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Poly(phenyl sulfone) anion exchange membranes with pyridinium groups for vanadium redox flow battery applications

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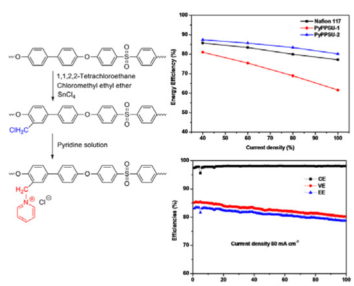
HIGHLIGHTS

- PyPPSU membranes are first fabricated and investigated for vanadium redox flow battery application.
- PyPPSU membranes show significantly low vanadium ions permeability.
- High VRFB cell efficiencies are obtained by using PyPPSU membranes.
- PyPPSU membrane shows stable performance in VRFB cycling test.

GRAPHICAL ABSTRACT



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ABSTRACT

To develop high performance and cost-effective membranes with low permeability of vanadium ions for vanadium redox flow battery (VRFB) application, poly(phenyl sulfone) anion exchange membranes with pyridinium groups (PyPPSU) are prepared and first investigated for VRFB application. PyPPSU membranes show much lower vanadium ions permeability (0.07×10^{-7}–0.15×10^{-7} cm^2 min^{-1}) than that of Nafion 117 membrane (31.3×10^{-7} cm^2 min^{-1}). As a result, the self-discharge duration of the VRFB cell with PyPPSU membrane (418 h) is about four times longer than that of VRFB cell with Nafion 117 membrane (110 h). Furthermore, the VRFB cell with PyPPSU membrane exhibits higher battery efficiency (coulombic efficiency of 97.8% and energy efficiency of 80.2%) compare with that of VRFB cell with Nafion 117 membrane (coulombic efficiency of 96.1% and energy efficiency of 77.2%) at a high current density of 100 mA cm^{-2}. In addition, PyPPSU membrane exhibits stable performance in 100-cycle test. The results indicate that PyPPSU membrane is high performance and low-cost alternative membrane for VRFB application.

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1. Introduction

Vanadium redox flow battery (VRFB) reported by M. Skyllas-Kazacos and coworkers [1] is a promising technology for energy storage system which provide solutions to overcome the intermittent nature of renewable energy and provide stable, reliable electricity for power grids [2]. In VRFB, membrane serves as physical separator to prevent cross-mixing of the positive and negative electrolytes while allowing the transport of ions (such as H^+, SO_4^{2-}, and HSO_4^-) to complete the electrical circuit. Nafion membrane served as the benchmark membrane for VRFB because of its high conductivity and good chemical stability. However, Nafion membrane has suffered from high cost and severe permeability of vanadium ions. Various modification methods (such as nanopartical incorporation [3,4], composite construction [5], multilayer

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structuring [6,7] and surface modification [8,9]) have been carried out to decrease the vanadium ions permeability of Nafion membrane. As a result, these membranes showed lower vanadium ions permeability and improved cell performance in VRFB cells. Clearly, these insights obtained from Nafion-based works would help the design of low-cost alternative membranes with superior properties.

Recently, alternative membranes such as cation exchange membranes [10–15], nanofiltration membranes [16–20] and anion exchange membranes [21–29] have been reported for VRFB application. Among these membranes, anion exchange membrane have received considerable attention for VRFB application, because the membrane enjoys lower vanadium permeability related to the Donnan exclusion effect between positively charged groups and vanadium ions. Both traditional quaternary ammonium group and pyridinium group can be served as ion exchange groups for anion exchange membrane. Pyridinium group showed more stability than quaternary ammonium group in oxidative vanadium electrolyte [28]. Moreover, pyridinium group, as a weak alkaline, can promote proton transport of membrane due to acid–base interactions [27]. In this paper, the low-cost poly(phenyl sulfone) with good commercial availability and chemical resistance was used to fabricate novel cost-effective poly(phenyl sulfone) anion exchange membranes with pyridinium groups (PyPPSU), and these membranes were first investigated in VRFB application. The membrane properties and VRFB cell performance were studied.

