



Harvesting energy from the marine sediment–water interface III. Kinetic activity of quinone- and antimony-based anode materials

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ABSTRACT

Benthic microbial fuel cells (BMFCs) consist of an anode imbedded in marine sediment, connected by an external circuit to a cathode in overlying water. Long-term power density of BMFCs is limited by mass transport of the anode reactants, the transport being attributed to natural processes, including diffusion, convection, and tidal pumping. In order to increase short-term power density of BMFCs and long-term power density of a more recently reported BMFC, which artificially augments mass transport of the anode reactants, new anode materials are reported here with faster kinetics for microbial reduction as compared to commonly used G10 graphite. Results indicate that the kinetic activities (KAs) of glassy carbon graphite with surface-confined anthraquinone-1,6-disulfonic acid (AQDS), graphite paste with an incorporated Sb(V) complex, and oxidized graphite, and oxidized graphite subsequently modified with AQDS is 1.9–218 times greater than the KA of plain G10 graphite.

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1. Introduction

Recent development of benthic microbial fuels (BMFCs) has demonstrated that they can generate useful power in remote environments [1–6]. This BMFC consists of a graphite plate anode (typically G10 graphite), embedded in marine sediment, and connected by an external circuit to a graphite plate cathode (also typically G10) or a graphite fiber bottle brush cathode, positioned in overlying water. It generates power by oxidizing sediment organic matter and simultaneously reducing oxygen dissolved in the overlying water. Prototype BMFCs have been demonstrated in salt and fresh water environments, including multiple coastal sites (near Tuckerton, NJ, USA; Newport, OR, USA; Narragansett, RI, USA) [2,5] and a riverine site (Potomac River, near Washington, DC, USA) [6]. When equipped with G10 graphite plate anode(s), BMFCs generate a maximum power density in the range of 20–32 mW m⁻² (anode geometric surface area) [6], at a cell voltage of ca. 0.35 V, depending on the site [2]. Current density is limited by mass transport of the anode reactants (organic matter) in sediment, the mass transport being as a result of natural processes, such as diffusion,

convection, sediment re-suspension, and tidal pumping. Voltage is limited by the natural redox gradient spanning the benthic interface between organic-rich sediment and oxygen-rich water. This benthic interface isolates the two half-cells of the BMFC. The redox gradient results from aerobic activity at the sediment top layer, being a common feature of the benthic interface of the continental margins, including bays and estuaries, and manifests as an open circuit voltage of ca. 0.75 V. The low voltage output of the BMFC can be converted to higher voltage, and used for the long-term powering of marine instrumentations, such as meteorological buoy [6].

In principle, the power density produced by a BMFC can be increased via raising the open circuit cell voltage [7] and/or the current density of the anode. The open circuit cell voltage is determined by the redox gradient, and can only be changed by replacing the inert anode with a sacrificial anode, such as aluminum [8–10], magnesium [11–14], aluminium–magnesium alloy [15], or manganese, the latter delivering a maximum potential of –1.38 V vs. Ag/AgCl, 3 M KCl reference electrode (henceforth abbreviated as Ag(RE)) [16]. Use of sacrificial anodes eliminates, however, the main advantage of BMFCs: their long-term operation without depletion.

Given the constraint on the open circuit cell voltage, the short-term power density of BMFCs (i.e., before depletion of anode reactants occurs) can be increased by improving the anode kinetics.

