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MEDIATED GAS DIFFUSION BIOCATHODES

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Oxygen-reducing biocatalysts such as laccase[1] and bilirubin oxidase[2,3] have several advantages over precious metal catalysts, including low-temperature activity, selectivity against common fuels, and manufacturability at relatively low cost. Biocatalytic electrodes achieve their maximum power density in structures that minimize transport limitations. When electron transfer between biocatalysts and a conducting surface is achieved by means of a mediating species, limitations may arise due to transport electrons, ions, and neutral reactants (substrates) within the electrode.

In an oxygen biocathode, one approach to improved substrate transport is to introduce a gas phase, leading to higher substrate concentrations and diffusion coefficients. However, this may in turn lead to further limitations in the aqueous phase, where high water content may be required to maintain adequate electronic and ionic transport. This talk will consider the tradeoffs inherent in the design and development of such electrodes, and describe recent progress toward high current-density gas diffusion biocathodes.

Liquid-feed bioelectrodes are typically immersed in an electrolyte. The electrolyte supplies dissolved reactant, hydration, and ionic conductivity to the electrode. Introduction of a gas-phase feed eliminates the latter two supplies, and the gas diffusion bioelectrode must be hydrated and ionically conductive independent of the feed.

Low-pH bioelectrodes rely on proton transport. While proton conductivity generally increases with decreasing pH, biocatalysts generally are deactivated at pH below 2. Thus the electrode pH can be tuned to optimized the balance between catalytic activity and proton conductivity. Figure 1 shows the pH dependence of oxygen reduction activity of the enzyme laccase, which is capable of reduction of oxygen to water at high potential. Because conductivity varies linearly with concentration, the optimum pH for such a laccase electrode is near pH 3.

The nature of the incorporated electrolyte effects performance significantly. Nafion®, incorporated successfully into unmediated laccase electrodes, has a negative impact on mediated electrodes [4]. Figure 2 shows current densities of Nafion®-based electrodes compared to electrodes with no Nafion®. Adjustment of pH using tetrabutylammonium indicates that electrolyte pH is a significant factor, consistent with Fig. 1.

Current efforts focus on incorporating improved electrolytes, including carboxylated polymers and bifunctional mediators.

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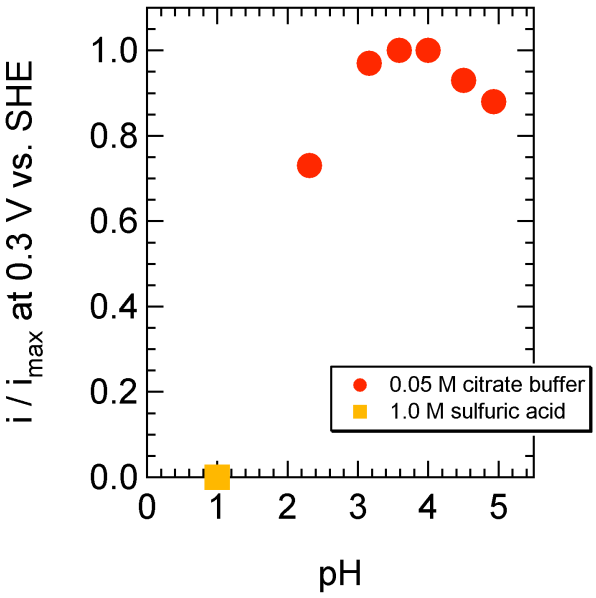

Figure 1. Effect of pH on laccase electrode performance, expressed as fraction of maximum current density. Rotating disc electrode at 1600 RPM. Electrolyte: 0.05 M citrate buffer or 1.0 M sulfuric acid, saturated with air.

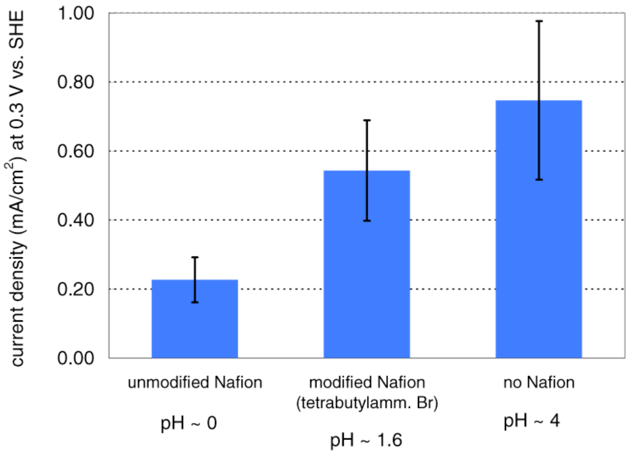

Figure 2. Effect of cast Nafion layer on laccase electrode performance. Rotating disc electrode at 3600 RPM. *Electrolyte:* citrate buffer (0.05 M, pH 4) saturated with air. *Nafion Loading:* 0.7 mg/cm^2.