Conductive Membrane Coatings for High-Rate Vanadium Redox Flow Batteries

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ABSTRACT: A conductive coating of carbon nanotubes (CNTs) and Naﬁon dispersion in water was deposited on a Naﬁon membrane via air-controlled electrospray. When the coated membrane was assembled into a large single cell of a vanadium redox flow battery (VRB) with a surface area of 35 cm², it was found that its cycling performance was greatly enhanced at much higher current densities than was afforded by the pristine Naﬁon membrane. A masking technique was also applied during the electrospraying process to create alternating domains of coated and uncoated membrane surfaces, which helped to mitigate the restriction of proton transport through the membrane due to the coating, while still decreasing the surface resistivity and thus the interfacial resistance of the membrane. Our results reveal that a very small mass of CNTs (∼0.015 mg CNT/cm²) enabled large improvements in the capacity retention and voltaic eﬃciencies of the vanadium redox battery during charging and discharging. This method has shown to be a reasonably fast, simple, and scalable technique for improving rate capability of VRBs, with the potential for extension to other redox ﬂow battery systems.

1. INTRODUCTION

Global electricity production from renewable sources has grown dramatically in recent years.1,2 While this new production ultimately drives energy generation portfolios toward a lower dependence on carbon-based electricity, the intermittent nature of renewable forms of electricity generation has proven diﬃcult to incorporate into regional electrical grids. Grid-scale electricity storage methods are a promising solution to the ineﬃciencies associated with unpredictable electricity generation. Redox ﬂow batteries have demonstrated the ability to be used as a reasonably low-cost, long-term electrical storage method. Speciﬁcally, vanadium redox ﬂow batteries (VRBs) have been of special interest because of their chemical stability, long life cyclability, and potential for high electrical capacity.3−5 VRBs take advantage of the four adjacent oxidation states of vanadium for the transfer of electrons via a redox reaction. The positive half-cell contains VO2+ which can be oxidized to VO2+ during charging; the negative half-cell contains V3+ which can be reduced to V2+ during charging. The vanadium salts are typically dissolved in sulfuri c acid. Accompanying these advantages are some research challenges. There have been a number of eﬀorts to improve the electrical conductivity of VRBs by physically or chemically altering the electrodes of the cell. Most VRBs use a carbon or graphite felt as porous cathodes and anodes—the large surface area from the felt is used to increase the number of reaction sites at which the redox reaction can occur. Many modiﬁcations to the electrodes have been investigated, including using various highly conductive carbons,6−16 metal catalysts,17−19 and doping the carbon felt with hydrophilic surface groups.20−23 Some works on casting membranes with conductive carbons incorporated into the bulk of the membrane have also been explored, typically focusing on graphene oxide or graphite as the carbon source.24−28 Substantial work has focused on selection and pretreatment methods for the Naﬁon family of membranes in VRBs.29−32 To our knowledge, little work has been conducted investigating the application of conductive carbons to the surface of premade membranes themselves. While other membrane modiﬁcation techniques involve poorly scalable casting or pretreatment techniques, our goal was to create a fast and inexpensive process to improve VRB performance. To this end, a new approach to improve the rate capability of VRBs involves

