OXYGEN REDUCTION KINETICS ON GRAPHITE CATHODES IN SEDIMENT

MICROBIAL FUEL CELLS

ELECTRONIC SUPPLEMENTARY INFORMATION

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MATERIALS AND METHODS

Laboratory-scale sediment microbial fuel cells

River sediment and water were collected from the South Fork Palouse River, at Pullman, Washington, USA (46° 43′ 48″ N / 117° 10′ 25″ W), and Pacific Ocean sediment and water were collected 15 yards offshore near Agate Beach at Newport, Oregon, USA (44° 39′ 31″ N / 124° 3′ 45″ W). The sediments were homogenized and used to fill 24 cm tall, 23 cm diameter (10 L) cylindrical plastic containers to a depth of 10 cm. Each container was then filled to within 3 cm from the top with water from its respective site. The containers were impermeable to light, except for small openings in the top for electrode wires and tubing. During normal operation, Aqua Culture MK-1504 air pumps were used to supply air at an approximate rate of 80 L/hr to an aquarium bubble stone in each SMFC. Two temperature controllers (Isotemp Refrigerated Circulator Model 910, Fisher Scientific, Pittsburgh, PA, USA) were used to manipulate the SMFC temperatures via 15.9 mm diameter coiled vinyl heat exchange tubing that was submerged under the sediments. Type I purified 18.3 MΩ·cm water (NANOpure Infinity, Thermo Scientific Barnstead, Dubuque, IA, USA) was added as needed to replace water that was lost through evaporation. The pH was 8.4 (0.1 standard deviation) for the river SMFCs, and 7.7 (0.2 standard deviation) for the ocean SMFCs.

Each cathode was submerged vertically to 4 cm below the air-liquid interface and 4 cm above the sediment. Initially, ocean sediment SMFC OCP values were recorded manually using a digital multimeter (Fluke 87V True RMS Industrial model, Fluke Corporation, Everett, WA, USA), but after 13 days an automated data acquisition unit (HP 34970A, Hewlett-Packard Company, Palo Alto, CA, USA) was used to record OCP automatically. Sub-sediment graphite anodes, identical in construction to the cathodes, were installed in all SMFCs for use in a later study.

Multi-channel potentiostat system

Because of the number of experiments and repetitions, a custom-made multi-channel potentiostat system (Figure S1) was made for polarizing the cathodes. This system is comprised of six independent three-electrode potentiostat channels and is controlled through a USB connection by a laptop computer. All of the potentiostat channels can be operated simultaneously, and each is individually controlled by a separate user-generated script file, allowing for the automated time-dependent polarization and current monitoring of six electrodes. The primary components of the multi-potentiostat system are the controlling computer, a digital to analog converter (DAC), six potentiostat boards, power supplies, and an analog to digital converter (ADC). During operation, the computer sends a signal to the DAC (16-channel 16-bit NI 9264, National Instruments, Austin, TX, USA), which controls the bias potential on each potentiostat board up to ±2 V (with an error of ±0.1 mV). The potentiostats (Model 1402, Custom Sensor Solutions, Inc., Oro Valley, AZ, USA) are low-cost circuits that are able to read from 1 nA to 5 mA of current, and were modified to fit our application: 1) the boards were changed from static to dynamic potentiostats by allowing for the potential bias to be derived from an external source, the DAC; 2) the active filter was altered to a 1 ms time constant; and 3) the last stage gain was changed to allow for a full 5 V span on the output. Each potentiostat has a reference, a counter, and a working terminal, which are connected by shielded coax cables. There are two power supplies (Model 1401, Custom Sensor Solutions, Inc., Oro Valley, AZ, USA), each providing power to three potentiostats. The output potential on each potentiostat, corresponding to the current flowing between the counter and working electrodes, is sent to the ADC (32-channel 16-bit NI 9205, National Instruments, Austin, TX, USA). The current data are then sent to the computer and recorded. A four-slot CompactDAQ USB chassis (cDAQ-9174, National Instruments, Austin, TX, USA) houses and supplies power for both converters, and provides the USB connection interface between the computer and the multi-potentiostat system. Molex connectors (Molex, Lisle, IL, USA) and 18 gauge stranded wire connect the potentiostats, power supplies, and converters. The system is operated using custom LabVIEW 8.5 software (National Instruments, Austin, TX, USA), allowing the user to control the potentials, the gain, and the sample rate. The gain control determines the potentiostat current magnitude range: <500 nA, <5 μA, <50 μA, <500 μA, or <5 mA. Six user-generated script files are used for temporal control of the potential for each potentiostat, and six data files are generated to record the current readings. The software and a complete construction manual are available upon request. For this study, the gain was set for a current magnitude of <5 mA. At this setting, the average instrument noise was ±0.5 μA, with 90% of the noise less than ±1 μA. The

