A Miniature Biofuel Cell

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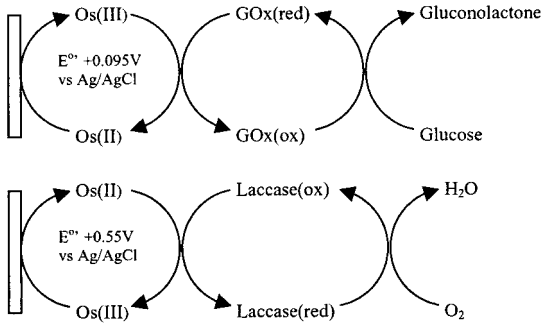
A biofuel cell, consisting of two 7-μm diameter, 2-cm long carbon fibers and operating at ambient temperature in a pH 5 aqueous solution is described. The areas of the anode and the cathode of the cell are 60 times smaller than those of the smallest reported (methanol oxidizing) fuel cell[1] and 180 times smaller than those of the smallest area biofuel cell.[2] The power density of the cell exceeds by a factor of 5 that of the highest power density earlier biofuel cell.[3] The electrocatalytic film of the microanode catalyzes the electrooxidation of glucose to gluconolactone (eq 1);[2−7] that of the microcathode catalyzes the electroreduction of O_2 to water (eq 2).[8−10] The film on the anode consists of the cross-linked electrostatic adduct of glucose oxidase (GOx) and a 0.1 V (vs Ag/AgCl) redox potential electron-conducting redox polymer, which electrically connects the GOx redox centers to one fiber. The film of the cathode consists of laccase and a 0.55 V (vs Ag/AgCl) electron-conducting redox polymer, electrically connecting the laccase redox centers to the second fiber. The power density of the cell is 64 μW/cm^2 at 23 °C and 137 μW/cm^2 at 37 °C, and its power output is 280 nW at 23 °C and 600 nW at 37 °C.

$$\text{glucose} \rightarrow \text{gluconolactone} + 2H^+ + 2e^- \qquad (1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2\,H_2O \qquad (2)$$

While the dimensions of electronic packages were shrinking through the past decades and CMOS circuits of reduced power consumption became available,[11] the size of their power source was not proportionately reduced. In applications where energy capacity was not the size-determining factor, the power source remained large, relative to the chip package because its case and seal were difficult to miniaturize. The case and the seal were necessary in batteries where the anode reacted with water or air, or if the electrolyte was corrosive. The lithium anode of high-energy density batteries is oxidized in humid air; the alkaline electrolyte of zinc−air and zinc−silver oxide batteries is corrosive. Small lithium and small zinc−silver oxide batteries have footprints of >10 mm^2. The smallest reported fuel cell, of 25-mm^2 size, electrooxidizes methanol, comprises a membrane, and is made by a multistep silicon chip-making process involving microlithography.[1] Larger biofuel cells[2−4] of lesser power density in which glucose is electrooxidized to gluconolactone at the anode (eq 1)[5−7] and dissolved O_2 is electroreduced to water at the cathode (eq 2),[8−10] have been described.

Scheme 1. Electron-Transferring Steps in the Electrocatalytic Oxidation of Glucose (top) and in the Electrocatalytic Reduction of O_2 (bottom)[a]



[a] The $Os^{2+/3+}$ centers and the enzymes are immobilized in the electron-conducting redox-polymer films.

The miniature cell delivers at 37 °C 0.6 μW, enough to power the slower and least power-consuming CMOS circuits.[11] The electron-transfer steps underlying the electrocatalytic reactions are shown at the top of Scheme 1 for the anode and at its bottom for the cathode.

