Ionically Conductive Polymer Gel Electrolytes Prepared from Vinyl Acetate and Methyl Methacrylate for Electric Double Layer Capacitor

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ABSTRACT: In order to obtain highly conductive polymer electrolytes for an electric double layer capacitor, three kinds of polymer gel electrolytes were prepared. Vinyl acetate (VAc) and methyl methacrylate (MMA) were copolymerized with divinyl adipate (DA) and ethylene glycol dimethacrylate (EGDMA), respectively, in propylene carbonate (PC) containing tetraethylammonium tetrafluoroborate (TEATFB) to form network polymer gel electrolytes. MMA was also copolymerized with butylene glycol DMA for comparison. The polymer gel electrolytes obtained were characterized by means of thermogravimetry, complex impedance analysis, and cyclic voltammetry for use in the electric double layer capacitor. The ionic conductivities of the polymer gel electrolytes were dependent on the TEATFB concentration, temperature, and crosslinking degree. The polymer gel electrolytes in the VAc-DA system exhibited higher room temperature conductivities (10^{-2} S/cm) than those in the MMA-EGDMA system. Further, the polymer gel electrolytes in the VAc-DA system showed good electrochemical stability windows ranging from -4.0 to 4.0 V versus Ag. Thermal analysis revealed that the polymer gel electrolytes in both systems were stable up to 150°C. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 12–18, 2000

Key words: ionic conductivity; polymer gel electrolyte; vinyl acetate-divinyl adipate; methyl methacrylate-ethylene glycol dimethacrylate; tetraethylammonium tetrafluoroborate

INTRODUCTION

Most electronic equipment with microprocessors and/or integrated circuit memories have back-up power sources on their circuits, and with an increasing demand for their miniaturization new types of battery have been developed. In particular, an electric double layer capacitor has recently been made as the electric power necessary for this equipment decreases. The electric double layer capacitor has the advantages of an extremely large electric capacity and high efficiency for repetition of charge–discharge.

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 the polymer electrolytes are poly(ethylene oxide) (PEO) and its network polymers and copolymers,[1] which have low glass transition temperature (T_g). The temperature dependence of the ionic conductivity of these polymer electrolytes can be described by employing the Vogel–Tammann–Fulcher semiempirical equation (non-Arrhenius form) with a concave curvature on the logarithmic plot against the reciprocal temperature.[2,3] Several other polymers having ester and amine groups in the main

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or side chains are also used as matrix polymers. Furthermore, Yamamoto et al. reported that the poly(vinyl alcohol)-lithium salt composites served as good solid electrolytes for the double layer capacitor.[4] However, it is difficult to use these solid polymer electrolytes for practical applications, because of their low conductivity at ambient temperature. Acceptable levels of conductivity in many PEO-based systems 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. The double layer capacitor requires a large amount of mobile ions to afford an effective double layer with a large value of capacitance.

Recently some researchers prepared polymer electrolytes with room temperature conductivities higher than 10^{-3} S/cm, which were achieved by plasticizing solid polymer electrolytes with small organic molecules such as ethylene carbonate (EC) and propylene carbonate (PC).[5–7] Chintapalli and Frech used tetraethylene glycol dimethyl ether as a plasticizer.[8] Abraham et al. encapsulated the plasticized polymer electrolytes within a porous polymer membrane to obtain sufficient mechanical strength.[9] Plasticizing additives increase the free volume and lower the T_g of the polymer.[10] Accordingly, they enhance the ionic conductivity by orders of magnitude.

In this article we report the properties of the polymer gel electrolytes in the vinyl acetate (VAc)-divinyl adipate (DA), methyl methacrylate (MMA)-ethylene glycol dimethacrylate (EGDMA), and MMA-butylene glycol DMA (BGDMA) systems prepared 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.[11] Considering that the maximum voltage for a capacitor is dominated by the voltage for electrolysis of the electrolyte solutions, organic electrolyte solutions are beneficial. PC with a higher dielectric constant and chemical and electrochemical stability is an important solvent for nonaqueous electrolytes in lithium batteries.[12] TEATFB is suitable as an electrolytic salt for the electric double layer capacitor, because tetraalkylammonium salts have good stability over a wide potential range.[13] In addition, we expected an interaction between the TEA cation and carbonyl oxygen similar to Lewis acid–base reactions.[14]

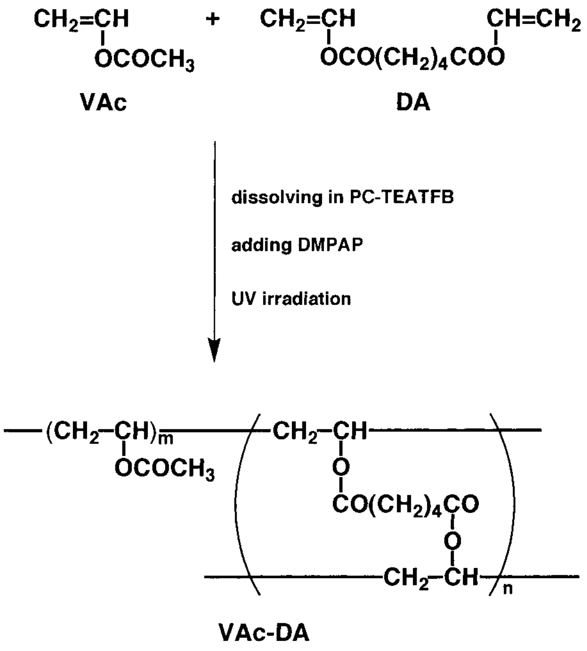

Figure 1 The synthetic route for polymer gel electrolytes in the VAc-DA system.

EXPERIMENTAL

Materials

VAc, MMA, and EGDMA were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). DA and 2,2-dimethoxy-2-phenylacetophenon (DMPAP) were reagent grade from Tokyo Kasei Kogyo Co., Ltd. (Tokyo). BGDMA was purchased from Aldrich Chemical Company Inc. (Milwaukee, WI). TEATFB (from Tokyo Kasei) was used after drying *in vacuo* for 24 h at 75°C. The commercial reagent grade of PC purchased from Kishida Chemical Co., Ltd. (Osaka, Japan) was distilled and dehydrated with molecular sieves (3 Å 1/8) before preparation of the electrolyte solutions. Acetone and methanol were distilled just before use. All other chemicals were reagent grade and used without further purification.

Preparation of Polymer Gel Electrolytes

The synthetic route for the polymer gel electrolytes in the VAc-DA system is shown in Figure 1. VAc was first mixed with DA in predetermined ratios (VAc : DA = 5 : 1, 10 : 1, 15 : 1, 20 : 1, 25 : 1, and 30 : 1). The resulting mixture solutions were blended with the same volume of PC solutions containing predetermined amounts of TEATFB (0.6, 0.8, 1.0, and 1.2 mol/dm^3) and DM-

PAP [0.2 (w/v) %]. Dry Ar was bubbled through 2 mL of the precursor solutions for 20 min in a quartz tube of 1.5-cm inner diameter. The water content of the solutions was determined with a Karl Fischer moisture meter (Hiranuma AQ-5). Then UV light (Ishii UV-LT10, 100 W) was irradiated for 90 min to polymerize the precursor solutions under a dry Ar atmosphere. Polymerization of the MMA-EGDMA and MMA-BGDMA systems was carried out in the same manner. The obtained gels were washed with PC and acetone and dried under a vacuum. IR spectra were recorded on a Hitachi 270-50 IR spectrophotometer by the KBr method.

Thermal Analysis

The thermal stability of the polymer gel electrolytes was investigated using a Seiko Instruments TG/DTA 320 and SSC 5200 thermal analyzer at the air flow rate of 20 mL/min. Each sample (ca. 5 mg) in Al sample pans was heated to 550°C at the heating rate of 10°C/min. The temperature was calibrated with pure indium.

Conductivity Measurement

The polymer gel electrolyte was sandwiched between two parallel stainless steel electrodes with 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 in the holder. The complex impedance of the polymer gel electrolytes was determined by the ac two-terminal method using an LCZ meter (Hioki 3531) at 10–65°C. The frequency range was from 50 Hz to 5 MHz, and the oscillation level was 1.0 V. The ionic conductivities of the polymer gel electrolytes were calculated using computer-assisted Cole–Cole plots of the complex impedance and the sample factors (thickness and electrode area). To examine the effect of moisture content on the conductivity behavior, a few measurements of the conductivity for the polymer gel electrolyte (VAc : DA = 5 : 1) containing water were also performed at ambient temperature.

Cyclic Voltammetry

In order to determine the stable electric potential windows, cyclic voltammetry for the VAc-DA and MMA-EGDMA systems was carried out in an Ar atmosphere at room temperature using a potentiostat (Hokuto Denko HA-151) and a function generator (Hokuto Denko HB-111) connected to an *x–y* recorder (Graphtec WX1100). A glassy carbon working electrode (3-mm diameter), a platinum counterelectrode, and an Ag/Ag^+ reference electrode for nonaqueous solution were adopted. The voltage sweep range was from −4 to 4 V, and the sweep rate was 100 mV/s.

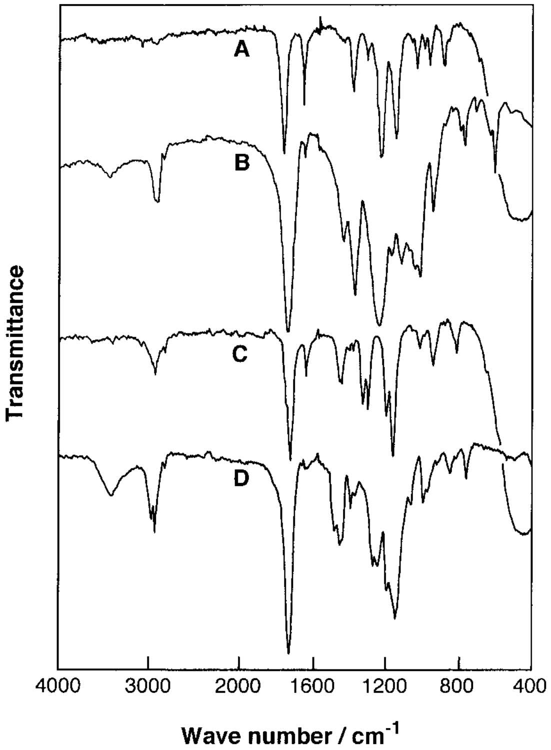

Figure 2 The IR spectra of monomer mixtures and polymer gels in the VAc-DA and MMA-EGDMA systems: (A) VAc : DA = 15 : 1 monomer mixture, (B) VAc : DA = 15 : 1 VAc-DA gel, (C) MMA : EGDMA = 20 : 1 monomer mixture, and (D) MMA : EGDMA = 20 : 1 MMA-EGDMA gel.

RESULTS AND DISCUSSION

In this study the polymer gel electrolytes were synthesized by photoinduced radical polymerization of the monomer mixture solutions. For mechanical and thermal stability the polymer gel electrolytes had a 3-dimensional network structure. Figure 2 shows the IR spectra of the monomer mixtures and polymer gels in the VAc-DA and MMA-EGDMA systems. After polymerization the absorption peaks at 1650 and 820 cm^{-1} assigned to the C=C bond disappeared, whereas

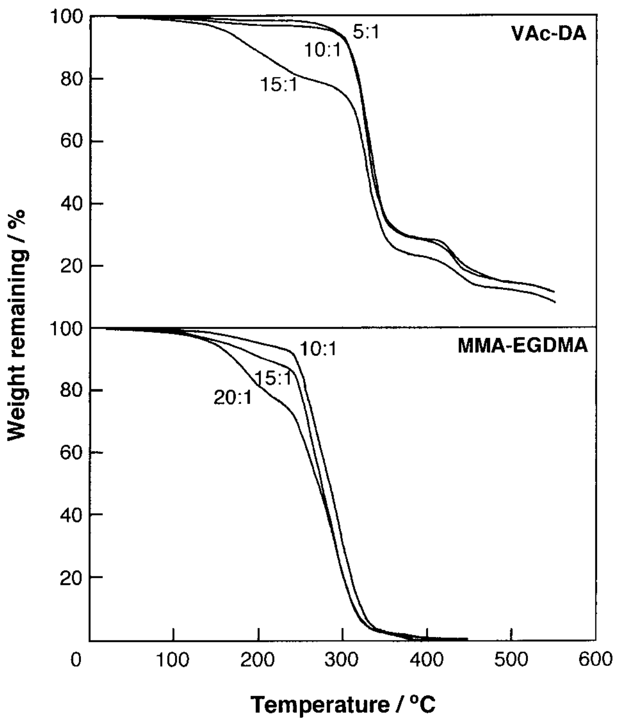

Figure 3 The thermogravimetric traces for the VAc-DA and MMA-EGDMA systems in air. The heating rate was 10°C/min. The numbers denote the molar ratios of VAc to DA and MMA to EGDMA.

the intensity of the absorption at around 2900 cm^{-1} assigned to the C—H bond increased in both systems. The resulting polymer gel electrolytes were colorless and transparent. However, the increase of the crosslinking agents gave hard and slightly turbid composites (VAc : DA = 5 : 1 and MMA : EGDMA = 10 : 1). All PC used for the preparation remained in the resulting polymer gel electrolytes, because the polymers were prepared by only the photopolymerization of the precursor solutions; evaporation of the solvent was not involved in this polymerization process.

The results of thermogravimetric analysis for the VAc-DA and MMA-EGDMA systems in air are shown in Figure 3. At a VAc : DA of 5 : 1 and 10 : 1, large weight losses are observed at 300°C and about 20% of the weight remains even at 400°C. These weight losses are attributed to the decomposition of the polymer network. Similarly, at an MMA : EGDMA of 10 : 1 and 15 : 1 large weight losses ascribed to the decomposition of polymer network are observed at 240°C. However, at a VAc : DA of 15 : 1 and MMA : EGDMA of 20 : 1 weight losses begin at around 150°C. It seems that they release volatile fragments at the lower temperature range due to the lower crosslinking degree. These results indicate that the VAc-DA and MMA-EGDMA systems are stable up to at least 150°C.

The ionic conductivity of the bulk of the polymer electrolyte strongly affects the electrostatic capacity. When the resistance of the electrolyte is high, a large IR drop is observed at the charge–discharge switching during the cycle.[13] In this case, the actual potential range utilizable for the charge–discharge is narrow. During the course of pursuing an electrolyte that exhibited the highest conductivity, optimization of the salt concentration, temperature, and crosslinking degree was carried out. As expected, the ionic conductivity of the polymer gel electrolytes depended on the water content. In Figure 4 the ionic conductivity of the VAc-DA (VAc : DA = 5 : 1) system containing 0.8 mol/dm^3 TEATFB increases with increasing water content in the system. This result can be explained by means of the affinity of the ammonium salt to water rather than PC.[15] Accordingly, the precursor solutions were polymerized under a dry Ar atmosphere.

