Ionically Conductive Polymer Gel Electrolytes Consisting of Crosslinked Methacrylonitrile and Organic Electrolyte

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ABSTRACT: To develop a highly ion-conductive polymer electrolyte, we copolymerized methacrylonitrile (MAN) with ethylene glycol dimethacrylate (EGDMA) in propylene carbonate that contained tetraethylammonium tetrafluoroborate (TEATFB), changing the TEATFB concentration and the MAN/EGDMA molar ratio. We characterized the obtained polymer gel electrolytes with complex impedance analysis and cyclic voltammetry, intending to apply them to electric double-layer capacitors. The ionic conductivities of the polymer gel electrolytes were dependent on the TEATFB concentration, the temperature, and particularly the crosslinking degree. The polymer gel electrolytes in this system exhibited high room-temperature conductivities ($>10^{-3}$ S/cm). Furthermore, these polymer electrolytes showed good electrochemical stability windows ranging from -4.0 to $+4.0$ V versus Ag. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2655–2659, 2002

Key words: ionic conductivity; polymer gel electrolyte; methacrylonitrile; ethylene glycol dimethacrylate; tetraethylammonium tetrafluoroborate; copolymerization; crosslinking; electrochemistry; gels

INTRODUCTION

Solid-state electrolytes are more desirable than liquid electrolytes for battery design and construction. In particular, solid polymer electrolytes have attracted strong interest because of their great potential in applications to solid-state ionic devices. The most commonly used matrix polymers for solid polymer electrolytes are poly(ethylene oxide) (PEO) and its copolymers.[1] Several other polymers with ester and amine groups in the main or side chains are also used as matrix polymers. However, it is difficult to use these polymer electrolytes for practical applications because of their low conductivity at ambient temperature. Acceptable levels of conductivity in many PEO-based electrolytes can be obtained only at elevated temperatures. The poor electrical contact at the electrode–electrolyte interface and the low solubility of salts in the polymer matrix are also disadvantages.

With respect to solid polymer electrolyte systems, increased ionic conductivities have been obtained in plasticized or gel-type polymer electrolytes with small organic molecules such as ethylene carbonate and propylene carbonate (PC) as plasticizers.[2–4] Chintapalli and Frech[5] used tetraethylene glycol dimethyl ether as a plasticizer. Plasticizing additives increase the free volume and lower the glass-transition temperature of the polymer.[6] Accordingly, they enhance the ionic conductivity by orders of magnitude. Highly plas-

ticized, crosslinked polymer gel electrolytes containing alkali metal salts often exhibit conductivities higher than 10^{-3} S/cm, even at subambient temperatures. In these systems, salt solutions are trapped in polymer matrices that keep the whole electrolytes mechanically stable. Therefore, ionic transport predominantly occurs in the liquid phase, and the polymer matrix plays an indirect, secondary role in achieving ionic conduction.[7] However, it has been reported that the nature of the polymer network is a determining factor in the conducting behavior of the system.[8,9] Moreover, Ward et al.[10] suggested that although the overall mechanism for conduction in gel electrolytes is the same as that in liquid electrolytes, that is, the similarities in the behavior of the gel and liquid systems are greater than the differences, polymers in some way interact with electrolyte components to modify the properties of gel electrolytes.

We have already reported polymer gel electrolytes of vinyl acetate–divinyl adipate and methyl methacrylate–ethylene glycol dimethacrylate (EGDMA) systems.[11] In this article, we report the properties of polymer gel electrolytes of the methacrylonitrile (MAN)–EGDMA system polymerized in PC containing tetraethylammonium tetrafluoroborate (TEATFB). Organic electrolyte solutions consisting of quaternary ammonium salts and PC are well known to have high performance as capacitors.[12] The goal is to develop a polymer gel electrolyte system with high room-temperature conductivity combined with high chemical and electrochemical stability and good mechanical properties.

EXPERIMENTAL

Materials

MAN, EGDMA, and 2,2′-azobisisobutylonitrile (AIBN) were purchased from Wako Pure Chemical Industries (Osaka, Japan). TEATFB, obtained from Tokyo Kasei Kogyo Co. (Tokyo, Japan) was used after drying in a vacuum oven for 24 h at 75°C. The commercial reagent grade of PC, purchased from Kishida Chemical Co. (Osaka, Japan), was distilled and dehydrated with molecular sieves (3A 1/8) before the preparation of the electrolyte solutions. Acetone was distilled just before use. All other chemicals were reagent-grade and used as received.

