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Synthesis and characterization of vinylimidazole-*co*-trifluoroethylmethacrylate-*co*-divinylbenzene anion-exchange membrane for all-vanadium redox flow battery

Chi Won Hwang [a], Hui-Man Park [a], Chang Min Oh [a], Taek Sung Hwang [a,*], Joonmok Shim [b], Chang-Soo Jin [b]

[a] Department of Applied Chemistry and Biological Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea
[b] Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon 305-343, Republic of Korea

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ABSTRACT

The VI-*co*-TFEMA-*co*-DVB (VTD) copolymer was synthesized by the solution polymerization of vinylimidazole (VI), trifluoroethylmethacrylate (TFEMA) and divinylbenzene (DVB). The VTD copolymer solution was quaternized with bromoethane (QVTD), and QVTD anion exchange membranes were prepared by the casting method. The chemical structure of the synthesized solution and the thermal stability of the prepared membrane were confirmed by FT-IR, ^{1}H NMR spectroscopy and TGA analysis. The following membrane properties were measured: bursting strength, thermal characteristics, chemical resistance, water content, ion exchange capacity, electrical resistance and ionic conductivity. The maximum values of bursting strength, ion exchange capacity and ionic conductivity were 4.53 kgf/cm^2, 1.92 meq/g dry and 0.0088 S/cm, respectively. The minimum values of water content and electrical resistance were 3.33% and 1.25 Ω cm^2, respectively. Compared to a commercially available membrane (AMX), the prepared membranes were more chemically resistant. After 150 charge–discharge cycles, the maximum current efficiency, voltage efficiency, energy efficiency and discharge capacity of an all-vanadium redox flow battery were determined to be 94.6%, 79.6%, 75.3% and 47.1%, respectively.

1. Introduction

Recently, the use of ion exchange membranes has sharply increased. Ion exchange membrane based processes are used in the following applications: desalting electro-dialysis for water treatment, water splitting electro-dialysis for the production of weakly acidic or basic substances, energy conversion and energy storage, such as in fuel cells and redox flow batteries (RFBs). Currently, redox flow batteries are being extensively researched because they are considered to be a potential energy source for the future [1,2]. The redox flow battery is a new fuel cell concept that stores energy in a liquid electrolyte. Oxidizable and reducible ions are dissolved in the electrolyte, which is stored in a large capacity tank. When energy is required, the electrolyte is supplied to the cell by a pump, and energy is charged and discharged through the ion exchange membrane during oxidation and reduction [3,4]. The vanadium redox flow battery (VRB), developed by Skyllas-Kazacos et al., is energy efficient and has a long life as well as a high energy discharge capacity. Additionally, with low production and maintenance costs, VRBs are a promising energy storage system. Therefore, VRBs are being extensively studied to develop a new generation of energy storage systems [5–12].

One of the key components of the VRB is the ion exchange membrane. The ion exchange membranes used in VRBs have selective proton permeability to simultaneously allow current flow and prevent the crossover of vanadium ions, which are present in both cationic and anionic electrolytes. Therefore, ion exchange membranes should have a high ionic conductivity and low vanadium crossover rate. Additionally, a high chemical resistance is also required to maintain membrane stability and energy efficiency over a long lifetime, even during exposure to strong vanadium electrolytes [13,14]. However, most ion exchange membranes are not chemically resistant. Thus, most membranes degrade by the oxidation of VO_2^+ ions in the vanadium electrolyte, which consequently reduces the durability of the membrane. Even if the ion exchange membrane possesses excellent chemical resistance, the crossover of vanadium ions occurs through the membrane by self-discharge [15,16]. Currently, cation exchange membranes, such as CMV (Asahi Glass Co., Japan) or Nafion (Dupont, USA), are being used as ion exchange membranes in VRBs. The CMV has inferior chemical resistance and a short lifetime, whereas the Nafion membrane has high proton conductivity and excellent stability in VO_2^+ aqueous solutions but is costly and has poor selectivity

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* Corresponding author. Tel.: +82 42 821 5687; fax: +82 42 822 8995.
E-mail address: tshwang@cnu.ac.kr (T.S. Hwang).

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between protons and vanadium ions. Therefore, the permeation of vanadium ions through cationic and anionic cells with different oxidation conditions causes a loss in electrical energy and reduced battery efficiency [17–22].

Current research on anion exchange membranes, which can be used in VRFBs, is focused on resolving problems and improving the ion exchange membrane [23–26]. Anion exchange membranes efficiently restrict the crossover of vanadium ions because of coulomb repulsion between the positively charged functional groups [27,28]. The use of AMV (Asahi Glass Co., Japan) and AMX (Tokuyama Soda. Co., Japan) membranes in VRBs has been evaluated, but because of low chemical resistance and reduced ionic conductivity, the potential of anion exchange membranes in practical applications has not yet been realized.

Therefore, in this study VI-*co*-TFEMA-*co*-DVB (VTD) copolymers were synthesized from fluorinated trifluoroethylmethacrylate (TFEMA), divinylbenzene (DVB) monomers, and vinylimidazole (VI) monomers, which provided a high ion exchange capability. The polymer was quaternized with bromoethane and treated with heat to produce partially fluorinated anion exchange membranes. Additionally, the structure of the synthesized VTD solution was analyzed by FT-IR and ^{1}H NMR. Basic performance and the properties of the developed anion exchange membrane were evaluated and measured, including thermal characteristics, bursting strength, water content, ion exchange capacity, electric properties, acid resistance, and VRB efficiency.