In making the cell, a cluster of 3-cm long, 7-μm diameter carbon fibers (Goodfellow, Cambridge, UK) was soaked in ethanol to allow their separation. Two of the separated fibers were placed in two 1-mm × 1-mm grooves machined into a 3-cm long polycarbonate support. One end of each fiber was fixed with epoxy, and the other end was electrically connected to a copper wire using conductive carbon paint (SPI, West Chester, PA). The carbon paint was allowed to dry and was then insulated with a layer of epoxy. A photograph, showing parts of the anode and the cathode, is seen in Figure 1. The active area of each fiber was 0.44 mm^2. Prior to their coating with the respective electrocatalysts the carbon fibers were made hydrophilic by plasma oxidation (1 Torr O_2 plasma, 2.5 min).[12] Phase-separation of GOx or laccase from their wiring polymers was prevented by electrostatic coupling of the polycationic wires and the enzymes, which are polyanions at or above pH 5. The anodic catalyst was made by cross-linking on a fiber $NaIO_4$-oxidized GOx (EC 1.1.3.4, from *Aspergillus niger*, Fluka, Milwaukee, WI) with the redox polymer poly{*N*-vinyl imidazole [Os(4,4′-dimethyl-2,2′-bipyridine)$_2$Cl]$^{+/2+}$-*co*-acrylamide}, ***I,*** redox potential $E^{0'} = +0.10$ V vs Ag/AgCl [7] using poly(ethylene glycol) diglycidyl ether (PEGDGE, M. W. 400, Polysciences, Warrington, PA) as cross-linker. Here 100 μL of 40 mg/mL GOx in 0.1 M $NaHCO_3$ was oxidized while shielded from light by 50 μL of 7 mg/mL $NaIO_4$ for 1 h; then 2 μL of the periodate-oxidized GOx was mixed with 8 μL of 10 mg/mL of ***I***, and the pH was adjusted to 5.0 with 2 μL of 0.2 M citrate buffer; then 0.5 μl of 2.5 mg/mL PEGDGE was added. The solution was applied to the carbon fiber in four aliquots of 5 μl each, with 1 h drying time allowed between applications. The film was then allowed to cure for 24 h. The electrocatalyst of the second fiber was made of laccase from *Coriolus hirsutus* (EC 1.10.3.2, SynectiQ, Denville, NJ) and poly(*N*-vinyl-imidazole) with one-fifth of the rings complexed with [Os(4,4′-dimethyl-2,2′-bipyridine)$_2$ (2,2′,6′,2″-terpyridine)]$^{2+/3+}$, ***II***, $E^{0'} = +0.55$ V vs Ag/AgCl.[8] The pH of 10 μL of the 10 mg/mL aqueous solution of ***II***

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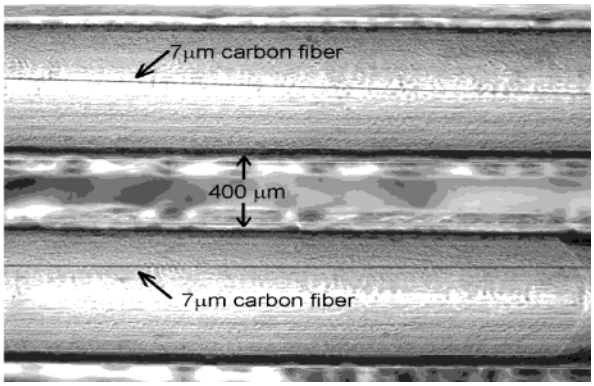

Figure 1. Segment of the cell, consisting of two 7-μm diameter carbon fibers.

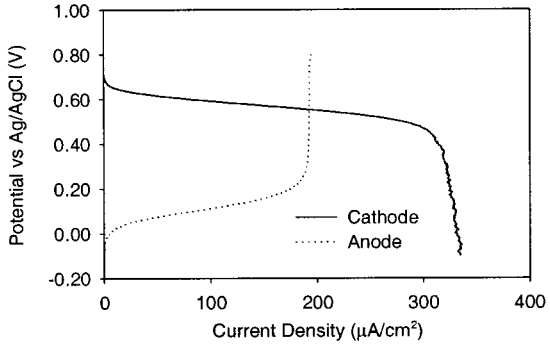

Figure 2. Polarization curves of the anode and the cathode. Quiescent solution, air, 23 °C, pH 5.0 citrate buffer (0.2 M), 15 mM glucose.

was adjusted with 2 μL 0.2 M citrate buffer to 5.0, and 2 μL of 30 mg/mL laccase and 4 μL of 10 mg/mL PEGDGE were added. The cathode fiber was coated and cured as described for the anode. The anode's coating contained ~0.3 units of glucose oxidase and the cathode's contained ~0.06 units of laccase. The assembled cell was immersed in an aerated 15 mM glucose, pH 5 citrate (0.2 M) buffer solution in a water-jacketed thermostated three-electrode (saturated KCl Ag/AgCl reference, Pt wire counter-electrode) cell. It was characterized using a CHI 832 electrochemical detector (CH Instrument, Austin, TX).

