



# A combined theoretical-experimental study of interactions between vanadium ions and Nafion membrane in all-vanadium redox flow batteries

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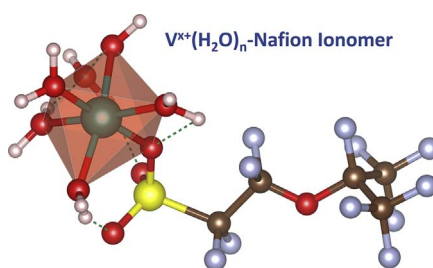
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## HIGHLIGHTS

- Nafion tends to have contact pair mechanism interactions with aqueous vanadium cations.
- Strong cation binding to Nafion induces peak splitting observed in IR spectra.
- DFT calculations help explain changes in IR spectra.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Vanadium redox flow batteries (VRFBs) are a promising solution for large-scale energy storage, but a number of problems still impede the deployment of long-lifetime VRFBs. One important aspect of efficient operation of VRFBs is understanding interactions between vanadium species and the membrane. Herein, we investigate the interactions between all four vanadium cations and Nafion membrane by a combination of infrared (IR) spectroscopy and density-functional-theory (DFT)-based static and molecular dynamics simulations. It is observed that vanadium species primarily lead to changes in the IR spectrum of Nafion in the  $\text{SO}_3^-$  spectral region which is attributed to the interaction between vanadium species and the  $\text{SO}_3^-$  exchange sites. DFT calculations of vanadium–Nafion complexes in the gas phase show that it is thermodynamically favorable for all vanadium cations to bind to  $\text{SO}_3^-$  via a contact pair mechanism. Car-Parrinello molecular dynamics-based metadynamics simulations of cation-Nafion systems in aqueous solution suggest that  $\text{V}^{2+}$  and  $\text{V}^{3+}$  species coordinate spontaneously to  $\text{SO}_3^-$ , which is not the case for  $\text{VO}^{2+}$  and  $\text{VO}_2^+$ . The interaction behavior of the uncycled membrane determined in this study is used to explain the experimentally observed changes in the vibrational spectra, and is discussed in light of previous results on device-cycled membranes.

## 1. Introduction

Redox flow batteries (RFBs) are currently experiencing rapid growth in interest as attractive candidates for large-scale energy storage applications because they are capable of storing multimegawatt-hours of

electrical energy from intermittent renewable sources such as wind and solar [1,2]. RFBs release or store energy when redox-active species dissolved in liquid electrolytes undergo electrochemical reactions at the electrode surfaces [3]. Out of many RFB chemistries that have been developed to date, the all-vanadium RFB (VRFB) has received the most

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attention [4–11]. Aqueous VRFBs use only one electroactive element (vanadium) for the entire redox cell with the  $V^{2+}/V^{3+}$  redox couple in the negative half-cell (anolyte) and the  $VO^{2+}/VO_2^+$  couple in the positive half-cell (catholyte) separated by an ion-exchange membrane to allow the migration of protons or sulfate/bisulfate. The use of the same element in both electrolyte reservoirs results in easier electrolyte regeneration and lower cross-contamination due to the crossover of vanadium ions through the membrane between the two electrolyte compartments. However, during long-term VRFB cell cycling, diffusion of vanadium ions through the membrane and their interaction with membrane constituents result in degradation of membrane components, capacity loss and electrolyte contamination [12]. Therefore, it is critical to understand how aqueous vanadium ions interact with the membranes at the molecular scale to help guide the design of more selective and chemically stable membranes.

The ideal membrane for VRFB applications should possess high selectivity to facilitate facile transport of protons or other supporting electrolyte anions or cations to complete the electrical circuit [13], but the membrane also needs to be impermeable to vanadium cations to prevent self-discharge reactions and capacity decay [14]. Other desired properties of the VRFB membrane include low water uptake, good physical strength, high chemical and thermal stability, and low production cost [15]. The most widely used membranes for RFBs are made of perfluorosulfonic acid (PFSA) polymers. Of particular importance among PFSA membranes is Nafion [16] characterized by its high ionic conductivity and high chemical stability, and it has been extensively used in fuel cells and batteries since its development in 1960s. Nafion is a sulfonated fluorocarbon polymer composed of a hydrophobic fluorocarbon teflon-based backbone with perfluoroether side chains terminated by strongly hydrophilic  $-CF_2SO_3H$  acid groups. In the presence of water, protons as well as the sulfonate groups of Nafion are in solvated form which greatly facilitates the hopping mechanism of protons. This hopping mechanism is widely known as the Grotthuss mechanism and is defined as the diffusion of protons through the H-bond network by the formation or cleavage of covalent OH bonds [17].

