



Quasi-solid polymer electrolytes using photo-cross-linked polymers. Lithium and divalent cation conductors and their applications

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Abstract

In this report, we will present the results on the photo-cross-linked poly-(ethylene glycol) diacrylate (PEGDA) based quasi-solid, i.e. gel, polymer electrolyte systems with lithium, magnesium and zinc trifluoromethanesulfonates [triflate; $M^n(\text{CF}_3\text{SO}_3)_n$] and their preliminary applications to primary cells. The Celgard[®] membrane-impregnated electrolytes were prepared in the same manner as Abraham et al. [K.M. Abraham, M. Alamgir, D.K. Hoffman, J. Electrochem. Soc. 142 (1995) 683]. The precursor solutions were composed of metal triflates, ethylene carbonate, propylene carbonate, and tetraethylene glycol diacrylate. The Celgard[®] #3401 membrane was soaked overnight in the precursor solution, then clamped between two Pyrex glass plates and irradiated with UV light to form a gel electrolyte. The maxima of the conductivity obtained were $4.5 \times 10^{-4} \text{ S cm}^{-1}$ at 12 mol% for LiCF_3SO_3 , $1.7 \times 10^{-4} \text{ S cm}^{-1}$ at 1 mol% for $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, and $2.1 \times 10^{-4} \text{ S cm}^{-1}$ at 4 mol% for $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ system, respectively. The Arrhenius plots of the conductivities are almost linear between 268 and 338 K with 15–25 kJ/mol of activation energy for conduction. The cell, $\text{Li}|\text{LiCF}_3\text{SO}_3\text{-SPE} + \text{Celgard}^{\text{®}} \#3401|(\text{CH}_3)_4\text{NI}_5 + \text{acetylene black}$, showed 2.86 V of OCV and could discharge up to 25% with respect to the cathode active material at a discharging current of 0.075 mA/cm². © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Photo-cross-linked polymer; Lithium trifluoromethanesulfonate; Magnesium trifluoromethanesulfonate; Solid polymer electrolytes; Primary cell; Tetramethylammonium pentafluoroborate

1. Introduction

It has been well known that poly-(ethylene oxide) (PEO) forms ionic-conductive complexes, i.e., solid polymer electrolytes (SPEs) [1,2] with salts of mono-, di-, or trivalent metals. However, values for the ionic conductivity are relatively low, in the range of 10^{-5} to $10^{-8} \text{ S cm}^{-1}$ at ambient temperature. Recently, Abraham et al. [3] reported the electrical conductivities of photo-cross-linked poly-(ethylene glycol)diacrylate (PEGDA)-based solid polymer electrolytes with lithium salts reinforced by a microporous membrane, i.e., Celgard[®]. We have reported on the application of the procedure to the multivalent cation salts, such as zinc halides [4], where the electrolyte of ZnI_2 (8 mol%) + ethylene carbonate (EC) (28%) + propylene carbonate (PC) (28%) + tetraethylene glycol dimethyl ether (tetraglyme) (28%) + tetraethylene glycol diacrylate (TEGDA) (8%) reinforced by Celgard[®] #2500 has the electrical conductivity of $4.3 \times 10^{-5} \text{ S cm}^{-1}$ at 298 K. In this paper,

we will present the results on the lithium, magnesium and zinc trifluoromethanesulfonates [triflate; $M(\text{CF}_3\text{SO}_3)_n$] systems with EC, PC, and TEGDA except for tetraglyme [5], and their preliminary applications to primary cells.

2. Experimental

2.1. Materials

Triflate salts, LiCF_3SO_3 (Kishida Chem., GR Grade), $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ (Fluka, > 98%), and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (Fluka, > 98%), were used as received. EC (TCL, EP Grade), PC (Kishida Chem., GR Grade), and TEGDA (Aldrich) were also used without further purification. A photoinitiator, Darocur[®] 1173, was donated by Japan Ciba Geigy. The Celgard[®] #3401 membranes, 25 μm thick and porosity of 38%, had been donated by the former dealer in Japan; polyplastics $(\text{CH}_3)_4\text{NI}_5$ was prepared from $(\text{CH}_3)_4\text{NI}$ (Tokyo Chemical Industry, GR Grade) and iodine (Kishida Chem., GR Grade) and recrystallized from methanol [6]. Li foil 0.67-mm thick was donated by Mitui Mining and

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Smelting Co., Ltd., try, Zn foil 0.80 mm thick and 99.99% was purchased from Nilaco. Mg anode was made by pressing Mg powder (Hayashi Pure Chemical Industries, EPR grade) under 422 MPa. Acetylene black (AB-7) was donated by Denki Kagaku Kogyo. All chemicals were stored in an argon-purged dry-box (UNICO, UN-650F).

