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Polymer 41 (2000) 3365–3369

polymer

Solvation of lithium salts within single-phase dimethyl siloxane bisphenol-A carbonate block copolymer

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Received 14 May 1999; received in revised form 12 July 1999; accepted 28 July 1999

Abstract

Dimethyl siloxane bisphenol-A polycarbonate block polymer was evaluated for its ability to dissociate lithium salts within a single-phase polymer matrix so as to invoke lithium ion conductivity. This strategy exploits the idea that carbonate oxygen, within a single-phase carbonate–siloxane polymer matrix, will facilitate extensive ionic dissociation of introduced lithium salts, and that furthermore elastomeric behavior of the matrix under ambient temperature conditions will lead to enhanced mobility of lithium ions. Since solvating capacity of the polymer matrix is dependent upon the presence of oxygen in a flexible molecular group dimethyl siloxane bisphenol-A polycarbonate was chosen because it contains a carbonate oxygen within the polymer matrix and is a flexible polymer when cured. Ionic conductivities similar to those reported for polyethylene oxide were observed due to the inclusion of a plasticizer solvent and lithium salt into the dimethyl siloxane bisphenol-A polycarbonate matrix. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Dimethyl siloxane bisphenol-A; Polymer electrolyte; Lithium salts

1. Introduction

The incentives for identification of elastomeric, lithium ion conducting polymer electrolytes possessing high ionic conductivities comes from an increasing demand for high energy density secondary batteries to be used in portable applications. This provides a driving force for reliable, long-life, low cost and environmentally friendly batteries possessing both high energy and power densities. Polymer electrolytes consist of polymer matrices combined with alkali metal salts. The ability of polymers, most notably polyethers, to chelate alkali metal cations is a prerequisite for achieving ionic conduction within these materials. Inherent features that should be present in technically useful polymer electrolytes would include (i) high ionic conductivity at or close to ambient temperatures, (ii) ionic transport numbers of unity for the cation of interest, (iii) the ability to maintain mechanical integrity and dimensional stability within a cell subjected to electrochemical cycling, (iv) possessing environmental stability, (v) possessing the ability to maintain stable interfacial regions between electrodes and (vi) be safe.

The solvating capacity of the polymer matrix depends upon the presence of oxygen within highly flexible molecular groups along the polymer chain. The mobility of cations within such polymer matrix is dependent upon the ability of the oxygen to coordinate with the lithium ion. This has been repeatedly demonstrated in the case of polyethylene oxide (PEO) [1]. Recent research on ethylene carbonate/propylene carbonate (EC/PC) based gel polymer electrolytes [2–7] are in support of polymer electrolytes incorporating carbonate-like structures. The high dielectric constants of liquid EC and PC permit extensive dissociation of lithium salts and their low viscosity provides an ionic environment that facilitates high ionic mobility [8,9]. The binding of carbonate entities to a silane-based matrix was investigated for bisphenol-A copolymers. The presence of dimethyl siloxane promotes elastomeric behavior in this single-phase material, which gives improved electrochemical performance and stability for lithium batteries incorporating polymeric solid electrolytes. Elastomeric behavior is important for flexibility which is why we investigated the dimethyl siloxane bisphenol-A polycarbonate matrix but ionic conductivities must be in the range of 10^{-3}–10^{-2} S/cm in order to be useful in a battery application. While bisphenol-A is a very flexible polymer when cured the T_g is very high and ionic conductivities are $>10^{-9}$ S/cm in the absence of plasticizer solvent and lithium salt. The research focused on increasing the ionic conductivity of the flexible polymer with the addition of methyl triacetoxysilane as a plasticizer solvent and lithium salts.

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PII: S0032-3861(99)00535-2

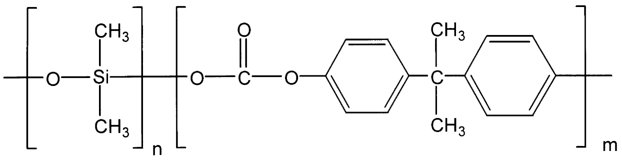

Fig. 1. Unit sequence for the bisphenol A carbonate block copolymer.