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increasing the electrical conductivity of the membrane itself using the electrospray deposition of conductive carbon mixed with a binder directly onto the membrane. In this method, a very small amount of highly conductive carbon can be deposited directly onto the surface of the cation exchange membrane, thereby increasing the electrical conductivity near the surface of the membrane without impeding proton transport through the membrane. This technique was investigated for use as both a stand-alone pretreatment of VRB membranes and as a complementary feature to existing electrode modifications.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Conductive Ink. The conductive ink consisted of three primary components—multiwalled carbon nanotubes (CNTs, Sigma), 20 wt % Nafion Dispersion (Ion Power, Newcastle, DE), and DI water. The CNTs add a highly conductive component to the spray, which improves the electrical conductivity across the surface of the membrane. The Nafion dispersion acted as a binder for the CNTs and the Nafion 117 membrane (Ion Power, Newcastle, DE) and was also a good surfactant when mixing the CNTs in water. The ink composition was important to both improve the rate capability of the battery and to allow for good processability when electrospraying. An ideal spray condition is realized when the conductive ink is able to be electrosprayed in a well-dispersed manner while hitting the membrane without complete solvent evaporation. This allows time for the remaining solvent to evaporate while the Nafion dispersion has a chance to relax and form a thin film. It was found that ink compositions with high water content would result in the spray collecting as a dry powder, which could be easily removed with abrasion. Some ink compositions with too much Nafion dispersion added would result in the spray not drying fast enough on the membrane, causing uneven distribution and dripping of the carbon ink down the substrate membrane. It was found that a carbon ink composition of 0.5 wt % CNTs, 15.0 wt % Nafion dispersion (20 wt % polymer), and 84.5 wt % DI water created a carbon ink with both good processability and performance. The coating after spraying was assumed to have no residual water, leading to a coating composition of about 14 wt % CNTs and 86 wt % Nafion polymer.

2.2. Processing Conditions. The carbon ink was ultrasonicated for 1 h before use. The solution was placed in a 5 mL syringe and sprayed through a homemade coaxial needle (tube gauge of 10 and shell gauge of 17) using a syringe pump (Harvard Apparatus). Dry air was applied through the shell of the coaxial needle at 10 psig. The use of air-controlled electrospraying helped increase the rate of spraying, as has been demonstrated elsewhere (see Figure 1). The Nafion 117 membrane (dry) was placed on a grounded copper current collector at a distance of 18 cm from the tip of the needle. A positive lead was attached to the needle, and the voltage was set to 18 kV. It was found that a flow rate of 0.05 mL/min was appropriate to balance deposition and solvent evaporation rates. The membranes seem to perform best when they were not completely covered by the carbon spray, so a copper mesh was used as a mask during spraying. The mesh had a series of 1 mm square holes, which allowed spraying through to hit the Nafion 117 membrane. Spray that did not go through the holes was stopped by the mask, creating a uniformly patterned series of domains with and without the carbon ink spray. Both sides of each membrane were sprayed in every case. Spray loadings of 0.015 mg CNT/cm², 0.035 mg CNT/cm², and 0.070 mg CNT/cm² per side were tested.

2.3. Electrochemical Measurements. The spray-coated membranes were tested using in situ electrical impedance spectroscopy (EIS) testing to measure the changes in resistance in the cell with the inclusion of the conductive membrane coating. An electrolyte consisting of 4 M H₂SO₄ and 1 M VOSO₄ was used for all testing. An ac voltage of 1 mV amplitude was used over a frequency range of 10⁴ to 10⁻² Hz to generate Nyquist plots of the pristine and coated membranes. Cyclic voltammetry (CV) was performed at rates of 20, 50, and 100 mV/s in a three-electrode glass cell using the above-mentioned electrolyte. The reference electrode used was Ag/AgCl, and the counter electrode used was a platinum wire. A 3.0 mm diameter circle of polished glassy carbon electrode (GCE) was coated with both the conductive coating and the Nafion dispersion alone to observe the difference in electrochemical activity at the membrane. A potential range between −0.85 and 1.5 V was explored. Four-point probe surface conductivity tests were also used to determine changes in surface electrical resistance with and without membrane coatings and with and without the use of a mesh mask. This involved pressing four parallel metal probes on the surface of the coated and uncoated membranes several times in various places on the membrane to get measurements of resistivity to electron flow between the probes. A current is passed between the outer two probes, and a corresponding voltage is measured between the inner two probes.

