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Mediated proton transport through Nafion 117 membranes imbibed with varying concentrations of aqueous $VOSO_4$ (VO^{2+}) and NH_4VO_3 (VO_2^+) in 2 M H_2SO_4

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HIGHLIGHTS

- VO^{2+} imbibed membrane's proton transport mediated strongly by viscosity.
- VO_2^+ imbibed membrane's transport strongly affected by hydrogen bonding network.
- Faster transport expected of VO^{2+} imbibed membrane compared to VO_2^+.

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ABSTRACT

We performed an extensive study on Nafion 117 membrane imbibed with various concentrations of aqueous ammonium metavanadate (NH_4VO_3), and vanadyl sulfate ($VOSO_4$), in 2 M H_2SO_4 over the temperature range of 20–100 °C, using ^{1}H NMR and AC Impedance spectroscopies. The objective was to determine the effect of the tetravalent (VO^{2+}) and pentavalent (VO_2^+) vanadium ions on the proton transport of Nafion 117.^{1}H NMR chemical shift and linewidth data show greater short-range proton transport for the VO_2^+ imbibed membranes compared with the VO^{2+}. However, the local environments seem to differ in that while the data for VO_2^+ imbibed membranes seem to follow more the trends observed for water hydrated Nafion 117, those for the VO^{2+} followed the trend of its aqueous bulk vanadium solvents, indicating that viscosity plays a larger role for the VO^{2+} imbibed membranes compared to the VO_2^+.

1. Introduction

The vanadium redox flow battery (VRB) is an excellent candidate for large-scale renewable electrical energy storage devices [1–5]. The VRB operates on redox couples of bivalent/trivalent (V^{2+}/V^{3+}) and tetravalent/pentavalent (VO^{2+}/VO_2^+) vanadium ions at the negative and positive electrodes respectively, with each cell consisting of an anode, a cathode and an ion exchange membrane (IEM). Energy is stored in the concentrated sulfuric acid solutions of vanadium electrolytes, which are separated by an IEM to allow translational diffusion of protons but prevent the mixing of the two electrolytes. Advantages such as long cycle life, flexibility in design, low cost, independent power and energy density outputs, room temperature operation and fast response time have resulted in the commercial use of VRBs for applications such as load leveling, UPS and hybrids of wind and solar energies devices.

In VRBs the high permeation of vanadium ions across cation exchange membranes (CEMs) leads to significant reduction in cell efficiency due to self-discharge and flooding from water molecules that solvate the vanadium ions [6–9]. In order to improve the VRB, reduction or elimination of vanadium ions permeation through the CEM is necessary. Because of this, we need a thorough understanding of the transport of the vanadium ions both in solutions and through CEMs, both of which are focus of our research group. We previously studied the fundamental transport of tetravalent and pentavalent vanadium ions of varying concentrations in a 2 M H_2SO_4 solution using variable temperature ^{1}H Nuclear Magnetic Resonance (NMR) and AC Impedance spectroscopy [10]. Results show transport processes being greatly dependent on solution

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viscosity, especially for the tetravalent vanadium ion (VO^{2+}). Additionally, ion association was observed and increased with increasing vanadium ion concentration, especially for VO^{2+}.

As a continuation of this study we performed variable temperature ^{1}H NMR and AC Impedance Spectroscopy studies of Nafion 117 imbibed with varying concentrations of the tetravalent and pentavalent (VO^{2+} and VO_2^+) oxidation states. As a membrane, Nafion are the most ubiquitous [9,11–39]. This is due to their high proton conductivity; and good chemical, thermal and physical stabilities. They are however, very expensive and permeable to parasitic ions or molecules. Additionally, their proton transport properties are very dependent on their level of hydration [23–34]. Structurally, Nafion membrane consists of a hydrophobic fluorocarbon backbone and hydrophilic pendant side chains of sulfonic acid groups. This duality has been blamed for its high cross-over of non-proton ions. Upon hydration, the microphase separation between the hydrophobic and hydrophilic regions forms water channels thereby creating additional ion transport pathways, which are typically 4 nm in diameter [33]. Adding to this, the fixed negatively charged sulfonic acid groups could facilitate positively charged ion adsorption as well as their diffusion in the membrane through Coulomb attractions. Both result in poor overall performance.

