weinheim
3. Fenton DE, Parker JM, Wright PV (1973) Polymer 14: 589
4. Armand MB, Chabagno JM, Duclot M (1979) Fast ion transport in solids. North Holland, New York, p 131
5. Killis A, Le Nest JF, Cheredame H (1980) Makromol Chem Rapid Commun 1: 595
6. Nicholas CV, Wilson DJ, Booth C, Giles JRM (1988) Br Polym J 20: 289
7. Capuano F, Croce F, Scrosati B (1991) J Electrochem Soc 138: 1918
8. Wiczcerek W, Such K, Florjanczyk Z, Stevens JR (1994) J Phys Chem 98: 6840
9. Bruce P (1995) Solid state electrochemistry. Cambridge University Press, Cambridge
10. Wiczcerek W, Florjanczyk Z, Stevens JR (1995) Electrochim Acta 40: 2251
11. Abraham KM (1993) In: Scrosati B (ed) Applications of electroactive polymers, chap 3. Chapman and Hall, London
12. Macfarlane DR, Sun J, Meakin P, Fasoulopoulos P, Hey J, Forsyth M (1995) Electrochim Acta 40: 2131
13. Stallworth PE, Greenbaum SG, Croce F, Slane S, Salomon M (1995) Electrochim Acta 40: 2137
14. Angell CA, Liu C, Sanchez E (1993) Nature 362: 173
15. Abbrent S, Lindgren J, Tegenfeldt J, Wendsjo A (1998) Electrochim Acta 43: 1185
16. Fauteux D, Massucco A, Mclin M, Van Buren M, Shi J (1995) Electrochim Acta 40: 2185
17. Wang Z, Huang B, Wang S, Xue R, Huang X, Chen L (1997) J Electrochem Soc 144: 778
18. Croce F, Scrosati B (1993) J Power Sources 44: 9
19. Thevenin JG, Muller RH (1987) J Electrochem Soc 134: 273
20. Dey AN, Sullivan BP (1970) J Electrochem Soc 117: 222
21. Dousek FP, Jansta J, Riha L (1973) J Electroanal Chem 46: 281
22. Geronov Y, Schwager F, Muller RH (1982) J Electrochem Soc 129: 1422
23. Appetecchi GB, Croce F, Scrosati B (1995) Electrochim Acta 40: 991
24. Xue R, Huang H, Menetrier M, Chen L (1993) J Power Sources 44: 431
25. Xu W, Siow KS, Gao Z, Lee SY (1999) Electrochim Acta 44: 2287