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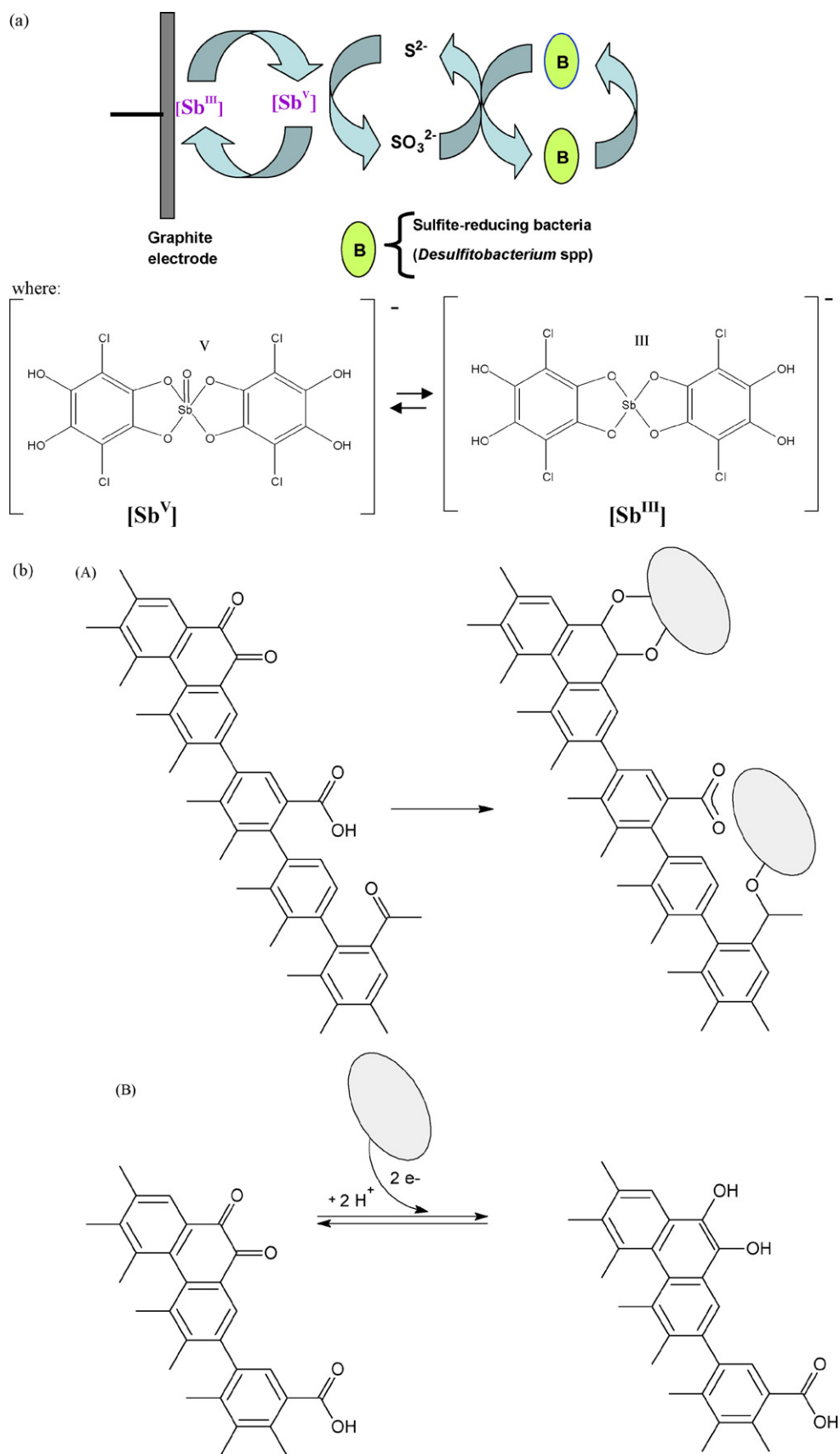


Fig. 1. (a) Schematic mechanism of the sulfide-mediated bacterial oxidation of *Desulfitobacterium* spp., with sulfide re-oxidation shuttled by Sb(V) complex (not drawn on scale). (b) Expected mechanism of adsorption (A) and mediated microbe oxidation (B) at the surface of electrochemically oxidized graphite. Shown are the oxygen-containing functional groups at the surface of oxidized graphite (*ortho*-quinone, carboxylic, and carbonyl groups). Circles correspond to the microbes colonizing the surface (not drawn on scale).