To improve the efficiency and stability of the VRB, replacement membranes are necessary. These membranes must be chemically and thermally stable, have high proton conductivity and low to non-existent vanadium ions permeability. Since the vanadium ions are much smaller (<1 nm) in diameter [35], there permeation through Nafion is uncomplicated. Efforts toward replacing Nafion have led to its alterations and the use of replacements membranes. Alterations include the incorporation of inorganic oxides such as SiO_2, TiO_2 and zirconium phosphate particles [36–38] into the polymer matrix in an effort to reduce hydrated pore diameters. The addition of a cationic charged layer on the surface of Nafion [39] resulted in reduced vanadium ions permeation, and single cell self-discharge. However, the higher area resistance of the modified membrane reduced the voltage and offered no improvement in the overall cell efficiency. Replacements include hydrocarbon type membranes, which are developed from thermoplastics by sulfonation and have good chemical and thermal stability, good mechanical properties and low cost [40,41]. These include cation exchange membranes such as sulfonated poly (ether ether ketone) SPEEK [41,42], which has more rigid structure and smaller hydrated pore diameters; and sulfonated polybenzimidazole (PBI) [43], which also have smaller pores (0.5–2.0 nm) [44,45], a more rigid structure and reduced vanadium cross-over. However they both suffer from smaller ionic conductivity and greater membrane resistance resulting in lower voltage efficiency with increased current density compared to Nafion.

Despite the extensive research effort, studies have failed to isolate and identify the critical contributors to observed improved membrane performances. This is due mainly to the complexity of the ionic environments and interactions that exist in hydrated IEMs in operating VRBs. Present in the hydrated IEM in an operational VRB are all four vanadium oxidations states. Additionally, water molecules (solvating and bulk), possibly sulfate and bisulfate ions, and protons are also present. The high concentrations of both the acid and metal ions create regions in the IEM where all species interact with and are affected by each other. Because of these, it is necessary to characterize the interactions and permeability of all vanadium species in the electrolyte solutions as well as in the IEM.

The objective of the present work is to determine fundamentally the effect of the tetravalent and pentavalent vanadium ions on Nafion's proton transport capability. NMR offers a direct and non-destructive probe of the nuclei local environment, providing information on physical characteristics over a wide time ($1–10^{-10}$ s) scale, depending on the particular experiment being performed [46,47]. Parameters such as NMR spin-lattice (T_1) relaxation time measurements and spectra can provide information on ion and molecular mobility and interactions. This is the first in a series of fundamental studies aimed at understanding the proton transport of Nafion and similar IEMs for possible application in VRBs.

2. Experimental

2.1. Sample preparation

The compounds $VOSO_4$ (97%), and NH_4VO_3 (98%), and the acid H_2SO_4 (99.99%) were purchased from Sigma Aldrich. 250 ml of 2 M H_2SO_4 was first prepared by combining the required volume of the acid with distilled water according to the $M_1V_1 = M_2V_2$ relationship, where M_i is the solute concentration and V_i is the total solution volume. Solutions of $VOSO_4$ and NH_4VO_3 were prepared by dissolving the required mass of the salt in 10 ml of 2 M H_2SO_4. The mass of $VOSO_4$ was calculated assuming it was anhydrous because the correct hydration number (up to 4) was unavailable. Nafion 117 membrane (purchased from Fuel Cell Inc.) was protonated by first boiling in distilled water for 1 h, then in H_2O_2 for 1 h, then in distilled water for another hour, followed by 3 h in 0.5 M H_2SO_4, and finally for 6 h in distilled water. All steps were performed at 80 °C. The imbibed membranes were prepared by immersing protonated Nafion 117 in the vanadium solutions for periods of four days. Concentrations were 0.05, 0.1, 0.2, 0.5, 1.0, and 2 M for $VOSO_4$; and 0.05, 0.1, 0.2 M for NH_4VO_3. Weight uptake measurements were performed on all samples.

For NMR measurements strips (3 mm × 25 mm) of the imbibed membrane were first patted dry with Chemwipes to remove the surface liquid, then cut and placed into 5 mm OD NMR tubes, which were then capped and sealed with parafilm to reduce moisture loss over the course of the measurement. All variable temperature measurements were performed on the same day successively to prevent membrane dehydration as can occur especially at elevated temperatures.

2.2. NMR measurements

^{1}H NMR measurements were performed on a Varian Unity Plus spectrometer with a 7.1 T superconducting magnet and a Varian four-frequency 5 mm probe. NMR spectra were obtained from the Fourier Transform of single π/2 pulses. Spin-lattice relaxation times (T_1) were determined by the Inversion Recovery (π-τ-π/2-acquire) pulse sequence using 15 τ values. Water was used as the reference and set to 0 ppm. The temperature range studied was 20–100 °C with wait times of 15–20 min for equilibration [10]. The spectra were fitted using the MestRenova version 7.1 program. The files were opened as FIDs, phase corrected using the program's manual Phase correction, and normalized to maximum height of 100. The linewidths were determined using the cross hair tool by sandwiching the width at the height of 50. The program itself calculates the difference between these points hence giving us the full width at half max. Errors in linewidth, chemical shift and T_1 were less that 5%.

2.3. Ionic conductivity measurements

In-plane ionic conductivity values were determined by AC Impedance Spectroscopy over the frequency range of $2.0–2 \times 10^6$ Hz, using a Solartron SI 1260 Impedance Phase Gain Analyzer and 1287 Potentiostat. The temperature range studied was 21–60 °C due to the dehydration of the membrane at higher