Performance Evaluation of a Hydrogen-Vanadium Reversible Fuel Cell

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Hydrogen-vanadium reversible fuel cells were tested using a Pt/C hydrogen electrode, carbon vanadium electrode and interdigitated flow fields at both electrodes. Vanadium electrolyte flow rate was varied to study its effect on mass transport performance. Two types of vanadium electrodes were explored, a single layer of high surface area carbon nanotube (CNT) electrode and three layers of nitric acid-treated carbon paper. Finally, four types of Nafion membranes were examined to determine the effect of membrane type and thickness on fuel cell charge and discharge performance. Higher performance was observed with higher vanadium flow rate, thinner membranes and a CNT vanadium electrode. Peak power density of greater than 540 mW/cm² was obtained using a NR212 membrane and CNT vanadium electrode.

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Manuscript submitted January 20, 2017; revised manuscript received March 10, 2017. Published March 22, 2017. This was Paper 381 presented at the San Diego, California, Meeting of the Society, May 29–June 2, 2016.

While charging, a hydrogen-vanadium fuel cell stores energy in the form of hydrogen and vanadium (V). During discharge, hydrogen is consumed at the negative electrode and vanadium (V) is reduced to vanadium (IV) at the positive electrode. Vanadium systems demonstrate no issues with membrane fouling or metal dendrite formation. For discharge, vanadium (IV) at the positive electrode is oxidized to vanadium (V) at the negative electrode. Vanadium systems demonstrated no issues with membrane fouling or metal dendrite formation. In a hydrogen-vanadium reversible fuel cell, the charge and discharge reactions are as follows:

**Vanadium (+) Electrode:**

\[
2V^{2+} + 2H_2O \xrightleftharpoons{charge \, discharge} 2V^{2+} + 4H^+ + 2e^-,
\]

\[E^\text{red} = +0.99 \text{V} \quad [1]\]

**H₂ (−) Electrode:**

\[2H^+ + 2e^- \xrightleftharpoons{charge \, discharge} H_2,
\]

\[E^\text{red} = +0.0 \text{V} \quad [2]\]

**Overall Reaction:**

\[2V^{2+} + 2H_2O \xrightleftharpoons{charge \, discharge} 2V^{2+} + 2H^+ + H_2,
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\[E^\text{cell} = +0.99 \text{V} \quad [3]\]

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Experimental

Three different studies were completed on the hydrogen-vanadium reversible fuel cell. In the first study, vanadium electrolyte flow rate was varied to determine the effect on mass transport performance at high current densities. For the second study, two types of vanadium electrodes were tested. In the third study, different proton exchange membrane types and thicknesses were explored. Table I lists the key parameters used for each study.
Vanadium electrolyte solution (500 mL) was prepared of 1 M vanadium(V) and 1 M vanadium(IV) by dissolving the appropriate amount of vanadyl sulfate (Sigma Aldrich) in 3 M sulfuric acid (H₂SO₄) and then charging the fuel cell to 50% state of charge (SOC) to make vanadium(V). Excess electrolyte was used to ensure that the electrolyte concentration remained relatively constant during the polarization measurements. The membrane electrode assembly (MEA) was prepared by either one of two ways. In the first method, the MEA was prepared by hot pressing a proton exchange membrane onto a 3 cm by 3 cm Pt-coated GDL (0.45 mg/cm² Pt loading, 0.16 mg/cm² Nafion ionomer, SGL35BC from TVN Systems, Inc.). In the second method, the MEA was prepared by hot pressing a proton exchange membrane between a 3 cm by 3 cm Pt-coated GDL (0.45 mg/cm² Pt loading, 0.16 mg/cm² Nafion ionomer, SGL35BC from TVN Systems, Inc.) and a nitric acid-treated 3 cm by 3 cm GDL (SGL10AA from Ion Power, Inc.) that was coated with Nafion solution on one side to allow hot pressing. SGL35BC electrode thickness was ~320 μm. The catalyst layer (loading of 0.45 mg/cm² Pt, 0.16 mg/cm² Nafion ionomer) was sprayed directly onto the microporous layer side of SGL35BC. TVN Systems, Inc. reported that the Pt catalyst used for the catalyst layer is commercially available (Tanaka) with Pt particle diameter of 1–2 nm. Commercially available membranes were purchased from Ion Power Inc. (DE, USA). MEAs were made using NR211 (~25 um thick), NR212 (~51 um thick), N115 (~127 um thick), or N117 (~183 um thick). Hot pressing was completed at 135 °C and 0.522 MPa (80 psi) for 5 min. Assembly of the fuel cell was carried out at 1.103 MPa (160 psi) using expanded polytetrafluoroethylene (PTFE) gaskets and interdigitated tantalum flow fields with 9.0 cm² flow area. The interdigitated flow field dimensions were 1.5 mm channel width, 1 mm channel depth and 2.5 mm shoulder width.

The vanadium electrode consisted of either a single CNT electrode or 3 layers of nitric acid-treated SGL10AA. The CNT electrode was prepared by growing nanotubes onto SGL10AA carbon paper using chemical vapor deposition as outlined in Reference 3. Nitric acid-treated SGL10AA was made using a 3-step process in order to improve electrode wettability. First, SGL10AA carbon paper was submerged in water while evacuating the air above the water using a vacuum pump at 0.03 MPa for 5 min. Then, the carbon paper was soaked in 2 M nitric acid for 24 h. Lastly, the carbon paper was thoroughly rinsed in deionized water and dried. 3 layers of SGL10AA were tested as the vanadium electrode because previous studies found that a single layer of SGL10AA did not have sufficient active area to provide high current density operation and when more than 3 layers were used the negative effect of increased transport distance from a thicker electrode became more dominant than the positive effect of having higher active surface area. In our previous studies with CNT electrodes in the hydrogen-bromine fuel cell we found that a single layer of CNT electrode on the bromine side yielded similar to or better performance than 3 layers of SGL10AA. The CNTs, which were grown onto the GDL carbon fibers, increase the active surface area available for the vanadium reaction while maintaining the same electrode thickness and transport distance of a single layer of SGL10AA electrode (~350 μm). Increased electrode thickness (i.e. 3 layers of SGL10AA) leads to greater transport distance and fuel cell resistance, therefore making a single layer CNT electrode more attractive than using 3 layers of SGL10AA.

Fuel cell testing was completed using a hydrogen pressure of 0.136 MPa (5 psig) and vanadium electrolyte flow rate of 5, 6, or 12 mL/min (Equivalence of 1.55, 1.86, and 3.72 A/cm², respectively, for the vanadium (V) concentration used, 1.735M at an OCV of 1.09V). All testing was completed at room temperature (~23 °C). The start-up procedure included cycling the reversible fuel cells in charge (1.3 V) and discharge modes (0.6 V) every 10 min for over 12 h. Prior to collecting all discharge and charge polarization curves, the vanadium electrolyte was charged to ~90% SOC. Multiple polarization curves were collected to ensure adequate membrane hydration and repeatable results.

Electrochemical impedance spectroscopy (EIS) was conducted on the hydrogen-vanadium fuel cell after operation in order to measure the total resistance of the fuel cell. EIS was also conducted on the fuel cell without the membrane in order to measure the electronic resistance of the fuel cell. Figure 1 shows the assembly layout for the reversible hydrogen-vanadium fuel cell.

**Results and Discussion**

Due to charging the vanadium electrolyte solution to ~90% SOC prior to collecting polarization curves, the open circuit potential (OCV) for the hydrogen-vanadium reversible fuel cell was approximately 1.09 V (as predicted by the Nernst equation). All polarization curves have been normalized using the OCV (i.e. cell voltage minus OCV) in order to more easily compare all cases. Figure 2 shows...
shows the polarization and discharge power density curves for the hydrogen-vanadium fuel cell using various vanadium flow rates (Study 1). We observe better mass transport performance at higher current densities as we increase the vanadium flow rate from 5 mL/min to 6 mL/min (1.55 and 1.86 A/cm², respectively, at the concentration used). During discharge at 5 mL/min, we start to observe a mass transport effect at around 100 mA/cm² and limiting current at 230 mA/cm². During discharge at 6 mL/min, we start to observe a mass transport effect at around 250 mA/cm² and limiting current above 350 mA/cm². This significant increase in performance after a 20% increase in flow stoichiometry is attributed to better transport of active materials to and removal of products from the porous electrodes because of deeper penetration of the electrolyte into the electrodes due to using interdigitated flow fields. When increasing the vanadium flow rate to 12 mL/min (3.72 A/cm² equivalence), we observe a more subdued increase in performance at higher current densities. Since the performance at 6 mL/min and 12 mL/min are similar, a vanadium flow rate of 12 mL/min is used for all subsequent studies to eliminate the mass transport effect caused by low vanadium flow rate. We did not observe further mass transport improvement when increasing the vanadium flow rate above 12 mL/min. Previous hydrogen-vanadium studies completed by Yufit et al. with serpentine flow fields required vanadium flow rates above 150 mL/min (with 25 cm² active area and serpentine flow fields) in order to minimize mass transport limitations.