Preparation of the Polymer Gel Electrolytes

Initially, MAN was mixed with EGDMA in predetermined molar ratios (MAN/EGDMA = 1:1, 3:1, 5:1, 10:1, 15:1, 17.5:1, 20:1, 25:1, 30:1, and 40:1). The resulting monomer mixtures were blended with the same volume of PC solutions containing predetermined amounts of TEATFB (0.6, 0.8, and 1.0 mol/dm^3) and AIBN (1.68 w/v %). Dry argon was bubbled through 2-cm^3 precursor solutions for 20 min in a quartz tube with an inner diameter of 1.5 cm. The water content of the precursor solutions was determined with a Karl Fischer moisture meter (Hiranuma AQ-5, Mito, Japan). Then, the precursor solutions were polymerized at 60°C for 10 h under a dry argon atmosphere. IR spectra of the obtained gels were recorded on a Hitachi 270-50 IR spectrophotometer (Tokyo, Japan) by the KBr method after the gels were washed with PC and acetone and dried *in vacuo*. The conversion of the monomers to the polymer gels was not determined.

Conductivity Measurements

Each polymer gel electrolyte was sandwiched between two parallel stainless steel electrodes with a cross-sectional area of 0.25 cm^2. The entire assembly was placed in a holder made of glass tubes, which functioned as a thermal reservoir. The temperature of the sample was measured with a thermocouple probe inserted in the holder. The complex impedance was determined by the alternating-current, two-terminal method with an LCZ meter (Hioki 3531, Veda, Japan) at 10–65°C. The frequency range was 50 Hz to 5 MHz, and the oscillation level was 1.0 V. The ionic conductivities of the polymer gel electrolytes were calculated from computer-assisted Cole–Cole plots of the complex impedance and the sample factors (thickness and electrode area). All experimental data reported are an average of at least three measurements.

Cyclic Voltammetry

Cyclic voltammetry was carried out in an argon atmosphere at room temperature with a potentiostat (Hokuto Denko HA-151, Tokyo, Japan) and a function generator (Hokuto Denko HB-111) connected to an x–y recorder (Graphtec WX1100, Yokohama, Japan). The working electrode was a glassy carbon electrode of 3 mm in diameter, and the reference electrode was an Ag/Ag$^+$ electrode for a nonaqueous solution. The counter electrode

was a platinum wire immersed directly in the polymer gel electrolyte. The voltage sweep range was -4 to $+4$ V, and the sweep rate was 100 mV/s.

RESULTS AND DISCUSSION

Although the affinity of ammonium salt to water rather than PC is known,[13] the moisture meter showed that there was no detectable amount of water in the precursor solutions, through which dry argon was bubbled for 20 min. Thus, the precursor solutions were immediately polymerized by radical polymerization under a dry argon atmosphere. Figure 1 shows the IR spectra of the monomer mixture and polymer gel in the MAN–EGDMA system in which the MAN/EGDMA molar ratio was fixed at 5:1. Both have an absorption peak at 2240 cm^{-1} assigned to the aliphatic nitrile groups. After polymerization, the absorption peaks at 1640 and 900 cm^{-1}, assigned to the C=C bond and the terminal methylene C—H bond, respectively, disappear, whereas the intensity of the absorption around 2950 cm^{-1}, assigned to the C—H bond, increases. It seems that the polymer gel electrolytes in this system have a three-dimensional network structure. The obtained poly-
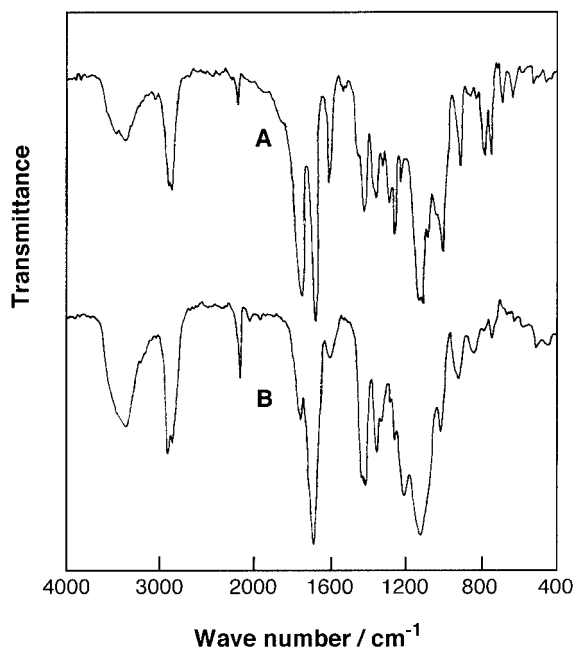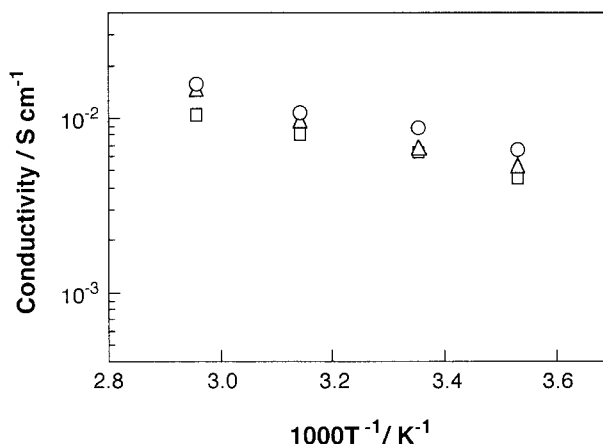