Unmodified polycarbonates, however, are poor candidates for complexing with supporting electrolytes. Most of them have T_g values well above ambient temperatures and crystallize easily [10]. However, we investigated the possibility of improving the solvating power of carbonate oxygen within the polymer matrix using dimethyl siloxane bisphenol-A carbonate block polymer (Fig. 1) with a molecular weight of 4000. The option, which we explored during this research, was the modification of the polycarbonate structure to obtain elastomeric properties through the introduction of silane plasticizer solvent into the polymer matrix to produce a single-phase polymer. To achieve this goal methyl triacetoxy silane was used as an elastomeric candidate. The ability to maintain high lithium ion conductivity in carbonate–siloxane polymer electrolytes is dependent in-part upon identifying polymeric materials with glass transition temperatures (T_g) which occur below ambient temperatures.

Target ionic conductivities, under ambient conditions, are in the 10^{-3}–10^{-2} S/cm range with ionic transport proceeding exclusively via lithium ions. In particular, the use of ionically conducting polymeric electrolytes facilitates the fabrication of thin-layer, flexible battery designs, provided that the polymer can maintain a reliable interelectrode spacing absent of electronic shorting. This contributes towards achieving low internal resistance and thereby improving electrochemical performance in terms of delivered energy density and discharge performance.

Incorporation of polymer electrolytes into electrochemical cells during the 1980s was restricted by inadequate ionic conductivity, with most materials possessing values between 10^{-9} and 10^{-5} S/cm at room temperature. The most widely studied material was poly(ethylene oxide) (PEO), incorporating lithium salts such as $LiClO_4$ and $LiCF_3SO_3$. This material, however, demonstrated ionic conductivities well below the target 10^{-3} S/cm at room temperature. PEO will be used as a control for this study. Methyl triacetoxy silane was studied as the crosslinker or plasticizer solvent for both PEO and bisphenol-A carbonate block polymers.

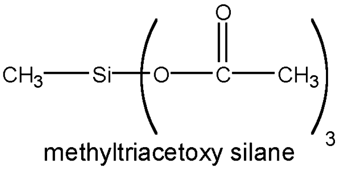

Fig. 2. Plasticizer solvent used for each single phase polymer.

Therefore, this investigation was directed towards achieving high lithium ion conductivity in single-phase carbonate–siloxane polymer electrolytes also anticipated to possess favorable elastomeric properties. Carbonate oxygen within the polymeric host was expected to facilitate effective ionic dissociation of introduced lithium salts.

2. Experimental

2.1. Materials

Lithium trifluoromethane sulfonate, acetonitrile and tetrahydrofuran were purchased from Aldrich and used without further purification. Methyltriacetoxysilane was purchased from United Chemical Technologies and used without further purification. Dimethyl siloxane bisphenol-A carbonate block polymer (mol. wt. 4000) was supplied by Dr Roger Kambour of General Electric Research and Development Center and used without further purification.

2.2. Preparation of polyethylene oxide and dimethyl siloxane bisphenol-A polymer electrolytes

Experimental procedure followed for the synthesis of polymers incorporating either polyethylene oxide or dimethyl siloxane bisphenol-A will now be discussed. Each experiment was set-up in the dry box in an argon atmosphere using a 250 ml three-neck round bottom flask. Polymer, lithium salt and plasticizer solvent (Fig. 2) were weighed and transferred to the round bottom flask followed by addition of solvent. Oxygen/lithium ratio for each polymer composition did not exceed 16. Composition of each polymer is found in Table 1. Upon completion of transfer of reactants the flask was capped to avoid introduction of oxygen and removed from the dry box. Upon removal from the box, the flask was flushed with argon while being equipped with an overhead stirrer in the central neck and a water jacket cooled condenser in the side neck of the flask. Solution was stirred for 24 h to ensure that dissolution had occurred. The temperature was varied between 35 and 50°C depending upon solution composition. The solution was then heated to 50°C and solvent removed under reduced pressure until a viscous polymer was present. Viscous solution was then poured from the flask onto a Teflon sheet then placed in a preheated (55°C) vacuum oven which was flushed with argon. Temperature was held constant and a partial vacuum of 5 in. was applied while raising the temperature to 85°C. After 1 h a full vacuum was applied while heating for 12 h followed by cooling to ambient temperature and bringing it up to atmospheric pressure while flushing with argon. When atmospheric pressure and ambient temperature were reached the polymer was immediately transferred to the dry box for storage in an inert atmosphere. The films were removed from the Teflon plate and thickness measured. The average thickness of each polymer was 0.10 mm. There was no

