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A Four-Electron O₂-Electroreduction Biocatalyst Superior to Platinum and a Biofuel Cell Operating at 0.88 V

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Catalysis of the electroreduction of O₂ to water determines the operating voltage and thereby the efficiency of the cathode in air batteries, the prime example of which is the zinc air battery, and in fuel cells, the best-studied examples of which are the methanol/air and the H₂/O₂ cells. When the current density is not limited by O₂ transport, the better the catalyst, the less the voltage loss for a cathode operating at a given current density. In the language of electrochemistry, the voltage loss is termed polarization or over-voltage. It is the excess voltage must be applied over the reversible potential of the O₂/H₂O half-cell in order to maintain the desired true current density, which is the current per unit true surface area, taking into account the surface topography or roughness, distinguished from the geometrical, or engineering, surface area. In engineered batteries or fuel cells, the ratio of the geometrical and true surface area is high. The specific surface of the platinum loaded carbon particles of fuel cell O₂ diffusion electrodes is >100 m²/g. The Pt weight fraction in the catalyst is ~0.05, and ~100 μg cm⁻² of Pt is loaded on their O₂ cathodes.¹ The engineering/true surface area ratio of these cathodes is ~2 × 10³, providing an engineering current density of ~1 A cm⁻² in H₂/O₂ or methanol/air fuel cells, when the true current density is about <0.5 mA cm⁻². Platinum, the classical catalyst for the electroreduction of O₂ to water, operates optimally near pH 0 in halide-free acids. The acids of choice are H₂SO₄, at temperatures below 50 °C, and H₃PO₄, at temperatures above 50 °C.²

Earlier, we showed that the polarization of a “wired” copper enzyme (bilirubin oxidase) bioelectrocatalyst coated carbon cathode was about half of that for pure, smooth platinum.³ Here we describe the fastest O₂ to water electroreduction catalyst to date. Its polarization at 37 °C and at a true current density of 0.5 mA cm⁻² is -0.07 V, approximately one-fifth of the 0.37 V polarization of platinum. Using the novel catalyst, we built a miniature compartmentless glucose–O₂ biofuel cell, operating optimally at 0.88 V, the highest operating voltage for a compartmentless or miniature cell.

To build a yet faster O₂ cathode, we used the copper enzyme laccase and “wired” it with a 100-fold more rapidly electron diffusing redox polymer (polymer I), shown in Figure 1. The synthetic strategy for the +0.55 V vs Ag/AgCl potential redox polymer I followed that for the reported glucose oxidase “wiring” polymer poly(4-vinylpyridine)[Os(*N,N'*-dimethyl-2,2'-biimidazole)₃]^{2+/3+} (polymer II, not shown).⁴ The osmium complex, with two 4,4'-dimethyl-2,2'-bipyridine ligands and one 4-aminomethyl-4'-methyl-2,2'-bipyridine ligand, was reacted to form amides with *N*-(5-carboxypentyl)pyridinium functions of poly(4-vinylpyridine) (PVP), introduced by partially quaternizing PVP with 6-bromohexanoic acid.

Unlike the earlier used “wires” of laccase and bilirubin oxidase, in which the redox functions were coordinatively bound to ring nitrogens of backbone imidazoles,⁵ polymer I has eight-atom long and flexible tethers between its Os complexes and its backbone.

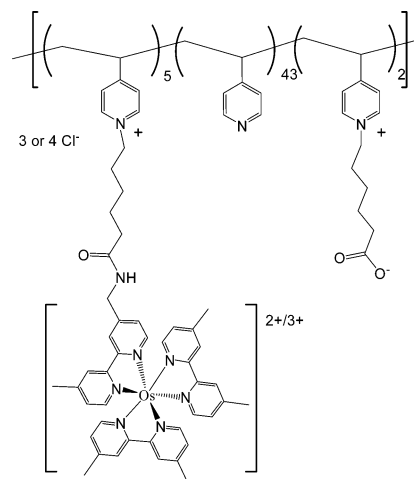


Figure 1. Polymer I. The pyridine-quaternizing functions are randomly distributed in the backbone.

