



Optimizing membrane thickness for vanadium redox flow batteries

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ABSTRACT

Two important intrinsic properties of proton exchange membranes for vanadium redox flow battery (VRFB) operation are proton conductivity and vanadium permeability. These characteristics are thickness-normalized quantities and depend on fundamental material parameters. However, the operational criteria of proton exchange membranes in these devices are the membrane resistance and vanadium crossover flux, both of which depend on membrane thickness. Herein, we explore the influence of the thickness of ion exchange capacity (IEC)-optimized sulfonated fluorinated poly(arylene ether) (SFPAE) membranes on their VRFB performance including charge/discharge behavior, charge depth, coulombic efficiency, voltage efficiency, energy efficiency and cell polarization. IEC-optimized SFPAE membranes with three different thicknesses (28 μm , 45 μm and 80 μm) were prepared and tested in this study. It was found that the combined effects of the ohmic loss and electrolyte crossover loss in the VRFB, which were governed by membrane thickness, resulted in an optimal membrane thickness of 45 μm for SFPAE under the conditions tested. Thicker membranes were observed to cause higher cell resistance while thinner membranes yielded larger vanadium crossover flux, both of which had negative impacts on the cell performance. The maximum power densities of the VRFBs assembled with 28 μm , 45 μm and 80 μm SFPAE membranes were 267 mW cm^{-2} , 311 mW cm^{-2} and 253 mW cm^{-2} respectively, much higher than that of the VRFB assembled with N212 membrane, which was 204 mW cm^{-2} . These results supported our previous observation that SFPAE was superior to N212 with regard to VRFB performance. The data also indicated that there is an optimum membrane thickness for a given set of properties through which the cell performance can be significantly improved while keeping the membrane material constant.

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1. Introduction

Recently, vanadium redox flow batteries (VRFBs) have received significant attention due to their potential as large-scale electric energy storage devices [1,2]. Several prototypes of VRFBs have been successfully implemented worldwide, and the technology is rapidly progressing toward widespread commercialization [3,4]. While much progress has been achieved during the last 5 years, the performance of VRFBs still needs to be improved in terms of their coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) to afford long-term and low-cost operation of the cells. To address these challenges, research effort has been focused on the control and optimization of VRFB separator properties, since the separator determines the CE of the cell and also contributes to a large portion of the ohmic loss which affects the overall VE and EE of these systems [5].

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Proton exchange membranes (PEM) have been successfully employed in VRFBs as the cell separator to transport ions between the catholyte and the anolyte while blocking the crossover of the electrolytes and preventing shorting of the electrodes [6]. Recent studies in this field have demonstrated that PEMs developed for hydrogen and methanol-fueled proton exchange membrane fuel cells (PEMFCs) can provide acceptable cell performance when employed in VRFBs [11–13]. NAFION[®], as the benchmark PEM, has been proven to be a sufficient separator to obtain good VE in a VRFB [7]. However, its high vanadium permeability leads to significant capacity loss and low CE, which has stimulated progressive efforts in the search for alternative PEM separator candidates [8–10]. Recent studies have demonstrated that randomly sulfonated aromatic backbone-based polymers are superior to their selectively sulfonated analogs in terms of ease of material synthesis and lower vanadium permeability [14]. Therefore these types of PEMs represent good candidates for use as VRFB separators.

The proton conductivity (σ) and vanadium permeability (P , the product of the diffusion coefficient of vanadium in the membrane, D , and the species partition coefficient from the solution phase

into the membrane phase, H) are two of the most important parameters for the operation of PEMs in VRFBs [15,16]. The σ can be converted to membrane resistance, R , through $R=L/\sigma S$ (L is thickness and S is the area for ion conduction), while P can be converted to crossover flux, J , through $J=P\Delta C/L$ (ΔC is the vanadium concentration difference of the electrolytes). The membrane resistance determines the VE while the vanadium crossover flux dictates the CE of the operating device. There is a tradeoff between these two fundamental material properties with thickness, through which the cell performance can be optimized for different baseline membrane properties. Generally, proper tailoring of the ion exchange capacity (IEC) of PEMs is the first and the most important step towards balanced proton conductivity and vanadium permeability after the backbone of the separator material is selected [16,17]. Further modifications such as hybridizing or blending with other desirable components like inorganic fillers can lead to better selectivity properties [18–20] and our thickness optimization observations in this work should be generally applicable to the use of many different types of ion exchange membranes in VRFBs.