potentiostat was calibrated and gave identical results to a Reference 600 Potentiostat (Gamry Instruments, Warminster, PA, USA).
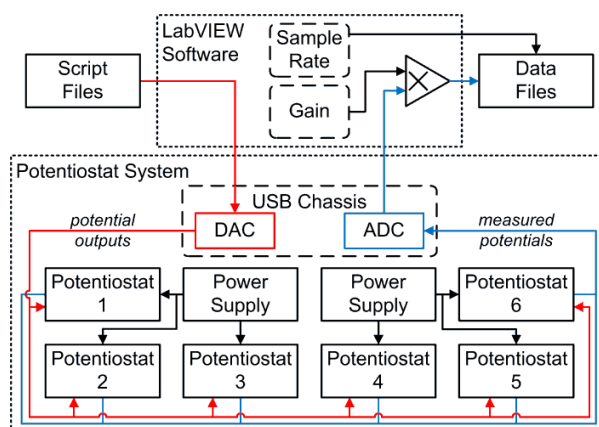

Figure S1. Diagram of the multi-potentiostat system. User-generated script files define how potential changes with time are read by the LabVIEW software and sent in real time to the digital to analogue converter (DAC), which controls the potentials of all six potentiostats. A potential proportional to the current between the working and counter electrodes of each potentiostat is sent to the analogue to digital converter (ADC) and to the LabVIEW software, where the potential is converted to a current reading and saved in a data file.

Polarization experiments

The polarization potentials began at +745 mV$_{SHE}$, a value that was more oxidizing than the cathode steady state OCP, and ended at -255 mV$_{SHE}$, a value that was more reducing than the cathode steady state OCP. Data were collected at every 100 mV interval.

Temperatures were maintained using the two temperature controllers connected to the heat exchange coils. A period of 12 hours was provided after each temperature change to allow for the SMFCs to reach steady temperatures before polarization began. All temperature measurements were performed using a thermocouple (Traceable Ultra 4339, Control Company, Friendswood, TX, USA). Because of the unequal effectiveness of the heat transfer coils in each SMFC at attaining the temperature set point, measurements were taken independently for each SMFC to ensure accurate temperature reporting. During the temperature-dependence polarization experiments, the oxygen concentration in the water was kept at saturation by bubbling air and was confirmed using a DO meter (Oakton DO 110 Series, Eutech Instruments, Singapore). The DO meter accounted for local atmospheric pressure, water temperature, and water salinity during measurements.

A period of 12 hours was provided between gas changes to allow for the SMFCs to reach a steady DO concentration. Two different oxygen concentrations were tested at room temperature: saturated and low (≤57% saturated). The DO meter was used to determine the concentration, and the actual values are reported in Results and Discussion. Matlab (The MathWorks, Inc., Natick, MA, USA) was used for all data parsing and analysis.

RESULTS AND DISCUSSION

Table S1. The acclimatization methods used in a selection of research papers that utilized cathodes of various materials in SMFCs or setups similar to SMFCs. Papers are alphabetized per year.

