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# Nonionic zeolite membrane as potential ion separator in redox-flow battery

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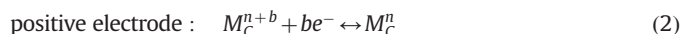
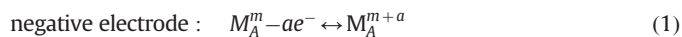
## ABSTRACT

The crystalline silicalite membrane has been demonstrated as an effective ion separator for acidic solutions of vanadyl sulfate and for potential application as a proton-permselective electrolyte membrane in the all-vanadium redox-flow battery. Silicalite contains uniform channels with an effective diameter of 0.56 nm, which permits the small  $\text{H}_3\text{O}^+$  ions to diffuse through but is impermeable to the large hydrated multivalent vanadium ions due to steric effects. Unlike conventional polymeric ion exchange materials, silicalite is nonionic and its proton conductivity relies on the electric field-driven  $\text{H}_3\text{O}^+$  transport through the sub-nanometer pores. The silicalite membrane exhibits high proton selectivity relative to vanadium ions and a significantly reduced self-discharge rate compared to that of Nafion ion exchange membranes.

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## 1. Introduction

Redox-flow batteries (RFBs) are promising for electrical energy storage in distributed renewable power systems and large-scale energy grids because of a number of advantages relative to solid state storage devices. Advantages include simple electrode reactions, separated cell stack and storage tanks, modularity, rapid recharge by direct solution replacement, small environmental footprint, and low cost [1,2]. The RFB operates by electrode reactions of dissolved ions constituting red-ox couples:



where  $M_A^m/M_A^{m+a}$  and  $M_C^n/M_C^{n+b}$  are reduced/oxidized states of metal ions in the negative (anode) and positive (cathode) compartments, respectively.  $M_A$  and  $M_C$  metal ions can be elementally identical or different [2]. As schematically shown in Fig. 1, during battery operations, the electrons go through the external circuit, while the nonreactive ionic charge carriers, often protons, transfer internally through the ion exchange membrane (IEM). The IEM not only plays a key role in determining the battery energy efficiency and lifetime but also contributes substantially to the RFB cost [3].

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Perfluorosulfonic acid polymers, such as Nafion<sup>®</sup> which is commonly considered as benchmark, were the first choice IEM candidates for RFB development because of their high proton conductivity and the good stability they had already demonstrated in proton-exchange membrane fuel cells. However, when used in the extremely acidic and oxidizing RFB aqueous electrolyte solutions, the polymeric IEMs experience metal ion crossover and polymer degradation that limit the cell efficiency and lifetime [1,4]. These deficiencies are inherent to the structural and chemical properties of the perfluorosulfonic acid polymers. Hydrated IEMs such as Nafion<sup>®</sup> films contain hydrophilic sulfonic acid groups that form nanometer-size water channels and pockets by self-organization within an otherwise hydrophobic matrix. These water channels are typically 2–4 nm in diameter and provide conduits for the fast transport of protons under the gradients of electrical or chemical potentials [5]. The flexible structure of the water-swollen polymer, however, also permits transport of the larger-size hydrated metal ions [4].

Reduction of metal ion crossover has been reported when inorganic or organic nanoparticles (e.g.,  $\text{SiO}_2$ ) are incorporated into the polymer matrix to reduce the width of the water channels [6] as well as when low-conductivity modifiers are incorporated to increase the transfer resistance for multivalent cations [7]. Attempts have also been made to reduce pore size of polymeric membranes by deposition of silica on the internal pore wall of nanofiltration membranes to improve the proton selectivity by increasing steric resistance to large cations [8,9]. There have also been efforts to develop partially fluorinated and nonfluorinated

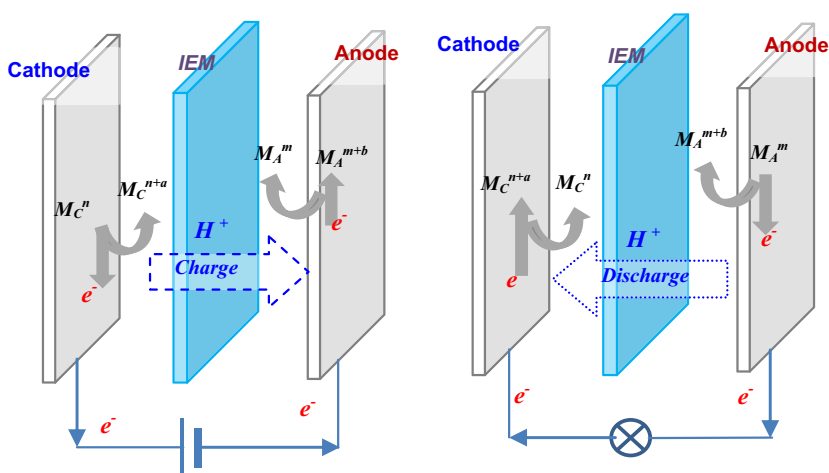


Fig. 1. Schematic showing the electron and proton transfer in an RFB during charging (left) and discharging (right) processes.

polymer IEMs for ion selectivity enhancement and cost reduction [10]. Despite substantial progress made in recent years, the improvement of ion selectivity by reducing the size of water channels is ultimately limited by the swelling and flexible nature of the perfluorosulfonic acid polymers. Furthermore, polymer degradation in strong oxidizing solutions remains a concern, especially for partial- or nonfluorinated IEMs [11].

