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New siloxane-based copolymers for use in anion exchange membrane fuel cells

Lee-Jin Ghil [a], Je-Deok Kim [a,b,*]

[a] Battery Materials Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044 Japan
[b] Polymer Electrolyte Fuel Cell Group, Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044 Japan

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ABSTRACT

New anion exchange membranes made by crosslinking poly(diphenyl-co-dimethylsiloxane) (DPh-DM) copolymers and incorporating quaternary ammonium groups via chloromethylation and alkalization to afford DPh-DM with quaternary ammonium groups (DPhQA-DM) for use in anion exchange membrane fuel cells (AEMFCs). The membranes were characterized by using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), water uptake, swelling, ion exchange capacity and hydroxide conductivity. The hydroxide conductivities of the DPhQA-DM copolymers were found to be greatly dependent on the amount of crosslinker used, molecular weight and the number of phenyl groups. DPhQA-DM 16L copolymer membrane was found to have a high hydroxide conductivity of 45 mS/cm at 80 °C. In addition, the membrane exhibited high ion exchange capacity and water uptake, as well as good thermal properties.

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1. Introduction

Fuel cells are promising energy sources because they provide clean and efficient energy for stationary and mobile applications [1–3]. Among all of the fuel cells so far reported, the majority of the effort has been directed towards the development of polymer electrolyte membrane fuel cells (PEMFCs) using proton exchange membranes (PEMs) because of their convenient features, such as low temperature operation, high power density, simplicity of the structures, easy storage, and supply and transport of fuels, which make them particularly suitable for vehicle and other mobile applications [3–5]. However, there are still challenges facing the commercialization of PEMFCs due to slow electrode kinetics and CO poisoning of expensive Pt-based electrocatalysts.

To overcome these problems, anion exchange membrane fuel cells (AEMFCs) have become the focus. AEMFCs use anion exchange membranes (AEMs) to replace the H^+ in PEMs with OH^- anions [6–10]. Compared to PEMFCs, AEMFCs have several important advantages, including (1) facile kinetics at the cathode [6,7], (2) a wide choice of fuels, such as hydrogen, methanol, ethanol, and hydrazine [7,8], and (3) significantly smaller amounts of noble metals used in AEMFCs. AEMs must have high hydroxide (OH^-) conductivities, good stabilities, and mechanical strengths to ensure that AEMFCs have sustainable and durable operations. Recently, new AEMs constructed mainly of copolymers prepared from quaternized comonomers with anions as the charge carriers, such as fluorinated polymers, including poly(ethylene-co-tetrafluoroethylene) (ETFE) [11], poly(vinylidene fluoride) (PVDF) [12], and hydrocarbon polymers, including poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) [13,14], poly(arylene ether sulfone) [15], poly (ether ketone) (PEK) [16], poly(vinyl alcohol) (PVA) [17,18] and so on, have been evaluated for use in AEMFCs. However, the existing AEMs are not as ion conductive and stable as the PEMs are, and thus, efforts have been devoted to developing better AEM materials.

To develop AEMs with excellent hydroxide conductivities and superior alkali stabilities, we focused on siloxane-based polymers. Polydimethylsiloxane (PDMS) has been used in various applications due to its thermal and chemical stabilities, flexible polymer chain backbone, alkali tolerance, and low price [19–22]. In addition, since polymer electrolytes require local relaxation and segmental motion to allow ion transport, we thought that PDMS with its excellent flexibility would be an ideal material for use as ionic conductors [22]. However, PDMS is intrinsically hydrophobic, and thus, it must be modified with hydrophilic end groups to be amphiphilic. Phase separation resulted in the formation of conductive channels, and these pathways should improve ion conductivities.

In this study, we prepared copolymers of PDMS with soft diphenylsiloxane (DPh) segments. Among different polymer

* Corresponding author at: Battery Materials Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044 Japan.
E-mail address: kim.jedeok@nims.go.jp (J.-D. Kim).

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structures for AEMs, block copolymers usually have higher water uptakes and ion conductivities due to their sequential hydrophilic/hydrophobic structures with ionic groups in the hydrophilic blocks, resulting in helpful hydration effects. The DPh segments act as impermeable fillers, physical crosslinks, and hydrophilic parts due to grafted quaternary ammonium (QA) groups. To avoid poor stability in aqueous solutions, reduce membrane swelling, and improve mechanical stability, the membrane was modified by the crosslinking the PDMS copolymer main chain with a methylhydrosiloxane-DM copolymer as a crosslinker. To enhance ionic dissociation and promote transport of the dissociated ions, we added QA groups. By crosslinking, chloromethylation, quaternization and alkalization, PDMS copolymers were synthesized. Their water uptakes, swelling behaviors, hydroxide conductivities, and thermal properties were determined.

2. Experimental

2.1. Materials

Poly(diphenyl-co-dimethylsiloxane) (DPh-DM copolymer) was obtained from Gelest, Inc. Methylhydro-co-dimethylsiloxane, the Pt-divinyltetramethyl disiloxane complex used, 1,1,2,2-tetrachloroethane (TCE), zinc chloride (CAS No. 7646-85-7), and trimethylamine (TMA) were purchased from Aldrich. Chloromethyl methyl ether (CMME) was obtained from TCI Inc., and hexane and sodium hydroxide were purchased from Wako.