2. Experimental

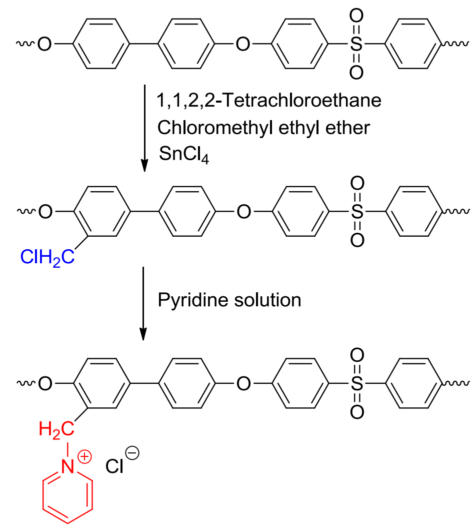
2.1. Materials

Poly(phenyl sulfone) (PPSU, Radel R-5500) (Solvay Advanced Polymers). 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), Pyridine (Sinopharm Chemical Reagent Co., Ltd) and other chemicals were commercially obtained and used as received.

2.2. Preparation of anion exchange membrane

Chloromethylated poly(phenyl sulfone) was prepared by chloromethylation reaction: after 5.0 g of poly(phenyl sulfone) had been dissolved in 75 mL tetrachloroethane, 0.7 mL $SnCl_4$ was added and then 5 mL of chloromethyl ethyl ether (CMEE) was added to the solution. The mixture was maintained at 50 °C for 10 h and poured into excess of ethanol. The precipitated polymer was dried at 60 °C under vacuum for 48 h. The degree of substitution of resulting polymer was calculated from ^1H NMR spectroscopy (Bruker Avance 500 M). The degree of substitution (DS) of chloromethylated poly(phenyl sulfone) (CMPPSU) was defined as the number of chloromethyl groups per polymer repeat unit.

After the CMPPSU had been dissolved in 1-methyl-2-pyrrolidone as a 10 wt. % solution, the solution was casted onto a smooth glass plate and evaporating the solvent at 60 °C for 9 h to obtain base membrane, and then the base membrane was treated with the method according to Zhang et al. [28]. The base membrane was immersed in 1 mol L^{-1} pyridine water solution at 40 °C for 72 h to obtain poly(phenyl sulfone) anion exchange membrane with pyridinium groups (PyPPSU) (Scheme 1). After that, the membrane was immersed into 5 wt. % HCl to neutralize residual pyridine, and then washed with excess deionized water to remove residual HCl. The thickness of PyPPSU membranes were in the range of 40–45 μm.



Scheme 1. Synthesis of poly(phenyl sulfone) anion exchange membrane with pyridinium groups (PyPPSU).

2.3. Characterization of membrane

The chemical structure of chloromethylated poly(phenyl sulfone) and PyPPSU membrane was confirmed using FT-IR analysis with a Varian 6400 FT-IR spectrometer.

The ion exchange capability (IEC) of membrane was determined by titration [21]. A dried PyPPSU membrane (in chloride form) was obtained under vacuum at 60 °C for 48 h, and then it was weighed and immersed in 25 mL 0.1 mol L^{-1} $NaNO_3$ solution for 48 h at room temperature. After that the solution was back titrated with 0.1 mol L^{-1} $AgNO_3$, and K_2CrO_4 was employed as indicator. 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 of PyPPSU membrane was determined by equilibrating the sample of membrane with deionized water at room temperature for 24 h. The membrane was wiped using absorbent paper and weighed immediately. Then the membrane was dried at 60 °C under vacuum for 48 h. Water uptake was calculated according to the following equation:

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

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

To evaluate the swelling ratio of the PyPPSU membranes in deionized water and vanadium electrolyte, membrane samples were dried at 60 °C under vacuum for 48 h, and then the length of membrane were measured. After that the membranes were soaked in deionized water and 1.5 M VO^{2+} in 3 M H_2SO_4 solution for 24 h, respectively. The swelling ratio was calculated according to the following equation:

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

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