Figure 2 shows the polarization curves of the microanode and microcathode at 23 °C. The glucose electrooxidation current reached its plateau near +0.1 V vs Ag/AgCl, and the O_2 electroreduction current near +0.5 V vs Ag/AgCl. In the quiescent solution the power density reached 64 μW/cm^2 (0.4 V, 160 μA/cm^2) at 23 °C and 137 μW/cm^2 (0.4 V, 343 μA/cm^2) at 37 °C. The actual power output of the cell was 280 nW (0.4 V, 700 nA) at 23 °C and 600 nW (0.4 V, 1.5 μA) at 37 °C (Figure 3). The cell operated for 24 h with <10% loss; after 72 h of continuous operation the power output dropped by ~25% (Figure 4).

Table 1 compares the characteristics of the cell with those of earlier reported biofuel cells. At 23 and 37 °C its power density was, respectively, 5- and 10-fold higher than that of the highest power density reported for a biofuel cell, which operated at 23 °C. [3] The increase in power density is derived from (a) the lessening of the concentration gradient upon replacement of the

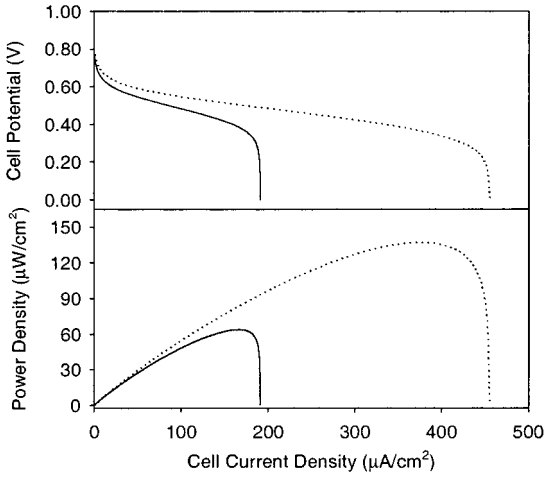

Figure 3. (Top) Polarization curve of the assembled cell. (Bottom) Dependence of the power output on the current. Conditions as in Figure 2. (Solid lines) 23°C; (dotted lines) 37 °C.

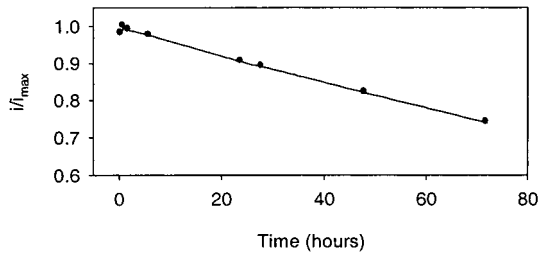

Figure 4. Stability of the micro-fuel cell. The external load in the test was 1 MΩ. Conditions as in Figure 2.

Table 1. Power Densities, Electrode Areas and Operating Potentials of Glucose−Air Fuel Cells

ref	[gluc], temp.	power density, μW/cm^2	electrode area, cm^2	operating potential,V
4	0.3 mM, 25 °C	5.1	32	0.3
3	0.1 M, 23 °C	12	12.6	0.4
2	1 mM, 25 °C	5	0.8	0.06
this study	15 mM, 23 °C	64	0.0044	0.4
this study	15 mM, 37 °C	137	0.0044	0.4

formerly used planar electrodes, to which mass transport is semi-infinite planar, by the microfibers, to which mass transport is cylindrical and (b) the use of cross-linked electrostatic adducts of enzymes with redox polymers of tailored redox potentials for transport of electrons between the fibers and the enzymes. Miniaturization is made possible by the absence of reaction of glucose at the cathode and the very slow reaction of O_2 at the anode, which, upon the immobilization of both bio-electrocatalysts, eliminate the requirement for a compartment-separating membrane,[2] and by the high current density of the four-electron electroreduction of O_2 to water at 0.5 V vs Ag/AgCl.[8]

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