2.2. Preparation of SPEs and primary cells

The Celgard[®] membrane-reinforced solid electrolytes were prepared in the same manner as reported by Abraham et al. [3] and in our previous papers [4,5]. Namely, precursor solutions were composed of LiCF_3SO_3 , $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, or $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, EC, PC, and TEGDA. A few drops of Darocur[®] were added to the precursor solutions of $(\text{EC}:\text{PC}:\text{TEGDA} = 73:16:3)_{100-X} [\text{M}^n(\text{CF}_3\text{SO}_3)_n]_X$. The Celgard[®] #3401 membrane, cut to 10 mm \times 10 mm, was soaked overnight in the precursor solution in a Teflon[®] FEP culture dish which was stored in a dark box placed in the dry-box filled with dried Ar gas. It was then clamped between two Pyrex[®] glass plates 3 mm thick and irradiated with UV light ($\lambda = 366$ nm) (UVP, UVL-21) for about 5 min to polymerize TEGDA to PEGDA.

The primary cell, $\text{M}[(\text{EC}:\text{PC}:\text{TEGDA} = 73:16:3)_{100-X} [\text{M}^n(\text{CF}_3\text{SO}_3)_n]_X + \text{Celgard}^{\text{®}} \#3401(\text{CH}_3)_4\text{NI}_5 + \text{AB-7}$ (where $X = 12$ for Li salt, 1 for Mg salt, or 4 for Zn salt) was constructed of each metal foil, SPE sheet, and a controlled amount of the cathode material (16 mg or 2.4 mA h for Li system and 32 mg or 4.8 mA h for Mg and Zn systems). The mixing ratio of $(\text{CH}_3)_4\text{NI}_5$ and AB-7 was 10:1 by weight. A dense graphite disk was used as a current collector of the cathode side. Glass-epoxy circuit boards with single Cu foil coated were used as the clamping plates and current collectors. The cell was molded with epoxy resin (Refine Tec, 27-770).

2.3. Electrochemical measurements

The conductivity of the Celgard[®] #3401-reinforced electrolyte, bounded by two stainless steel disk electrodes was determined with an AC bridge (DELICA Elec. Meas. Instr., Mini Bridge D1S) with 0.5 V at 20 kHz between 268 and 338 K using a gastight cell made of Neoflon[®] CTFE, stainless steel, and O-rings. The specimen was set into the cell in the dry-box. The measuring frequency has been determined from the preliminary experimental results using a frequency response analyzer (Solartron, 1255) between 1 Hz and 2 MHz and a conventional personal computer system (NEC, PC9801RX2).

The constant current discharging characteristic of the cell, $\text{M}[\text{M}^n(\text{CF}_3\text{SO}_3)_n\text{-SPE} + \text{Celgard}^{\text{®}}[(\text{CH}_3)_4\text{NI}_5 + \text{AB-7}]$, was measured using a potentiostat (Hokuto Denko, HA-301), a conventional microcomputer (NEC, PC9821-Ne3), and an A/D convertor (TORICA, HACARASS) with the data sampling interval of 0.2 to 45 s at ambient temperature.

3. Results and discussion

Each metal triflate was dissolved to 16, 6, or 8 mol% in the precursor solutions for the system of Li, Mg, or Zn, respectively. The prepared polymer electrolyte was a quasi-solid, i.e., gel, as a bulk and a Celgard[®]-reinforced state, of which the thickness was 25 to 36 μm .

From a preliminary experimental result on the complex impedance measurement using the frequency response analyzer between 1 Hz and 2 MHz for 4 mol% $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ system using stainless steel electrodes, the semicircle intercepts the axis at 20 kHz, which value corresponds to the bulk resistance of the electrolyte. Thus, 20 kHz has been selected as the measuring frequency of the AC bridge.

