



The use of polybenzimidazole membranes in vanadium redox flow batteries leading to increased coulombic efficiency and cycling performance



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ABSTRACT

An issue with conventional vanadium redox flow batteries (VRFB) with Nafion membranes is the crossover of vanadium ions, resulting in low coulombic efficiency and rapid decay in capacity. In this work, a VRFB with a polybenzimidazole (PBI) membrane is tested and compared with the Nafion system. Results show that the PBI-based VRFB exhibits a substantially higher coulombic efficiency of up to 99% at current densities ranging from 20 mA cm⁻² to 80 mA cm⁻². More importantly, it is demonstrated that the PBI-based VRFB has a capacity decay rate of as low as 0.3% per cycle, which is four times lower than that of the Nafion system (1.3% per cycle). The improved coulombic efficiency and cycling performance are attributed to the low crossover of vanadium ions through the PBI membrane.

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1. Introduction

Pressing concerns on the environmental impacts of burning fossil fuels and their limited reserves have led to a growing global usage of renewable energy, such as wind and solar energy. The wide deployment of renewables is, however, hindered by a viable energy storage technology. Among a wide range of energy storage technologies, flow batteries offer several unique advantages, including the system scalability, long cycle life, and high energy efficiency [1–4]. In particular, the all-vanadium redox flow battery (VRFB) has been regarded as one of the most promising technologies, primarily because it uses the same element in both half-cells, which avoids the problem of cross-contamination between the two half-cell electrolytes [5,6].

A typical VRFB consists of two porous electrodes and two circulating electrolyte solutions separated by a membrane, as shown in Fig. 1. The membrane acts as a key component, not only separating the positive electrolytes and negative electrolytes, but also providing an ionic conduction pathway between the two electrolytes during the charge and discharge process. To date, the most widely used membranes in VRFBs system are perfluorosulfonic cation exchange membranes (typically Nafion) due to their high ionic conductivity and decent chemical stability. However,

Nafion membranes suffer from a high crossover rate of vanadium ions, which results in a decrease in the coulombic efficiency and capacity fading after prolonged cycling. Previous studies reported two main reasons for the high vanadium crossover with Nafion membranes. First, the chemical structure of currently employed Nafion consists of hydrophilic sulfonic acid groups and a hydrophobic Teflon backbone. Once hydrated, the microphase separation between hydrophilic sulfonic acid groups and the hydrophobic Teflon backbone forms water channels, which create unwanted ion transport pathways. These water channels are typically 4.0 nm in diameter [7], which is much larger than the size of hydrated vanadium ions (typically 0.6 nm [8]), allowing free movement of vanadium ions through Nafion membranes. Second, the negatively charged functional groups from Nafion membranes facilitate the adsorption and diffusion of positively charged vanadium ions in the membrane due to electrostatic attraction. In order to improve VRFB's performance, efforts have been made to reduce vanadium crossover [9–16]. For example, inorganic particles like SiO₂, TiO₂ and zirconium phosphate have been introduced into Nafion membranes in an attempt to reduce the size of water channels, thereby decreasing vanadium permeability [9–11]. Some alternative CEMs such as SPEEK membranes, which possess more rigid structures and narrower water channels, have proven to exhibit a lower vanadium permeability, but have not completely eliminated the problem [12–15]. Further reduction in the vanadium permeability of CEMs is limited by the negatively charged functional groups.