2.4. Diffusion Tests. A 2-chamber side-by-side diffusion cell (Permegear) was used to measure the diffusivity of both vanadium ions and hydrogen ions across the Nafion 117 membrane. Vanadium diffusion rates were measured by placing 3.4 mL of 1 M VOSO₄ in 4 M H₂SO₄ in the donor chamber of the diffusion cell and 3.4 mL of 1 M MgSO₄ in 4 M H₂SO₄ in the receptor chamber of the cell. MgSO₄ was added to balance the contribution of osmotic pressure from the added vanadium salt that could impact the perceived diffusion rate. Samples
accomplished by using a constant current charge of 15 mA/cm². The upper cutoff voltage was set at 1.7 V and the lower cutoff voltage was 0.8 V. This cycle was repeated 5 times to ensure maximum conversion to V(V) in the cathode and V(III) in the anode. The V(V) was then removed from the system and replaced with more of the original V(IV) solution, and the process was repeated.

2.5. Single-Cell Testing. Membrane coatings were assessed using single-cell testing in an in-house flow cell system. Included in the system were two glass chambers for electrolyte storage, from which electrolyte was pumped through 1/4″ i.d. tubing to and from the flow cell (Tygon 2375 Ultra tubing, Watson-Marlow 323E Pump). Each side of the cell consisted of symmetric acrylic end plates with push-to-connect tube fittings, a graphite current collector, a Viton gasket, a polypropylene flow frame, and an HDPE gasket. These parts were separated by a Nafion 117 membrane with or without a coating. The total exposed area of the membrane and the graphite current collector was a 7 cm by 5 cm rectangle, totaling 35 cm². Each side of the cell had a 2 mm space between the membrane and the current collector, in which a piece of 3 mm thick porous graphite felt (PAN-based, AVCarb) was compressed for good electrical contact. The felt was used as received and was not pretreated in any way. The electrolyte used in all tests was 1 M VOSO₄ (Alfa Aesar) in 4 M H₂SO₄. This was prepared by first dissolving the appropriate mass of VOSO₄ into 4 M H₂SO₄. This solution, containing V(IV), was then electrochemically oxidized while being pumped through the flow cell. This was accomplished by using a constant current charge of 15 mA/cm² and an upper cutoff voltage of 1.7 V. This cycle was repeated 5 times to ensure maximum conversion to V(V) in the cathode and V(III) in the anode. The V(V) was then removed from the system and replaced with more of the original V(IV) solution, and the process was repeated. This generated more V(V) at the cathode and V(II) at the anode. The single-cell tests were then run using these freshly generated electrolyte solutions. The electrolyte volume used was 25 mL for the catholyte and 25 mL for the anolyte, with a flow rate of 30 mL/min. Current densities between 30 and 50 mA/cm² were explored. All single-cell cycling tests were carried out using a battery analyzer (3 A/5 V, MTI). Cycling involved charging and discharging repeatedly at a specified constant current density. The upper cutoff voltage was set at 1.7 V and the lower cutoff voltage was set at 0.8 V. Cycling tests were assessed by Coulombic efficiency, voltammetry, energy efficiency, and capacity retention.

3. RESULTS AND DISCUSSION

The coated membranes and the coating itself were thoroughly analyzed to investigate the impact of the coating on electrochemical activity and overall performance of the battery.

3.1. Optical Analysis. Scanning electron microscopy (SEM) was used to analyze the surface of the membrane (Figure 2). The thickness and homogeneity of the coating were considered as important aspects regarding the reproducibility of membrane coatings using these methods. Both surface and cross-section imaging was conducted. It was found that the carbon coatings were typically between 3 and 5 microns in thickness. The coatings seemed to form discrete regions of CNT aggregates, connected together with the Nafion dispersion binder. These regions are likely formed because of the rapid evaporation of small amounts of residual water left in the ink after it hits the surface of the membrane. The coatings showed that the CNTs were predominantly encapsulated in droplets of Nafion dispersion, providing anchoring sites that proved to be resistant to delamination or degradation during cycling.