In practice, not only protons but also significant amounts of water and vanadium ions are transferred across the Nafion membrane during the VRFB operation. In the past, the effect of hydration on ionic conductivity of Nafion has been extensively examined both experimentally and theoretically [18,19]. In the context of VRFBs, despite a series of both experimental and theoretical investigations [20–23], it remains ambiguous whether the contact pairs with covalent-type bonding between vanadium ions and sulfonate sites of Nafion are formed, or if these species interact electrostatically through the solvent molecules thus exhibiting solvent-separated ion pair-type interactions. Several computational studies have recently focused on understanding the interaction mechanisms between vanadium ions and Nafion, but the results were inconclusive [20,22]. It is also still unclear why after VRFB cycling only the  $VO^{2+}$  species were experimentally identified inside Nafion membranes [21], while all four vanadium cations are present in the system. Although different types of cation- and anion-exchange membranes have been developed in recent years that are characterized by better ion selectivity and lower costs than Nafion, even the behavior of Nafion as the prototypical PFSA membrane in the presence of vanadium ions at the molecular level is still lacking. Detailed microscopic information about the interaction of Nafion with aqueous vanadium ions versus other metal ions would enable the development of efficient strategies to prevent vanadium crossover and decrease capacity fading of the VRFBs.

In a recent modeling study employing density-functional-theory (DFT) calculations at the B3LYP/6-311G++ level of theory [22] interactions between hydrated vanadium cations and triflic ( $CF_3SO_3H$ ) acid mimicking the terminal functional group of PFSA membranes were investigated in the gas-phase in conjunction with a continuum solvation model. It was suggested that none of the vanadium cations should covalently bind to the sulfonate group of triflic acid, but rather interact

with the  $SO_3^-$  site through the hydration shell (solvent share mechanism). It should be noted, however, that although triflic acid does resemble Nafion as both have fluorinated backbone and sulfonic acid head group, the polymer chain of Nafion is different making it a much weaker acid (by about three orders of magnitude) than triflic acid with a  $pK_a$  value of about  $-6$  [18,19]. Another recent gas-phase DFT study has focused on the interaction between the aqua-vanadyl ion  $VO(H_2O)_5^{2+}$  and the  $SO_3^-$  group of Nafion using a small Nafion ionomer model [20]. The authors investigated the energetics of vanadyl binding to  $SO_3^-$  through both solvent share and contact pair mechanisms, but the results were not conclusive as to what interaction mechanism should be more favorable.

It should be pointed out that the questions about the interaction mechanisms of Nafion with many other aqueous cations is still largely unresolved despite years of research [23–27]. For instance, it was suggested that  $Li^+$ ,  $Na^+$  and  $K^+$  should bind covalently to the sulfonate sites of Nafion preserving the 3-fold local symmetry, based on the combination of IR spectroscopy and gas-phase DFT calculations [25,26]. However, these results seem to contradict other DFT-based computational studies of  $Li^+$  interacting with triflate  $CF_3SO_3^-$  [28] and  $Na^+$  interacting with  $SO_3^-$  of Nafion [19] which show preference for these cations toward monodentate binding. This type of covalent interaction should break the local  $C_{3v}$  symmetry of the terminal  $SO_3^-$  group which may affect the  $SO_3^-$  IR spectral region.

In this paper we present the results of our systematic investigation of the interaction between all four aqueous vanadium cations and the sulfonic acid group of Nafion by means of IR spectroscopy and DFT-based static and molecular dynamics simulations.

## 2. Experimental details

An approximately 150  $\mu m$  thick Nafion membrane was prepared by solvent casting from an alcohol dispersion containing 20 wt% Nafion (DE2021, Ion power, New Castle, DE) at 80 °C followed by drying at 65 °C under vacuum for 24 h. The complete removal of solvent was confirmed by the absence of solvent peaks in the infrared spectrum of the membrane. The membrane was subsequently stored under vacuum at room temperature and used to generate vanadium complex samples within 72 h of preparation. To generate vanadium complex samples the 2.5 cm $\times$ 1 cm sections of the Nafion membrane were soaked in a salt solution containing the vanadium ion of interest for 24–48 h rinsed in de-ionized (DI) water to remove residual ions and dried under vacuum at 30 °C for 24 h before collecting spectra under a constant flow of dry nitrogen. Spectra were collected on a Vertex 70 spectrometer (Bruker, Billerica, MA) equipped with a wide band Mercury-Cadmium-Telluride (MCT) detector. The oxidation states of vanadium were confirmed by the color of the solution, and more precisely by UV–Vis measurements (see Supporting Information for more details). When removed from solution, the membrane acquired the color of the solution, and maintained this color for the next 4–5 days. In the case of  $V^{2+}$  oxidation occurred rapidly upon removing the membrane from solution, and therefore the spectra were obtained directly after removing the membrane from solution and after drying overnight.

Measurements were conducted in attenuated total reflection geometry on a horizon ATR accessory (Harrick, Pleasantville, NY) at 45° incident angle with a Ge attenuated total reflection (ATR) crystal. All spectra were collected as an average of 400 scans at 4  $cm^{-1}$  resolution. The resultant spectra were 2 point baseline corrected in the Opus software package (Bruker, Billerica, MA) with no further spectral manipulations performed.

## 3. Computational details

### 3.1. Gas-phase calculations

The structure of Nafion used in this study is shown in Fig. 1. For

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