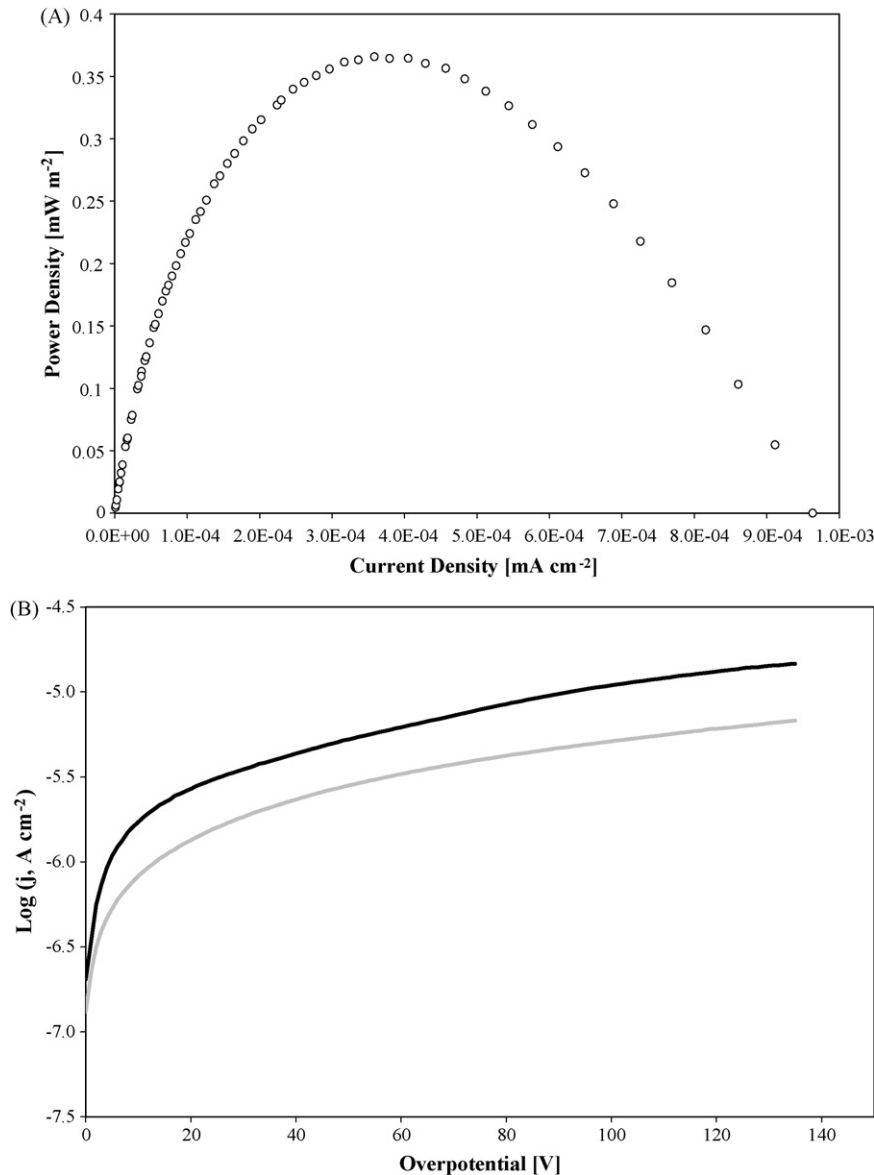


Fig. 2. (A) Power curve recorded with graphite rod (PGR) electrode modified with a thin film of Sb(V) complex. (B) Tafel plots recorded in a fuel cell equipped with carbon paste anode, which contains Sb(V) complex (black line) relative to a carbon paste electrode with no added antimony complex (grey line). Overpotential range: 0–140 mV vs. OCP, scan rate: 0.1 mV s⁻¹; reference electrode: Ag/AgCl, 3 M KCl.

Furthermore, long-term power density of a recently described BMFC variant [17] that uses a pump to accelerate mass transfer of the anode reactants may also benefit from improved anode kinetics. In another approach, pumping of the anodic half-cell produced power densities greater by a factor of 5–10 as compared to the still standing system [18].

Strategies for increasing current density in the absence of mass transfer limitations rely on (i) enlarging the specific surface of the anode and/or (ii) improving the electrocatalytic activity of the anode. Owing to the microbial nature of the anode reactions [3], we have employed strategies that take advantage of microbial reduction catalysts. Previously we reported the use of graphite anodes modified with anthraquinone-1,6-disulfonic acid (AQDS), 1,4-naphthoquinone, and microcrystalline magnetite [3]. Results indicated that 1.5–2.1 times greater power densities could be attained with modified electrode materials relative to plain graphite. In this paper we evaluate the use as the anode material of graphite modified with a sulfide-oxidizing Sb(V) complex, able

to shuttle electrons between microbes and the graphite electrode [19]. We also investigate the utilization of oxidized graphite, rich in quinone-like and carboxylic groups, which facilitate microbial oxidation, and we examine the performance as anode material of oxidized graphite subsequently modified with AQDS. These results indicate a significant improvement in power production as compared to unmodified G10 graphite.

