COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A miniature biofuel cell operating at 0.78 V

Nicolas Mano,*[a] Fei Mao,[b] Woonsup Shin,[ac] Ting Chen[a] and Adam Heller*[a]

[a] *Department of Chemical Engineering and Texas Material Institute, The University of Texas at Austin, Austin, TX 78712, USA. E-mail: mano@mail.utexas.edu*

[b] *Therasense Inc, 1360 South Loop Road, Alameda, CA 94502, USA*

[c] *Department of Chemistry, Sogang University, Seoul, South Korea*

Received (in Cambridge, UK) 28th November 2002, Accepted 13th January 2003
First published as an Advance Article on the web 21st January 2003

We report the highest voltage miniature biofuel cell to date, a membrane-less cell operating at 37 °C in pH 5 buffer at 0.78 V.

Although implantable sensors and integrated amplifier-transmitter circuits with footprints smaller than 1 mm^2 and volumes smaller than 1 mm^3 are available, the sizes of implantable autonomous sensor-transmitter systems are much larger because of the size of their power source. The sizes of off-chip batteries are defined by the size of their case and seal, the sizes of on-chip fuel cells,[1] and by the size of their hydrogen or methanol storage unit. Thus, an alternative power source, which can be manufactured and operated in small packages, is needed for the miniaturization the microelecronic devices operating in a biological environment.

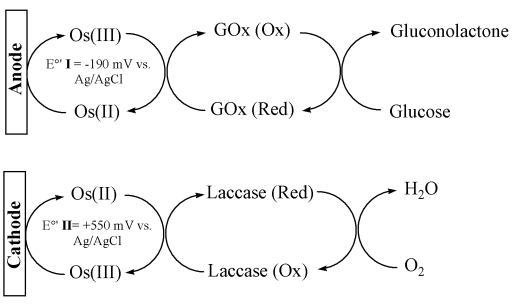
The volume of many of the earlier biofuel cells exceeded 1 cm^3 and the areas of their electrodes were >1 cm^2. They required membranes to separate their anode and cathode compartments to prevent the substrate-reduced mediators of the anode from reaching the cathode compartment, where they would have been oxidized, and to prevent their cathode mediators from reaching the anode compartment, where they would have been reduced.[2–4]

A miniature case-less and compartment-less glucose–O_2 biofuel cell was reported by Chen *et al*.[5] Like the cell reported here, it consisted of two 7 μm diameter 2 cm long carbon fibers, an anode on which glucose was electrooxidized to gluconolactone and a cathode on which dissolved O_2 was electroreduced to water. The electrocatalyst immobilized on the anode comprised a 0.1 V *vs*. Ag/AgCl potential redox polymer, electrically connecting the redox centers of the co-immobilized glucose oxidase (GOx) to the fiber. The immobilized electrocatalyst on the cathode comprised a 0.55 V *vs*. Ag/AgCl potential redox polymer connecting the redox centers of its laccase to the other fiber. The cell, which produced 0.6 μW at 0.4 V at 37 °C operated at pH 5 and in the absence of chloride, because the enzyme of the cathode, laccase, was inactive at physiological pH and NaCl concentration.[6–8] The cell described here is similar, but it operates at +0.78 V in a glucose containing, air equilibrated, citrate buffer solution (pH 5, 20 mM citrate) at 37 °C.

The electrodes were designed to allow their operation in the same solution, obviating the need for a membrane to separate the anode and cathode compartments. The electron transfer catalyzing films on the electrodes, each formed of an enzyme and an electron conducting redox polymer (Scheme 1) were immobilized to avoid the detrimental reverse reactions that would take place if they were allowed to diffuse to the opposite electrode. To avoid phase separation of the enzymes and their connecting redox polymers, the polymers were polycations, forming electrostatic adducts with the enzymes which were polyanions at neutral pH. Excessive loss of current by electroreduction of O_2 at the glucose oxidizing anode, maintained at a reducing potential, was avoided by designing the GOx connecting redox polymer **I** (Scheme 1) so that the rate of electron transfer from the reduced GOx to polymer **I** was much faster than the rate of electron transfer to O_2.[9] Similarly, the electrocatalyst of the cathode did not catalyze the electrooxidation of glucose even though the electrode operated at + 0.4 V *vs*. Ag/AgCl.[10,11]

