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Harvesting energy from the marine sediment–water interface II Kinetic activity of anode materials[☆]

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Abstract

Here, we report a comparative study on the kinetic activity of various anodes of a recently described microbial fuel cell consisting of an anode imbedded in marine sediment and a cathode in overlying seawater. Using plain 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. Here, graphite anodes incorporating microbial oxidants are evaluated in the laboratory relative to plain graphite with the goal of increasing power density by increasing current density. Anodes evaluated include graphite modified by adsorption of anthraquinone-1,6-disulfonic acid (AQDS) or 1,4-naphthoquinone (NQ), a graphite-ceramic composite containing Mn^{2+} and Ni^{2+}, and graphite modified with a graphite paste containing Fe_3O_4 or Fe_3O_4 and Ni^{2+}. It was found that these anodes possess between 1.5- and 2.2-fold greater kinetic activity than plain graphite. Fuel cells were deployed in a coastal site near Tuckerton, NJ (USA) that utilized two of these anodes. These fuel cells generated ca. 5-fold greater current density than a previously characterized fuel cell equipped with a plain graphite anode, and operated at the same site.

Keywords: Microbial fuel cell; Magnetite; Tafel plots; Kinetic activity; Power density

1. Introduction

Recently a microbial fuel cell was demonstrated, at two coastal marine sites, that is being developed to operate low-power consuming marine deployed scientific instrumentation (Fig. 1) (Tender et al., 2002). This fuel cell consists of a graphite plate anode buried in marine sediment connected by an external circuit to a graphite plate cathode positioned in overlying seawater. Open circuit cell voltage is typically 0.75 ± 0.03 V. Maximum power density is typically 10–20 mW/(m^2 geometric area of the anode), depending on the discharge potential and geochemical characteristics of the site (Tender et al., 2002). Such a fuel cell generates power by oxidizing sediment organic matter with seawater oxygen. It does so by utilizing a naturally occurring redox gradient that spans oxidant-rich seawater and reductant-rich sediment millimeters to centimeters beneath the sediment surface (Tender et al., 2002; Reimers et al., 2001). The redox gradient results from microbial activity in marine sediment; it is a common feature of the seafloor of continental margins and the source of the fuel cell voltage (Froelich et al., 1979). Cathodic current is attributed to reduction of seawater oxygen owing to similarity of the cathode to that of seawater batteries (Wilcock and Kauffman, 1997). Anodic current is a result of two types of concurrent reactions: (i) oxidation of sediment reductants and (ii) reduction of the anode by microorganisms that colonize the anode. Sediment of continental margins is often

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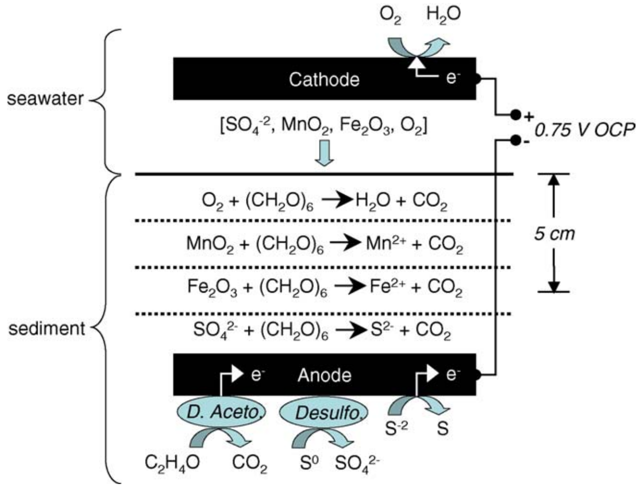

Fig. 1. Schematic representation of the operating principle of the mediator less sea floor microbial bio-fuel cell (based on refs: Avila et al., 2000; Bard and Faulkner, 2001; Bond et al., 2002). See explanations in text.

rich in organic matter. Microbial oxidation of this organic matter is limited by flux of oxidants from overlying seawater (listed in Fig. 1 below the cathode in order of increasing oxidation potential). Sediment dwelling microorganisms therefore utilize a depth dependent succession of oxidants in order of decreasing oxidation potential with increasing sediment depth, given that less potent oxidants liberate less energy per equivalent organic matter oxidized (represented in Fig. 1 as glucose) (Reimers et al., 2001).

Fig. 1 illustrates the operating principle of the mediator less sea floor microbial bio-fuel cell. In the generalized case illustrated here, microbes in the sediment surface layer preferentially reduce O_2 in oxidation of organic matter, leaving MnO_2, Fe_2O_3, and $SO_4{}^{2-}$ unutilized. MnO_2 is then microbially reduced in the next lowest sediment layer, Fe_2O_3 in the third sediment layer, and $SO_4{}^{2-}$ in the forth sediment layer. As a consequence, each layer accumulates more potent reductants (Mn^{2+}, Fe^{2+}, and S^{2-}) with increasing sediment depth. This reductant gradient generates the open circuit voltage of the fuel cell, and renders the sediment imbedded electrode the anode and the seawater electrode the cathode. At least three reactions have been determined to occur at the anode: (1) oxidation of S^{2-} to S^0; the importance of dissolved and solid state sulfides as electron donors in anoxic marine sediments has been recently emphasized (Reimers et al., 2005), and the amplification of the biogeochemical cycle of sulfur and iron by the fuel cell deployed in the Yaquina Bay estuary discussed (Ryckelynck et al., 2005); (2) microorganisms colonizing the anode in the family Geobacteracea (most similar to *Desulfuromonas acetoxidans*) oxidize acetate in sediment and directly reduce the anode; (3) microorganisms colonizing the anode most similar to species in the *Desulfobulbus* or *Desulfucapsa* genera oxidize anode generated S^0 to $SO_4{}^{2-}$. The enrichment of anodic biofilms in *Desulfobulbus* or *Desulfucapsa* genera was reported by Lovley et al. (Holmes et al., 2004a,b). These microorganisms may mediate electron transfer by either direct bacterial transfer, i.e., without addition of exogenous electron transfer mediators (Tender et al., 2002; Bond et al., 2002) (e.g., in the case of Geobacteracea) (Bond and Lovley, 2003) or by excretion of redox components (Mahadevan et al., 2006). Sustained current is attributed to continual replenishment of electrode reactants by diffusion (anode and cathode) and seawater flow (cathode) (Bond et al., 2002). A fuel cell operating at one of the deployment sites for the past ~1.5 years continuously sustains approximately $30\,mW\,m^{-2}$ ($90\,mA\,m^{-2}$) at a cell voltage of 0.3 V, with no indication of exhaustion. Kinetic activity of the anode, which limits overall power current density (and thus power generation), was determined by separate measurement of anode and cathode overpotentials (Reimers and Tender, 2002).

In order to increase the current density and, as a result, the power density of fuel cells of this design, we focused attention on enhancing the kinetics of microbial reduction of the anode. Specifically, graphite anodes modified with or incorporating known microbial oxidants where evaluated in comparison to plain graphite. A kinetic activity (KA) for each type of anode is therefore reported. KA was determined by normalization of the average i_0 for each anode type by i_0 of a plain graphite anode determined in a cell of the same configuration. Our described research is justified by the observation that all anodes evaluated here demonstrated greater KA than graphite (considered, by convention, equal to 1.0). The KA of graphite–ceramic composite anodes containing Mn^{2+} and Ni^{2+} was 2.2 (highest) and for AQDS-modified graphite anode was 1.7. Fuel cells deployed in a previously utilized coastal site near Tuckerton, NJ, USA (Tender et al., 2002; Reimers et al., 2001) utilizing these anode materials generated, before onset of mass-transfer limitation, ~5-fold greater current density than a fuel cell equipped with a plain graphite anode.

2. Experimental

2.1. Anode preparation

2.1.1. Anodes modified with AQDS and NQ

For the laboratory evaluation, graphite disks (9.53-cm diameter, 1.27-cm thick, LG grade 10, Graphite Engineering and Sales, Greenville, MI, USA) were lightly sanded, rinsed with dionized water (DIW), then modified with anthraquinone-1,6-disulfonic acid (AQDS) by immersion in $50\,mmol\,L^{-1}$ AQDS (>97%, purity, Fluka Chemika, Buchs, Switzerland, used as received) in $0.1\,mol\,L^{-1}$ perchloric acid (prepared from 70% $HClO_4$, A.C.S. reagent grade, Aldrich, used as received) for 48 h, at room temperature. The concentration of the AQDS solution was set by the solubility of the quinone in perchloric acid, while the duration of immersion was optimized by colorimetric monitoring. These electrodes were then rinsed with copious amounts of DIW (18.2 Mohm cm, Milli-Q Synthesis System, Milipore). In a similar fashion, graphite disk electrodes were modified with 1,4-naphthoquinone (NQ) by soaking in $63\,mmol\,L^{-1}$ NQ in ethanol (200 proof, 95.5% purity, A.C.S. reagent grade, Aldrich, used as received), for 72 h. A water insulating oceanographic bulk head connector and matching 18-AWG cable (Impulse Enterprise, San Diego, CA, USA) was used as previously described