2. Experimental/materials and methods

2.1. Anode preparation

2.1.1. Oxidized graphite anodes

Graphite plates (2.54 cm × 7.62 cm, 1.27-cm thick, LG grade 10, Graphite Engineering and Sales, Greenville, MI, USA) were cleaned with aluminum oxide (240J) sandpaper, washed with de-ionized water (DIW), and dried in the oven at 120 °C. Then, they were electrochemically oxidized according to the methodology elaborated

by Bélanger and coworkers [20], via bulk electrolysis with coulometry, at +1.85 V vs. Ag(RE), in an aqueous supporting electrolyte, containing 20 wt.% of H₂SO₄. Optimum values of charge for graphite oxidation were in the range of 70–115 C cm⁻². Upon passing more charge through the electrode, the graphite plate may become brittle.

Alternatively, cleaned glassy carbon (GC) electrodes (Bioanalytical Systems, Inc., IN, BAS) were oxidized according to the same procedure (GC does not become brittle). Formation of surface confined quinone/hydroquinone groups was monitored by cyclic voltammetry (CV), which evidenced the growth of a peak pair centered around +0.35 V vs. Ag(RE) [20].

2.1.2. Oxidized graphite anodes modified with AQDS

Graphite plates oxidized as described above were modified with AQDS by immersion in 20 mmol L⁻¹ AQDS (>97% purity, Fluka Chemika, Buchs, Switzerland, used as received) in DIW (18.2 MΩ cm, Milli-Q® Synthesis System, Milipore) for 48 h, at room temperature. These electrodes were then rinsed with copious amounts of DIW. Electrical connections to each electrode were made by means of water insulating oceanographic bulk head connectors and matching 18-AWG cables (Impulse Enterprise, San Diego, CA, USA) [2].

2.1.3. Anodes modified with Sb(V) complex [Sb^VO(CHL)₂]Hex

An efficient sulfide oxidizing Sb(V) complex, hexadecylpyridinium bis(chlorinato) Sb(V), abbreviated as [Sb^VO(CHL)₂]Hex, was prepared according to the procedure reported by Karayannis and coworkers [19] (see structure in Fig. 1a). Purity of the synthesized compound and its sulfide-oxidizing ability were demonstrated by CV [19]. Complex adsorbed on the surface of a GC electrode was scanned in the range from -0.6 to +0.1 V vs. Ag(RE), at the sweep rate of 0.100 V s⁻¹. One peak pair was detected, at the formal potential $E^0 = -0.17$ V vs. Ag(RE), which corresponds to the oxidation-reduction of the antimony metal center [19].

Spectroscopically pure graphite rods (PGR) were cleaned according to Gorton and coworkers [21], then modified by applying onto their circular end 1.5 mM solution of [Sb^VO(CHL)₂]Hex in acetone, and evaporating the acetone at ambient temperature, for 15 min. After rinsing the surface repeatedly with DIW, the side of each graphite rod was insulated by wrapping it in Parafilm "M"® (American Can Co., Greenwich, CT), such that only the rod's end was exposed to the sediment. Anodes for control experiments consisted of plain graphite disc electrodes, lightly sanded and rinsed with DIW.

Alternatively, the same antimony complex was incorporated in a carbon paste electrode (BAS kit), and evaluated relative to an unmodified carbon paste electrode. Such electrodes were prepared by filling with carbon paste the hole of a Model MF-2010 Carbon paste electrode body (3.0-mm inner diameter, BAS). Electrical contact was made by means of the copper rod mounted in the center of the Teflon body of the electrode. Unmodified carbon paste for control experiments consisted of CPO carbon paste (CF-1010, BAS), i.e., paste of uniform graphite particles mixed with a paraffin binder (for use in aqueous media). Modified carbon paste was prepared by incorporating Sb(V) complex in the carbon paste; 1 part of Sb(V) complex and 10 parts of carbon paste were meticulously hand-mixed in a mortar with a pestle. After packing the modified or plain CPO carbon pastes into the electrode body, the surface was polished on a Watman® silicon treated filter paper (1 PS, Cat. No. 2200 125), while applying a slight manual pressure to the electrode body. In all setups plain graphite served as the counter electrode (cathode). Each electrode was connected to the electrochemical workstation via an alligator clip.

