Characterization of Flow-Through Porous Electrodes for Microfluidic Electrochemical Cells

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Fig. 1: Tafel plots for V(II)/V(III) oxidation and reduction on carbon electrode materials.

Within the last decade, microfluidic fuel cells[1] and redox batteries[2] have attracted much interest as a reduced cost alternative to traditional electrochemical cells for low power applications. In these cells, reactant separation is achieved through the formation of a microfluidic colaminar interface between the fuel and oxidant. For these devices, it has been observed that flow-through porous electrodes allow for higher current densities than their planar counterparts.[3] Understanding the nature and limits of these performance enhancements is crucial to device optimization.

The present study focuses on the vanadium redox reaction for flow-through porous carbon. With four oxidation states, vanadium electrolytes can be used as both fuel and oxidant in electrochemical cells. During the development of the vanadium redox battery at UNSW, it was established that the following redox couple, otherwise referred to as V(II)/V(III):

$$V^{3+} + e^- \rightleftarrows V^{2+} \qquad E^o = -0.496 \, V_{SCE}$$

had lower reaction kinetics than the vanadium oxidant redox couple otherwise known as V(IV)/(V).[4,5] This has also been observed more recently[6,7] and is the motivation for using this redox couple to characterize the flow-through electrodes in the present study.

Preliminary investigations using a three electrode electrochemical cell in a stirred solution of 50/50 V(II)/V(III) were performed on two carbon electrode materials, namely Toray carbon paper (TGPH-060) without any hydrophobic treatment, and simple carbon graphite pencil leads (Pentel, C505). The carbon paper electrodes are cut into 1mm width strips to simulate the electrodes being used in the microfluidic device, whereas the pencil leads used for comparison have a cylindrical structure with a 0.5mm diameter. Although the current density presented in Fig. 1 is calculated by dividing by comparable geometric surface area, the specific surface area is quite different for both electrodes and has been measured by porosimetry to be several orders of magnitude larger for Toray ($\sim 4 \, m^2g^{-1}$). The measured exchange current densities were $j_0 = 4 \times 10^{-4} Acm^{-2}$ for the Toray electrodes and $j_0 = 1 \times 10^{-5} Acm^{-2}$ for the graphite rod. This order of magnitude difference is smaller than that expected by the differences in surface area. This indicates that the stirring of solution, even at high rotation rates, may not be sufficient to access all parts of the porous carbon electrode.
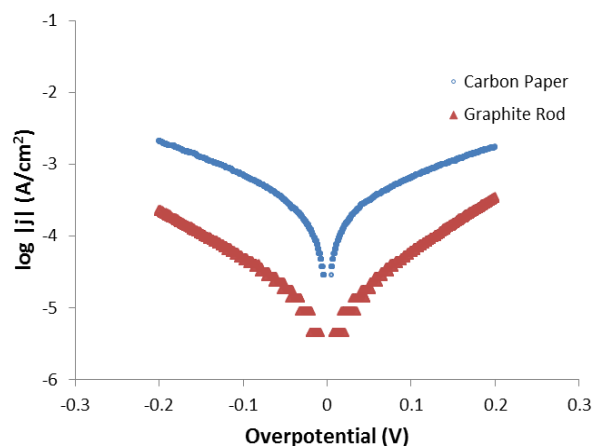
To address the above issues, a microfluidic version similar to the experimental apparatus developed by Alkire[8] has been constructed. A microchannel is fabricated with previously published soft lithography techniques[3] and houses both a working and counter electrode. The apparatus is designed to allow both upstream and downstream reference electrode measurements. Solutions of V(II)/V(III) of various concentrations are driven through the microchannel at various flow rates with the help of a syringe pump (MA1 70-2209, Harvard Apparatus). The mass transport properties of porous carbon electrodes are characterized empirically to determine what flow rates and concentrations are suitable for determination of kinetic reaction parameters. Measured kinetic parameters and mass transport limits are then compared between materials to determine which ones are advantageous for microfluidic electrochemical cell applications.

Acknowledgements

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