Aqua-vanadyl ion interaction with Nafion® membranes

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Lack of comprehensive understanding about the interactions between Nafion membrane and battery electrolytes prevents the straightforward tailoring of optimal materials for redox flow battery applications. In this work, we analyzed the interaction between aqua-vanadyl cation and sulfonic sites within the pores of Nafion membranes using combined theoretical and experimental X-ray spectroscopic methods. Molecular level interactions, namely, solvent share and contact pair mechanisms are discussed based on vanadium and sulfur K-edge spectroscopic analysis.

Keywords: ion exchange membrane, redox flow battery, X-ray absorption spectroscopy, TD-DFT

INTRODUCTION

Nafion®, a perfluorinated cation exchange membrane, has wide technological applications ranging from fuel cells, batteries, to sensors. The excellent chemical stability combined with high proton conductivity and exceptionally wide functionality arises from the stable tetrafluoroethylene (TFE) backbone and acidic sulfonic groups in the pore structure of Nafion. In particular, its applicability in strong acidic and oxidative chemical environments has made it a central component in vanadium redox flow batteries (VRFB) (Zhang et al., 2010; Schwenzer et al., 2011). As a promising stationary energy storage system, VRFB requires cost effective long-term operation capabilities under a wide temperature range. Although, the chemically stable Nafion provides the necessary proton conductivity, it is also permeable for vanadium ion diffusion through its pore structure leading to substantial capacity decay during VRFB operation (Luo et al., 2013). Hence, designing a highly ion-selective membrane is the main challenge in realizing wide range commercial deployment of VRFB technology. However, a molecular level analysis of how the solvated vanadium ions diffuse through the spatially confined Nafion pores must precede any rational design approach of a highly ion-selective membrane.

Typically, cation permeation through Nafion is believed to be a result of its electrostatic interaction with negatively charged sulfonic acid sites within their pore structure (Hsu and Gierke, 1983). Inside the Nafion pore structure, the cations can interact with sulfonic sites though various mechanisms. For example, if the cations are fully solvated within these spatially encapsulated solutions, then it is expected that their solvation structure could effectively screen the electrostatic interaction with sulfonic sites. In this scenario, the solvent molecule as part of solvation sphere can interact with the sulfonic site, i.e., solvent share type interaction, and experience charge driven diffusion behavior. In

