Harvesting Energy from the Marine Sediment–Water Interface

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Pairs of platinum mesh or graphite fiber-based electrodes, one embedded in marine sediment (anode), the other in proximal seawater (cathode), have been used to harvest low-level power from natural, microbe established, voltage gradients at marine sediment–seawater interfaces in laboratory aquaria. The sustained power harvested thus far has been on the order of 0.01 W/m² of electrode geometric area but is dependent on electrode design, sediment composition, and temperature. It is proposed that the sediment/anode–seawater/cathode configuration constitutes a microbial fuel cell in which power results from the net oxidation of sediment organic matter by dissolved seawater oxygen. Considering typical sediment organic carbon contents, typical fluxes of additional reduced carbon by sedimentation to sea floors < 1000 m deep, and the proven viability of dissolved seawater oxygen as an oxidant for power generation by seawater batteries, it is calculated that optimized power supplies based on the phenomenon demonstrated here could power oceanographic instruments deployed for routine long-term monitoring operations in the coastal ocean.

Introduction

Microbial decomposition of marine sediment organic matter consumes a succession of oxidants based on energy of reaction and regulated by supply across the sediment–water interface (*1*). In organic-rich sediments it is common to observe oxygen reduction at the sediment surface, nitrate, manganese, and iron reduction within the next few centimeters, and sulfate reduction over another meter or so (*2*). As each oxidant is successively exhausted and its byproducts generated, distinct depth-dependent chemical profiles develop in sediment pore waters resulting in a voltage drop as large as 0.75 V within the top few centimeters of the sediment column (*3, 4*). Here we show that this potential gradient can sustain low-level power for prolonged periods if tapped by

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a simple fuel cell-like device consisting of an electrode shallowly embedded in marine sediment (anode), connected through an external load to a second electrode in seawater (cathode). Unlike conventional fuel cells or seawater batteries (*5–8*) the described device is intended to operate in an environment (i.e., marine sediment/seawater interface) in which fuel (sediment organic detritus) and oxidant (dissolved seawater oxygen) are both natural and continually renewed resources.

Experimental Section

Marine sediment–seawater interfaces (i.e., ocean floors) were simulated in our laboratories in aquaria containing seawater and marine sediment (collected from either a salt marsh near Tuckerton, NJ, U.S.A. at approximately 39°30.5′N, 74°19.6′W or an estuarine site within Raritan Bay, NJ, 40°27.5′N, 74°04.4′W). After equilibration of the sediment at 22 °C, under circulating aerated seawater (salinity = 34 psu), multiple pairs of coplanar, electrochemically cleaned (*9*) 20 or 100-cm² (geometric area) 52-mesh platinum electrodes (Alfa Aesar) were positioned about the sediment–seawater interfaces (Figure 1) and held in place by Plexiglas, polycarbonate or glass frame and rod rigs (not illustrated). Electrical contact to each electrode was made with a 20-gauge marine insulated wire (Ancor). Each wire terminus was silver epoxied (Epotek) to the platinum, and the contact was encapsulated in insulating water-resistant epoxy (Torr-Seal). Carbon fiber-based anodes and cathodes of 100 cm² geometric area were also examined. These consisted of 27 g of loose-packed 8-micron diameter, 0.25-in. long, carbon fiber (Alfa-Aesar) sandwiched between fiberglass screens with Plexiglas frames. Electrical contact to each electrode was made by a 9-cm² platinum mesh electrode wired as above and inserted between the fiberglass screens in physical contact with the carbon fiber. Resistances on the order of 5 ohms were measured across various positions on each electrode when dry suggesting that fiber–fiber contact provided conductivity throughout the electrode. For both electrode types initial placement of the anode (sediment embedded electrode) disrupted the interface–homogenizing local sediment and collapsing the voltage gradient. Monitoring the open circuit potential between the electrodes (i.e., when the external circuit resistance was greater than 1×10^6 Ohm so that no appreciable current was observed) showed partial reestablishment of the voltage difference to approximately 0.3 V to 0.4 V (anode negative voltage with respect to cathode) within minutes after anode placement, and complete reestablishment of the voltage gradient to approximately 0.7 V on the order of 1–2 days. Once the voltage gradient stabilized, current flow through an external circuit was initiated by connecting the two planar electrodes through a variable load causing a reduction in the voltage difference.