In addition to chemical composition and properties, the thickness of the membrane has direct implications on the cell performance and longevity. For instance, the thickness of the membrane affects the amount of undesired species crossover during charging/discharging, which governs the capacity loss/fade and thus the long-term performance of VRFBs. Recent work has shown that species crossover in a VRFB occurs as a result of three transport mechanisms in the membrane: convection, diffusion, and migration [21]. Along with the polymer backbone type and electrolyte chemistry, the rate and relative importance of these species transport mechanisms in the membrane is also reported to be highly dependent on the thickness of the membrane [21]. Thickness controls the ion transport resistance and alters the magnitude of the driving forces governing the species transport during VRFB operation. In particular, the rate of the osmotic convection and diffusion was shown to be highly sensitive to the membrane thickness [21,22].

In addition to capacity loss, the thickness of the membrane also plays a key role in the cell ohmic resistance and membrane mechanical properties such as compressibility and osmotic stability. While the mechanical strength of the membranes is enhanced with thickness, the VE of the overall system is diminished because of the increased ohmic resistance. Furthermore, the CE of the system is observed to increase with a thicker membrane due to the lower amount of vanadium species crossover. Therefore, the thickness of the membranes can simultaneously influence the CE and VE of flow batteries through membrane resistance and electrolyte crossover, similar to the role of membrane IEC or changes in intrinsic membrane properties during blending/hybridization. Despite its importance, few systematic studies have been performed to understand the role of membrane thickness on the cell performance and assess the importance of optimizing the membrane thickness for a given set of VRFB operational conditions. Herein, we reported our effort on the investigation of the influence of membrane thickness on VRFB cell performance using an IEC-optimized ionomer.

2. Experimental

2.1. Materials

Fluorinated sulfonated poly(arylene ether) (SFPAE) with an IEC of 1.8 meq g^{-1} , room temperature proton conductivity of 61 mS cm^{-1} and VO_2^+ permeability of $7 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ was synthesized according to our previous report [16]. Membranes with three different thicknesses (28 μm , 45 μm and 80 μm) were

obtained by casting different amounts of 8 wt% SFPAE solution in N,N' -dimethylacetamide onto glass plates followed by drying at 80°C for 24 h. All reagents were purchased from common commercial suppliers and used as received.

2.2. VRFB construction

A VRFB cell was constructed according to our previous work [22,23]. The battery was composed of a symmetric cell consisting of two graphite current collectors, two carbon felt electrodes with an area of 10 cm^2 , two PVDF spacers, two PVDF endplates and the membrane separator to isolate the anolyte and catholyte. Viton gaskets ($\sim 0.8 \text{ mm}$) were placed in between each of the components to avoid leakage of the electrolyte. The electrolyte tanks were filled with $1.4 \text{ M VO}_2^+ + 2.0 \text{ M H}_2\text{SO}_4$. The electrolyte volume in the positive tank was 100 mL while 50 mL of electrolyte was used in the negative tank. We used double amount of the electrolyte in the positive tank because the oxidation of V^{4+} to V^{5+} is a one electron reaction while the reduction of V^{4+} to V^{2+} is a two electron reaction. Silicone tubing was used to connect the electrolyte tanks and the cell. Two peristaltic pumps were used to feed the electrolytes to the cell continuously at a flow rate of 100 mL min^{-1} . Nitrogen was purged to the electrolyte tanks to protect the vanadium species from oxidation.

2.3. Electrochemical measurements

All electrochemical measurements were conducted using a custom-designed fully automated redox flow battery testing system. For charge/discharge experiments, a constant current program was used with an upper limit voltage of 1.7 V and a lower limit voltage of 0.7 V to determine the end of the charge/discharge processes under each current density studied. For polarization curve measurements, the current was scanned with the lower limit voltage of 0.2 V to determine the end of the polarization curve. The VRFBs were first fully charged at 80 mA cm^{-2} , then the discharge current was scanned from 0 A to 700 mA cm^{-2} with steps of 10 mA cm^{-2} . The hold time at each step was 30 s. The voltage after 30 s was recorded and plotted against current density. The CE, VE and EE of the cell were calculated from the following equations:

$$\text{CE} = \frac{t_d}{t_c} \times 100\% \quad (1)$$

$$\text{VE} = \frac{V_d}{V_c} \times 100\% \quad (2)$$

$$\text{EE} = \text{CE} \times \text{VE} \quad (3)$$

where t_d is the discharging time, t_c is the charging time, V_d is the average discharging voltage, and V_c represents the average charging voltage.

3. Results and discussion

3.1. Charge/discharge behavior

The charge/discharge behavior of a VRFB is usually quantified as the voltage change of the cell as a function of charge/discharge time. When charging a VRFB, the voltage increases gradually with time until the concentration of uncharged species is too low to support the charging rate and then a sudden increase in the charge voltage occurs. This point is generally considered as the end point of the charging process. Similarly, when discharging a VRFB, the voltage decreases gradually with discharge time until the concentration of the charged species becomes insufficient to

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