addition, higher cation concentration, charge, temperature along with pore geometry can lead to contact pair formation where the cation can directly bind to sulfonic acid sites (Komoroski and Mauritz, 1982). The interaction between cations and sulfonic sites often can significantly impact the overall membrane performance. For instance, if the contact pair is formed with covalent type bonding, it could lead to fouling process and decrease the overall cation permeability including the proton conductivity. Hence, it is essential to gain a molecular level understanding of vanadium ion interaction with the Nafion membrane in order for the rational design of membranes tailored for high performance VRB operation. Unfortunately, such study focused on the interactions of vanadium ions within the Nafion membrane is still elusive. Our previous analysis of the Nafion–vanadyl ion interaction is based on nuclear magnetic resonance (NMR) and x-ray photoelectric spectroscopy (XPS) methods (Vijayakumar et al., 2011, 2012), which has inherent limitations in terms of internal solvent dynamics and surface sensitivity, respectively. To overcome these experimental limitations, we employed the vanadium and sulfur K-edge x-ray absorption (XAS) analysis in combination with density functional theory (DFT) based computational methods. This combined approach can help us shed light on the aqua-vanadyl ion interaction with the sulfonic sites.
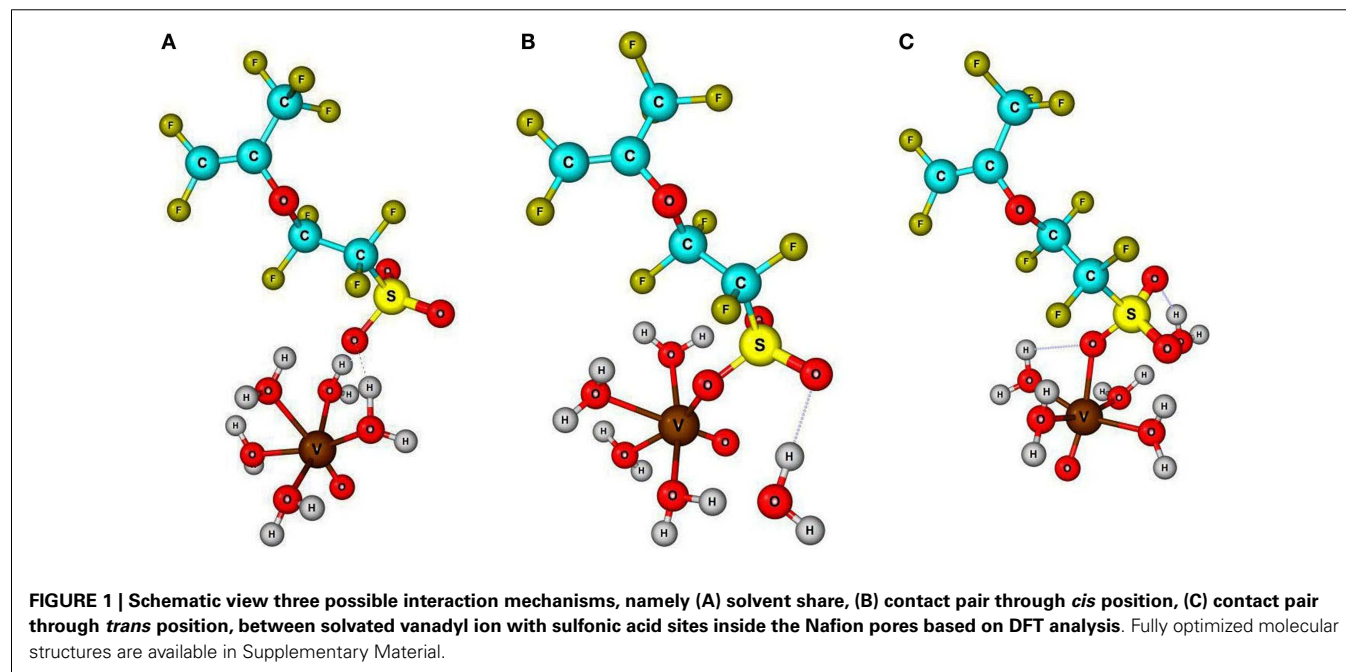
MATERIALS AND METHODS

All the measurements described herein were done using the commercial Nafion® 115 membrane. To probe the vanadyl ion interaction, the membrane was soaked in 1 M vanadium (IV) sulfate aqueous solution for 24 h at room temperature. The soaked membrane is washed with distilled water and dried in open air to remove any surface adsorbed vanadium species. Both vanadium and sulfur K-edge x-ray near edge spectroscopic (XANES) data

