Composition Dependence of Glucose Oxidation at Mediated Glucose Oxidase Bioanodes

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Research in Enzymatic biofuel cells holds significant technological promise for sustainable energy generation by combining renewable catalysts with fuel flexibility. In the past decade, research interest has grown due to potential applications such as biosensors, portable electronics, and implantable power [1].

However, the limitations of enzymatic biofuel cells for such applications are low stability of the electrode and low current density. To mitigate these disadvantages, research efforts have focused on new materials, enzyme engineering, design of mediated and direct electron transfer architectures, and electrode structure.

In mediated enzyme electrodes, electrons are transferred between the enzyme and electrode surface via a redox species. Previous studies have documented the parameters affecting mediated GOx electrodes and the effect of the composition, mediator structure, pH etc [2]. Our previous work describes the optimization of mediator redox potential for a laccase-catalyzed oxygen reduction electrode [3]. This result leads us to our current research, focused on composition dependence of the electrode structure, in terms of the balance between loadings of enzyme and mediator.

The electrode under study is a 3 mm diameter glassy carbon rotating disk electrode, modified with a film consisting of glucose oxidase crosslinked with poly(N-VI$_{12}$[Os(bpy)$_2$Cl]$^{1+/2+}$. The electrochemistry of this electrode, both in terms of mediator redox kinetics and glucose oxidation at pH 7, is studied as a function of GOx, mediator, and crosslinker mass loading. Fig. 1 illustrates the cyclic voltammogram (glucose-free) and polarization curves (with glucose) of the modified electrode at 40 wt% GOx, 60 wt% redox polymer for a total loading of 0.726 mg cm^{-2}. As shown in Fig. 2, glucose-free peak current remains steady at low GOx content, decreasing as mediator content diminishes. Similarly, as shown in Fig. 3, and optimum glucose conversion current density is found at 40 wt% GOx, where the catalytic and electron transport properties are balanced.

A mathematical model is used to predict the electrode activity. A key consideration is the film thickness, l, which is assumed to vary according to:

$$l = k_m \gamma_m + k_e \gamma_e$$

where γ_m and γ_e are the mass loadings of mediator and enzyme, respectively, and k_m and k_e represent the effective densities of each component. Electrode thickness is measured independently and correlated to component loading, yielding estimates for the effective densities.

The outcome of this study will be improved quantitative understanding of mediated enzyme electrode behavior, applicable to engineering of biofuel cells, bioreactors, and sensors.

REFERENCES

1. S. C. Barton, J. Gallaway and P. Atanassov, *Chem. Rev.,* **104**, 4867-4886 (2004).

2. N. Mano, F. Mao, and A. Heller, *J. Electroanal. Chem.,* **574**, 347–357 (2005).

3. J. W. Gallaway and S. Calabrese Barton, *J. Am. Chem. Soc.,* **130**, 8527-8536 (2008).
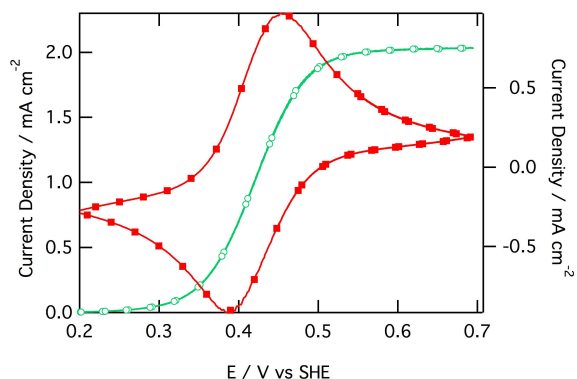
Figure 1. CV of mediated GOx enzyme electrodes produced from 40 wt% GOx (Scan rate 50 mV/s, Glucose-free). Polarization curve (50mM Glucose, 1000 rpm, scan rate 1 mV/s).
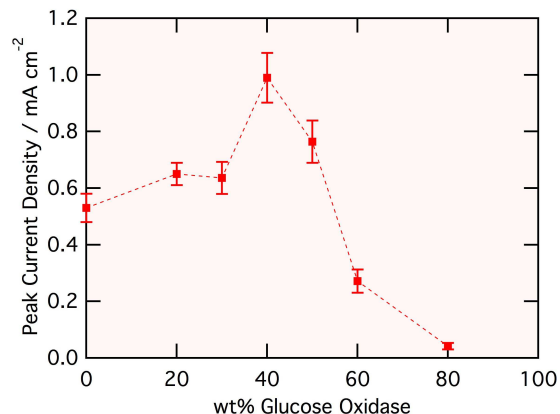

Figure 2. Dependence of glucose-free current density on the wt% GOx. Scan rate 50 mV/s.
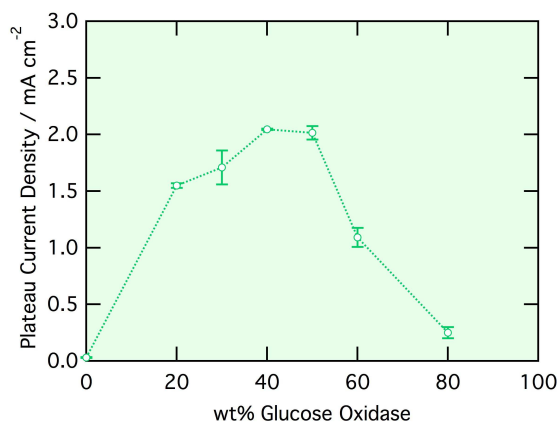

Figure 3. Dependence of the current density on the wt% GOx. 50mM Glucose, 1000 rpm, scan rate 1 mV/s.

Experiments conducted at 38°C, 250 mM PBS pH 7,under N$_2$.