Table 1
Polyethylene oxide compositions evaluated (PEO: polyethylene oxide, BPA: bisphenol-A carbonate block polymer, PDMS: polydimethylsiloxane, silanol terminated)

Polymer no.	Polymer (g)	Cross-linker	Lithium salt $LiCF_3SO_3$	Ionic conductivity (S/cm, 25°C)	Glass transition T_g (°C)
PO301	PEO (1.32)	None	0.290 g	1×10^{-5}	−41.35
PO401	PEO (1.30)	0.030 g	0.290 g	5.1×10^{-6}	−42.72
PO701	PEO (0.93), PEG (0.26)	0.13 g	0.270 g	3×10^{-6}	−42.10
PO801	PEO (1.34)	None	0.600 g	5.3×10^{-7}	−40.05
P1003	BPA (0.560)	None	0.2845	7×10^{-9}	62.35
P1101	BPA (0.561)	0.062	0.0540	4.3×10^{-6}	56.20
P1201	BPA (0.668)	0.070	0.120	4.4×10^{-6}	57.65
P1501	BPA (0.560)/PDMS (0.12)	0.062	0.0523	8.1×10^{-7}	

indication of separation of phases upon curing as was observed with several other polymer mixtures. Each film was homogeneous and flexible.

2.3. Polymer membrane characterization

2.3.1. Glass transition temperature

Measurements were performed using a Shimadzu DSC - 50 differential scanning calorimetry equipped with a TA-50WS Thermal Analyzer. Each polymer was weighed and transferred to an aluminum pan. Each polymer was evaluated over a temperature range of −150 to 150°C, where polymer electrolyte transition from glassy to elastomeric state is characterized by an endothermic process.

2.3.2. Ionic conductivity

Conductivity cells were prepared by placing the polymer between two glass slides onto which gold electrodes have been evaporated. Contact was made using spring-loaded Pogo contacts to which contact wires were soldered (Fig. 3). The spring contact provides a firm uniform contact onto which current will be dispersed to the electrode surface. Glass microscopic slides were first deposited with chromium using an Edwards Coating System Model E306A. Chromium was deposited at 1 Å/s until a thickness of 100 Å was deposited. Chromium was deposited first to provide a rough surface for the gold to adhere to. Gold was deposited at 1–2 Å/s until a total thickness of 1000 Å was reached. The area of each electrode is $0.196\ \mathrm{cm}^2$. Electrodes were then positioned between two 1 in. × 1 in. Teflon plates. Cell assemblies were equipped with metal screws for proper tightening of the cell. The cell was assembled in the dry box in an argon atmosphere then placed an apparatus (Fig. 4) so that testing could be completed outside of the dry box. Ionic conductivity measurements were performed as a function of frequency.