Introduction of the tethers increased 100-fold the apparent electron diffusion coefficient D_{app} of the hydrogel, formed upon cross-linking, with poly(ethylene glycol)diglycidyl ether (PEGDGE), and hydration in pH 5 citrate buffer. D_{app} was determined, through the Randles–Sevcik equation, by cyclic voltammetry.⁴ D_{app} of the novel hydrogel was $(7.6 \pm 0.3) \times 10^{-7}$ cm² s⁻¹. That of the earlier used laccase “wire”, PVI-Os-tpy, was only $(6.2 \pm 0.8) \times 10^{-9}$ cm² s⁻¹. The activation energy for electron diffusion in polymer I was reduced from 48.3 kJ mol⁻¹ for PVI-Os-tpy to 30 kJ mol⁻¹.

Cross-linking makes the “wired” enzyme films more rigid, reducing the collision rate of the redox functions and thereby D_{app} . The long tethers facilitate the collisional electron transfer between neighboring polymer redox centers and sweep electrons from large volumes of the hydrated redox polymer,⁶ just as they do in the “wire” designed for glucose oxidase, having long tethers between its backbone and its redox centers.⁴ Because the eight-atom long tethers increased D_{app} 100-fold, we were able to raise the PEGDGE cross-linker weight fraction from 0.050 for the PVI-Os-tpy laccase “wire” without the tethers to 0.072 for polymer I. The resulting better cross-linked gel was adherent to carbon and leatherlike. At pH 5, a current density of 0.5 mA cm⁻² was reached only at a polarization as large as -0.16 V for the polymer without the tethers, PVI-Os-tpy (Figure 2, fine line), while it was reached at a mere -0.07 V for polymer I. (Figure 2, bold line). Under the (stagnant) conditions of the experiment, the O₂ transport limited current density for the “wired” laccase coated 7 μm diameter carbon fibers (in pH 5 citrate buffer) was 1 mA cm⁻², so that, at 0.5 mA cm⁻², O₂ transport did not limit the current density. Under the same conditions, the polarization of a 6 μm diameter platinum fiber in 0.5 M H₂SO₄ was -0.37 V versus the reversible O₂/H₂O half-cell potential (Figure 3).³ Unlike the platinum fiber cathode, which is poisoned by alcohols including glucose, the bioelectrocatalyst-based cathode is stable to glucose for >1 week at 37 °C.

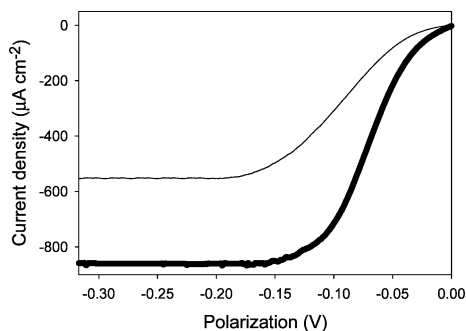


Figure 2. Polarization of the 7 μm diameter, 2 cm long carbon fiber cathode modified with laccase “wired” by PVI-Os-tpy, which has no tethers between its redox centers and its backbone (fine line),⁵ and polymer I, with 8-atom long tethers (bold line). The film contained 45.6 wt % laccase, 47.2 wt % polymer I, and 7.2 wt % PEDGE. 0.1 M pH 5 citrate buffer, quiescent solution, under air, 37 $^{\circ}\text{C}$. Scan rate 1 mV s^{-1} .

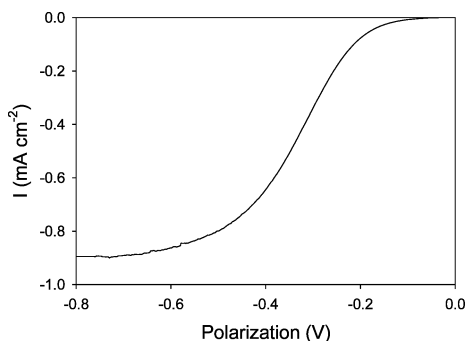
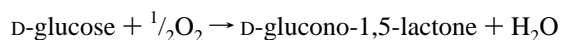


Figure 3. Polarization of the 6 μm diameter, 2 cm long smooth solid platinum fiber cathode in 0.5 M H_2SO_4 . Quiescent solution, under air, 37 $^{\circ}\text{C}$. Scan rate 1 mV s^{-1} .