Figure 5 depicts the TEATFB concentration dependence of the conductivities for the VAc-DA and MMA-EGDMA systems. As compared with conventional aqueous and organic electrolytic solutions,[16] the polymer gel electrolytes show slightly lower ionic conductivity. This phenomenon is reasonably explained by the lower mobilities of ions in the polymer gel electrolytes than those in the liquid electrolytes, which are due to the crosslinked polymer networks. Nevertheless,

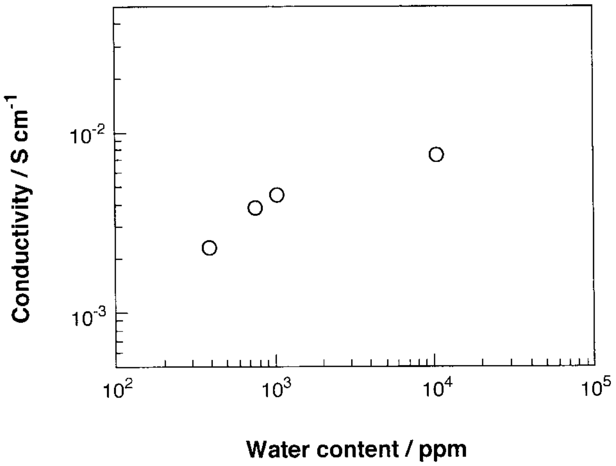

Figure 4 The dependence of ionic conductivity on water content for the VAc-DA system with a VAc : DA of 5 : 1 and 0.8 mol/dm^3 TEATFB.

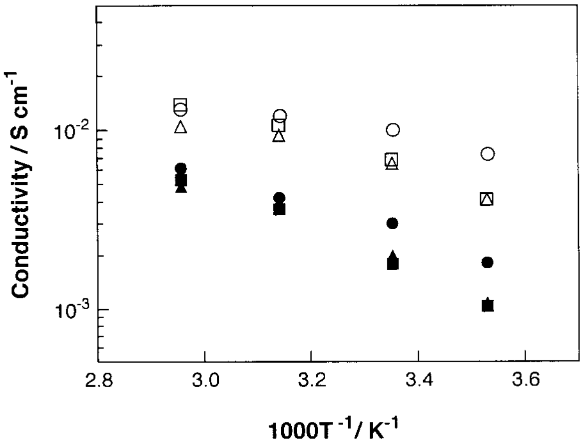

Figure 5 The dependence of ionic conductivity on TEATFB concentration for the VAc : DA = 20 : 1 VAc-DA and MMA : EGDMA = 20 : 1 MMA-EGDMA systems: (△) 0.6 mol/dm^3, (○) 0.8 mol/dm^3, (□) 1.0 mol/dm^3, (▲) 0.8 mol/dm^3, (●) 1.0 mol/dm^3, and (■) 1.2 mol/dm^3. The open and closed symbols represent the VAc-DA and MMA-EGDMA systems, respectively.

the ionic conductivity increases with increasing concentration of TEATFB as the charge carrier and reaches a maximum value at 0.8 mol/dm^3 TEATFB in the VAc-DA system. In the MMA-EGDMA system, on the other hand, the conductivity reaches a maximum at 1.0 mol/dm^3 TEATFB. Polymer electrolytes usually show a maximum ionic conductivity at 1 mol/dm^3 of the salt concentration.[17] The decrease in the conductivity at higher salt concentrations can be attributed to the ion-association effect. In practice some turbidity was observed for the polymer gel electrolyte when the salt concentration was higher than 1.0 mol/dm^3. The ion-association effect induces a decrease in the number of free charge carriers, which is due to an increase of the paired ions at higher salt concentrations in the system. The temperature dependence of the ionic conductivity has been described in terms of various empirical expressions. The simplest is the Arrhenius form that is the most appropriate for thermally activated ionic motion. Figure 5 also shows the Arrhenius plots for the polymer gel electrolytes in both systems. The conductivities increase with increasing temperature, but the Arrhenius plots are nonlinear, suggesting the migration of small molecules in the polymer matrix.[18] The motion of carrier ions in the polymer gel electrolytes is thought to be strongly coupled to the structural relaxation of the polymer chains. Therefore, it seems that the polymer gel electrolytes behave as a system in which the mechanism of ion diffusion involves ion–polymer segment coupling such as conventional polymer electrolytes.[2]