A standard course of polymer electrolyte conductivity measurements was based on the fact that the high frequency limit of the complex impedance is generally equal to electrolyte resistance. Electrolyte conductivity, σ, is then derived from series resistance, R_s, electrode surface area, A, and polymer electrolyte membrane thickness, d, as $\sigma = d/(AR_s)$. Impedance measurements were conducted using an electrochemical impedance setup comprising PAR Potentiostat/Galvanostat Model 273 and Schlumberger SI 1260 Impedance/Gain-Phase Analyzer. The setup was controlled and the complex impedance parameters were acquired and analyzed by Zplot software. An ac voltage amplitude of ±10 mV was used in a potentiostatic mode to ensure only a small perturbation of polymer electrolyte steady-state

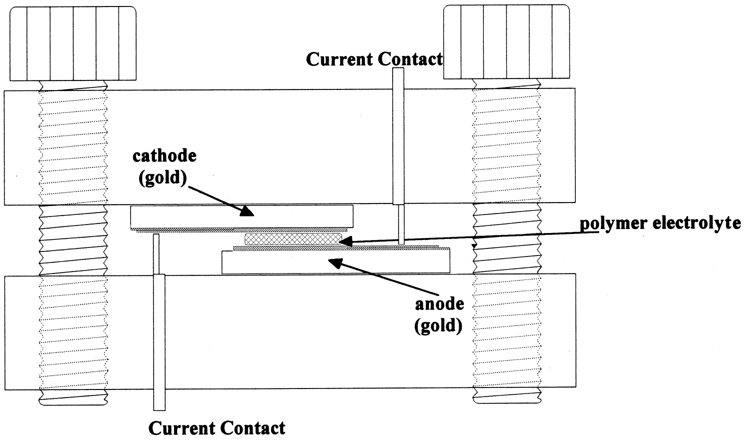

Fig. 3. Schematic of cell assembly used to measure ionic conductivity of polymer electrolytes.

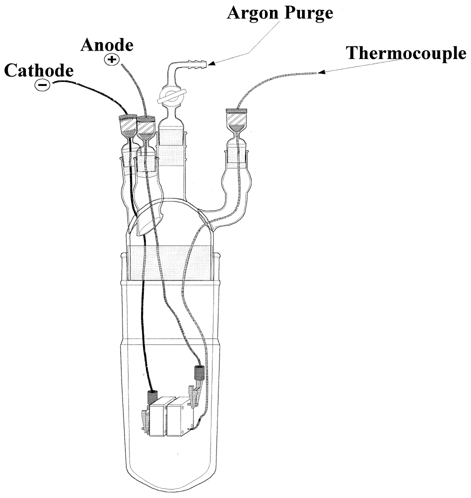

Fig. 4. Schematic of the apparatus used to perform inert atmosphere conductivity measurements.

conditions. Since only series resistance of the electrolyte was of interest, the frequency was limited to (100 kHz–1 Hz) range.

3. Results and discussion

Polymers were prepared using various solvent systems and temperatures in order to produce a polymer film with the desired properties for this application. PEO membranes were used as a control since much work has been accomplished in this area [11–13]. Composition, ionic conductivities and T_g for each membrane evaluated is listed in Table 1. We have found that texture, stability and flexibility are dependent upon the plasticizer and solvent system used for each polymer composition. Each time lithium salts and crosslinker were added to the dimethyl siloxane bisphenol-A polycarbonate polymer a single-phase material was produced. When the bisphenol-A was subjected to several heat–cool down cycles, lithium salts and crosslinker did not separate from the single-phase material and reproducible results were observed. This was confirmed by examining each film under the microscope (Leitz microlab epi-fluorescence microscope at 100X in darkfield mode). As the PEO polymer was subject to several heat–cool down cycles it was observed that the lithium salts were separating from the polymer matrix.

Transference number measurements were not performed at this stage, but ionic character of the conductivity was confirmed by the temperature dependence of the conductivity measured in a limited (20–75°C) temperature range: the cumulative mobility of ionic species in the polymer electrolytes above their glass transition temperatures indicated activation energies 0.2–0.7 eV, typical of rubbery polymers. Series resistance represents all ohmic contributions (i.e. current collectors, electronic resistance contributions and interfacial ohmic drop). Results found in Fig. 5 indicate that our new polycarbonate polymer shows stability and reproducibility over the temperature range of 25–60°C.