The 2 cm long, 7 μm diameter carbon fibers (Goodfellow, Cambridge, UK) were coated by the reported procedure.[5,9] Each fiber was placed in a 1 mm × 1 mm groove machined into a 2 cm long polycarbonate support and its end was cemented to a copper wire using conductive carbon paint (SPI, West Chest, PA). The carbon paint was allowed to dry and then insulated with the epoxy. The active area of each fiber was 0.44 mm^2. Prior to their coating the 7 μm diameter fibers were made hydrophilic by exposure to a 1 Torr O_2 plasma for 3 min.[12] The anodic catalyst consisted of the crosslinked adduct of 35 wt% of glucose oxidase, 60 wt% of poly(*N*-vinylimidazole) (PVI)–$[Os(N,N'\text{-dialkylated-}2,2'\text{-bisimidazole})_3Cl]^{2+/3+}$ (polymer **I**), 4.7 wt% of poly(ethylene glycol) (400) diglycidyl ether (PEDGE, Polysciences). The cathodic catalyst was made of 44.8 wt% laccase from *Corsiolus hirsutus* (SynectiQ, Dover, NJ), 48.8 wt% of the polycationic redox copolymer PVI–$[Os(2,2',6',2''\text{-terpyridine-}4,4'\text{-dimethyl-}2,2'\text{-bipyridine})_2Cl]^{2+/3+}$ (polymer **II**), crosslinked with 6.4 wt% PEDGE.

Operation at 0.78 V was achieved by substituting the earlier used[5] anodic polymer PVI–$[Os(4,4'\text{-dimethyl-}2,2'\text{-bipyridine})_2Cl]^{+/2+}$ by PVI–$[Os(N,N'\text{-dialkylated-}2,2'\text{-bisimidazole})_3Cl]^{2+/3+}$ (**I**).[9] Polymer **I** differs from the earlier used redox polymers[13,14] in its redox potential, in the tethering of its redox centers to the polymer backbone and in the coordination of its $Os^{2+/3+}$ centers. The redox potential of its $[Os(N,N'\text{-alkylated-}2,2'\text{-bisimidazole})_3]^{2+/3+}$ centers is highly reducing, −190 mV *vs*. Ag/AgCl, unprecedented for immobilized polymeric mediators accepting electrons at a high rate from $FAD/FADH_2$ centers of GOx. The feature of the polymer enabling the reduction of the overvoltage for driving electrons of $GOx/FADH_2$ centers to the redox polymer is the tethering of the complexed osmium redox centers to the polymer backbone through a 13-atom long



Scheme 1 Schematic diagram of the compartment-less biofuel cell. The two electrodes, coated with different crosslinked electrostatic adducts of enzymes and redox polymers reside in the same compartment. At the anode (top) electrons are transferred from glucose to glucose oxidase (GOx), from GOx to redox polymer **I**, then from **I** to the electrode. At the cathode (bottom), electrons are transferred from the cathode to redox polymer **II**, from **II** to laccase and from laccase to O_2. The electrons generated by the glucose anode, which is poised at a reducing potential, pass an external load R and reduce O_2 at the cathode, poised at an oxidizing potential.

DOI: 10.1039/b211796g

flexible spacer. The tether allowed approach of the redox centers of the polymer and the enzyme and facilitated collisional electron transfer between neighboring polymer redox centers by sweeping electrons from large volumes of the hydrated crosslinked redox polymer. In redox polymer **I** the osmium centers are completely surrounded by bidentate dialkylated bisimidazole ligands, improving their stability to ligand substitution reactions.

Fig. 1 shows the polarization curves of the microanaode and microcathode at 37 °C. As shown in Fig. 1, the anodic redox polymer enables the electrooxidation of glucose at a current density of 360 μA cm^{-2} already at −100 mV *vs.* Ag/AgCl, only 190 mV oxidizing *versus* the estimated GOx redox potential at pH 5.3.[15] The oxygen electroreduction current density was 580 μA cm^{-2} at + 0.5 V *vs.* Ag/AgCl. The power output of the cell operating at 0.78 V in a quiescent solution was 1.2 μW, corresponding to a power density of 268 μW cm^{-2} (Fig. 2, heavy line), well over the 137 μW cm^{-2} at 0.4 V reached in the earlier laccase-based miniature cell where the anodic redox polymer was PVI–[Os(4,4′-dimethyl-2,2′-bipyridine)$_2$Cl] $^{+/2+}$ (Fig. 2, fine line).[5] When the cell operated continuously at 0.78 V and at 37 °C for one week, it lost ~10% of its power per day.

In summary, we describe a miniature case-less biofuel-cell producing 1.2 μW, with a power density, 2.68 μW mm^{-2} twice the output of an earlier cell which also operated at pH 5 and in the absence of chloride.[5] The operating voltage of the cell, 0.78 V *vs.* 0.4 V, suffices to drive silicon integrated circuits.[16]

The study was supported by the Office of Naval Research (Grant number N00014-02-1-0144).