3.2. Electrochemical Measurements. 3.2.1. Cyclic Voltammetry. Three-probe CV tests were conducted at different scan rates to measure the impact of the conductive ink on the electrochemical activity of the vanadium redox reaction in the catholyte. The conductive ink was used to coat a GCE and was compared to a GCE coated with only the Nafion dispersion. This test was run to compare the electrochemical activity of the coated Nafion membrane and the pristine Nafion membrane. The standard reduction potential of the oxidation of VO²⁺ to VO₃⁺ (cathodic reaction) is about 1.00 V, whereas the standard reduction potential of the reduction of V³⁺ to V²⁺ (anodic reaction) is about −0.26 V compared to the standard hydrogen electrode. These two coatings were tested over a series of potential scan rates, ranging from 20 to 100 mV/s (see Figure 3a,b). It was found that when compared to the Nafion dispersion coating, the conductive ink peak current increased during both the cathodic and anodic reactions. This larger induced current is indicative of greater electrochemical activity of both relevant vanadium redox reactions on the surface of the electrodes. It should also be noted that no anodic peak was observed at both high and low scan rates with the Nafion coating. This shows that the kinetics of the anodic reaction are slow compared to those of the cathodic reaction, as is consistent with other literature studies. A small peak appears for the anodic reaction in the case of the conductive ink, showing that the addition of CNTs helps facilitate the anodic reaction. When current density is increased, the overpotential (peak voltage difference from standard reduction potential) will typically increase accordingly. When comparing a lower scan rate (20 mV/s) to a higher scan rate (100 mV/s), the observed
increase in the overpotential for the electrode coated with a conductive ink is much lower than the electrode coated with Na\textsubscript{ion} dispersion. This indicates the ability of the CNT-based conductive ink to allow for a highly efficient redox reaction, even at higher current densities.

### 3.2.2. Electrical Impedance Spectroscopy.

EIS testing was also conducted on the in-situ cell, probing the resistance of the membranes with different coating thicknesses with and without the use of a mesh mask. This test was used primarily to test if the proton conductivity through the membrane was impacted with the use of the coating. It was found that the proton conductivity, and hence resistance contribution from the membrane, was nearly unchanged with the addition of the conductive ink. There was a very low Ohmic resistance, on the order of 0.1 ohms, as shown at the high frequency intercept of the real axis in the Nyquist plots (Figure 4). When the conductive ink coating was applied to the Na\textsubscript{ion} membrane, the charge transfer resistance did not change noticeably. The charge transfer resistance was difficult to estimate precisely in both the coated and pristine cases, as the system was difficult to keep at a steady state in the slower, low frequency regime of the test. It is likely that the charge transfer resistance was effectively the same in both cases because of the fact that the majority of the battery setup (electrodes and electrolyte) was unchanged during these tests. Thus, any improvement in performance of the battery can likely be attributed to the formation of a highly electrically conductive network (CNTs) with tethered reaction sites (end groups of CNTs) focused on the interface between the membrane and the felt electrodes. The key message from these data is that despite the addition of a layer of a conductive ink to the surface of the membrane, the observed resistance to proton transport through the membrane was largely unhindered.

### 3.2.3. Surface Resistivity Measurements.

Four-probe surface resistivity measurements of each membrane were also conducted to test the resistance to electron transport across the surface of the membrane with different coating masses. The surface resistivity of each membrane was measured and is shown in Figure 5. The addition of the conductive ink at a
deposition mass of ∼0.01 mg CNT/cm² caused the electrical surface resistivity to decrease by about half, when compared to the pristine Nafton membrane. The surface resistivity decreased further when larger masses of the conductive ink were added. Membranes coated without the mesh mask showed a slightly lower resistivity than those coated with the mask. This was expected, as there was a larger mass of conductive carbons reaching the membrane in a continuous film, as compared to the discontinuous masked membrane. The main results from these tests show that there is a noticeable improvement in electrical conductivity across the surface of the membrane with the addition of the coating, and a greater mass of coating leads to lower electrical resistance across the surface. This is relevant to the vanadium battery performance, as electrons can be effectively transferred to the current collector when the vanadium redox reactions occur, especially closer to the interface of the membrane and the felt electrode. Ideally, the surface of the membrane would have a very low electrical resistance, but this must be balanced with diffusive restrictions of protons imposed by the addition of the coating.