2.2. Electrochemical cells

As already reported, a benthic interface can be reassembled in the laboratory, using harvested sediment and seawater [3]. Sediment (collected with a clean shovel and clean PVC bucket) and seawater (collected with a clean Nalgene carboy) utilized here originated from the Rutgers University Marine Field Station, Tuckerton, NJ, USA (39°30.5'N, 74°19.6'W). This sediment was previously characterized and no attempt was made to preserve the redox gradient [2–4]. When using BAS electrodes, the anodes were positioned in ~180 mL of wet sediment (as collected), added to clean 250-mL beakers. Each beaker was then filled to ~230 mL with seawater, which unsettled some sediment. For the graphite plate electrodes (geometric surface area 19.4 cm²) we employed clean 2-L beakers; the anodes were positioned in ~1.7 L of wet sediment (as collected), each beaker being filled to ~1.9 L with seawater, which unsettled some sediment. Within hours, the sediment re-settled to the bottom of the beaker. A glassy carbon (BAS) or a plain graphite disk counter electrode and a Ag(RE) were then positioned in the overlying seawater; the open circuit voltage measured between the anode and counter electrode was typically 0.73 V. No procedures were employed for maintaining these cells, except for the periodic addition of DIW in order to compensate for losses by evaporation. When operated at room temperature, these cells can maintain an open circuit voltage of 0.675–0.750 V for at least 6 months.

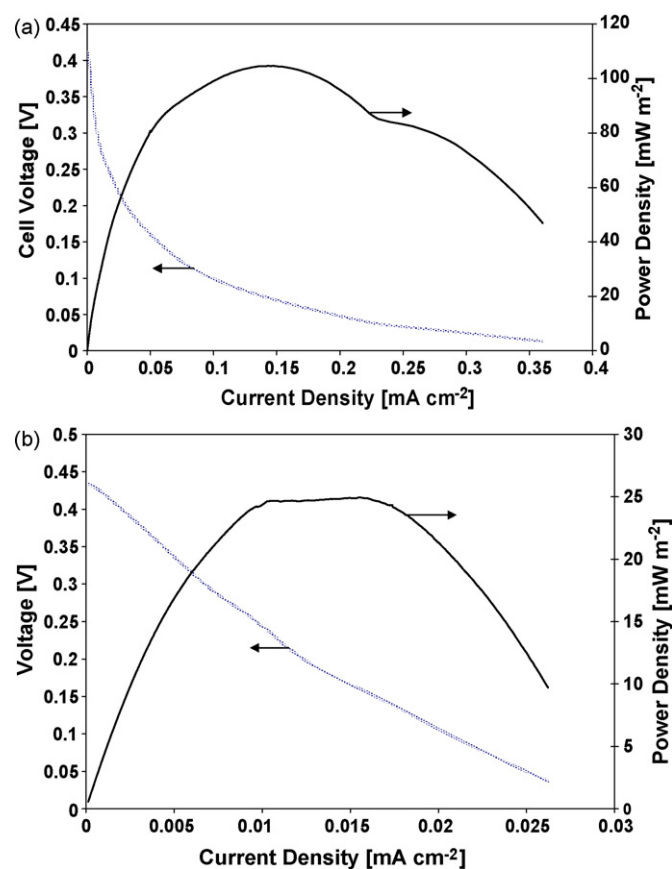


Fig. 3. Cell voltage and power density vs. current density (etc.) curves for a fuel cell operated with (a) Sb(V) complex-modified graphite paste anode and (b) plain graphite paste anode, respectively. Plots were recorded in two-electrode geometry with a plain graphite cathode, in sediment and seawater collected from Tuckerton, NJ, USA.

