

Short communication

# Nafion/SiO<sub>2</sub> hybrid membrane for vanadium redox flow battery

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Received 15 December 2006; received in revised form 20 January 2007; accepted 24 January 2007

Available online 2 February 2007

## Abstract

Sol–gel derived Nafion/SiO<sub>2</sub> hybrid membrane is prepared and employed as the separator for vanadium redox flow battery (VRB) to evaluate the vanadium ions permeability and cell performance. Nafion/SiO<sub>2</sub> hybrid membrane shows nearly the same ion exchange capacity (IEC) and proton conductivity as pristine Nafion 117 membrane. ICP-AES analysis reveals that Nafion/SiO<sub>2</sub> hybrid membrane exhibits dramatically lower vanadium ions permeability compared with Nafion membrane. The VRB with Nafion/SiO<sub>2</sub> hybrid membrane presents a higher coulombic and energy efficiencies over the entire range of current densities (10–80 mA cm<sup>-2</sup>), especially at relative lower current densities (<30 mA cm<sup>-2</sup>), and a lower self-discharge rate compared with the Nafion system. The performance of VRB with Nafion/SiO<sub>2</sub> hybrid membrane can be maintained after more than 100 cycles at a charge–discharge current density of 60 mA cm<sup>-2</sup>. The experimental results suggest that the Nafion/SiO<sub>2</sub> hybrid membrane approach is a promising strategy to overcome the vanadium ions crossover in VRB.

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**Keywords:** Vanadium redox flow battery; Nafion/SiO<sub>2</sub> hybrid membrane; Vanadium permeability

## 1. Introduction

Vanadium redox flow battery (VRB) proposed by Skyllas–Kazacos group [1–4] in 1985 has received considerable attention due to its long cycle life, flexible design, fast response time, deep-discharge capability, and low pollution emitting in energy storage [5–16]. As shown in Fig. 1, the VRB consists of two electrolyte tanks with the electrolytes of V(IV)/V(V) and V(II)/V(III) in sulfuric acid solution, two pumps, and a battery stack section where the redox electrode reaction takes place. The electrolytes are pumped into the stack separated by an ion exchange membrane. Ion exchange membrane is one of the key materials for VRB and usually used to provide proton conduction to maintain the electrical balance and effective separation of the anode and cathode electrolytes. The ideal membrane for VRB should possess low vanadium ion crossover, high ionic conductivity, and good chemical stability. Previous studies showed that most early types of commercial ion exchange membranes (e.g., Selemion CMV, DMV, Asahi Glass Co., Japan) are unsuitable due to their degradation by V(V) in VRB [17].

Perfluorosulfonic polymers such as Nafion are the most commonly used proton exchange membrane material owing to their high proton conductivity, good chemical and thermal stability [18]. However, Nafion membrane suffers from the crossover of methanol and vanadium ions when used in direct methanol fuel cell (DMFC) [19,20] and VRB [12,21], respectively, which results in decreases in energy efficiency. There has been extensive research activity in the modification of Nafion based membrane to reduce the methanol permeability, for example, recasting with inorganic nanoparticles, [22] surface modification with metal thin film, [23] surface modification with layer-by-layer self-assembly polyelectrolyte, [19] hot-pressing with other proton conducting membrane, [24] and *in situ* sol–gel reaction to incorporate inorganic oxide nanoparticles within the pores of Nafion [25]. All of above modification methods may also be used to decrease the crossover of vanadium ions through Nafion membrane and, in general, improves the performance of VRB.

Since the pioneer work by Mauritz et al. [26–29], sol–gel derived Nafion/SiO<sub>2</sub> hybrid membranes have been successfully used in DMFC due to the simple dealing procedure (see Fig. 2) and lower methanol permeability. Nafion/SiO<sub>2</sub> hybrid membranes can reduce the crossover of methanol because of the polar clusters (pores) of the origin Nafion, which is the dominating reason for methanol permeating, had been filled with SiO<sub>2</sub>

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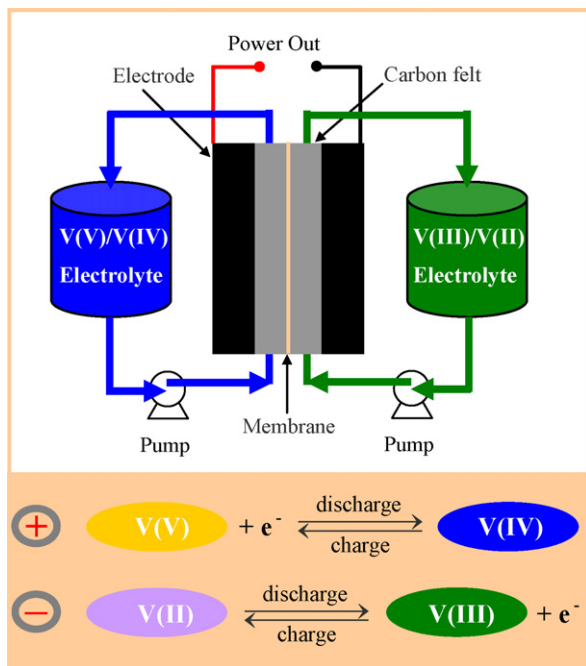


Fig. 1. Schematic illustration of vanadium redox flow battery (VRB).