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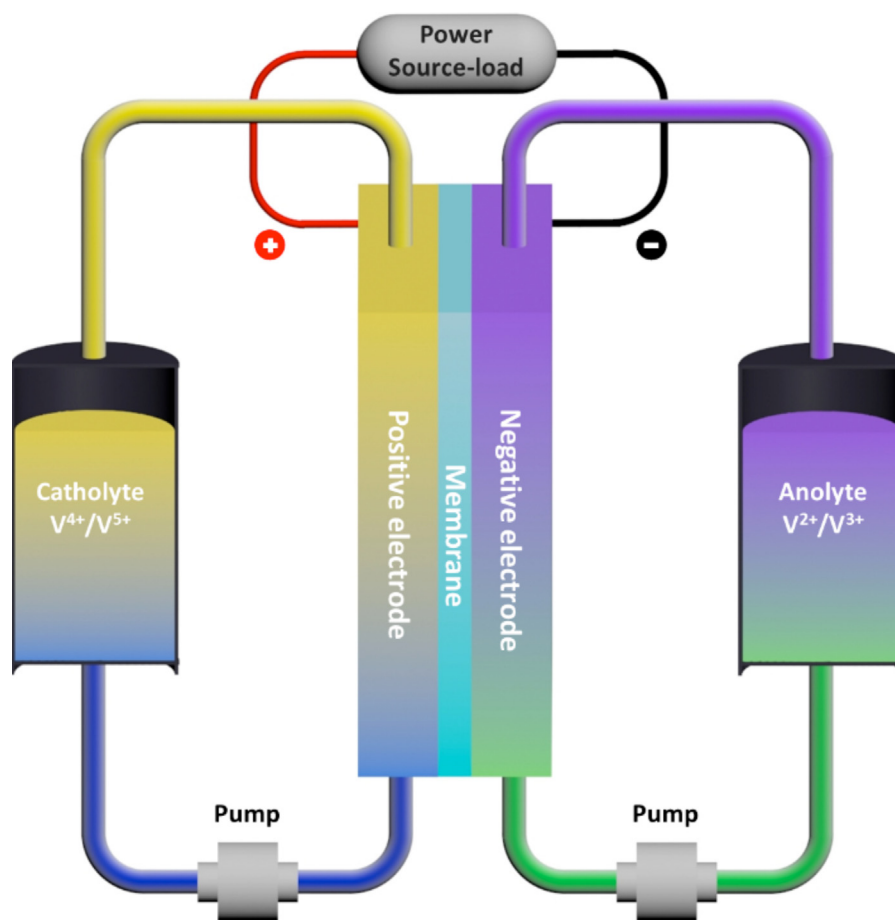


Fig. 1. Schematic of vanadium redox flow batteries.

Xu *et al.* [17] recently demonstrated a zeolite membrane for flow batteries, suggesting that effective separation of protons from vanadium ions can be achieved by using porous membranes with small pore sizes due to the size exclusion effect. Considering the fact that the Stokes radius of hydrated vanadium ions is much larger than that of H_3O^+ , it is possible to separate protons from vanadium ions by using a porous separator [18]. A porous separator may be a likely solution to eliminating vanadium crossover, since it contains no functional groups, but the brittleness of zeolite membranes is a serious limiting factor in practical applications. Therefore, a porous polymer membrane with small pore sizes that offers better mechanical properties is highly desired.

The PBI membrane has been widely investigated for nano-filtration [19,20] and high-temperature proton exchange membrane fuel cells [21–26]. The chemical structure is illustrated in Fig. 2. PBI has a highly chemically stable polymer backbone, making it especially suitable for VRFBs, which has a strong acidic and oxidizing environment. Previous studies show that the pore size of PBI membranes should range from 0.5 nm to 2.0 nm [19,20] (much smaller in comparison to that of Nafion membranes and other alternative ion exchange membranes at typically 2–4 nm in diameter), which helps to reduce vanadium ion crossover significantly. The objective of this work is to employ the PBI membrane as a porous separator for a VRFB system and conduct a comparison study with the Nafion-based system through investigating conductivity, vanadium ion permeability and cell performance. It is demonstrated that the vanadium permeability of a PBI membrane is two orders of magnitude lower than that of the

Nafion system, indicating that effective separation of protons from vanadium ions is achieved. A PBI-based VRFB demonstrates a coulombic efficiency of up to 99% at current densities ranging from 20 mA cm^{-2} to 80 mA cm^{-2} , as opposed to a coulombic efficiency of 82% to 94% seen in a Nafion-based VRFB.

2. Experimental

2.1. Membrane preparation

A PBI membrane, 30 μm in thickness, was provided by Yick-Vic. It should be noted that the ionic conductivity of a pure PBI membrane is extremely low, i.e. $10^{-12} \text{ S cm}^{-1}$ [27] and have nearly no pores. Thus, the PBI membrane was pretreated by immersion in 4M H_2SO_4 for 7 days to form the porous membrane. The PBI membrane was then thoroughly washed in DI water to remove excess sulfuric acid. Nafion® 211 (thickness: 25 μm) was examined as a benchmark under the same conditions.

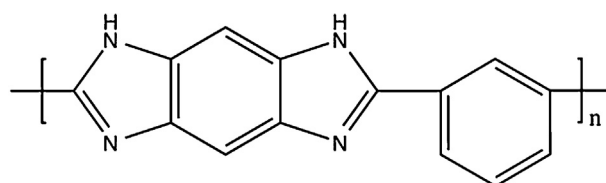


Fig. 2. Chemical structure of PBI.

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