| Paper	Initial acclimatization	Cathode Type	Cathode Material
Donovan et al. 2011 [1]	open circuit	plate	graphite
Gong et al. 2011 [2]	open circuit (2 weeks in seawater), followed by the cell being held at ~0.4 V $_{Ag/AgCl}$	brush	carbon
Parot et al. 2011 [3]	polarized (-0.2 V$_{Ag/AgCl}$)	plate	stainless steel
An et al. 2010a [4]	open circuit	felt	graphite
An et al. 2010b [5]	closed circuit	felt	graphite
De Schamphelaire et al. 2010a [6]	open circuit and closed circuit were tested for both types of cathodes	felt / fibers	graphite / stainless steel
De Schamphelaire et al. 2010b, 2008 [7,8]	open circuit	mat	graphite
Hong et al. 2010 [9]	closed circuit	felt	graphite
Martins et al. 2010 [10]	closed circuit	paper	carbon
Saravanan et al. 2010 [11]	open circuit	plate	graphite
Song et al. 2010 [12]	closed circuit	plate	graphite
Xu et al. 2010 [13]	open circuit	plate	graphite
Yuan et al. 2010 [14]	closed circuit	cloth assembly	Pt/C catalyst over Ni conductive paint on cloth
Hong et al. 2009 [15]	closed circuit	felt	graphite coated with Pt
Nielsen et al. 2009 [16]	cell held at 0.4 V $_{Ag/AgCl}$	fibers	carbon
Donovan et al. 2008 [17]	open circuit	wires	stainless steel
Dumas et al. 2008 [18]	closed circuit (attached to sacrificial zinc anode)	plate	stainless steel
Faimali et al. 2008 [19]	polarized (-0.2 V$_{Ag/AgCl}$ and other potentials)	plate	stainless steel
Hong et al. 2008 [20]	open circuit / open circuit	plate / felt	graphite / graphite
Liu et al. 2008 [21]	closed circuit	rods	graphite
Dumas et al. 2007 [22]	closed circuit / closed circuit	plate / plate	stainless steal / stainless steal
He et al. 2007 [23]	closed circuit	foam	carbon coated with Pt
Nielsen et al. 2007 [24]	open circuit / cell held at 0.4 V $_{Ag/AgCl}$	brush / brush	carbon / carbon
Rezaei et al. 2007 [25]	closed circuit	paper	carbon coated with Pt
Reimers et al. 2006 [26]	cell held at 0.6 V $_{Ag/AgCl}$ / open circuit	brush / rod	carbon / graphite
Bergel et al. 2005 [27]	polarized (-0.1 to -0.4 V$_{SHE}$)	plate	stainless steel
Tender et al. 2002 [28]	closed circuit	plate	graphite
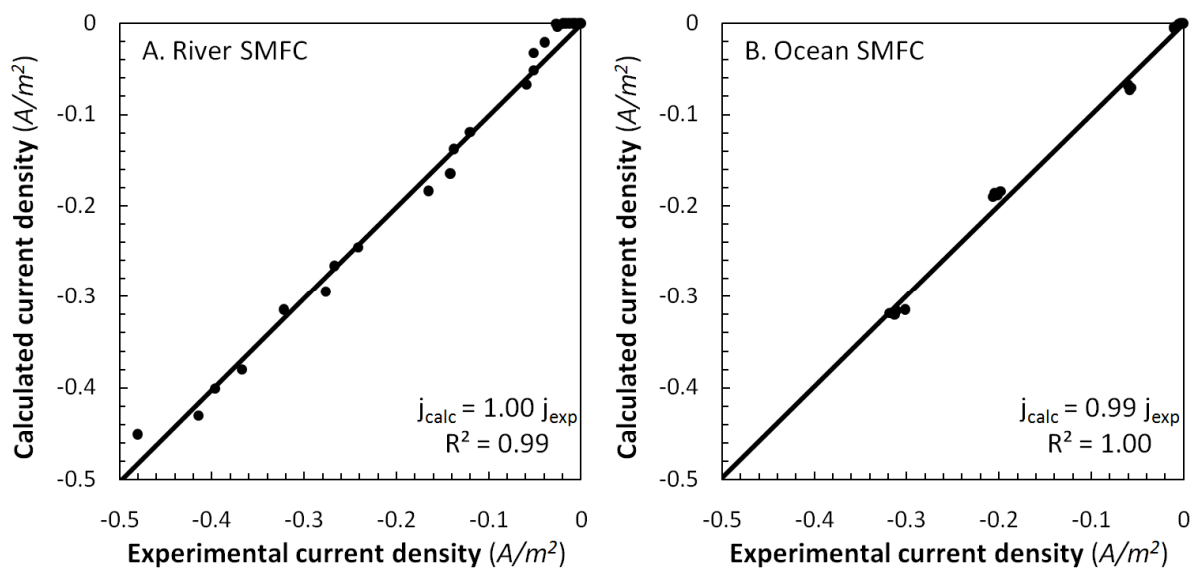
Figure S2. Plots comparing calculated current density with experimental current density for both the A) river and B) ocean SMFCs. The black line represents a linear fit, and the line equation and coefficient of determination (R^2) are shown.

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