Voltage and current sustained by the two-electrode devices under variable loads were monitored for experimental periods ranging from minutes to months using a data-logging, high-impedance multimeter (HP 34970A) or a high input impedance multimeter (Keithley 916) as an ammeter and potentiostat (PAR 263 A) as a voltmeter. Finally, the sediments were electrochemically characterized by profiling (adjacent to the devices) with Pt-redox (Microelectrodes Inc.), voltammetric (*10*) (yielding O_2 data), and pH (*11*) microelectrodes (the Rartian Bay sediment only) and sampled with 7.5 cm diameter core tubes. The cores were sectioned into vertical intervals of 0.25–0.5 cm under N_2, and pore waters were extracted by centrifugation. Analytical methods applied to separated and then filtered pore water samples included
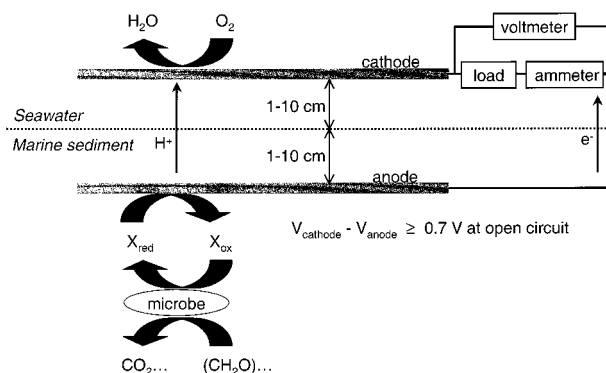
FIGURE 1. Schematic of experimental setup showing coplanar electrodes straddling marine sediment−seawater interface. Due to distinct differences in chemical composition of the seawater and sediment established by microbial decomposition of organic matter, an open circuit voltage of approximately 0.7 V is observed between the electrodes. The working model (described in text) for observed power generation involves net oxidation of sediment organic matter by dissolved seawater oxygen, catalyzed by sediment microbes and mediated by one or more secondary electron-transfer mediator (X). Separation of reactants, necessary to isolate electrode half reactions and allow flow of electrons through the external circuit, is maintained by microbial oxygen depletion in the top layer of sediment.

spectrophotometric determinations of total dissolved sulfide, ammonium, nitrate, and phosphate (12), ICP-mass spectrometric analysis of total dissolved iron and manganese (predominantly Fe^{2+} and Mn^{2+}) (13), and flow injection analysis of total dissolved CO_2 (14).

Results and Discussion

Depth-dependent chemical characterization of the laboratory maintained sediments is shown in Figure 2. As expected, oxygen depletion was observed within the top 1−2 mm of both sediment types owing to the high energy of oxic microbial respiration (1). Also evident was utilization of less energetic oxidants by microbes lacking access to oxygen deeper in the sediment. In the salt-marsh sediment (Figure 2A), nitrate (not shown) and manganese and iron oxides were reduced within the top 5 mm of sediment. Deeper down, sulfate reduction was dominant, yielding high concentrations of dissolved sulfide, ammonium, total-CO_2, and phosphate. In the estuarine sediment (Figure 2B) a broader region of iron reduction was observed in association with a pH minimum, and little sulfide accumulated in the pore waters due to rapid rates of iron sulfide precipitation (15). Potential (E)-depth profiles of the sediments examined here show increasing negative voltage with increasing depth below the oxic zone (3) resulting in voltage reductions of approximately 0.7 V within the top 4 cm of the sediment−seawater interface.