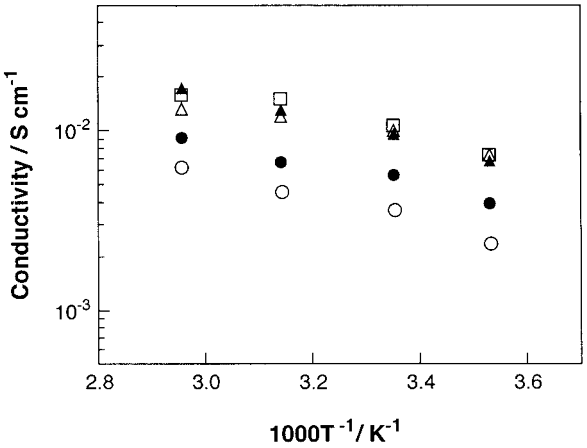

Figure 6 The dependence of ionic conductivity on crosslinking degree for the VAc-DA system (0.8 mol/dm^3 TEATFB) at VAc : DA = (○) 10 : 1, (●) 15 : 1, (△) 20 : 1, (▲) 25 : 1, and (□) 30 : 1.

Figures 6 and 7 exhibit the crosslinking degree dependence of the conductivities for the polymer gel electrolytes in the VAc-DA and MMA-EGDMA systems, respectively. At the lower crosslinking degree in the VAc-DA system, the temperature dependence of the conductivity obeys the Arrhenius type equation, suggesting that the conductivity is thermally activated. At the higher crosslinking degree, on the contrary, the Arrhenius plots are nonlinear, which reflects the migration of small molecules in the polymer matrix as

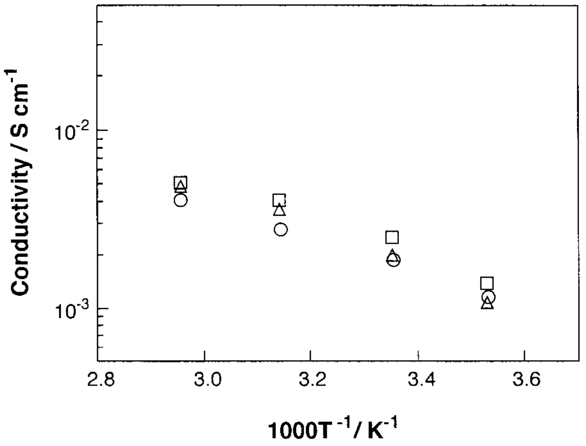

Figure 7 The dependence of ionic conductivity on crosslinking degree for the MMA-EGDMA system (0.8 mol/dm^3 TEATFB) at MMA : EGDMA = (○) 10 : 1, (△) 20 : 1, and (□) 30 : 1.

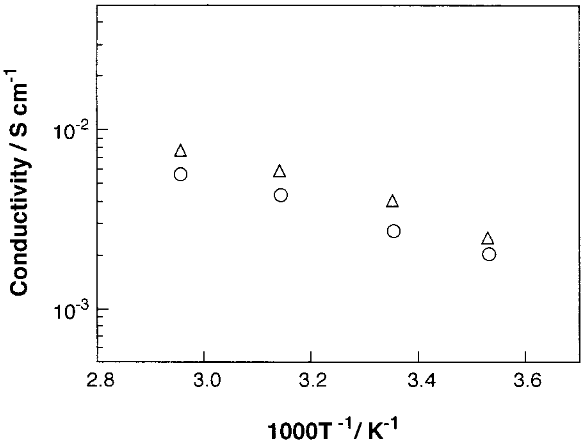

Figure 8 The ionic conductivity for the MMA-BGDMA system (0.8 mol/dm^3 TEATFB) at MMA-BGDMA = (○) 10 : 1 and (△) 20 : 1.