3.3. Diffusion Testing. Membranes coated with varying amounts of the conductive ink were assessed for ionic permeability using diffusion testing. These tests used the diffusion of vanadium(IV) ions through the membrane as an analogue for proton diffusion through the membrane, as proton diffusion proved difficult to be measured accurately because of the protonated nature of the Nafton membrane. Figure 6 shows the change in the measured vanadium ion concentration in the receptor chamber of the diffusion cell as a function of time. There seemed to be some trend showing the reduction of vanadium ion crossover with increased coating mass, although the relative differences are quite small. This would support the theory that the regions of no coating created when using the mesh mask allow for a combination of reasonably fast ion transport through the membrane coupled with low electrical resistance. Very little vanadium ion restriction was observed when comparing either of the “0.015 mg CNT/cm² mesh” or “0.035 mg CNT/cm² mesh” cases to the pristine membrane case.

3.4. Single-Cell Tests. Each membrane was assessed using a single-cell vanadium flow system. This cycling test shows the true utility of any alteration to the VRB—the discharge capacity and efficiencies must be maintained over a large number of cycles, or the battery will face issues regarding potential longevity. Each test consisted of 100 cycles in the voltage window of 0.8 to 1.7 V. Charge and discharge capacities were monitored over the cycling period. Membranes were tested with varying masses of the conductive ink sprayed on them to assess the impact of membrane thickness, mass of CNTs, and ink surface coverage on VRB performance. First, the system was tested with the pristine Nafton 117 membrane. It was found that the membrane showed good capacity retention and cyclability at lower current densities, around 30 mA/cm² and lower. This changed dramatically, however, when current densities were increased. As charge and discharge current densities were increased to between 40 and 50 mA/cm², discharge capacities dropped precipitously (see Figure 7). This is attributed to the inability of the vanadium redox reaction to occur quickly enough—limited by slow kinetics of the redox reaction from too few reaction sites or high bulk resistance in the cell. Previous work has theorized that the availability of hydroxyl groups attached to highly electrically conductive material on the electrode can improve the reaction rate of the redox couple based on reaction mechanisms proposed in the literature. This is also likely the case in this system. Membranes sprayed with the conductive ink were tested at the same current densities for the same number of cycles. Initial tests utilized membranes sprayed with 2.5 mL of the conductive ink on each side of the Nafton 117 membrane. The conductive ink contained 0.13 mg CNT/mL solution. It was found that this led to poor performance of the VRB over time, as the capacity was not retained after many cycles. The capacity retention was diminished at a current density of 30 mA/cm² when compared to the pristine Nafton case. It was theorized that the thickness and relative hydrophobicity of this coating were negatively impacting the ability of protons to transport easily through the membrane, rapidly increasing cell polarization and diminishing VRB capacity before the specified cutoff voltage was reached. To address this issue, a twofold strategy was employed. First, the volume of the ink sprayed was reduced to 0.50 mL per side to reduce the total overall

Figure 6. Vanadium diffusion across Nafton 117 membranes with varying amounts of the conductive ink coating. The diffusion cell setup is shown in the inset.