To form a compartmentless miniature glucose– O_2 biofuel cell, the novel cathode was combined with a glucose electrooxidizing anode. The 7 μm diameter carbon fiber anode was coated with “wired” glucose oxidase (GOx). The “wire” chosen was polymer II, having a reducing redox potential and 13-atom long flexible tethers binding the redox centers to the backbone to increase D_{app} . The effective collection of the electrons from the glucose-reduced GOx allowed poisoning of the anode at a potential as reducing as -0.10 V vs Ag/AgCl.⁴

The power of the cell made of the two 7 μm diameter, 2 cm long carbon fibers, its cathode coated with the polymer I “wired” laccase, and its anode with the polymer II-“wired” GOx (35 wt. % GOx, 60 wt. % polymer II and 5 wt. % PEDGE), peaked at 0.88 V. This value represents the highest operating voltage in a miniature biofuel cell, the power density reaching 350 $\mu\text{W cm}^{-2}$ (Figure 4).

Because the thermodynamic potential for the cell reaction



is 1.18 V⁷ and because in the novel cell the power reached its peak when the cell operated at 0.88 V, just 300 mV below the reversible cell voltage, the average kinetic loss for the six electron transferring steps (glucose \rightarrow GOx \rightarrow anodic “wire” \rightarrow anode; cathode \rightarrow cathodic “wire” \rightarrow laccase \rightarrow O_2) was remarkably low, only 50 mV.

Methods: 4-Aminomethyl-4'-methyl-2,2'-bipyridine (amino-dme-bpy) was synthesized according to the reported procedure,⁸ but using crude 4-bromomethyl-4'-methyl-2,2'-bipyridine.⁹ Os(dme-bpy)₂Cl₂ and amino-dme-bpy were reacted by refluxing in DMF/

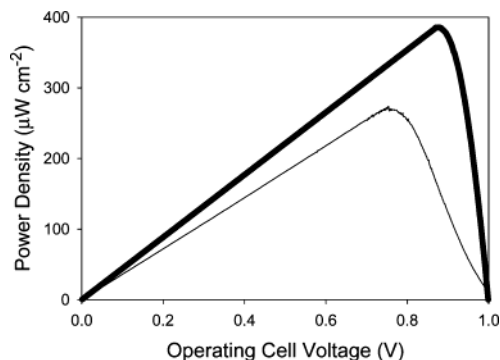


Figure 4. Dependence of the power density on the cell voltage for the cell made with a 7 μm diameter, 2 cm long carbon fiber anode coated with “wired” glucose oxidase and with a 7 μm diameter, 2 cm long carbon fiber cathode coated with the PVI-Os-tpy “wired” laccase⁵ (fine line) and with the novel polymer I “wired” laccase cathode (bold line). 15 mM glucose. Other conditions as those in Figure 2.

methanol/water (1:1:1) for 36 h to form [Os(dme-bpy)₂(amino-dme-bpy)]Cl, which was isolated and purified as described.¹⁰ The chloride was converted, by ion exchange, to the PF_6^- salt. Polymer I was obtained by linking, through amide bonds, the resulting osmium complex to poly(4-vinylpyridine), quaternized with 6-bromohexanoic acid, following the procedure of Mao et al.⁴ The composition of polymer I (Figure 1) was confirmed by ^1H NMR and elemental analysis. The electrodes were prepared as described.^{5,11}

In summary, by introducing long and flexible tethers in the “wire” of laccase, which electrically connected the reaction centers of the enzyme to the cathode, we increased the apparent electron diffusion coefficient, D_{app} , 100-fold. By doing so, we formed a catalyst allowing the electroreduction of O_2 to water (at pH 5) at a greatly reduced voltage loss relative to that for pure and smooth platinum (at pH 0). At a current density of 0.5 mA cm^{-2} , the overpotential was -0.07 V, approximately one-fifth of the 0.37 V overpotential of Pt. A miniature, membraneless glucose– O_2 biofuel cell, built with the novel cathode, operated at the highest voltage to date, 0.88 V while producing 350 $\mu\text{W cm}^{-2}$ in a stagnant pH 5 citrate buffer at 37.5 $^{\circ}\text{C}$.

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