were recorded in fluorescence mode at Stanford synchrotron radiation light source (SSRL), on beam line 4–3. The vanadium and sulfur K-edge XANES peak positions are calibrated using absorption edge of sulfur powder and vanadium metal foil. Ground state quantum chemistry calculations were performed with the ADF 2013 software package. Both geometry optimization and energy barrier analysis carried out using the in-build PBE exchange-correlation functional with the D3 dispersion and triple-zeta double polarization (TZ2P) basis set on all atoms. The Gibbs free energy (G) of each structure was calculated using bond energy, solvation energy, entropy, and internal energy terms, which are computed with inbuilt program in ADF package (te Velde et al., 2001). For geometry optimization and energy calculation, only the side chain with terminal sulfonic sites (SO_3^-) is considered as it is crucial part of the Nafion pore structure. The TFE backbone is severely hydrophobic and not expected to interact with aqual-vanadyl ion and subsequently not analyzed in this study. The XANES spectra are calculated using time dependent density functional theory (TDDFT) with the NWChem quantum chemistry suite (Valiev et al., 2010). Averaged spectra were generated by sampling 20 geometries near the optimized structure and 1.0 eV Lorentzian broadened. The absorbing centers V and S were represented with the Sapporo-QZP-2012 (Noro et al., 2012) all electron basis set, while the remaining atoms were treated with the 6-311G** basis set (Krishnan et al., 1980). The BHLYP exchange-correlation functional (Lee et al., 1988; Becke, 1993) was used for all the TDDFT XANES calculations.