Figure 3 illustrates the observed short-term dependency of voltage and power density (product of voltage and current density) vs current density for two of the first devices examined by measurement of short-term, steady-state current and voltage following stepwise reduction of external circuit resistance. Both devices consisted of a platinum mesh anode and cathode with one examined in salt-marsh sediment (Figure 3A), the other in the estuarine sediment (Figure 3B). Figure 3 illustrates at least three important points. First, it shows a current can be sustained by the device without complete collapse of the voltage gradient. Second, the voltage vs current density dependencies of both devices are similar in form regardless of differences in sediment composition. (However, the similarity in amount of power obtained by the two sediment types examined here may be coincidental in light of our ongoing examinations of power harvesting from
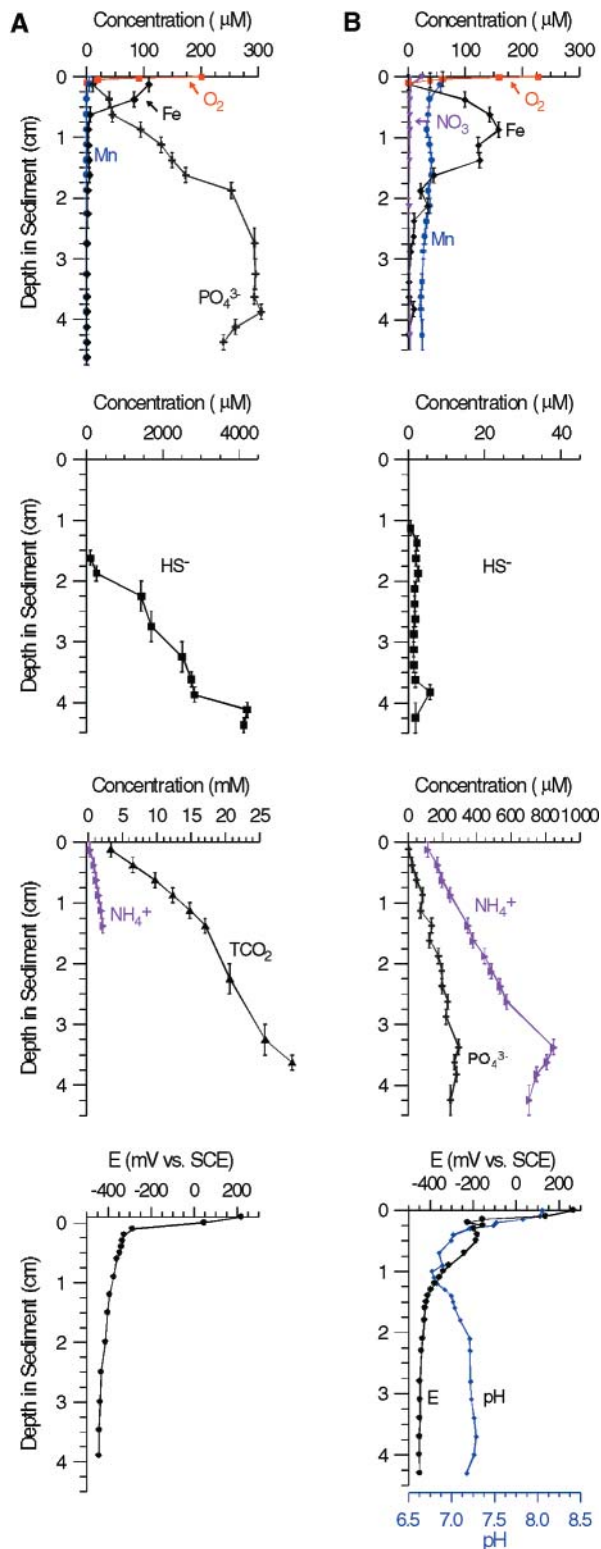
FIGURE 2. Chemical and voltage vs depth characterization of (A) a salt-marsh sediment and (B) estuarine sediment used in this study. Vertical bars indicate the thickness of sections separated for pore water extraction. Ammonium concentrations in samples from > 1.5 cm depth from the salt-marsh core are not reported because they exceeded the maximum standard prepared for the analyses (2.4 mM). SCE refers to a standard calomel electrode.

other sediment types.) Third, both dependencies are fuel cell-like in form (16). Interpretation of the voltage vs current density dependencies considering the devices as fuel cells suggests power is limited at low current densities (<0.1 μA
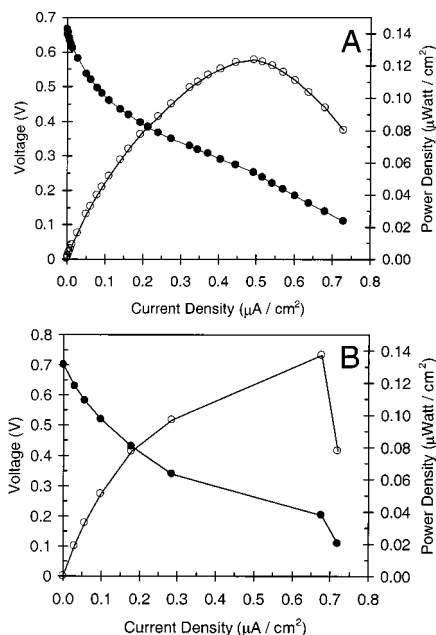
FIGURE 3. Short-term steady-state voltage (●) and power density (○) vs current density dependencies for platinum mesh devices in (A) the salt-marsh sediment and (B) the estuarine sediment characterized in Figure 2. Current and voltage values were taken from when the change in voltage was less than 2 mV in 100 s (A) or from readings 15 min after the external resistance was changed (B).
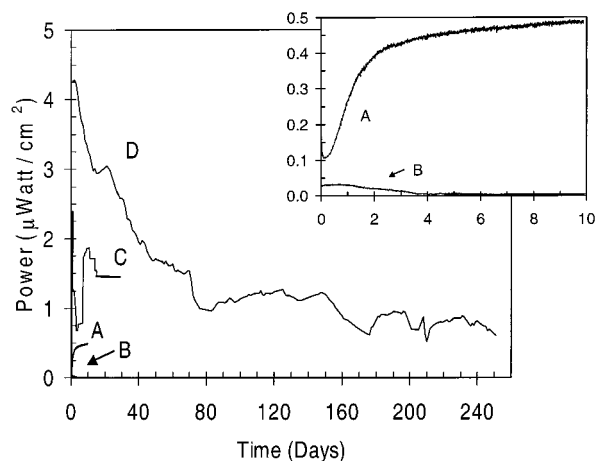

FIGURE 4. Power vs time for long-term discharges of various devices described in the text. Records A and B are enlarged in the inset to facilitate their comparison.

cm^{-2}) by kinetics of electrode reactions, at intermediate current densities (between 0.1 μA cm^{-2} and 0.5 μA cm^{-2}) by internal resistance (i.e., that of the sediment and seawater between the electrodes to ion flow), and at large current densities (>0.5 μA cm^{-2}) by mass transfer of electrode reactants and/or products. Mass transfer in the fine-grained, low-permeability sediments of the kind that surrounded the anodes in this study is most probably limited by molecular diffusion through interstitial waters (2). At lower temperatures, this limitation will therefore decrease cell performance to a greater extent.

Figure 4 illustrates measured power vs time for various devices discharged for prolonged periods of time. Curve A pertains to a 10-day discharge in estuarine sediment across a 50 000-Ohm external resistance for a device in which both the anode and cathode consisted of a single 20-cm^2 platinum mesh surface (characterized in Figure 3B). The experiment

