Kinetics and Transport in Porous Biofuel Cell Electrodes
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For high-rate applications such as biofuel cells and bioreactors, bioelectrocatalysts must be deployed in high-surface area, porous electrodes that maximize electron transfer between enzymes and solid phases, and allow for transport of reactants and products in fluid phases. Our research group has studied such porous bioelectrodes extensively, beginning with the use of carbon papers as electrode substrates, and including modifications with nanomaterials and pore forming strategies to enhance transport properties. We have developed modeling strategies to quantify the effect of various treatments on rate limiting steps and overall electrode performance.

This talk will discuss our recent work in this area, particularly in the modification of single carbon fibers with nanotubes as a test platform for studying multiscale porosity in bioelectrodes [1,2]. Carboxylated carbon nanotubes were coated onto carbon microfiber electrodes to serve as a support for immobilized glucose oxidase and an associated mediator. With oxygen-free glucose oxidation currents exceeding 15 mA cm^{-2} at 0.5 V/Ag|AgCl, we consider this approach a useful platform for the design of micro-environments in porous bioelectrodes.

Macropores were introduced into nanotube matrix by templating with polystyrene beads, and were found to increase the electrochemically active surface area and glucose oxidation current density by two fold at a nominal polystyrene mass fraction of 73%. Focused ion beam cut cross sections reveal complete adsorption of the enzyme-hydrogel matrix into the CNT layer (Fig. 1).

A high-rate NADH oxidizing electrode was fabricated by incorporating poly(azine) electrocatalysts into a high surface area layer of carboxylated carbon nanotubes (CNTs) [3,4]. Conformal deposition of poly(methylene green) (PMG) and poly(toluidine blue) (PTBO) on the carboxylated CNT-modified electrodes was achieved by cyclic voltammetry (Fig. 2).

A model of convective and diffusive transport in porous rotating disk electrodes is described for quantitative analysis of porous bioelectrodes. The model accounts for both convection and diffusion in the electrolyte outside of PRDE, which allows for better fitting to experimental data.

REFERENCES

Figure 1. Scanning electron micrographs of focused ion beam revealed cross sections. a) CNT coating (no PS particles) at 2 µg cm^{-1}; b) PS+CNT coating at PS mass fraction of 73 wt%; c) PS+CNT coating after heat treatment. d) Hydrogel coated CFME at loading of 13 µg cm^{-1} Vertical lines, especially those in (b), are artifacts from ion beam polishing.

Figure 2. Surface characterization of CNT and PMG-CNT. a. SEM image of CNT; b. SEM image of PMG-CNT; c. EDS spectrum of CNT; d. EDS spectrum of PMG-CNT