RESULTS AND DISCUSSION

The vanadyl ion normally exists as a distorted octahedral structured cation $[VO \cdot 5(H_2O)]^{2+}$ in aqueous solution. The molecular structure of vanadyl cation with its solvation phenomena in redox flow battery electrolyte has previously been reported (Vijayakumar et al., 2010, 2014). This distorted octahedral cation has five
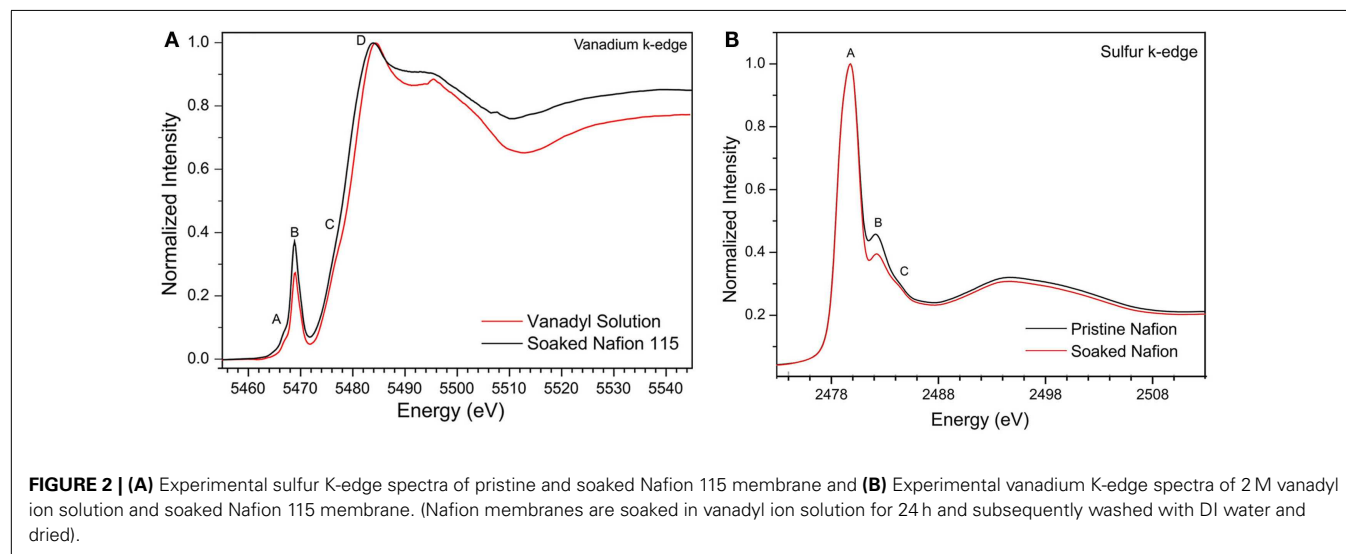
liable water molecules in octahedral coordination along with one vanadyl oxygen (V=O), which constitutes the first coordination sphere. This aqua-vanadyl ion can diffuse into the Nafion membranes forming electrostatic interactions with negatively charged sulfonic acid sites within the membrane pore structure. The diffusing aqua-cation can interact through the solvent share mechanism where the water molecule from first solvation can interact with sulfonic site through hydrogen bonding interaction. Alternatively, the sulfonic site can directly bond with the central vanadium atom via V–O bonding. This direct bonding represents a contact pair mechanism where the symmetry of the bond with respect to the native vanadyl oxygen (V=O) can result in either *cis* or *trans* positions. Schematic view of optimized geometry for solvent share, *cis* and *trans* contact pair mechanisms are shown in **Figure 1** (optimized molecular structures are available in Supplementary Material). To evaluate these three different possible vanadyl ion specific interactions and possibly identify the dominant mechanism within Nafion pores, we employed the ground state DFT calculations. All three possible structures were constructed from prior optimized vanadyl and Nafion side chain molecular structure and subsequently optimized without any geometry restrictions. From these optimized structure, respective room temperature (295 K) Gibbs energy were calculated. Surprisingly all three structures shows similar energy (± 0.6 eV) indicating nearly equal probability of formation inside the Nafion pores. It should be noted here that, our DFT calculations only involves a single side chain molecule and vanadyl ion whereas the experimental conditions contain complex cluster of sulfonic sites, bulk water, and multiple vanadyl ions engaging in highly correlated interactions. Nevertheless, the main focus of this article is to explore the molecular interaction between sulfonic sites and vanadyl ion. To verify the possibility of these different types of sulfonic site – vanadyl ion interactions within Nafion membranes, we carried out XANES measurements on pristine Nafion, vanadyl ion solution, and soaked Nafion membrane.