The Arrhenius plots of the conductivities of the electrolytes showing the highest values for each system are shown in Fig. 1, where the conductivity values were not corrected with the membrane tortuosity defined by Abraham et al. [3]. They are almost linear between 268 and 338 K with a value of 15–25 kJ/mol for the activation energy for conduction, suggesting the conduction mechanism of the electrolytes, i.e., carriers of which migrate in the solvent molecules of a quasi-solid, gel, phase impregnated in the polymer matrix of PEGDA [7]. It suggests that conductivity does not depend on the segmental movement of polymer according to the Williams-Landel-Ferry (WLF) equation [8] such as the PPO- LiClO_4 system [9].

The conductivity values at 298 K are plotted against the concentration of metal salts in Fig. 2. Between 1 and 6 (Mg) or 1 and 8 (Zn) mol% of metal salts, their ionic conductivities are of the same order as that for the LiCF_3SO_3 system, i.e., 10^{-4} S cm^{-1} at 298 K. The maxima of the conductivities were obtained as 4.5×10^{-4} S cm^{-1} at 12 mol% for LiCF_3SO_3 , 1.7×10^{-4} S cm^{-1} at 1 mol% for $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, and 2.1×10^{-4} S cm^{-1} at 4 mol% for $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ system, respectively. These ten-

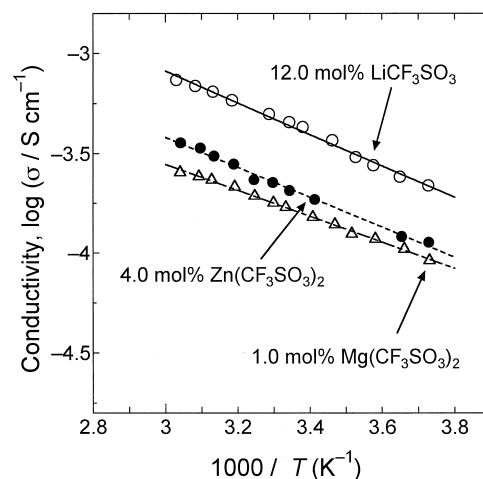


Fig. 1. Arrhenius plots of the electrical conductivities of solid polymer electrolytes with 12 mol% LiCF_3SO_3 , 1 mol% $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, and 4 mol% $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ systems reinforced in Celgard[®] #3401 membranes.

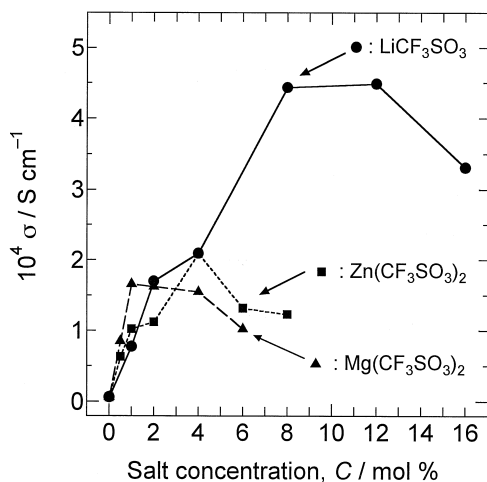


Fig. 2. Electrical conductivity of solid polymer electrolytes with LiCF₃SO₃, Mg(CF₃SO₃)₂, and Zn(CF₃SO₃)₂ systems reinforced by Celgard® #3401 membranes with respect to the metal salt concentration measured at 298 K.

dependencies are also similar and clearer at elevated temperatures. These values are almost one order greater than those of the halide system reported previously [4]. The reason for this is thought to be due to the higher dissociation constant of triflate anion than the halide anion. At the low metal salt content of 1 mol%, the electrical conductivities were the order of Mg > Zn > Li salts, i.e., conductivities of divalent salts were greater than that of monovalent salt. Between 2 and 4 mol%, the conductivities were almost the same values for all salts, that is, depending on the kind of the metal, the suitable concentrations of the metal salts showing the maximum conductivity differ from each other.

