



Gel polymer electrolytes based on poly(methacrylamide) derivative having branched pendant with terminal nitrile groups

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ABSTRACT

We prepared new gel polymer electrolytes composed of a poly(methacrylamide) derivative having tri(cyanoethoxymethyl) group (PMCA), poly(ethylene glycol)dimethacrylate (PGM400), lithium bis(trifluoromethylsulfonyl)amide (LiTfSA) and propylene carbonate (PC). The gel polymer electrolytes were prepared by photo-initiated radical polymerization using 2-benzoyl-2-propanol as an initiator. The highest ionic conductivity for the obtained gel polymer electrolytes was 0.38 mS cm^{-1} at 293 K and 2.46 mS cm^{-1} at 343 K. Analysis of IR spectra of the gel electrolyte films suggested that lithium ions interacted with both nitrile groups in PMCA and carbonate groups in PC at higher lithium salt concentration. In contrast, lithium ion was solvated preferentially by the nitrile groups of PMCA at lower lithium salt concentration even in the presence of PC. The gel polymer electrolytes showed oxidation stability up to ca. 4.6 V against a lithium electrode. Reversible plating and stripping responses of lithium on a nickel electrode in the gel polymer electrolytes were also confirmed by cyclic voltammetry.

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1. Introduction

Rechargeable lithium ion batteries (LIBs) have been widely used in portable electronic devices and electric vehicles because of their high energy density and long cycle life [1,2]. However, typical LIBs using flammable liquid electrolytes have the potential to leak the liquid electrolyte and catch fire. To address the safety concerns, many scientists have developed LIBs using dry solid polymer electrolytes in which the polymer matrix serves as solid solvent of lithium salt. Because lithium ion transport is coupled with segmental motions of the polymer matrix, solid polymer electrolytes exhibit low ionic conductivities ranging from 10^{-7} to $10^{-4} \text{ S cm}^{-1}$ at room temperature, and therefore their practical application has been limited so far [3].

Unlike the dry solid polymer electrolytes, gel polymer electrolytes are consisting of cross-linked polymer networks swollen by organic liquid electrolytes such as propylene carbonate (PC) or ethylene carbonate (EC) containing lithium salts [4]. In the gel polymer electrolytes, lithium ions are mainly solvated by the liquid solvents and the liquid electrolyte is supported by the interaction with the polymer matrix. Therefore, the gel polymer electrolytes show high ionic conductivity and can suppress the solvent volatilization and the electrolyte leakage. As a result, the gel polymer electrolytes are expected to supersede solid polymer electrolytes and conventional organic liquid electrolytes. A number of polymer networks including poly(ethylene oxide) (PEO), poly(methacrylate)

(PMMA), poly(vinylidene fluoride) (PVDF), poly(acrylonitrile) (PAN), or poly(vinyl alcohol) (PVA) have been studied as the polymer matrix for the gel polymer electrolytes [5–15].

Introduction of functional branched groups into main chains of the polymer matrix has been a reasonable approach to enhance the ionic conductivity of the dry solid polymer electrolytes. Walkowiak et al. have proposed the solid polymer electrolyte prepared from polysiloxane with three $\text{OCH}_2\text{CH}_2\text{OCH}_3$ units [16]. The ionic conductivity of the polysiloxane-based electrolyte was improved to $10^{-3} \text{ S cm}^{-1}$ at 298 K. In our previous studies [17,18], we have proposed the dry solid polymer electrolyte prepared from polyoxetane with multi-armed side chains of terminal nitrile groups. The ionic conductivity of the polyoxetane-based electrolyte was $10^{-4} \text{ S cm}^{-1}$ at 293 K. Because the side chains of the matrix polymers have high flexibility and strong interaction with lithium ions allowing faster mobility and greater dissociation of lithium ions, the dry solid polymer electrolytes exhibited high ionic conductivity. Similarly, a gel polymer electrolyte prepared from the polymer with multi-armed side chains is expected to have enhanced ionic conductivity. However, there are few studies on this topic to the best of our knowledge.