FIGURE 1 | Schematic view three possible interaction mechanisms, namely (A) solvent share, (B) contact pair through *cis* position, (C) contact pair through *trans* position, between solvated vanadyl ion with sulfonic acid sites inside the Nafion pores based on DFT analysis. Fully optimized molecular structures are available in Supplementary Material.
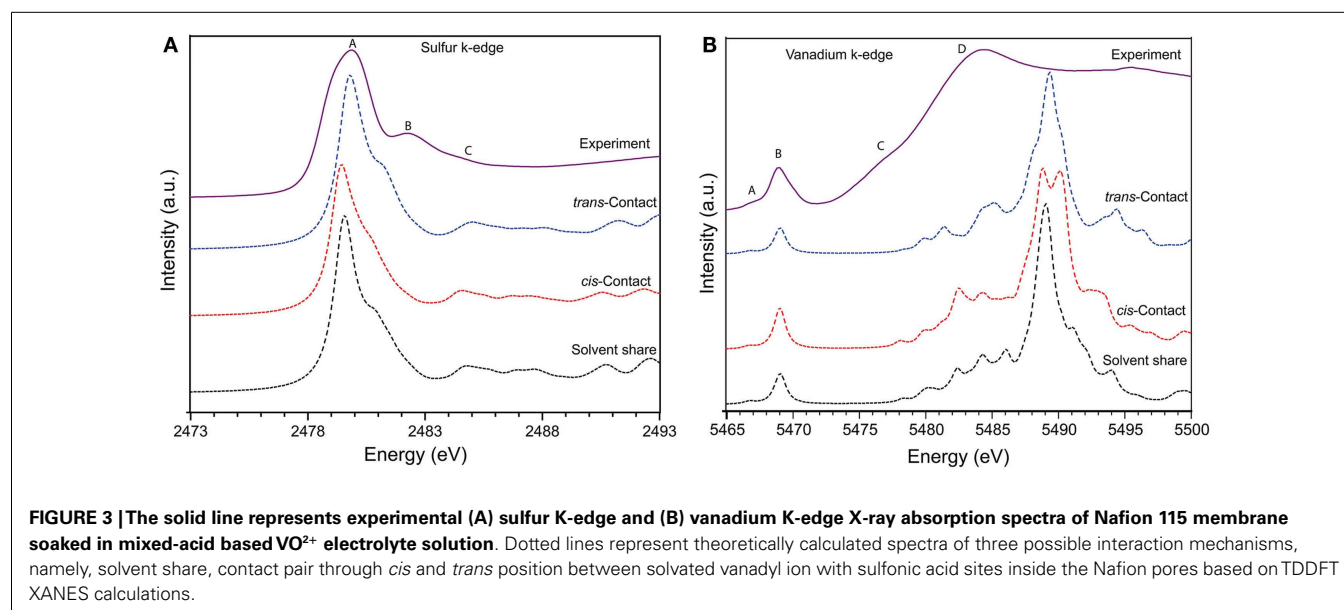
The vanadium K-edge spectra of pure vanadyl ion electrolyte solution and soaked Nafion membrane show very similar spectrum (see **Figure 2A**) with pre-edge absorption peaks (A and B) followed by shoulder peak (C) on strong absorption curve (peak D). While the strong absorption peak (D) and shoulder peak (C) represents dipole allowed $1s \rightarrow 4p$ transition and $1s \rightarrow 4p$ shakedown transition respectively, the pre-edge peaks (A and B) represents dipole forbidden $1s \rightarrow 3d$ transition indicating distorted octahedral symmetry of vanadyl molecular structure (Wong et al., 1984). The intensity of the pre-edge peaks is known to arise due to deviation of centrosymmetry around the absorbing V center allowing for strong $3d \rightarrow 4p$ mixing. Empirically, the intensity of pre-edge absorption peaks will give direct indication of the distortion in vanadium molecular structure, especially deviation from centrosymmetry, provided other factors such as oxidation state and ligand field strength remain comparable. For the soaked Nafion membrane, the dominant pre-edge peak (B) grows about 20% relative to the pure electrolyte solution, indicating the average ligand bond lengths are contracted and vanadyl molecule experiences more disorder inside Nafion pores. Now we can correlate this observation to DFT calculated molecular structure of vanadyl ion interacting with sulfonic sites of Nafion membranes (see **Figure 1**). The molecular size parameter can be defined as an average ligand bond length, $R = \left(\frac{1}{n}\right) \sum_{i=1}^{n} (r_i)$, where r is each individual ligand bond length and n is the total number of ligands ($n = 6$ for vanadyl molecules). The DFT optimized structure of vanadyl ion interacting with Nafion through solvent share and contact pair mechanism shows similar molecular size parameter ($R = 2.03 \pm 0.02$ Å), but lower than the pure vanadyl molecule ($R = 2.07$Å). This is in good agreement with increased intensity of pre-edge absorption in vanadium K-edge peaks of soaked Nafion membrane. Now we can focus on the main absorption peaks (C and D), where the soaked Nafion membrane register slight blue shift (~0.5eV) relative to the pure vanadyl solution (see **Figure 2A**). Typically, the shift in main absorption peaks is due to changes in any combination of valence, electronegativity of the