2.2. Crosslinking

We used DPh-DM copolymers with different molecular weights and numbers of phenyl groups (mol%) (Table 1). Vulcanization of vinyl terminated siloxanes was performed by using platinum-catalyzed hydrosilylation with stoichiometric amounts of polymer, and crosslinker [23]. The DPh-DM copolymer and methylhydro-co-dimethylsiloxane as a crosslinker were mixed in hexane, and then the mixture was cast on Teflon sheets below 0 °C. Next, a solution of Pt-divinyltetramethyl disiloxane complex dissolved in xylene as a catalyst was added dropwise into a Teflon dish, and then it was cured at 0 °C for 6 h, followed by vacuum oven drying at 60 °C for 6 h. DPh-DM copolymer and crosslinker were mixed in mole ratios of 1:0.5, 1:1, 1:2, 1:3, and 1:4. The crosslinking scheme is shown in Fig. 1.

2.3. Chloromethylation

Friedel-Crafts chloromethylation occurs at the activated aryl ring between the isopropylidiene and ether bond by adding CMME and a Lewis acid catalyst (e.g., $ZnCl_2$) to afford a halomethylated polymer (Fig. 2) [24]. A flask was charged with crosslinked DPh-DM copolymer and 20 mL of TCE. A solution of CMME and $ZnCl_2$ was added dropwise to the mixture and stirred at 35 °C for 72 h. After chloromethylation was finished, the membrane was washed with methanol three times and dried at 80 °C for 24 h. The chloromethylated DPh-DM copolymer, i.e., DPhCl-DM copolymer, was obtained.

Table 1
Physical properties of the DPh-DM copolymers.

Copolymer	Molecular weight	Phenyl group (mol%)
DPh-DM 16H	55,000	15–17
DPh-DM 5H	60,000	4–6
DPh-DM 16L	19,000	15–17
DPh-DM 5L	14,000	4–6

2.4. Quaternization and alkalization

Solid-state alkaline electrolytes are typically prepared by amination of halomethylated polymers with tertiary amines, such as trimethylamine (TMA) and triethylamine (TEA) (Fig. 2). Chloromethyl groups were converted to quaternary ammonium (QA) groups by immersing the DPhCl-DM membrane in a 35 wt% TMA aqueous solution at room temperature for 72 h. To replace the Cl^- anion in the membrane with OH^-, the membranes were placed in a 1 M aqueous sodium hydroxide solution at room temperature for 72 h and then washed with DI water three times to afford DPhQA-DM. The obtained DPhQA-DM copolymers were stored in a closed vessel filled with DI water before being used in the performance tests.

2.5. Measurements and characterization

Attenuated total reflection (ATR) spectroscopy was performed using an infrared (IR) spectrophotometer (Nicolet-6700, Thermo Scientific) in the frequency range of 4000–400 cm^{-1}.

The thermal stabilities of the samples were determined using thermogravimetric analysis (TGA) with a TG/DTA 6000 (SII Co., Ltd). The samples were heated from RT to 800 °C at 5 °C/min in oxygen. Al_2O_3 powder was used as a reference material.

The water uptake values of the samples were determined from the sample masses before and after hydration. Before the measurement, the membranes were cut into 10 mm × 10 mm squares, and then the squares were dried for 24 h at 100 °C in a vacuum oven. The masses of the dry membranes, W_{dry}, were determined before the membranes were immersed in deionized water for 1 h at 100 °C. After treatment, the surface water on the membranes was removed, and then the masses of the wet membranes, W_{wet}, were measured. The values of the water uptake (WU) were calculated using the following equation:

$$WU(\%) = [(W_{wet} - W_{dry})/W_{dry}] \times 100 \quad (1)$$

The swelling ratios (SRs) of the samples were determined by using the thickness expansion ratios, which were determined by measuring the changes in the thicknesses of the dry and wet membranes. The SR values were calculated via the equation:

$$SR(\%) = [(T_{wet} - T_{dry})/T_{dry}] \times 100 \quad (2)$$

where T_{wet} was the thickness of the wet samples in DI water at given temperatures and T_{dry} was the thickness of the dry membranes.

The ion exchange capacities (IECs) of the samples were measured by using titration. The samples were immersed in 20 mL portions of an HCl (0.01 M) standard solution for 24 h. Then the HCl solution mixtures were titrated with a standardized NaOH (0.01 M) solution to pH 7. The IEC values were calculated using the following:

$$IEC(meq./g) = (M_1V_1 - M_2V_2)/W_{dry} \quad (3)$$

where M_1 (M) and V_1 (mL) are the concentrations and volumes of the initial HCl solutions. M_2 (M) and V_2 (mL) are the concentrations and volumes of the standardized NaOH solution used for titration. W_{dry} (g) is the mass of the dry sample.

The hydroxide conductivity measurements were performed using a method similar to that used for proton conductivity measurements, in which a four probe method is used. The hydroxide conductivities of the membranes were calculated using four-point probe impedance spectroscopy at different temperatures by using a PGSTAT302N electrochemical instrument (Autolab). Under N_2 atmosphere, the cell temperatures were 30, 40, 60,

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