In this study, a gel polymer electrolyte based on the polymer matrix having branched nitrile functional groups was reported. Poly(methacrylamide) with tri(cyanoethoxymethyl) group (PMCA) was employed as the main polymer matrix, and poly(ethylene glycol) dimethacrylate (PGM400) was used as cross-linker (Fig. 1).

The gel polymer electrolyte was swollen by non-aqueous liquid electrolyte consisting of lithium bis(trifluoromethylsulfonyl)amide

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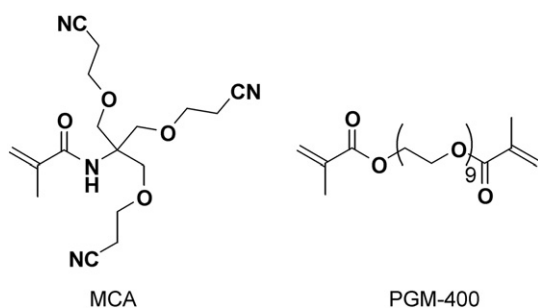


Fig. 1. Structure of MCA and PGM400.

(LiTfSA) and propylene carbonate (PC). The thermal properties and lithium ion solvation were characterized with DSC and FTIR techniques respectively. Ionic transport properties such as ionic conductivity were determined for the obtained gel polymer electrolytes. Electrochemical stability of the gel polymer electrolytes and depositing and stripping of lithium in the gel polymer electrolytes were also investigated.

2. Experimental

2.1. Materials

All reagents were used as received unless otherwise described. Propylene carbonate (PC) and lithium bis(trifluoromethanesulfonyl)amide (LiTfSA) were lithium battery grade and used as received. MCA was prepared by the literature procedure [19]. Structure of MCA was confirmed by ^1H and ^{13}C NMR, FT-IR, and TOF-MS techniques.

2.2. Preparation of gel electrolyte films

Typical procedure of P(MCA-GM400)-based gel polymer electrolytes was as follows. MCA (0.16 g, 0.46 mmol), PGM400 (0.03 g, 0.054 mmol), LiTfSA (0.135 g, 0.47 mmol) and 2-benzoyl-2-propanol (5 μL , 0.04 mmol) were dissolved in PC (0.10 mL, 1.18 mmol). The mixture was stirred at room temperature for 1 h in the dark. The mixture was then poured into an aluminum foil dish and irradiated with a handy UV lamp (254 nm, 8 W, SLUV-8, distance between the lamp and the liquid surface in the aluminum foil dish was 3 cm) for 10 min at room temperature (from 273 K to 298 K). The resulted gel polymer electrolytes is abbreviated as P(MCA-GM400)(LiTfSA) n that contains n mol% of LiTfSA relative to the molar amount of PC; for example, P(MCA-GM400)(LiTfSA)40 was prepared from 0.47 mmol of LiTfSA and 1.18 mmol of PC (namely, 40 mol% of LiTfSA relative to PC). The molar ratio of P(MCA-GM400) relative to PC was fixed at MCA/GM400/PC = 46/5.4/118 while lithium salt concentration was varied relative to the molar amount of PC as denoted by n . The molar ratio of MCA to cross-linker PGM400 was fixed at 46 to 5.4 in this investigation.

2.3. Measurements

Infrared spectra were recorded with a FTIR spectrophotometer (IRPrestage-21, Shimadzu). Peak fitting in the spectra was performed by using peak separation and analysis software (PeakFit™ ver. 4.12, Seascolve Co.). The spectra were fitted by a Gaussian–Lorentzian function for the spectroscopic analysis. DSC measurements were performed with a differential scanning calorimeter (DSC3100S, Bruker AXS) at heating rate of 10 K min^{-1} under nitrogen flow. The DSC sample was hermetically sealed in an aluminum pan. For electrochemical measurements, the resulted gel polymer electrolytes were put between two stainless steel plates (15 mm in diameter) in glove box filled with argon and sealed in 2032 type coin cell holder. Ionic conductivity of P(MCA-GM400)-based gel polymer electrolytes was measured with an LCR meter (HIOKI 3532-80 chemical impedance meter, 50 mV_{p-p}, 5 Hz–