Figure 7. Comparison of cycling results using coated and pristine Nafton 117 membranes at different current densities. All coated membranes were electrosprayed with 0.070 mg CNT/cm² of the conductive ink.
thickness of the coating. A copper mesh mask with a grid of 1 mm square holes was also placed over the membrane during the coating process in an effort to generate ordered domains of coated and uncoated regions on the surface of the membrane. This was to allow some discrete domains to remain pristine and uncoated, while coating adjacent domains with the conductive ink. The goal was to permit high proton transport, while improving the electrical conductivity between the membrane and the graphite felt. The results of these changes yielded improvements in the capacity retention during cycling, especially at higher current densities (see Figure 7). After this improvement, all tests on coated membranes were conducted at the higher rate of 50 mA/cm². The volume sprayed was further reduced to approach a lower limit for improvements when reducing CNT loading. Loadings of 0.070, 0.035, and 0.015 mg CNT/cm² were tested at 50 mA/cm² to see their effect on capacity retention and battery performance (see Figure 8). As the spray volumes were reduced, a lower volume of coating seemed to yield an improvement in initial discharge capacity and capacity retention during cycling. Greater improvement in discharge capacity retention was realized by further reducing spray loadings from 0.035 to 0.015 mg/cm². This seemed to indicate that there is an important balance between the mass and topology of the coating necessary to improve the overall capacity retention and VRB performance. As the thickness of coating is reduced, proton transport through the membrane likely approaches rates closer to that in the pristine case (as was demonstrated in diffusion testing), while contributing a highly electrically conductive bridge between the membrane and the graphite felt. Single-cell tests were conducted wherein the same conductive ink coating volumes sprayed onto Naion membranes and the graphite felt. This was to allow some discrete domains to remain pristine and uncoated regions on the surface of the membrane. It was found that even when a loading of 0.15 mg CNT/cm² of the conductive ink was sprayed onto each piece of the graphite felt (ten times the volume that was sprayed onto the best-performing membrane), the VRB single-cell tests underperformed those using only 0.015 mg CNT/cm² of the conductive ink sprayed directly onto the membrane. This is likely due to the Coulombic and voltaic efficiencies from each of these tests, which are shown in Figure 9. The trends seen in Figure 8 are further illustrated here, as each of the tests has a similar Coulombic efficiency and differing voltaic efficiencies. The coatings with the highest voltaic efficiencies also tended to have the best capacity retention. This may indicate the importance of focusing the conductive ink at the interface of the VRB, as opposed to simply maximizing the overall mass of the conductive ink in the electrodes. This is likely due to the formation of a highly conductive CNT network, as compared to the random distribution of the material throughout the graphite felt. It should be noted that the pristine membrane case was unable to adequately discharge at a constant current of 50 mA/cm², so the values reflected for the pristine membrane voltaic efficiencies in Figure 9 are likely measured in the range of 35–45 mA/cm². This choice was made for the sake of comparison at a higher current density, and it is expected that these values will be higher than they realistically should be for the pristine case. To determine the robustness of these coatings, coated membranes were analyzed via SEM and Fourier transform infrared (FTIR) both before and after 200 cycles, as shown in Figure 10. It was found that there was little to no observable change in the surface characteristics of the coating via both the SEM images and the FTIR spectra. This further demonstrates the promise for the use of these conductive coatings in VRB applications.

4. CONCLUSIONS

A very thin CNT-based conductive carbon coating (∼0.015 mg of CNT/cm²) onto Naion 117 membranes can improve the rate capability of VRBs. Despite a slightly higher electrical surface resistivity, thinner coatings seemed to yield the highest starting discharge capacities and highest capacity retention over a large number of cycles. The use of a copper mesh mask during the electrospaying process created discrete, ordered domains of coating coverage, which seemed to allow for adequately high proton transport during cycling, while still decreasing the surface resistivity of the membrane, and thus the interfacial resistance. This coating technique could be used as a fast, stand-alone pretreatment of membranes before use in a VRB. It could also be used in tandem with other electrode enhancement techniques or on other types of ion-exchange membranes to yield a more efficient battery.
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Notes
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ABBREVIATIONS
CNT carbon nanotube
VRB vanadium redox flow battery

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