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Selective ion transport for a vanadium redox flow battery (VRFB) in nano-crack regulated proton exchange membranes



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ABSTRACT

To develop new cost-effective and high performance ion exchange membranes (IEMs) for redox flow battery applications, poly(arylene ether sulfone) random copolymer membranes (BPSHs) with surface nano-crack coatings (P-BPSH) were prepared using a hydrophobic atmospheric plasma treatment. The effect of the nano-cracks on the membranes' ion transport properties and the performance of the vanadium redox flow batteries (VRFBs) were evaluated to better understand the feasibility of using this technique in membrane ionic selectivity. The ion-selective nano-crack surface significantly improved the proton selectivity, from 32.95 to 74.20, over vanadium (VO^{2+}) ions. Consequently, the VRFB cell assembled using a P-BPSH-60 membrane showed higher coulombic and energy efficiencies compared to a VRFB with a pristine BPSH-60 membrane. The energy efficiency of the P-BPSH-60 membrane (85.37%) is comparable to that of a Nafion[®] 117 membrane (85.11%). The improved battery performance demonstrated that the surface nano-crack coating layer effectively blocked the transport of vanadium ions through the IEM without distinct reduction of the proton conductivity. The results suggest a promising strategy to enhance membrane proton selectivity over vanadium ions.

1. Introduction

Redox flow batteries (RFB), which are highly energy efficient and have standalone modular design, have attracted much scientific and public interest for their energy storage applications [1,2]. Among the various available RFB technologies, the vanadium redox flow battery (VRFB) is one of the most promising techniques and has received extensive attention and commercialization [3–5]. In VRFBs, vanadium is utilized to form both negative and positive electrolytes, so cross-contamination is less detrimental than in other flow batteries [6]. Ion exchange membranes (IEMs) play a very important role in the VRFB system as they prevent electrode shorting while still allowing the movement of ionic charge carriers to complete the circuit [3]. Generally, an ideal membrane for VRFB applications should exhibit the following characteristics: 1) low vanadium ion and water molecule permeation rates to minimize self-discharge; 2) high proton conductivity/low area resistance to minimize voltage efficiency loss; 3) good chemical stability under operational conditions; and 4) low cost [6,7].

Sulfonated fluoropolymer copolymers such as DuPont's Nafion[®] membranes have been widely investigated and employed as membrane separators in VRFBs due to their good chemical stability and commercial availability [8,9]. However, Nafion[®] membranes are costly, and can be about 41% of the flow cell stack's total cost [10]. A relatively high vanadium cross-over flux is another issue with the Nafion[®] membrane, leading to a lower coulombic efficiency (CE) and more significant capacity loss in the standby state. To suppress the vanadium ion permeation rate in Nafion[®] membranes, many efforts have been conducted to modify its properties. Teng et al. reported a VRFB with a hybrid membrane of Nafion[®] containing SiO_2 . They organically modified the silicate, which improved the coulombic efficiency and showed a slower self-discharge rate when compared to the VRFB with pristine Nafion[®] [11]. Zeng et al. also lowered the vanadium ion permeability and water transfer rate by modifying the surface of Nafion[®] with polypyrrole [12]. Considering the high price of pristine Nafion[®], these membranes are still not commercially attractive for large-scale devices, even with the modification strategies that improved battery performance. Therefore, alternative methods using low-cost materials must be employed.

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