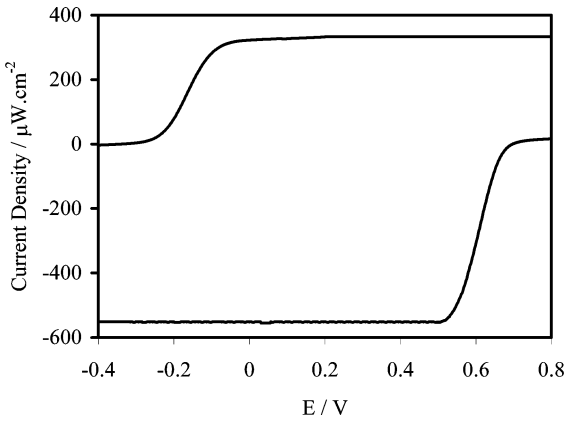


Fig. 1 Polarization curves of the anode and the cathode. Quiescent solution under air, 37 °C, pH 5, 20 mM citrate, 15 mM glucose solution.

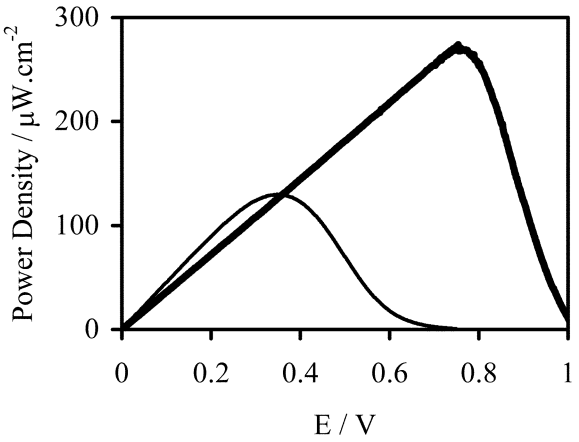


Fig. 2 Dependence of the power density on the cell voltage when the anode polymer is PVI–[Os(4,4′-dimethyl-2,2′-bipyridine)$_2$Cl]$^{+/2+}$ (fine line) or PAA–PVI–[Os(*N*,*N*′-dialkylated-2,2′-bisimidazole)$_3$Cl]$^{2+/3+}$ (heavy line). Other conditions as in Fig. 1.

Notes and references

1 S. C. Kelley, G. A. Deluga and W. H. Smyrl, *AIChE J.*, 2002, **48**, 1071.
2 G. T. Palmore, H. Bertschy, S. H. Bergens and G. M. J. Whitesides, *Electroanal. Chem.*, 1998, **443**, 155.
3 G. Davis, H. A. O. Hill, W. J. Aston, I. J. Higgins and A. P. F. Turner, *Enzyme Microb. Technol.*, 1983, **5**, 383.
4 I. Willner, G. Arad and E. Katz, *Bioelectrochem. Bioenerg.*, 1998, **44**, 209.
5 T. Chen, S. C. Barton, G. Binyamin, Z. Gao, Y. Zhang, H.-H. Kim and A. Heller, *J. Am. Chem. Soc.*, 2001, **123**, 8630.
6 S. C. Barton, H.-H. Kim, G. Binyamin, Y. Zhang and A. Heller, *J. Phys. Chem. B*, 2001, **105**, 11917.
7 S. C. Barton, H.-H. Kim, G. Binyamin, Y. Zhang and A. Heller, *J. Am. Chem. Soc.*, 2001, **123**, 5802.
8 S. C. Barton, M. Pickard, R. Vasquez-Duhalf and A. Heller, *Biosens. Bioelectron.*, 2002, **17**, 1071.
9 N. Mano, F. Mao and A. Heller, *J. Am. Chem. Soc.*, 2002, **124**, 12962.
10 N. Mano, H.-H. Kim, Y. Zhang and A. Heller, *J. Am. Chem. Soc.*, 2002, **124**, 6480.
11 N. Mano, H.-H. Kim and A. Heller, *J. Phys. Chem. B*, 2002, **106**, 8842.
12 A. Sayka and J. G. Eberhart, *Solid State Technol.*, 1989, **32**, 69.
13 A. Heller, *J. Phys. Chem. B*, 1992, **96**, 3579.
14 A. Heller, *Acc. Chem. Res.*, 1990, **23**, 128.
15 M. T. Stankovich, L. M. Schopfer and V. Massey, *J. Biol. Chem.*, 1978, **253**, 4971.
16 R. R. Harrison and C. Koch, *Analog. Interg. Circuits Signal Process*, 2000, **24**, 213.