Table 1
Electrocatalytic activity of chemically modified graphite anodes relative to plain graphite (based on exchange current density and current density values at three overpotential values, obtained from Tafel plots)^a

Anode material	Anode potential ^a (mV vs. Ag/AgCl, sat. KCl)	Kinetic activity ^{a,b} (KA, relative units)
Plain GC ^c or graphite ^{c,d,e}	−411 ± 16	1.0
AQDS-modified GC ^c or plain graphite ^d	−403 ± 15	1.7
Sb(V) complex in graphite paste ^e or film on GC ^c	−224 ± 20	1.9
Oxidized GC ^c or graphite ^d	−350 ± 10	57.8
AQDS-modified oxidized GC ^c or graphite ^d	−350 ± 10	217.8

^a Mean values of 5–8 independent experimental runs.

^b Based on Tafel plots recorded in the overpotential range from 0 to 85 mV, and determined as the mean value of the ratios extracted at three overpotential values: $\eta = 60$, 70, and 80 mV.

^c Projected geometric surface area of the anode: 0.04 cm².

^d Projected geometric surface area of the anode: 23.2 cm².

^e Projected geometric surface area of the anode: 0.018 cm² (all experimental parameters are identical to b).

2.3. Electrochemical measurements

Electrochemical measurements were performed by means of a Model 660a Electrochemical Workstation (CH Instruments, Austin, TX). Multiple Tafel plots, i.e., $\log(\text{current density})$ vs. overpotential, were recorded in the three-electrode configuration, the potential of each anode (working electrode) being swept at the rate of 0.10–1.0 mV s^{−1}, in the overpotential range from $\eta = 0$ to 100–140 mV (in most cases), where $\eta = 0$ corresponds to the open circuit potential (OCP) of the anode vs. the reference electrode. At least 8 h were required for a stable OCP value being re-established between measurements.

Precaution was taken for rendering our methodology consistent, and making it suitable for a meaningful comparison of different electrodes. Therefore, Tafel plots acquired with modified electrodes were compared to Tafel plots obtained with controls, i.e., non-modified anodes, recorded in the same system. For both modified and control electrodes, current densities were extracted, and compared at three overpotential values: $\eta = 60$, 70, and 80 mV.

Discharge curves were obtained in two-electrode configuration, with the working electrode relative to the counter electrode, the latter being connected to both the counter and reference electrode entries of the potentiostat. Current was monitored at diminishing ohmic resistance of the external circuit, while the cell voltage decreased from its initial open circuit to the short-circuit value.

3. Results and discussion

Catalytic activity exhibited by the Sb(V) complex in the oxidation of sulfide was probed by CV (recorded in the potential range from −0.400 to +0.100 V vs. Ag(RE), at the scan rate of 50 mV s^{−1}) by adding accurately known amounts of aqueous 0.050 M Na₂S solution to the supporting electrolyte (0.100 M phosphate buffer, pH 6.5). Our results (not shown) reproduced those reported by Karayannis and coworkers [19]. In the presence of Sb(V) complex, the peak corresponding to sulfide oxidation showed up at a potential value more negative by ca. 300 mV as compared to sulfide oxidation in the absence of the complex.

Mechanism of the anticipated catalytic effect of [Sb^VO(CHL)₂]Hex complex in oxidizing sulfide is shown schematically in Fig. 1a. Sulfite-reducing bacteria (such as *Desulfitobacterium* spp.) may make use in their anaerobic respiration of SO₃^{2−} ions, converting them into sulfide. The latter is changed back to sulfite upon interacting with the oxidized form of the antimony complex [Sb^VO(CHL)₂]Hex, noted as [Sb^V], which, on its turn, is reduced to [Sb^{III}(CHL)₂]Hex, abbreviated as [Sb^{III}]. As sulfide is considered the main inorganic specie involved in the electron transfer (ET) proceeding at the anode [22,23], its fast regeneration is critical for efficient power production. Given the greater geometric surface

area of the carbon paste electrode, as compared to a glassy carbon disk of the same size, in control experiments we used an unmodified CPO carbon paste electrode. As the latter has a surface area comparable to the modified carbon paste, the recorded increase in KA can be attributed to the presence of the antimony complex, rather than to the increased surface area. Tabled data reveal that the open circuit electrode potential of Sb(V) complex modified anodes is lower than that of plain graphite; the greater kinetic ability of the antimony electrodes allows, however, for obtaining greater power densities.