bonding ligands, coordination number and specific structural features of vanadium molecule. Due to its interaction with Nafion the valence state of vanadyl (VO^{2+}) and coordination numbers are not affected whereas overall structure is affected due to the difference in electronegativity of oxygen as part of water and sulfonic molecules. Hence, this slight blue shift is similar to the pre-edge peak intensity and merely represents a structural disorder in vanadyl structure.

The sulfur K-edge XANES spectrum of both pristine Nafion and soaked Nafion shows very similar features with one broad asymmetric peak centered at 2480.2 eV (peak A) followed by shoulder type resonances around 2482 and 2483 eV (peak B and C). The high intense broad peak A can be ascribed to an antibonding (C–S) σ* MO of A1 symmetry, whereas the shoulder type peak B and C represents (S–O) π bonding (Damian Risberg et al., 2007). It is evident that, the soaked Nafion shows slightly reduced intensity for peak B and C (see **Figure 2B**) indicating the possible change in S–O bond length of sulfonic sites due to interaction with vanadyl ions. Our DFT optimized geometry reveals that the typical S–O bond distance (1.46 ÅÅ) of sulfonic site is elongated due to its solvent share type interaction (1.57 ÅÅ) and contact pair interaction (~1.51 ÅÅ) with vanadyl ion. However, the cumulative effect of this bond elongation would be minimal as only one S–O bond is influenced by vanadyl ion interaction with sulfonic site [i.e., (SO_3^-)]. Meanwhile, the C–S bonds mostly remain uninterrupted (±0.01 ÅÅ) due to vanadyl ion interaction (Damian Risberg et al., 2007). Overall, unlike the vanadyl ion structural distortion, the sulfonic site of Nafion side chain retains its chemical structure, which is reflected in similar sulfur K-edge spectra of pristine and soaked Nafion membrane. Despite these observations, it is still unclear about the preferred type of interaction between sulfonic sites and vanadyl ion inside Nafion pores. To further explore the possible interactions, we calculated the XANES spectra for all three interaction models and compare with experimental spectra (see **Figure 3**). Our ensemble averaged TDDFT XANES calculations for the S and V K-edges are in fair agreement with experiment. As can be seen **Figure 3A**, there are

FIGURE 2 | (A) Experimental sulfur K-edge spectra of pristine and soaked Nafion 115 membrane and **(B)** Experimental vanadium K-edge spectra of 2 M vanadyl ion solution and soaked Nafion 115 membrane. (Nafion membranes are soaked in vanadyl ion solution for 24 h and subsequently washed with DI water and dried).

FIGURE 3 | The solid line represents experimental (A) sulfur K-edge and (B) vanadium K-edge X-ray absorption spectra of Nafion 115 membrane soaked in mixed-acid based VO^{2+} electrolyte solution. Dotted lines represent theoretically calculated spectra of three possible interaction mechanisms, namely, solvent share, contact pair through *cis* and *trans* position between solvated vanadyl ion with sulfonic acid sites inside the Nafion pores based on TDDFT XANES calculations.

no significant differences between the *trans* contact, *cis*-contact, and solvent share, respectively. This suggests that the experiment can be a combination of all three configurations. For the V K-edge spectra, the pre-edge features A and B are captured well while features C and D are in reasonable agreement. As in the S K-edge spectra, there are no significant differences in the V K-edge spectra of the three configurations. It is clear that, the experimental spectra could be summation of contributions from all three bonding environments as shown in **Figure 1**. This is in good agreement with our DFT based Gibbs energy calculation, where the energy requirement for these different configurations are similar and represent possibilities of such bonding interaction between Nafion and solvated vanadyl ion.

CONCLUSION

Predictive level understanding about chemical interaction between solvated cation and Nafion membranes is imperative for designing optimal membranes for all vanadium redox flow battery technology. However, the challenge is to employ the efficient tools to probe the molecular level interaction inside the nano size pores of Nafion membranes. Herein, we employed a combined experimental and theoretical analysis of core-level vanadium and sulfur K-edge spectroscopy to analyze the possible chemical interactions such as, solvent share, *cis*- and *trans*-contact pair formation between solvated vanadyl ion and sulfonic sites of Nafion membranes. The DFT-based energy calculation predicted both solvent share and contact pair interactions are probable. The TD-DFT calculated core-level vanadium and sulfur K-edge excitations for these chemical interactions were quite similar, and matches well with experimental spectra. This reveals that both contact pair and solvent share interactions between diffusing vanadyl ion and sulfonic sites of Nafion are probable as predicted by DFT calculations. However, the pore size, vanadyl ion concentration, electric field, and temperature can greatly influence the energy barrier for contact pair and solvent share interactions and result in preference over other interaction.

Apparently, more detailed studies are warranted to gain quantitative view about these interactions and subsequently move toward designing of optimal membranes for redox flow batteries.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at http://www.frontiersin.org/Journal/10.3389/fenrg.2015.00010/abstract

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