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Quaternized adamantane-containing poly(aryl ether ketone) anion exchange membranes for vanadium redox flow battery applications

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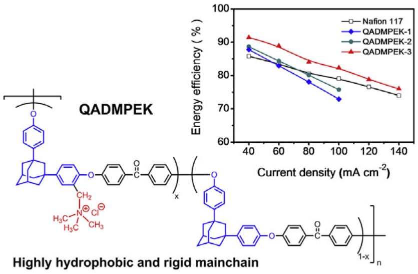
HIGHLIGHTS

- New adamantane-containing poly(aryl ether ketone) membranes are prepared for VRFB.
- QADMPEK membranes show significantly low vanadium ions permeability.
- High battery efficiency of VRFB with QADMPEK membranes are obtained.
- QADMPEK membranes show high stability in VRFB.

GRAPHICAL ABSTRACT



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ABSTRACT

Quaternized adamantane-containing poly(aryl ether ketone) anion exchange membranes (QADMPEK) are prepared and investigated for vanadium redox flow batteries (VRFB) application. The bulky, rigid and highly hydrophobic adamantane segment incorporated into the backbone of membrane material makes QADMPEK membranes have low water uptake and swelling ratio, and the as-prepared membranes display significantly lower permeability of vanadium ions than that of Nafion117 membrane. As a consequence, the VRFB cell with QADMPEK-3 membrane shows higher coulombic efficiency (99.4%) and energy efficiency (84.0%) than those for Nafion117 membrane (95.2% and 80.5%, respectively) at the current density of 80 mA cm^{-2}. Furthermore, at a much higher current density of 140 mA cm^{-2}, QADMPEK membrane still exhibits better coulombic efficiency and energy efficiency than Nafion117 membrane (coulombic efficiency 99.2% vs 96.5% and energy efficiency 76.0% vs 74.0%). Moreover, QADMPEK membranes show high stability in *in-situ* VRFB cycle test and *ex-situ* oxidation stability test. These results indicate that QADMPEK membranes are good candidates for VRFB applications.

1. Introduction

Vanadium redox flow batteries (VRFB) are promising energy storage devices for renewable energy and power grids [1]. As key materials in VRFB, membranes are used to prevent cross-mixing of the positive and negative electrolytes while allowing the transport of ions to complete the electrical circuit. Of these membranes, the

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most common membrane investigated for VRFB is commercial available Nafion membrane due to its high conductivity and excellent chemical stability. However, Nafion membrane has suffered from high cost and severe permeability of vanadium ions. Recently, VRFB have benefited from a large number of alternative membrane studies, where cation exchange membranes [2–4], anion exchange membranes [5–14], porous membranes [15–18] and amphoteric ion exchange membranes [19–21] have been reported for VRFB application. All of these alternative membranes demonstrated great promise for VRFB applications and laid a firm foundation for the further development of alternative membranes with high performance. However, enhancing durability in oxidative vanadium electrolyte still remained a significant challenge in this fields. It has been demonstrated that restricting water uptake and swelling behavior of the membrane can improve the chemical stability of the ion exchange membrane by inhibiting the absorption of VO_2^+ and further delaying the membrane degradation [4,14,22].

Adamantane has rigid spherical cycloaliphatic-cage structure, which imparts it with high melting point (269 °C) and excellent thermal stability [23]. The bulky and rigid adamantane incorporated in to the backbone of polymer resulted in much higher T_g than that of polysulfone derived from bisphenol A, because the former has greater resistance to segmental motion [24]. In this paper we reported on an unique anion exchange membrane derived from adamantane-containing poly(aryl ether ketone), where the bulky, rigid and highly hydrophobic adamantane segment can restrict the water uptake and swelling of membrane, the as-prepared membrane was employed for VRFB application, and showed high stability attribute to the introduction of adamantane segment, the other properties of membrane and VRFB cell performances were also investigated in detail.

2. Experimental

2.1. Materials

1,3-Dibromoadamantane (Luzhou Dazhou chemical Ltd., China), chloromethyl ethyl ether (CMEE) (Henan wanxiang technology & trade co., Ltd), tin tetrachloride ($SnCl_4$) (Sinopharm Chemical Reagent Co., Ltd), vanadyl sulfate ($VOSO_4$) (Shanghai Luyuan Fine Chemical Plant), 4,4′-difluorobenzophenone (DFB) (Changzhou Huashan Chemical Co., Ltd). All chemicals were chemically pure grade or better and were used as supplied.

