Abstract:

In this work, we describe the development of a microfluidic vanadium redox fuel cell with micropatterned electrodes. Mass transport has been identified as a limiting factor in microfluidic fuel cells; here, we address this by using smaller size scales to decrease diffusion, distance, and time. The cells use carbon paper electrodes, or micropatterned carbon films made from a polymer precursor. The polymer precursor is fabricated by phase separation micro-molding (PSµM) using Torlon® polyamide-imide and carbonizing at 800°C in nitrogen. Conductivity tests show sheet resistances of 0.028Ω·cm, which is comparable to carbon paper. X-ray photoelectron spectroscopy (XPS) shows promising surface composition. Future work will focus on testing in a working fuel cell of our design.

Introduction:

Microfluidic fuel cells have gained research interest in recent years and are seen as a future power source for portable electronic devices. The transport phenomena on the micro-scale allows for operation without a proton exchange membrane; leading to simple, robust cell designs. Recent work points to the benefits of architectures using flow-through porous electrodes [1]. Reactant transport has been identified as a major source of losses in these cells and can be addressed by decreasing the size scales in the electrodes. Our work focuses on enhancing reactant transport through the use of novel system designs exploiting micro-/nano structures. The fuel cell design uses stackable “Lego®” manifolds separated by thin, micro porous electrodes made from Toray® carbon paper or micropatterned carbon films (Figure 1).

The patterned carbon films are fabricated by phase separation micromolding (PSµM), followed by a pyrolysis step to carbonize the polymer. PSµM was explored by Vogelaar, et. al. [2], and allows us to make perforated carbon electrodes with 5 µm pores. The fabrication is discussed in detail in the next section. The short diffusion distances at these scales will allow for higher efficiency and power density.

Material and Methods:

Perforated carbon electrodes were fabricated from polymer precursor films cast using PSmµM. Here, we used a solution of 16% Torlon (Solvay) polyamide-imide, and 64% n-methyl-2-pyrrolidone (BDH) and 20% acetone (Acros). The polymer solution is spin-coated onto a silicon mold (1 × 1 cm array, 10 µm pegs) and then exposed to high humidity air, which acts as the non-solvent causing the polymer to “crash” out of solution (Figure 2). The film can then be removed from the mold in water. After removing any remaining NMP by soaking in DI water, the film is taken and cured at 200°C for 1 hour. The polymer film is carbonized by pyrolysis in a nitrogen environment. The furnace is heated from room temperature to 400°C at a rate of 300°C/hr, after a 1 hr dwell, the temperature is raised to 600/800°C at a rate of 120°C/hr and held again for 1 hr.

Figure 1: (a) Schematic diagram of a vanadium redox fuel cell with porous flow through electrodes.
X-ray photon spectroscopy (XPS) was performed on the polymer films and carbonized films. A survey scan, followed by narrow width scans of the C 1s and N 1s were done in each case. Sheet resistance measurements were made using the standard 4 point probe technique (CDE ResMap system).

Results and Discussion:

To check the morphology of the polymer precursor and carbonized electrode scanning electron imaging was done on a Zeiss Supra SEM (Figure 3). The polymer precursor was frozen in liquid nitrogen, under these conditions brittle fracture mechanics occur. Here, we see a uniform closed pore structure with 1-5 µm pores and a thin surface layer. During the carbonization process the pores collapse as the film is heated above the glass transition temperature, giving a solid carbon film. Reductions in film area up to 73% are seen due to the collapsing pores. The larger patterned holes shrink to ~ 5 µm, but are otherwise unaffected. This shrinkage is beneficial in that the mold features can be significantly larger than the final features.

X-ray photon spectroscopy (XPS) was performed to characterize the electrode surface (Figure 4). The O 1s and N 1s peaks are significantly reduced after the 800°C bake, and the atomic mass percent of carbon is increased from 75.8 to 89.2%. Sheet resistance was measured to be 0.028Ω·cm after an 800°C bake, and is comparable to that of the carbon paper. These initial results show that PSµM followed by a high temperature carbonization process is a promising fabrication technique for fabricating porous carbon electrodes due to the reduction in pore size. Future work will focus on testing the electrodes and fuel cell design.

References:
