Development of Advanced Carbon Electrodes for use in Microfluidic Vanadium Redox Fuel Cells

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Abstract:
We report on the current progress to develop advanced carbon electrodes with improved performance in microfluidic vanadium redox cells. In vanadium cells, carbon electrodes are typically used as a conductor and catalyst. Carbon fiber paper electrodes have had a silver nanolayer applied to function as an integrated current collector. This resulted in a 34.2% decrease in sheet resistance in the material, in turn increasing the cell performance; however the voltage generated by the cell caused electrostripping of the deposited silver. In addition, graphite electrodes were microfabricated using pyrolyzed micropatterned polyamide-imide films. The microfabricated graphite electrodes are designed to have a smaller pore size than the carbon paper electrodes, allowing for shorter diffusional distances, reducing mass transport losses. These advancements should decrease ohmic losses and increase the performance of the microfluidic fuel cell.

Introduction:
The advancement of fuel cell technology is amongst the most pursued topics in the effort to develop alternative energy generation methods. Microfluidic fuel cells are a relatively new development which take advantage of the characteristics of laminar flow to control the interaction between the fuel and oxidant entering the cell. Because the fuel and oxidant are able to flow concurrently and separately in a single microfluidic channel, it is possible for the cell to function without the need of a physical barrier such as a proton exchange membrane.

Microfluidic vanadium redox fuel cells commonly use carbon paper as an electrode and as a catalyst for the reaction. Carbon paper electrodes, which are made from sheets of interlaced carbon fibers, are not without a few drawbacks. The carbon paper electrodes have a relatively high resistivity when compared to that of metallic electrodes. This results in ohmic losses in the cell. Further, the carbon paper sheets have a larger pore size than desired, resulting in greater mass transport losses, and fuel cross over due to large diffusion distance with the catalyst.

The application of a silver (Ag) nanolayer acting as an integrated current collector could aid in increasing the conductivity of the carbon paper, and reducing the ohmic losses of the electrode. Additionally, it is possible to use micromolding and carbonization techniques to microfabricate a new graphite electrode tailored with small pore sizes for use in the cell.

Experiment:
Our microfluidic cell consisted of a series of interconnected square manifold pieces, with ports designed to allow the flow of the fluid in and out through the corners (see Figure 1). The fuel entered the cell through one port, then flowed over and through one of the carbon electrodes. Through a lower port, oxidant flowed into the cell and through a separate carbon electrode. The two flows met in a gap between the two electrodes, and exited through the waste port. The manifold pieces were fabricated using 3D printing (Bjet Connax 500).

The carbon paper electrodes were made with Torray carbon paper (Torray, Inc.) The silver current collector was deposited using electron-beam evaporation (CVC SC4500 e-gun evaporator). In a side experiment attempting to maximize the carbon surface area on the Ag-coated electrode, we fabricated an electrode that...
had a micropatterned Ag current collector. We generated a comb-shaped Ag pattern using photolithography (with Microchem Microspray™ photo-resist) and etching (Transene TFA etchant, diluted 1:9).

The microfabricated graphite electrodes were manufactured using micromolded polyamide-imide films (see Figure 2).

First a peg-array (10 µm and 20 µm diameter, 50 µm height) micromold was manufactured using photolithography and DRIE (Unaxis 770 Deep Si Etcher). A polymer solution (Torlon polyamide-imide, NMP, acetone) was spincoated on to the micromold. The mold was then introduced to a humid environment, resulting in a vapor-induced phase separation. The film was immersed in water and then released from the mold. Finally the films were carbonized by heating to 800°C in a nitrogen environment. This resulted in a highly porous glossy carbon electrode.

Results:

The sheet resistance of the Ag-coated carbon paper was measured using 4-terminal resistance mapping (CDE ResMap™). A 34.2% decrease in sheet resistance was measured. Performance tests were then performed for the carbon paper electrode and the Ag-plated carbon electrode (see Figures 3 and 4). The Ag-plated carbon electrode had a maximum current density 13 times higher than the carbon paper alone with a 6 ml/hr flow rate.

Discussion and Conclusions:

There has been some inconsistency with the measurements of the cell performance, particularly with the uncoated carbon-paper electrode performance. This may be due to trapped air bubbles in the cell assembly, which resulted in dramatically reduced surface area on the carbon electrode. Future work will be focused on improving the cell assembly and design to achieve proper flow of fuel and oxidant.

While the Ag did result in higher performance, the potential caused by the cell, caused electrostripping of the silver layer, rendering it as an unsuitable metal for use as a current collector. We suspect gold will be a much more suitable candidate, and should serve as an effective current collector.

Future Work:

Our next step is to test the microfabricated graphite electrode, and compare it to standard carbon paper electrode performance. We are working on methods to reduce the air bubble presence in the cell. We intend on repeating all Ag-coated electrode fabrication, patterning, and performance testing using an evaporated gold current collector. Finally, we intend on gold-coating the microfabricated graphite electrode and measuring performance.

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References: