



Influence of aminosilane precursor concentration on physicochemical properties of composite Nafion membranes for vanadium redox flow battery applications



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HIGHLIGHTS

- Nafion membranes were modified via sol-gel condensation of aminosilane.
- The effect of aminosilane loading on the membrane properties is studied.
- High loadings of aminosilane result in strong anisotropy of membranes.
- An optimum aminosilane loading is found.
- Vanadium redox batteries with composite membranes have improved energy efficiency.

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ABSTRACT

A series of composite proton-exchange membranes have been prepared via sol-gel modification of commercial Nafion membranes with [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane. The structure and physico-chemical properties (water uptake, ion-exchange capacity, vanadyl ion permeability, and proton conductivity) of the prepared composite membranes have been studied as a function of the precursor loading (degree of the membrane modification). If the amount of the precursor is below 0.4/1 M ratio of the amino groups of the precursor to the sulfonic groups of Nafion, the composite membranes exhibit decreased vanadium ion permeability while having relatively high proton conductivity. With respect to the use of a non-modified Nafion membrane, the performance of the composite membrane with an optimum precursor loading in a single-cell vanadium redox flow battery demonstrates enhanced energy efficiency in 20–80 mA cm⁻² current density range. The maximum efficiency increase of 8% is observed at low current densities.

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1. Introduction

Vanadium redox flow batteries (VRB) have recently attracted much attention as promising electrochemical energy storage devices for stationary applications, due to a number of advantages including independent power and energy sizing, long cycle life, fast response, and no self-discharge during storage [1–4].

VRB consists of positive and negative electrolytes (VO₂⁺/VO²⁺ and V³⁺/V²⁺ redox couples in acidic solution, respectively) stored in two separate tanks, two pumps, and a membrane electrode assembly, where electrochemical reactions take place [3,5]. An ion exchange membrane (IEM) in an essential battery component as it separates the electrodes, prevents cross-mixing of the positive and negative electrolytes, and provides proton transport to complete the electrochemical circuit. A membrane suitable for VRB applications should be stable against oxidation by VO₂⁺ cations as well as to reduction by V²⁺ cations, it should exhibit high proton conductivity to provide high voltage efficiency of the battery as well as low

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vanadium permeability to ensure high Coulombic efficiency, and eventually low water transport for longer cycle life.

Perfluorinated polysulfonic acid (PFSA) membranes such as Nafion are the most widely used in VRBs [4,6,7]. The unique properties of PFSA membranes are determined by their microphase-separated structure; the polytetrafluoroethylene (PTFE) backbone forms continuous hydrophobic domains providing excellent mechanical properties and chemical stability, while side chains containing sulfonate groups form ion-conducting domains of hydrophilic channels with diameter of several nanometers [8]. Such unique structure ensures good cationic conductivity of PFSA membranes yet reduces selectivity to transport of protons to other cations. As such, the use of Nafion membranes in VRBs suffers from pronounced crossover of vanadium cations [9] through the membrane which leads to severe capacity loss.

Various methods have been proposed to improve the ionic selectivity of Nafion and suppress the crossover of vanadium cations [6]. These methods include coating Nafion membranes with thin films of polycations (polyethylenimine [10] or polyaniline [11]), surface modification of membranes (via layer-by-layer assembly of polyelectrolyte complexes [12–15] or adsorption of cationic silica nanoparticles [16]), and incorporation of inorganic or composite organic–inorganic nanoparticles inside the hydrophilic channels of Nafion [17–21]. The latter modification results in partial blocking of Nafion hydrophilic channels by nanoparticles and yields lower swelling degrees as well as suppressed vanadium cation permeability of the modified membranes.

In this work we report for the first time that a modified Nafion composite membrane can be prepared via soaking dry Nafion membrane in a solution of [*N*-(2-aminoethyl)-3-aminopropyl]trimethoxysilane (AATMS, a cationic silica precursor) followed by the *in situ* hydrolysis. The amount of the precursor uptaken by the membrane could be easily varied by altering the concentration of AATMS in the soaked solution. This process allowed us to prepare Nafion membranes with a varied degree of modification and to systematically elucidate the effect of the degree of modification on the properties of the resulting composite membranes. In particular, we studied the influence of AATMS concentration during modification on the ion exchange capacity, water uptake, in-plane and through-plane proton conductivity, and vanadium permeability of the membranes. The membranes showing suppressed vanadium cation permeability and reasonably high proton conductivity were tested in single VRB cells.

2. Experimental

2.1. Materials

Commercially available Nafion 115 membrane material (Aldrich) was used. According to the manufacturer data, the membrane thickness was 125 μm , and the Nafion equivalent weight was of 1100 g mol^{-1} . Prior to use, the membrane was conditioned via sequential boiling in distilled water (1 h), aqueous H_2O_2 (3 wt%, 1.5 h), distilled water (1 h), aqueous H_2SO_4 (0.5 M, 1.5 h), and distilled water (1 h). The treated membrane will be further referred to as the pristine one.

[*N*-(2-Aminoethyl)-3-aminopropyl]trimethoxysilane (97%, abcr GmbH) was used as received. This silica precursor is abbreviated as AATMS throughout this paper.

The following inorganic salts were used in this work: NaCl (Khimmed, Russia) in the ion-exchange capacity test (Section 2.4), $\text{VOSO}_4 \times 4\text{H}_2\text{O}$ (Chempur GmbH) in the V(IV) permeability (Section 2.6) and single-cell (Section 2.7) tests, and $\text{MgSO}_4 \times 5\text{H}_2\text{O}$ (Khimmed, Russia) in the V(IV) permeability test (Section 2.6). The crystal hydrates composition was determined by means of TGA.

2.2. Membrane modification

The membranes modification was carried out as follows. The Nafion 115 specimens (0.8–1.0 g each) were incubated in a large volume of water (3 d, the water was exchanged with fresh portion 6 times during the incubation) to wash out the excess of sulfuric acid and dried in air at 60 °C overnight. The dry specimens were immersed in 35 mL of a solution of AATMS in isopropanol and left overnight for saturation with the precursor. The specimens were then rinsed with distilled water and incubated in 40–50 mL of water overnight for partial hydrolysis of the silica precursor. Subsequently, the specimens were again rinsed with distilled water to wash out the precipitate that might be formed at the surface, and the swelling medium was changed to a 2.5 M aqueous solution of sulfuric acid to ensure the complete hydrolysis. These modified membranes were incubated in a large volume of distilled water (3 d, the water was exchanged with fresh portion 6 times during the incubation) in order to wash out any low-molecular admixtures or side products and then stored in 2.5 M aqueous sulfuric acid prior to other experiments.

The amount of the AATMS precursor (each molecule of the precursor contained 2 amino groups) in the saturating solution was chosen so that the amount of the amino groups introduced into the membrane corresponded to a desired fraction of the charged groups in the Nafion specimen (10–400%).

The reference (non-modified) membrane was treated similarly, but no silica precursor was added to isopropanol at the saturation stage.

In a special experiment we checked whether the preliminary swelling of the membrane in isopropanol had any influence on the sol-gel process and the properties of the resulting modified membrane. To do so, the dried pristine Nafion 115 specimens were incubated in isopropanol up to constant mass. After that, the membranes were immersed in a solution of AATMS; further treatment was identical to the above-described procedure.

2.3. Morphology

Microscopy images of the membranes surface were obtained using Carl Zeiss Supra 40 scanning electron microscope.

In order to obtain thin (about 100 nm) cross sections, the membranes were cut using a Reichert-Jung ultramicrotome with an ultra 35° DiATOME diamond knife. Those ultrathin sections were placed onto an ultrathin film-substrate from the water surface of the knife reservoir. Transmission microscopy images of those cross sections were obtained by means of LEO912AB (Carl Zeiss, Germany) transmission electron microscope as 2048 \times 2048 px digital images.

2.4. Ion exchange capacity determination (IEC)

Prior to determination of the Nafion membranes ion-exchange capacity (related to the apparent equivalent weight of the polymer), the specimens were incubated in a large volume of distilled water (3 d, the water was exchanged with fresh portion 6 times during the incubation) in order to wash out the excess of sulfuric acid. After that, the specimens were dried in air at 60 °C overnight and weighed; the determined mass was considered that of the dry polymer.

The dry specimens were incubated in 30 mL of 2 M aqueous NaCl solution during 48 h which facilitated the substitution of protons contained in the membrane with sodium ions. The membrane was then removed from the solution and washed with water. The external solution was combined with the washings, and the resulting mixture was titrated with 0.050 M NaOH. Having known

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