2.2. Synthesis of adamantane-containing poly(aryl ether ketone)

The monomer 1,3-(4-hydroxyphenyl)adamantane (1,3-ADM) was synthesized from 1,3-dibromoadamantane and phenol according to the literature procedure [25]. As depicted in Scheme 1, the adamantane-containing poly(aryl ether ketone) (ADMPEK) were synthesized as following method:

4, 4′-Difluorobenzophenone (DFB) (0.1 mol), 1,3-ADM (0.1 mol), anhydrous potassium carbonate (0.14 mol), sulfolane (40 mL), and toluene (20 mL) were charged to a three-neck flask equipped with a mechanical stirrer, Dean–Stark trap, and reflux condenser. Under nitrogen purge, the reaction mixture was refluxed for 2 h at 140 °C. After refluxing, the Dean–Stark trap was drained to remove the toluene, and the temperature was maintained at 180 °C for another 20 h. Following the reaction, the viscous solution was diluted with 60 mL of sulfolane, and then the solution was precipitated into water. The intrinsic viscosity for ADMPEK in chloroform at 25 °C was measured on an Ubbelohde capillary viscometer as an indication of molecular weight.

2.3. Preparation of anion exchange membrane

An illustrative synthesis for chloromethylated adamantane-containing poly(aryl ether ketone) (CADMPEK) was provided as following. Adamantane-containing poly(aryl ether ketone) (5.0 g) had been dissolved in nitrobenzene (75 mL), then, chloromethyl ethyl ether (CMEE) (5 mL) and calculated $SnCl_4$ were added to the polymer solution. The temperature of polymer solution was maintained at 30 °C for 10 h. Then, the polymer solution was precipitated with excess of ethanol. The obtained polymer was dried at 60 °C under vacuum for 48 h. The degree of substitution (DS) of CADMPEK was calculated from ^1H NMR spectroscopy (Bruker Avance 500 M). A series of CADMPEK with different DS were prepared by altering the amount of $SnCl_4$.

Preparation of membrane: CADMPEK was dissolved in 1-methyl-2-pyrrolidone to form a 10 wt % solution. Then, the solution was casted and heated on a smooth glass plate (60 °C, 9 h), after that, the resulting base membrane was immersed in trimethylamine solution (33 wt%) (40 °C, 72 h) to obtain quaternized adamantane-containing poly(aryl ether ketone) membrane (QADMPEK) (Scheme 1). The thickness of QADMPEK membranes was in the range of 40–45 μm.

2.4. Characterization of membrane

^1H NMR (Bruker Avance 500 M) and FT-IR analysis (Varian 6400 FT-IR spectrometer) were used to confirm the chemical structure of ADMPEK and CADMPEK, respectively.

The ion exchange capability (IEC) of membrane was determined by titration. QADMPEK membrane (in chloride form) was dried under vacuum (60 °C, 48 h), and then the membrane was weighed and immersed in 25 mL of 0.1 mol L^{-1} $NaNO_3$ solution for 48 h at room temperature. After that the solution was titrated with 0.05 mol L^{-1} $AgNO_3$ over a potentiometric titrator (ZD-2, Shanghai INESA & Scientific Instrument Co., Ltd, China). IEC was calculated according to the following equation:

$$IEC = \frac{V_{AgNO_3} \times C_{AgNO_3}}{M}$$

where V_{AgNO3} was the volume of $AgNO_3$ solution, C_{AgNO3} was the concentration of $AgNO_3$ solution, and M was the weight of dried membrane, respectively.

Water uptake was calculated according to the following equation:

$$Water\ \ uptake(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

where W_{wet} and W_{dry} were the weights of the membrane in wet and dry state, respectively.

The swelling ratio was calculated according to the following equation:

$$Swelling\ \ ratio = \frac{L_1 - L_0}{L_0} \times 100\%$$

where L_1 and L_0 were the length of the soaked membrane and dry membrane, respectively.

The area resistances of the membranes were measured by electrochemical impedance spectroscopy (EIS) over a frequency range from 100 kHz to 1 Hz (CH Instruments Electrochemical Workstation, CHI 660E) [26]. The conductivity cell was separated with membrane, and each cell was filled with 1.5 M $VOSO_4$ in 3 M H_2SO_4. The effective area S of membrane was 1 cm^2 r_1 and r_2