1 MHz) under various temperature conditions from 293 K to 343 K. Temperature was adjusted using a temperature regulated bath (EYELA, NCB-3100). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements were performed with a three-electrode cell. In the case of LSV measurements, the cell had a platinum plate (5 mm by 5 mm) as a working electrode, a lithium tip (2.5 mm by 5 mm) as a reference electrode, and a lithium foil (10 mm by 10 mm) as a counter electrode. In the case of CV measurements, the cell had a nickel plate (5 mm by 5 mm) as a working electrode, a lithium tip (2.5 mm by 5 mm) as a reference electrode, and a lithium foil (10 mm by 10 mm) as a counter electrode. P(MCA-GM400)-based gel polymer electrolytes were sandwiched with these electrodes. The similar cell configuration was reported in our previous paper [20]. LSV and CV measurements were performed with a computer-controlled potentiogalvanostat (HZ-5000, Hokuto Denko) under Ar atmosphere (dew point was at 193 K) at room temperature.

3. Results and discussion

3.1. Preparation of gel electrolyte films

P(MCA-GM400)-based gel polymer electrolytes were prepared by photo-polymerization using 2-benzoyl-2-propanol as a photo-radical initiator. The obtained gel polymer electrolytes were transparent, colorless, rubbery and flexible as shown in Fig. S1 (Supplementary Material). The successful polymerization of P(MCA-GM400)-based gel polymer electrolytes was confirmed by FTIR spectroscopy. Fig. 2 shows FTIR spectra of (a) MCA, (b) PGM400, (c) PC and (d) P(MCA-GM400). From these results, the peaks derived from carbonate group of PC (1782 cm^{-1}), nitrile group of MCA (2250 cm^{-1}) and ester group of PGM400 (1651 cm^{-1}) were all observed by FTIR spectrum of P(MCA-GM400). Disappearance of peak derived from double bond (935 cm^{-1} and 942 cm^{-1} , solid allows in Figure) of the cross-linker and MCA was also observed by FTIR spectrum of P(MCA-GM400). These results suggest that P(MCA-GM400)-based gel polymer electrolyte was formed by photo-radical polymerization.

We tried to prepare the gel electrolyte films with other molar ratio of PGM400 to MCA. The resulted gel films with lower molar ratio of PGM400 to MCA were mechanically weak films. Thus we fixed that the molar ratio of PGM400 to MCA was 46 to 5.4 in this investigation.

Glass transition temperature (T_g) was determined by DSC measurement of P(MCA-GM400)-based gel polymer electrolyte films and listed in Table 1.

T_g value of cross-linked P(MCA-GM400) without PC, P(MCA-GM400)-PC-free, was 264 K. This value is lower than that of homopolymer of MCA, PMCA (T_g = 278 K), suggesting that PEO moiety of the cross-linker PGM400 influenced the lower T_g for P(MCA-GM400)-PC-free. T_g values of P(MCA-GM400)-based gel polymer electrolytes containing PC were in the range of 192 K to 202 K, and much lower

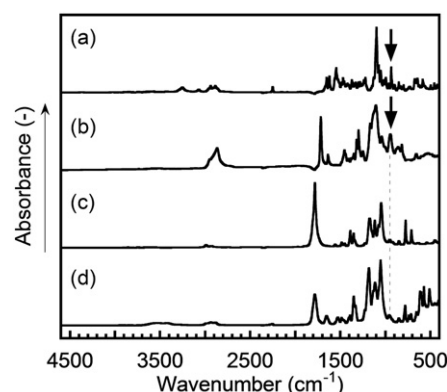


Fig. 2. FTIR spectra of (a) MCA, (b) PGM400, (c) PC and (d) P(MCA-GM400).

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