2. Experimental

2.1. Materials

The following chemicals were used in the experiments: 1-vinylimidazole (VI) from Aldrich, with a purity of 99%, as the polymerized monomer; 2,2,2-trifluoroethylmethacrylate (TFEMA) from Esstech, with a purity of 99%; and divinylbenzene (DVB) from Aldrich, with a purity of 80%. Additionally, α,α′-azobis(isobutyronitrile) (AIBN) from Junsei, with a purity of 98%, was used as the polymerization initiator. The synthesized copolymer was quaternized with 98% pure bromoethane from Junsei and N,N-dimethylformamide (DMF) from Samchum, with 99% purity, was used as a solvent. All the reagents in the experiment were used as received. No additional purification processes were performed prior to use.

2.2. Preparation of anion exchange membranes

2.2.1. Copolymer synthesis

VI-*co*-TFEMA-*co*-DVB (VTD) copolymers were synthesized following the mechanism illustrated in Fig. 1. Briefly, DMF solvent, VI monomers, TFEMA, DVB, and AIBN initiator were added to a 1 L capacity four-hole flask reactor. A stirrer, sample input port, cooler, and nitrogen injection device were attached according to the directions described in Table 1. The reaction was performed at 50 °C for 24 h under a nitrogen atmosphere. To obtain a pure solution of VTD copolymers, the reactants were filtered through distilled water to remove excess monomers and solvent and dried inside a vacuum oven at 30 °C for 24 h.

2.2.2. Quaternization

Quaternization reactions were performed using bromoethane to add functional groups to the synthesized VTD copolymers. After dissolving the VTD copolymers in DMF solvent, the molar equivalent of bromoethane was added to 2 mol of VI to synthesize the VTD (QVTD) ion exchangers. The reaction was performed at 50 °C for 24 h under a nitrogen atmosphere. To obtain pure QVTD ion exchangers, the reactants were treated with distilled water and dried in a vacuum oven at 30 °C.

2.2.3. Preparation of anion exchange membranes

Synthesized QVTD ion exchangers were dissolved in DMF while adjusting the viscosity. Air pores were removed, and the membrane was cast to a 150 μm thickness using a doctor blade. The membrane was dried and heated in an oven from 70 to 130 °C with incremental increases in temperature. The dried mass was precipitated in a 1 M KOH solution for 24 h, and a QVTD anion exchange membrane was prepared with OH– groups.

2.3. Confirmation of structure

FT-IR and ^{1}H NMR spectral analyses were performed to confirm VTD copolymer and QVTD ion exchanger synthesis. FT-IR spectral analysis was performed using the ATR method and a FT-IR spectrometer (IR Prestige-21) from Shimadzu with a measurement range of 4000–600 cm^{-1} at 4 cm^{-1} resolution (number of scans = 20). A FT-NMR spectrometer (JNM-AL400) from JEOL Korea Ltd. was used to perform ^{1}H NMR spectral analysis using tetramethylsilane and deuterated chloroform as the standard and solvent, respectively.

2.4. Membrane characterization

The bursting strength was measured to determine the mechanical strength of the QVTD anion exchange membrane. A Universal Testing Machine (EZ Test/CE) from Shimadzu was used to measure the bursting strength according to the standard testing method ASTM D3786.

TGA was performed to analyze the thermal stability of the QVTD anion membrane. The test was performed using a TGA analyzer (Q500) from TA Instruments that was operated in the temperature range of 25–700 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

To measure the acid resistance of QVTD anion exchange membranes, a prepared membrane was deposited in 1 M HCl and stirred for 45 days at room temperature. The change in membrane weight was measured.

To measure the water content of QVTD anion exchange membranes, a membrane was cut into 3 cm × 3 cm pieces and stored in distilled water for 24 h. The moisture from the surface of the cut pieces was removed, and the weight of the membrane was measured. After completely drying and weighing the cut pieces, the moisture content was determined by substituting the values into Eq. (1):

$$\text{W.C. } (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

To substitute Cl$^-$ for functional groups, the prepared membranes were placed in a 1 M NaCl solution. The Mohr titration method was used to measure the ion exchange capacity of the QVTD anion exchange membrane. The anion exchange membrane was then placed in a 0.5 M Na_2CO_3 solution to substitute CO_3^- for functional groups. After adding 1–2 drops of 5% potassium chromate solution, titration with $AgNO_3$ was performed until a reddish brown precipitate was observed. To determine the ion exchange capacity, the amount of consumed $AgNO_3$ was substituted into the following equation:

$$\text{IEC (meq/g)} = \frac{V_{AgNO_3} \times C_{AgNO_3}}{W_{dry}} \times 100 \tag{2}$$

where V_{AgNO_3} is the volume of silver nitrate that was used during titration (ml), C_{AgNO_3} is the concentration of silver nitrate (meq/ml), and W_{dry} is the weight of the dry membrane (g).