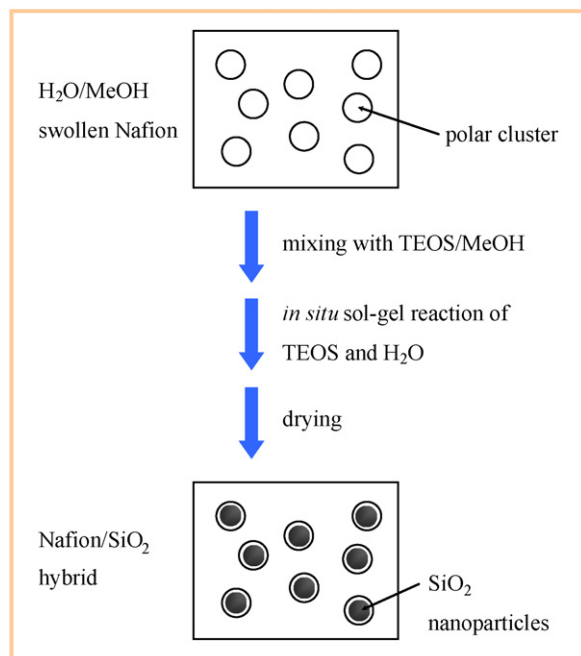


Fig. 2. Schematic depiction of the preparation of Nafion/SiO<sub>2</sub> hybrid membrane.

nanoparticles during the *in situ* sol–gel reaction with TEOS, as shown in Fig. 2 [25,29].

The specific nanostructure of Nafion/SiO<sub>2</sub> hybrid membranes inspired us that this kind of membrane maybe also can lower vanadium ion permeability compared with Nafion membrane. In this work, Nafion/SiO<sub>2</sub> hybrid membrane was measured their ion exchange capacity (IEC), proton conductivity, water uptake, and vanadium ion permeability in comparison with the pristine Nafion 117 membrane. Then, Nafion/SiO<sub>2</sub> hybrid membrane was employed as the separator in VRB, and the cell performance was also evaluated and discussed. Experiment results show that the Nafion/SiO<sub>2</sub> hybrid membrane approach is a promising strategy to inhibit vanadium ions crossover in VRB.

## 2. Experimental

### 2.1. Preparation of Nafion/SiO<sub>2</sub> hybrid membrane

All membranes used in this work were Nafion 117 and denoted as Nafion. Prior to modification, the Nafion membrane was treated according to the standard procedure that is 60 min in a 3 wt.% H<sub>2</sub>O<sub>2</sub> solution at 80 °C, 30 min in deionized water at 80 °C, and 30 min in 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at 80 °C. After each treatment, the membrane was rinsed in deionized water to remove traces of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. The membrane was stored in deionized water before use.

Samples were dried at 110 °C under vacuum to determine the initial, dry H<sup>+</sup> form weight before the sol–gel reaction. Nafion/SiO<sub>2</sub> hybrid membrane was prepared according to the *in situ* sol–gel method reported by Mauritz et al. [26–29] Fig. 2 illustrates the preparation of Nafion/SiO<sub>2</sub> hybrid membrane [25,29]. In a typical synthesis, a 6 cm × 6 cm dry Nafion membrane was first swollen overnight in stirred solutions of MeOH:H<sub>2</sub>O = 5:1 (vol/vol) at room temperature. Then the pre-mixed tetraethylorthosilicate (TEOS)/MeOH solutions were introduced into the flask with the Nafion membrane so that the H<sub>2</sub>O:TEOS ratio was 4:1 (mol/mol) while maintaining stirring. After 3 min for the sol–gel reaction, the membrane was removed from the flask, and then quickly soaked in MeOH for 1–2 s to wash away excess reactants adhering to the surface. Finally, the membrane was surface-blotted and dried at 100 °C under vacuum for 24 h. The resulted Nafion/SiO<sub>2</sub> hybrid membrane had a silica content of 9.2 wt.% (see Table 1). The sample was stored in deionized water before use.

### 2.2. Membrane characterization

The water uptake of the membranes was defined as mass ratio of the absorbed water to that of the dry membrane. It can

Table 1  
Comparison of general properties between Nafion and Nafion/SiO<sub>2</sub> hybrid membrane

Membrane	Silica content (wt.%)	Thickness (μm)	Water uptake (wt.%)	IEC (mmol g <sup>-1</sup> )	Conductivity (mS cm <sup>-1</sup> )
Nafion	–	215	26.0	0.97	58.7
Nafion/SiO <sub>2</sub>	9.2	204	21.5	0.96	56.2

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