Figure 2 Arrhenius plots of the ionic conductivities of the polymer gel electrolytes with a MAN/EGDMA molar ratio of 25:1: (○) 1.0, (△) 0.8, and (□) 0.6 mol/dm^3 TEATFB.

mer gel electrolytes were colorless and transparent. However, an increase in the crosslinking agent, EGDMA, gave hard and slightly turbid composites (MAN/EGDMA = 1:1 and 3:1). All PC used still remained in the polymer gel electrolytes because the polymerization was performed at a lower temperature and the evaporation of the solvent was not involved in the polymerization process.

During the course of our pursuit of a polymer gel electrolyte that exhibited the highest conductivity, optimization of the salt concentration and the amount of the crosslinking agent was carried out. Figure 2 depicts the dependence of the ionic conductivities of the polymer gel electrolytes on the TEATFB concentration, in which the MAN/EGDMA molar ratio was fixed at 25:1. According to the results obtained in a previous study,[11] the concentration of TEATFB was increased to 1.0 mol/dm^3. The conductivities increase with the increasing concentration of TEATFB was and reach the highest value at 1.0 mol/dm^3 TEATFB. This result seems plausible because polymer electrolytes usually show a maximum ionic conductivity at a 1 mol/dm^3 salt concentration.[14] The temperature dependence of the ionic conductivity, which reflects the migration of carrier ions in the matrix, has been described in terms of various expressions. The simplest is the Arrhenius form, which is the most appropriate for thermally activated ionic motion. However, the temperature dependence of the ionic conductivity of the solid polymer electrolytes with a concave curvature on the Arrhenius plots can be described with the Vogel–
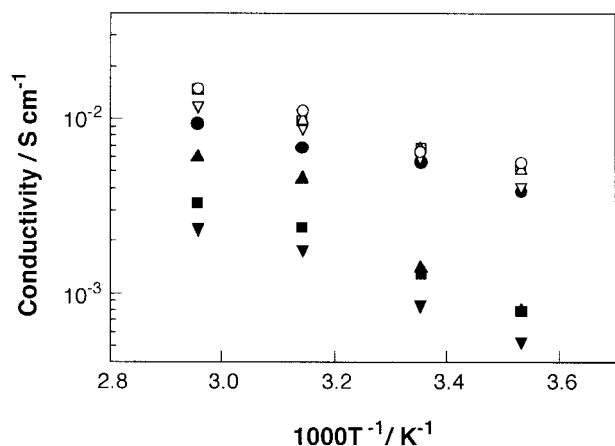

Figure 1 IR spectra of (A) the monomer mixture and (B) the polymer gel with a MAN/EGDMA molar ratio of 5:1.

Figure 3 Arrhenius plots of the ionic conductivities of the polymer gel electrolytes containing 0.8 mol/dm³ TEATFB: (○) MAN/EGDMA = 40:1, (△) MAN/EGDMA = 30:1, (□) MAN/EGDMA = 25:1, (▽) MAN/EGDMA = 20:1, (●) MAN/EGDMA = 17.5:1, (▲) MAN/EGDMA = 15:1, (■) MAN/EGDMA = 10:1, and (▼) MAN/EGDMA = 5:1.

Tammann–Fulcher semiempirical equation.[15,16] Figure 2 also shows the Arrhenius plots of the ionic conductivities of the MAN–EGDMA gel electrolytes. In this system, the conductivities increase with increasing temperature, and the Arrhenius plots are almost linear, suggesting that the conduction is thermally activated. In view of the activation energies of the ionic conductivities of the MAN–EGDMA gel electrolytes (12–15 kJ/mol), the migration of the dissolved ions may be independent of the thermal relaxation of the polymer chains, contrary to the ionic conduction mechanism in well-known solid polymer electrolytes such as PEO. Therefore, it is thought that the solvent is the main conduction medium, and the role of the polymer matrix is structural integrity in this case.