Here we demonstrate the nonionic molecular sieve zeolite film for effective proton/metal ion separation and its potential application as an alternative electrolyte membrane in an all-vanadium RFB (VRFB). Zeolites are crystalline aluminosilicates with large porosity and uniform pore sizes of molecular scale defined by specific crystallographic structures. Membranes of small pore siliceous zeolites such as MFI-type, which have no ion exchange capacity, have been theoretically and experimentally shown to separate water from dissolved alkaline metal ions by size-exclusion (steric) effects [12,13]. The zeolite membranes allow transport of water molecules but reject metal ions, which are strongly hydrated in aqueous solutions, making them too large to enter the zeolitic channels. Because the number of water molecules tied to a metal ion increases with the ion charge density, the hydrated multivalent metal ions involved in RFB systems are typically very large ( $> 0.6$  nm [14]). However, proton exists in water in the form of  $\text{H}_3\text{O}^+$  hydronium, which is a polyatomic ion with charge density too small to form hydration shells and thus has a much smaller size. In this study, the siliceous MFI-type zeolite (i.e., silicalite) membrane supported on macroporous  $\alpha$ -alumina disc has been investigated for ion separation and as an IEM in the VRFB system. The silicalite is known to be intrinsically inert in oxidizing environments and chemically stable in strongly basic and acidic solutions. The material contains nearly cylindrical channels with an effective diameter of 0.56 nm, which is expected to be permeable for  $\text{H}_3\text{O}^+$  but inaccessible to the large hydrated multivalent metal ions.

## 2. Experimental

### 2.1. Membrane preparation and characterization

The silicalite membrane was supported on a 25-mm diameter porous  $\alpha$ -alumina disc that had a thickness of 2 mm, porosity of  $\epsilon=27$ –30%, and an average pore size of  $d_p \sim 0.07$   $\mu\text{m}$ . For the in-situ synthesized silicalite membrane, the effective area ( $A_{\text{eff}}$ ) is given by ( $\epsilon A_m$ ), where  $A_m (=2.54$   $\text{cm}^2)$  is the straight forward area of the membrane excluding the area covered by the O-ring seals.

The zeolite membrane was synthesized by in-situ crystallization from an aluminum-free precursor solution with a molar composition of 0.33( $\text{SiO}_2$ ):0.1(TPAOH):0.017(NaOH):5.56( $\text{H}_2\text{O}$ ). The tetrapropylammonium hydroxide (TPAOH) is the structure directing agent (SDA). The synthesis procedure is similar to that reported in our previous publication [15]. The hydrothermal crystallization was conducted in an autoclave at 180  $^\circ\text{C}$  and autogenous pressure for 17 h. The hydrothermal synthesis process was repeated once to minimize the intercrystalline pores after the first film growth. The membrane recovered from the synthesis solution was thoroughly washed by DI water, dried at 100  $^\circ\text{C}$  overnight, and then fired at 500  $^\circ\text{C}$  for 6 h to activate the zeolitic pores by burning off the SDA molecules. Although a very small amount of  $\text{Al}^{3+}$  ions from the substrate could incorporate into the zeolite framework near the zeolite/substrate interface, the membrane was previously verified to be aluminum-free near the outer surface [16]. The silicalite membrane was tested by helium permeation and proton diffusion before template removal to verify the absence of pinholes. After calcination, the membrane was further tested by permeation of pure helium and a 50(v)/50(v)  $\text{CO}_2/\text{H}_2$  gas mixture, respectively, at room temperature and atmospheric pressure to check the quality of the membrane.

### 2.2. Ion permeation

The proton/vanadyl ion ( $\text{VO}^{2+}$ ) transport selectivity values of the silicalite membrane, the bare alumina substrate, and commercial Nafion<sup>®</sup> 117 membrane were evaluated by the conventional diffusion experiment [9] performed in the RFB cell described in the next section. During the measurement, 20 ml of 4/7 M  $\text{VO}^{2+}$  ( $\text{VOSO}_4 \cdot 4\text{--}6\text{H}_2\text{O}$ , 99.9%, Aldrich) sulfate solution in 4/7 M  $\text{H}_2\text{SO}_4$  was circulated on one side of the membrane and 20 ml of 1 M  $\text{MgSO}_4$  solution was circulated on the other side. The 1 M  $\text{MgSO}_4$  solution was used in the permeate side to minimize the osmotic pressure difference and maintain equivalent ionic strengths between the two sides. The pH value and  $\text{VO}^{2+}$  concentration in the  $\text{Mg}_2\text{SO}_4$  solution were continuously monitored using a pH meter (Thermo Scientific Orion 320) and a UV/vis spectrometer (with actual  $\text{VO}^{2+}$  detection limit of  $\sim 0.0001$  M), respectively. The  $\text{H}^+/\text{VO}^{2+}$  ion selectivity ( $\alpha_{\text{H}^+/\text{V}^{4+}}$ ) of the zeolite membrane was then estimated based on their respective measured fluxes. A diffusion study was also performed on an identical zeolite membrane with the permeate side filled with DI water instead of the 1 M  $\text{MgSO}_4$  solution to observe the  $\alpha_{\text{H}^+/\text{V}^{4+}}$  and  $\text{H}^+$  flux under osmotic pressure.

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