represented by curve B was identical to that of curve A except the sediment was autoclaved with the device in place and with the chemical gradients established, so as to kill sediment microbes without eliminating the voltage gradient. When discharged, the voltage across the device in the autoclaved sediment collapsed rapidly, and significantly less current was observed (Figure 4B). Comparison of curve A and curve B suggests continued microbial activity is central to observed power generation because this activity sustains the voltage gradient. Curve C pertains to a 15-day discharge in salt-marsh sediment across a 5000-Ohm resistance for a device in which both the anode and cathode consisted of six 100-cm^2 platinum mesh electrodes pressed into physical contact. This device generated roughly 3-fold more power than that of a device in which both anode and cathode consisted of single platinum mesh electrodes (characterized in Figure 3A). The dip and rise in power that occurred within the first 2 days of discharge is nearly always observed with platinum electrodes and is speculated to result from the onset of increased microbial activity due to anode regeneration of microbial oxidant(s) (described below). Still greater power generation is represented by curve D, which pertains to the first 250 days of an ongoing discharge across a 300-Ohm external resistance in which both the anode and cathode consisted of graphite fibers pressed between two sheets of fiberglass mesh (area = 100 cm^2) in salt-marsh sediment. The discontinuity between days 10 and 14 and the subsequent rise in power is a measurement artifact due to temporary removal of the ammeter from the external circuit. The abrupt drop in power beginning on day 71 resulted from a change in temperature from 21.2 °C to 16.7 °C. Given concentrations of candidate anode reactants (i.e., microbe-generated reductants) in these sediments (Figure 2) and the magnitudes and duration of the observed currents, we suspect that reoxidation of these species is not the ultimate source of power. We speculate that net oxidation of sediment organic matter, which was present at concentrations of approximately 0.5 M reduced carbon per liter of wet sediment in the salt-marsh sediment (or ~5−6% dry weight) (11), is the source of power. The organic carbon content of the estuarine sediment was 3−3.5% dry weight, which is very typical for fine-grained sediments in coastal and continental margin environments (17).

Based on power generation characteristics illustrated by Figures 3 and 4 and drawing from microbial fuel cell literature (5, 6) and seawater battery literature (7, 8), we model the system as follows (Figure 1). At the anode (sediment embedded electrode) oxidation of a microbe-produced reductant (represented as $X_{red} \rightarrow X_{ox}$) occurs, stimulating reuse by microbes (i.e., species X is an electron-transfer mediator) and promoting additional oxidation of sediment organic matter. In the salt-marsh sediments, the anode reaction may be ($HS^- \rightarrow S_{(s)} + H^+ + 2e^-$) or ($HS^- + 4H_2O \rightarrow SO_4^{-2} + 9H^+ + 8e^-$), whereas in the estuarine sediments the anode reaction may be ($2Fe^{2+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 2e^-$). Multiple chemical species including humic compounds may also participate in electron transfer (18). At the seawater immersed electrode (cathode) oxygen reduction (i.e., $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ or $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) (7, 8) occurs. Following Froelich et al. (1) and Berner (2) the net reaction is oxidation of sediment organic matter by dissolved oxygen ($CH_2O + O_2 \rightarrow CO_2 + H_2O$) catalyzed by sediment-dwelling anaerobes and mediated by the intermediate oxidants reduced in anaerobic respiratory reactions. Separation of organic matter and oxygen necessary to channel electrons through an external circuit is maintained by microbial oxygen depletion within the oxic layer between the anode and cathode. Although still conjectural, this model is intriguing because it suggests large regions of the ocean floor may be utilized for energy harvesting requiring only placement of optimized

electrodes. The viability of dissolved seawater oxygen as an oxidant for power generation has been established by the use of seawater batteries with cathode energy densities on the order of 0.5 W m^{-2} in oxic seawater (*7*). Since sediments on continental margins (<1000 m deep) are typically 2−3% by dry-weight organic carbon, and since typical fluxes of reduced carbon to the sea floor of continental margins due to sedimentation are on the order of 2−10 mol C m^{-2} y^{-1} (*17, 19*), this supply of organic fuel could provide on the order of 0.1 amps m^{-2} × 0.5 V ≈ 0.05 W m^{-2} constantly. Many oceanographic instruments have power requirements on the order of 0.1 W and only periodic operation requirements. If anodic current densities can be increased, it is conceivable that meter-dimensioned devices based on the phenomenon described here could provide near-perpetual worthwhile power. Our ongoing investigations are focused on identifying the electrode reactions, understanding microbial aspects, optimizing electrodes with respect to power density, and examining prototype devices interfaced with environmental sensors in natural marine settings to correlate oceanographic parameters such as water velocity, dissolved oxygen, salinity, and temperature with power generation.

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