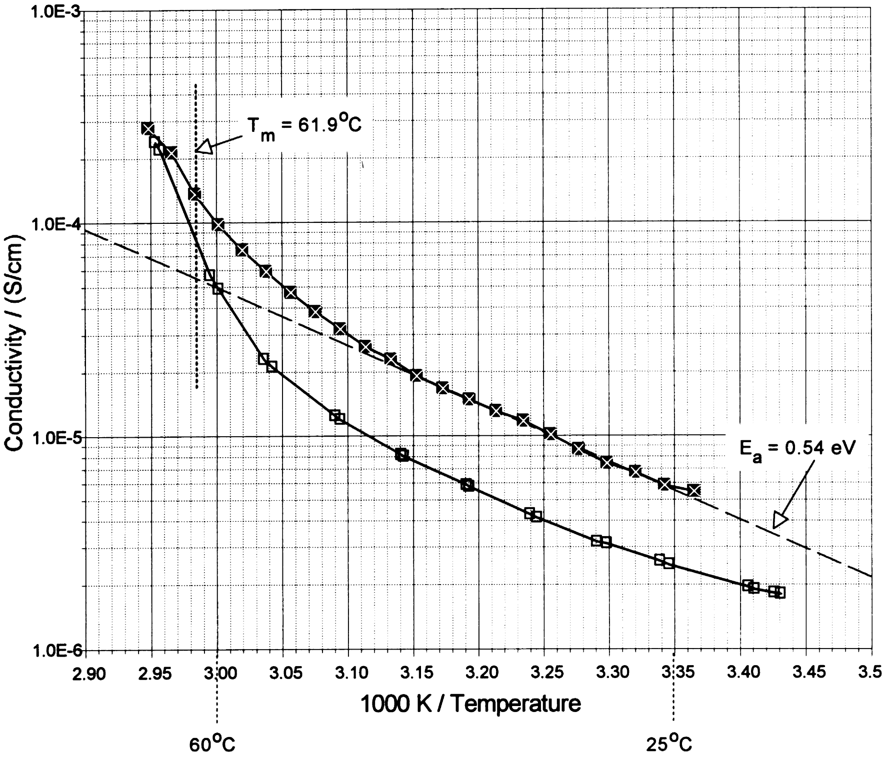

Fig. 5. Temperature dependence for conductivity of PEO polymer P0401.

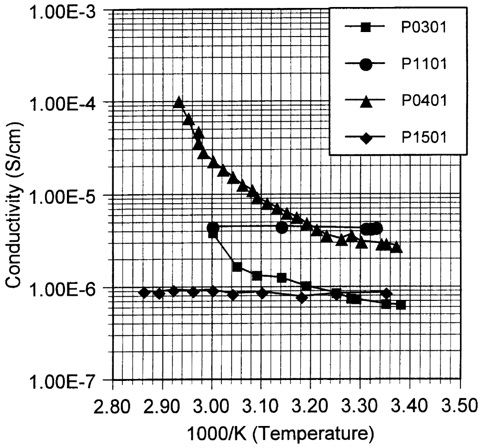

Fig. 6. Conductivities of various polymer compositions over a defined temperature range.

This is indicated by the linear response whereas the PEO membrane composites behave in an exponential manner at elevated temperatures indicating lack of stability at increased temperature. This was confirmed when the cell was disassembled and lithium salts had separated from the polymer matrix. These studies have helped in understanding the polymer system and its limitations. (Fig. 6).

4. Conclusions

Ionic conductivity of the bisphenol-A carbonate block polymer improved with the addition of lithium salts and plasticizer while still maintaining its rubbery texture and flexibility. Polymer P1501 exhibited the strongest similarities to PEO polymers with a glass transition temperature of $-47.2°C$ and an ionic conductivity of 8.11×10^{-7}. This is a significant improvement over bisphenol-A without additives. This improvement does not meet the necessary requirement for polymer electrolyte in battery applications but does reinforce the concept of increased ionic dissociation of introduced lithium salts in the presence of carbonate oxygen.

Acknowledgements

The novel polymer electrolyte program described herein was sponsored by DOD Army Research Development and Engineering Center under a DOD Small Business Innovation Research contract.

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