Figure 3 compares the fuel cell performance of a CNT vanadium electrode to the one made from 3 layers of nitric acid-treated SGL10AA (Study 2). We observe improved performance for the CNT electrode at higher current densities. The limiting currents for the CNT electrode and the 3 layer SGL10AA electrode were 0.7 A/cm² and 0.55 A/cm², respectively. The mass transport limitation observed in Figure 3 during charge for V_SGL10AA_NR212 arises due to the increased electrode thickness when using 3 layers of SGL10AA (≈1050 μm) versus 1 layer of CNT electrode (≈350 μm). From previous studies with the hydrogen-bromine system, a single layer of this CNT electrode was found to have active surface area equivalent to greater than 10 layers of conventional carbon electrode with an additional benefit of reduced thickness and therefore shorter transport distance from the flow channels. Therefore, the increased performance can be attributed to the higher active surface area available to the CNT electrode. This leads to lower activation loss, faster transport, and lower ohmic resistance. The ohmic resistance of the electrolyte near the active area is reduced since the local current density per active site is lower when the total current is distributed over a larger area.

Figure 4 compares the fuel cell performance when using various types and thicknesses of Nafion membranes (Study 3). Identical positive (3 layers of SGL10AA) and negative (SGL35BC) electrodes, flow fields, hydrogen pressure, and electrolyte flow rate (12 mL/min) were used for each cell. We observe improved performance as membrane thickness decreased and a peak power density of more than 300 mW/cm² with NR211. Thinner membranes lead to lower cell ohmic resistance or faster hydronium ions transport across the membrane during charge and discharge.

Figure 5 compares the discharge polarization curves before and after iR correction for various membrane types and thicknesses. The fuel cell resistance measured using EIS for NR211, NR212, N115, and N117 were 0.04, 0.068, 0.104, and 0.166 ohms, respectively. Full iR-corrected discharge polarization curves remove all ohmic losses in the fuel cell, including the ohmic resistance of the membrane. This allows us to directly compare the kinetic and mass transport effect for the various membrane types and thicknesses. First, with the ohmic resistance of the membranes removed, we observe similar kinetic performance in the low overpotential region for the two groups of membranes, the extruded N115/N117 membranes and the solution-cast NR211/NR212 membranes. Next, we are able to identify the current density in which the mass transport effect starts to negatively impact the discharge polarization curves. For the extruded N115/N117 membranes, the mass transport effect starts at 0.18 A/cm². However, mass transport doesn’t start to negatively impact the solution-cast NR211/NR212 membranes.
During discharge, we start to observe a mass transport effect at around 500 mA/cm² and limiting current at 700 mA/cm². However, during charge, we don’t observe a mass transport effect within the overpotential or current density range evaluated. Based on the polarization curves in Figure 6, we observe very high kinetics on both charge and discharge, but mass transport losses take over during discharge as the overpotential is increased. Our studies show a 3–4 times increase in peak power density over the previous hydrogen-vanadium studies conducted by Yufit, et al. The performance enhancement is attributed to using interdigitated vice serpentine flow fields, thinner proton exchange membranes, and advanced CNT electrodes.

Summary

We conducted a performance study on a reversible hydrogen-vanadium fuel cell using interdigitated flow fields at both electrodes. Two different types of vanadium electrodes (CNT and nitric acid-treated SGL10AA) were explored, as well as various types of proton exchange membranes. The hydrogen-vanadium fuel cell shows promising performance by achieving peak power greater than 540 mW/cm².

Further investigation is needed to determine whether electrospon nanofiber composite membranes made of perfluorosulfonic acid (PFSA) fibers and inert fibers to control membrane swelling will be suitable for the hydrogen-vanadium fuel cell. Electrospon nanofiber composite membranes offer the potential of lower vanadium crossover and lower membrane resistance. Therefore, these membranes may lead to increased fuel cell performance and cycling efficiency.

Acknowledgments

The authors wish to acknowledge the financial support from the University of Kansas (KU) Madison and Lila Self Fellowship. Supplies for this work were supported by the National Science Foundation through grant no. EFRI-1038234. The authors also like to thank Dr. Venkata Yarlagadda for providing the high surface area carbon nanotube electrodes, Yuanchao Li for his assistance in preparing the nitric acid-treated electrodes and Dr. Alan Pezeshki for the lengthy discussions related to the all-vanadium flow battery.

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