described above. Moreover, as can been seen in Figure 6, the lower the crosslinking degree, the higher the conductivity, and then the conductivity saturates at a VAc : DA of 20 : 1. Similarly, as shown in Figure 7, the lower the crosslinking degree, the higher the conductivity, and the conductivity saturates at an MMA : EGDMA of 10 : 1. It is apparent that these polymer gel electrolytes lead to a 2 orders of magnitude increase in the room temperature conductivity as compared to the PEO-based polymer solid electrolytes. The highest room temperature conductivity is 1.0×10^{-2} S/cm at a VAc : DA of 30 : 1. The ionic conductivities of the polymer gel electrolytes in the VAc-DA system are higher than those in the MMA-EGDMA system. At this point it seems that the lower conductivity for the MMA-EGDMA system than that for the VAc-DA system is attributable to the shorter crosslinker EGDMA. The polymer gel electrolytes in the MMA-BGDMA system were prepared for comparison using the crosslinker BGDMA, which is as long as DA. In the MMA-BGDMA system sturdy polymer gel electrolyte was not obtained at an MMA : BGDMA of 30 : 1. Figure 8 shows that the conductivity at an MMA : BGDMA of 20 : 1 is higher than that at an MMA : EGDMA of 20 : 1. This result indicates that the ionic conductivity is also influenced by the crosslinker length.

A stable potential window is of practical importance for capacitor electrolytes, because it determines the maximum operational voltage of the capacitor. Figure 9 displays the cyclic voltammograms for the VAc-DA and MMA-EGDMA systems at a sweep rate of 100 mV/s. A rise in the Faradaic current corresponds to an increase in the electrochemical decomposition of the electrolytes. The polymer gel electrolytes in the VAc-DA system have good stability over a wide potential range from −4.0 to 4.0 V, which is defined as a potential region where no appreciable Faradaic current flows (<0.5 mA), and the capacitive current is very small. No apparent difference in the voltammograms is observed for the polymer gel electrolytes with different crosslinking degrees. In the MMA-EGDMA system, on the other hand, the potential window range is rather narrow: −3.0 to 4.0 V. The actual stable window for the capacitor using an activated carbon fiber cloth (ACFC) may be somewhat narrower, because the specific surface area of the ACFC is relatively large.[13] However, 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 dc range.

In conclusion, the polymer gel electrolytes in this study showed good ionic conductivity at room temperature. In particular, the polymer gel electrolyte in the VAc-DA system showed excellent conductivity as compared with the MMA-EGDMA

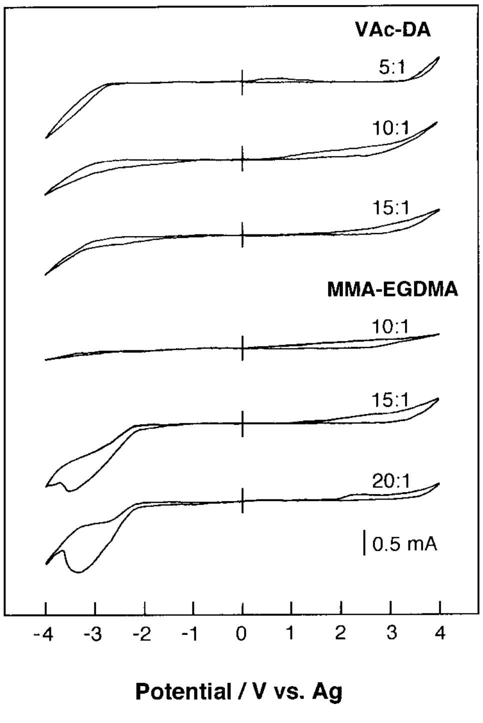

Figure 9 Cyclic voltammograms for the VAc-DA and MMA-EGDMA systems containing 0.8 mol/dm^3 TEATFB using a glassy carbon working electrode, Pt counterelectrode, and Ag/Ag$^+$ reference electrode. The sweep rate was 100 mV/s.

system and was almost the same as that of liquid electrolytes. Furthermore, the VAc-DA system is stable over a wide potential range and is suitable for the electrolyte in electric double layer capacitors.

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