Schematic mechanism by which oxidized graphite is likely to enhance the ET rate of microbial oxidation is shown in Fig. 1b. By increasing the surface density of oxygen-containing functional groups (*ortho*-quinone, carboxylic, and carbonyl groups) the graphite electrode enables for better adsorption of the microbes (Fig. 1b(A)), and thus for an easier ET with the electrode. Also, the *ortho*-quinone groups may efficiently mediate microbial oxidation (Fig. 1b(B)).

Antimony complex incorporated in thin film coatings on graphite rods (PGR) generated power curves of classical shape (shown in Fig. 2A). In our approach, Tafel plots were employed for the relative comparison of KAs. Such plots were recorded for each modified electrode and compared to plots obtained for an unmodified electrode of identical size and geometry, in the same system, under identical conditions, and recorded one after the other. As revealed by Fig. 2B, when using antimony complex incorporated in the anode the KA increased by a factor of 1.9 relative to plain graphite (this value being an average of the ratios extracted at three overpotential values: $\eta = 60$, 70, and 80 mV); such a rise can be termed as significant. Conclusions drawn from Tafel plots were validated by an alternative electrochemical technique, i.e., by discharge curves recorded in the two-electrode configuration. For carbon paste loaded with antimony complex (Fig. 3a) the maximum power density was ca. 4.2 times greater as compared to plain carbon paste (Fig. 3b). The activity of the carbon paste electrode with incorporated Sb(V) complex was unchanged over the time frame of our investigation (3 weeks). Therefore, one can assume that there was no measurable loss of the complex to the sediment and the aqueous solution, owing to the extremely low solubility of Sb(V) complex in water. This insolubility explains why the activity of antimony complex thin films did not decay over 2 months.

Hence, anodes modified with antimony complex show promise for power production in sulfur-rich sediments or sewer waters. Maximum power densities were ca. 250 times greater for a carbon paste electrode modified with antimony complex (Fig. 3a), as compared to surface films containing Sb(V) (Fig. 2A). An explanation may reside in a much lower packing of the thin films with Sb(V) complex, as compared to carbon paste electrodes. Also, since heterogeneous electrocatalysis is an interfacial phenomenon, which

shares many features of heterogeneous catalysis [24], the greater the contact surface area of the catalyst (the antimony complex) exposed to the substrate, the more efficient the electrocatalysis is.

As previously emphasized [3,25], there is a strong rationale for utilizing quinone-modified materials as the anode: (i) a number of microbes (other than *Geobacter*) secrete quinones, and use them as exogenous ET mediators in mineral respiration, and (ii) some microbes (including *Geobacter*) can utilize added quinones as exogenous ET mediators in mineral respiration. Grounds for choosing oxidized graphite as the anode material are that graphite surfaces naturally include quinone-like and carboxylic functional groups [20], and the surface density of these oxygen-containing functionalities can be increased significantly by electrochemical oxidation. In addition, the electrochemical pretreatment increases the specific area of the graphite and its ability to colonize microbial communities [25]. The greater specific surface area of electrodes enables for a better adsorption of various ET mediators, including quinones. Thus, power density can be increased by combining electrochemical oxidation with subsequent adsorption of quinones. As revealed by Table 1, the electrochemical pretreatment improves KA by a factor of 57.8, while the pretreatment combined with the adsorption of AQDS yields a very spectacular increase, by a factor of 217.8 (both determined relative to plain graphite). The enhanced ability of oxidized graphite to adsorb and retain AQDS, as compared to plain graphite, is shown by the relative increase of kinetic activities: KA (AQDS-modified oxidized graphite)/KA (oxidized graphite) = 3.8, while the ratio KA (AQDS-modified graphite)/KA (plain graphite) is of only 1.7.

4. Conclusions

As it is stable over extended time periods, the explored benthic microbial bio-fuel cell is a promising power source for many low-power marine-deployed instruments, including seismic detectors and monitoring devices. In order to increase the power density of such fuel cells, new electrode modification strategies have been explored, and an efficient technique for evaluating their kinetic activity reported. Anode materials treated with inorganic or organic charge transfer mediators, an antimony complex and anthraquinone-1,6-disulfonic acid, respectively, have proven kinetically advantageous over plain graphite. Quinone-modification of previously oxidized graphite electrodes yielded an increase of the kinetic activity by a factor of 218. When deployed in real marine or river environment, large size fuel cells equipped with such modi-

fied anodes will allow for determining their stability of operation and lifetimes.

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