It is suggested that the carrier in the electrolyte are the ions produced by dissociation of dissolved salts in the solvent molecules impregnated in the polymer matrix, because more than one order increase in the conductivity is

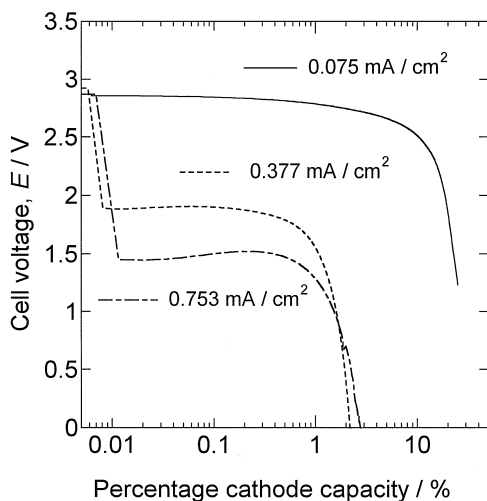


Fig. 3. Discharging characteristics of the cell, Li|LiCF₃SO₃-SPE + Celgard® #3401(CH₃)₄NI₅ + AB-7, at ambient temperature.

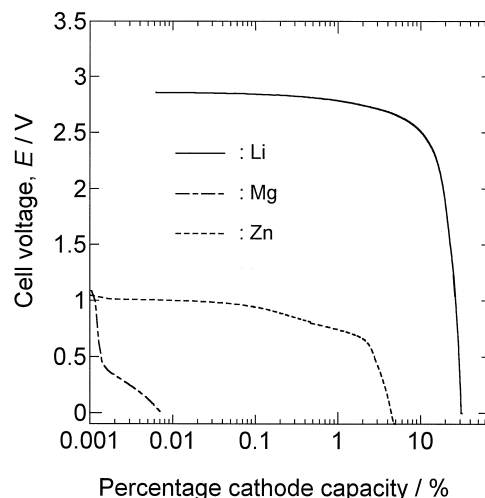


Fig. 4. Discharging characteristics of the cells, M|Mⁿ(CF₃SO₃)_n-SPE + Celgard® #3401(CH₃)₄NI₅ + AB-7, with 0.075 mA/cm² at ambient temperature.

observed by the addition of metal salts of 1 mol%. The carrier of the metal salt free sample is not clear. Relatively high value of its conductivity may be partially due to the remaining proton and hydroxyl ions.

The open circuit voltages of the primary cells with apparent working area of 1.3 cm², M|M-SPE + Celgard®(CH₃)₄NI₅ + AB-7, were 2.86 V for Li, 1.12 V for Mg, and 1.06 V for Zn, respectively. At a discharging current of 0.10 mA/cell, or 0.075 mA/cm², Li|Li-SPE + Celgard®(CH₃)₄NI₅ + AB-7 cell could discharge for 25% with respect to the amount of the cathode active materials, 2.4 mA h, at the cut-off voltage of 1.2 V as shown in Figs. 3 and 4. At the higher current density, such as 0.377 or 0.753 mA/cm², the discharge capacity was very much lower as shown in Fig. 3. On the other hand, the cell with the Zn system attained 3% of theoretical capacity, 4.8 mA h, at the cut-off voltage of 0.5 V, and that of the Mg system attained less than 0.01% of 4.8 mA h even at 0 V. However it became 18% at the cut-off voltage of 0.5 V when the amount of the cathode active materials became 32 mA h even in the Mg cell. Therefore, the reason for such a low discharging capacity with the low amount of the active material is thought to be due to the loss by sublimation and direct combination of the metal with iodide.

4. Conclusion

By changing the anion of the divalent metal salts containing solid polymer electrolytes impregnated in photo-cross-linked polymer from halides to triflate, the electrical conductivity became higher as 4.5×10^{-4} S cm⁻¹ at 12

mol% for LiCF_3SO_3 , $1.7 \times 10^{-4} \text{ S cm}^{-1}$ at 1 mol% for $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, and $2.1 \times 10^{-4} \text{ S cm}^{-1}$ at 4.0 mol% for $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ system, respectively. The cell, $\text{Li}|\text{LiCF}_3\text{SO}_3\text{-SPE} + \text{Celgard}^\circledast \#3401|(\text{CH}_3)_4\text{NI}_5 + \text{AB-7}$, showed 2.86 V of OCV and could discharge up to 25% with respect to the cathode active material (2.4 mA h) with a discharging current density of 0.075 mA/cm^2 .

Acknowledgements

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