The ionic conductivities of the polymer gel electrolytes consisting of MAN–EGDMA, PC, and TEATFB were further investigated as functions of the MAN/EGDMA molar ratio and temperature. Figure 3 exhibits the dependence of the ionic conductivities of the polymer gel electrolytes on the amount of the crosslinking agent, in which the TEATFB concentration was fixed at 0.8 mol/cm³. The physical characteristics of the gels varied from a stiff gel at MAN/EGDMA = 5:1 to a soft gel at MAN/EGDMA = 40:1. As can be seen from Figure 3, the conductivities increase with a decreasing amount of the crosslinking agent and saturate at MAN/EGDMA = 20:1. At the lower

EGDMA content, the temperature dependence of the conductivity obeys the Arrhenius-type equation, which suggests again that the migration of the dissolved ions is independent of the thermal relaxation of the polymer matrix. At the higher EGDMA content, on the contrary, the Arrhenius plots are nonlinear, suggesting that the motion of dissolved ions in the polymer gel electrolytes is slightly coupled with the structural relaxation of the polymer chains. Consequently, the polymer gel electrolytes seem to behave as a system in which the mechanism of ion diffusion involves ion–polymer-segment coupling such as solid polymer electrolytes. At MAN/EGDMA = 15:1, one can see the discontinuity. Reiche et al.[17] also observed similar discontinuities in the Arrhenius plots of conductivities at low plasticizer contents for gel electrolytes based on oligo(ethylene glycol) dimethacrylates and speculated that they were a result of the homogenization of the heterogeneous gel electrolyte due to the successive softening of the polymer network with temperature. A further investigation should address this point.

It was reported that the content of liquid electrolyte should be higher than 80 wt % to ensure high ionic conductivity of polymer electrolytes.[18] In our system, however, the polymer gel electrolytes lead to an increase of 2 orders in magnitude in the room-temperature conductivity in comparison with the PEO-based solid polymer electrolytes, even though the content of liquid electrolyte is about 50 wt %. The highest room-temperature conductivity is 7×10^{-3} S/cm at MAN/EGDMA = 40:1. The ionic conductivities in this system are comparable to those of the conventional liquid electrolyte solutions. This phenomenon is reasonably explained by much the same mobility of ions in this polymer gel electrolyte as those in the liquid electrolytes.

A stable electric potential window is of practical importance for capacitor electrolytes because it determines the maximum operational voltage of the capacitor. To determine the stable potential window, we carried out cyclic voltammetry. The curves in Figure 4 refer to the first cyclic voltammograms recorded for the MAN–EGDMA gel electrolytes containing 0.8 mol/dm³ TEATFB. There was a very small decrease in peak currents for repeated cycles, and redox was reversible in all cycles. A rise in the Faradaic current may correspond to an increase in the electrochemical decomposition of the electrolytes. The polymer gel electrolyte at MAN/EGDMA = 20:1 has good stability over a wide potential range, from −4.0 to
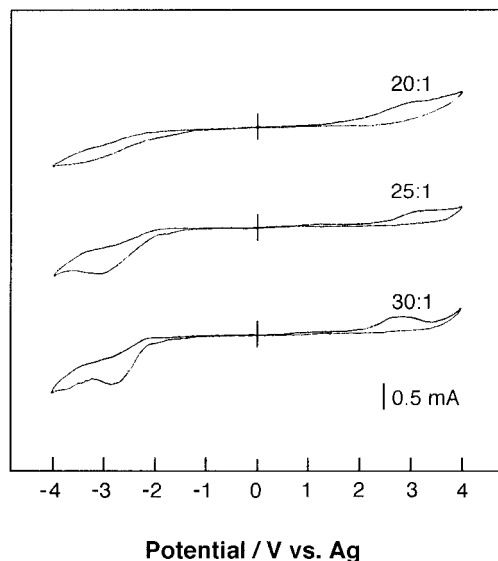
Figure 4 Cyclic voltammograms for the MAN–EG-DMA gel electrolytes containing 0.8 mol/dm^3 TEATFB obtained with a glassy carbon working electrode, an Ag/Ag$^+$ reference electrode, and a Pt counter electrode. The sweep rate was 100 mV/s.

+4.0 V, which is defined as a potential region in which there is no appreciable Faradaic current flows ($<$0.5 mA) and the capacitive current is very small. A slight difference in the voltammograms is observed for the polymer gel electrolytes with different amounts of the crosslinking agent. The lower the EGDMA content is, the higher the reduction peaks are. The actual stable window for the capacitor with an activated carbon-fiber cloth (ACFC) may be somewhat narrower because the specific surface area of the ACFC is relatively large.[19] Nevertheless, the polymer gel electrolytes in this study are practically applicable because most of the electric double-layer capacitors are essentially operated in the 0.8–2.8-V direct-current range.

In conclusion, the polymer gel electrolytes in the MAN–EGDMA system showed good ionic conductivity at ambient temperature. In particular, the room-temperature conductivity was almost the same as that of the corresponding neat ionic liquids. Moreover, the MAN–EGDMA gel electrolytes were stable over a wide potential range and may be suitable for the electrolyte in electric double-layer capacitors.

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