

# MICROBIAL FUEL CELLS GENERATING ENERGY FROM THE MARINE SEDIMENT/WATER INTERFACE. KINETIC STUDIES ON ANODE MATERIALS

Leonard M. Tender<sup>a</sup>, Daniel A. Lowy<sup>b</sup>,  
J. Gregory Zeikus<sup>c</sup>, Doo Hyun Park<sup>d</sup>

<sup>a</sup>Center for Bio/Molecular Science and Technology, Naval Research Laboratory, Washington, DC 20375 USA

<sup>b</sup>Nova Research, Inc., Alexandria, VA 22308, USA

<sup>c</sup>Departments of Microbiology and Molecular Genetics, Michigan State University, East Lansing, MI 48824

<sup>d</sup>Department of Biological Engineering, Seokyeong University, Seoul 136-704, Korea

## INTRODUCTION

We compare the kinetic activity (KE) of various anodes of a recently described microbial fuel cell consisting of an anode imbedded in marine sediment and a cathode in overlying seawater [1,2]. This fuel cell generates power by oxidizing organic-rich marine sediment with seawater oxygen. Using graphite anodes, it was demonstrated that a significant portion of the anodic current results from oxidation of sediment organic matter catalyzed by microorganisms colonizing the anode and capable of directly reducing the anode without added exogenous electron-transfer mediators [2,3]. Here, graphite anodes incorporating known microbial oxidants are evaluated in the laboratory relative to graphite with the goal of increasing current density. Anodes examined include graphite modified with anthraquinone-1,6-disulfonic acid (AQDS) [4] or 1,4-naphthoquinone (NQ), a graphite-ceramic composite containing  $\text{MnSO}_4$  and  $\text{NiCl}_2$  [5], and graphite modified with a graphite paste containing  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_3\text{O}_4$  and  $\text{NiCl}_2$ . It was found that all of these anodes possess greater KA than graphite. Fuel cells deployed with these anodes in a previously utilized coastal site near Tuckerton, NJ, USA ( $39^\circ 30.5' \text{ N}$ ,  $74^\circ 19.6' \text{ W}$ ) [1] at short times before onset of mass-transfer limitation generated ~5-fold greater current density than fuel cells equipped with graphite anodes.

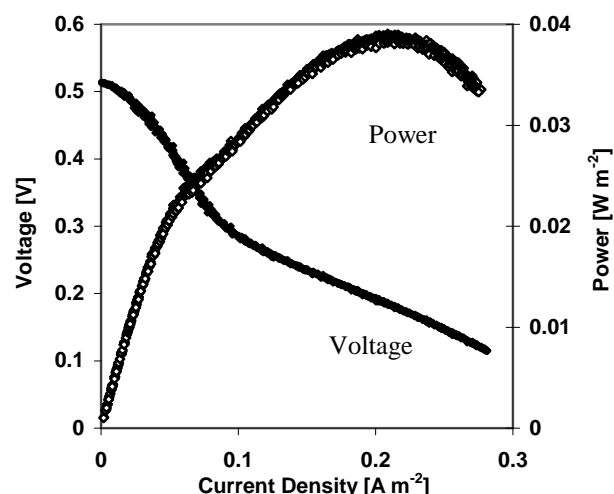
## EXPERIMENTAL

Two- and three-electrode mode electrochemical measurements were performed with a Model 660a Electrochemical Workstation (CH Instruments, Austin, TX) equipped with a Faraday cage. The sediment/sea water interface was reassembled in the laboratory with sediment and seawater from Tuckerton, NJ. Working electrodes (WE) were graphite and modified graphite anodes (listed above), buried in marine sediment. (Anode preparation methods will be described in an upcoming paper [6].) Graphite disk cathode, immersed in seawater, was the counter electrode and  $\text{Ag}/\text{AgCl}$ , sat.KCl (BAS) served as the reference. Multiple Tafel plots were recorded for each anode by sweeping voltage at  $1 \text{ mV s}^{-1}$  from the open circuit potential (OCP) of the anode vs. the reference electrode, corresponding to  $\eta = 0 \text{ mV}$ , to  $\eta = 100$  ( $\eta$  is the overpotential). At least 8-hr was required for a stable OCP to re-establish between measurements. For each Tafel plot,  $i_o$  was determined by extrapolation to  $\eta = 0$  of a linear regression ( $R^2 > 0.99$ ) between  $\eta = 60 \text{ mV}$  to  $\eta = 80 \text{ mV}$ .

For real/life experiments a fuel cell similar to that previously described [1] was used to evaluate a 48.6-cm diameter, 1.27-cm thick AQDS-modified graphite disk anode and a graphite disk cathode of identical size.

## RESULTS

Laboratory evaluation of the five types of graphite-based anodes, expressed as relative KA with respect to plain graphite, provided the following order of decreasing KA values: graphite-ceramic containing  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$ : 2.2, graphite paste containing  $\text{Fe}_3\text{O}_4$ : 2.1, graphite paste containing  $\text{Fe}_3\text{O}_4 + \text{Ni}^{2+}$ : 1.7, AQDS-modified graphite: 1.7, NQ-modified graphite: 1.5, unmodified graphite: 1.0. Voltage and power density vs. current density curves recorded with the fuel cell deployed in Tuckerton (see Figure) show that the optimum current density ( $200 \text{ mA m}^{-2}$ ) and power density (ca.  $40 \text{ mW m}^{-2}$ ) are attained at a cell voltage of ca. 0.2 V. This power density is 1.6 times greater than the one reported for plain graphite. [1]



**Figure:** Voltage and power density vs. current density curves for a benthic fuel cell operating on the seafloor near Tuckerton, NJ, USA; it generates power by oxidizing organic-rich marine sediment with seawater oxygen. (May 11, 2001, anode modified with AQDS.)

## CONCLUSION

As they require low investment costs and are stable over extended time periods, the explored microbial bio-fuel cells are promising sources for many low-power applications, including seismic detectors and monitoring devices. Modified graphite anodes open new avenues towards achieving enhanced power densities.

## REFERENCES

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