INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 21847–21856

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Performance evaluation of activated carbon-based electrodes with novel power management system for long-term benthic microbial fuel cells

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ARTICLE INFO

Article history:
Available online 22 July 2014

Keywords:
Benthic microbial fuel cell (BMFC)
Activated carbon (AC)
Carbon fiber brush (CB)
Activate carbon nanofibers (ACNF)
Power management system (PMS)

ABSTRACT

Underwater benthic microbial fuel cell (BMFC) systems were studied as a long-term sustainable power source for low-energy aquatic instruments (e.g. sensors). Different electrode materials and a power management system (PMS) arrangement were investigated in the lab-scale BMFCs over 12 weeks. An activated carbon (AC) cathode without catalyst layer (CL) was examined as a low-cost cathode material, and the results showed that AC cathode with a diameter of 5 cm and 20% weight polytetrafluoroethylene (PTFE) was the most effective. Granular Activated Carbon (GAC) column was used as a cost-effective anode for biofilm growth. The efficiency and durability of GAC was compared with other anodes with high surface area (e.g. carbon fiber brush (CB) and activated carbon nanofibers (ACNF)). Although, CB and ACNF outperformed GAC, and could be used as the model anodes in underwater BMFCs, high mechanic strength and durability of GAC are advantageous for long-term operations in benthic applications. Evaluation of a caged BMFC system equipped with multiple pairs of AC cathode and GAC anode showed the peak power and current densities of 0.56 W/m^2 and 0.25 A/m^2 respectively. A PMS was developed and coupled with batch mode BMFC system, to boost the output voltage to 3.3 V necessary for the working load.

Introduction

Marine exploration is vital for understanding oceanic systems and behavior, with technologies focusing on underwater communication, monitoring, and remote sensing. These underwater devices are often used for long-term deployment, and require stable and lasting power supplies [1,2]. Currently, rechargeable batteries are used to power underwater sensors, but high costs associated with installation, diving, and replacement pose severe challenges for long-term underwater operation [1,3]. It is, therefore, critical to deploy a low-cost, robust power generation system for such purposes. Microbial fuel cell (MFC) systems fulfill these requirements using natural microorganisms and organic/inorganic nutrients

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http://dx.doi.org/10.1016/j.ijhydene.2014.06.095

Abbreviations

AC	activated carbon
ACNF	activated carbon nanofibers
BMFC	benthic microbial fuel cell
CB	carbon-fiber brush
CC	carbon cloth
COD	chemical oxygen demand
DC	direct current
η	efficiency
GAC	granular activated carbon
MFC	microbial fuel cell
OCP	open circuit potential
ORR	oxygen reduction reaction
PBS	Phosphate Buffer Saline
Pt	platinum
PMS	power management system
PMOS	P-type metal-oxide-semiconductor
PTFE	polytetrafluoroethylene
R_{ext}	external resistance
$R_{ext\text{-}w}$	working external resistance
SEM	scanning electron microscope
Vc	charge start voltage
V_d	discharge start voltage

contained in sediment and water to produce electrical current. In benthic MFCs (BMFCs), anaerobic microorganisms growing on anode degrade organic substrates in sediment and generate electrons which flow through an external circuit to reach the aerobic cathode placed in water [4,5]. The distinct advantages of BMFCs, in respect to conventional power supplies, are sustainable power production using natural resources, reduced costs, and elimination of dangerous and expensive deep-sea maintenance.

As such, MFCs have been extensively researched for wastewater treatment [6–8], nevertheless, BMFCs have only been investigated in last decade as a potential power supply for underwater devices [9–11]. Studies have indicated a promising prospect for BMFCs, but there are challenges for practical applications. For instance, the dynamic variability of underwater environment could change the power output of BMFCs. Bioturbation due to diverse aquatic organisms causes electrode passivation/fouling and affects the long-term stability of BMFCs. Although microbially mediated redox reactions establish a stable potential difference of 0.5–0.8 V [5,10,11], lab-scale BMFC systems have been able to only achieve power densities between 10 and 100 mW/m^2[11, 12], and the total power of MFCs deployed in field is still less than 100 mW. Numerous methods of improving power output for scale-up BMFC systems have been considered, such as revamping electrode configurations [12], utilizing novel electrode materials [13], and optimizing electronic systems [2,12].

One of the major problems in MFCs is low voltage generation (0.3–0.9 V) [9,10,14,15]. The physical structure of MFCs has been studied using various configurations involving multiple MFCs and/or electrodes [12,16,17]. For real world applications in underwater environments, distributed and multi-anode/cathode configurations were developed for improved robustness and power and current densities [18]. The multi-anode structure has several anodes sharing a single common cathode. This configuration increases durability by avoiding an impairment of the entire system, so that the effect of one anode malfunction would be negated by the remaining functional anodes and the system could continue to generate current.

The cathodes in BMFC systems float in overlying marine waters, and thus require the use of non-corrosive materials. Traditional MFCs used abiotic cathodes often consisting of costly metal catalyst (e.g. Pt) as the electron mediator for oxygen reduction reaction (ORR) [6,19]. Long-term stability of Pt-loaded cathodes is a critical problem for MFCs treating wastewater [6,13] and BMFCs in underwater environment [4,5,18] due to the cathode fouling, which experiences the catalytic activity loss over time. Such disadvantages can be overcome by using biofilm-based cathodes (termed as biocathodes) [20–23]. Biocathodes are economically viable, as they utilize the biofilm to promote electron transport process. Subsequently, biocathodes must have high surface area and conductivity [23]. Activated carbon (AC) cathode have been found to have comparable performance as Pt-coated cathodes in traditional MFCs treating organic wastes [20,21,24], but have not been tested in BMFCs. In fact, AC has high surface area for mass transfer and biofilm growth, and low cost of preparation which makes it a promising candidate for long-term BMFC application.

BMFC anodes must be resistant to corrosion and degradation as they are embedded in sediments and extreme environments. Mass transfer diffusion limitations and loss of available organic substrates (as the electron donors) over time deteriorate anode functioning [5].This necessitates the anodes to have high surface area for the growth of anaerobic electrogenic bacteria and have a durable structure to withstand bioturbation for long-term deployment [25]. Graphite, stainless steel, and carbon cloth have been examined as anodes [26–28]; however, these materials have problems with high cost, low robustness, fouling, or installation difficulties [4]. Granular activated carbon (GAC) possesses the key features of durability, high surface area, low cost, and easy implementation, and has been successfully used in MFCs treating wastewater [7]. In addition, two novel carbon-based materials have been studied for high biofilm growth and excellent electron transfer capacity. Carbon brush (CB), in which thousands of carbon fiber tips per square centimeter of brush are bonded on a core metal rod (e.g. titanium) to generate high surface area [29], can be easily emplaced in sediments for biofilm growth. Activated Carbon nanofiber (ACNF) is a good biofilm support substrate with high electron conductivity, and has been used in MFCs treating wastewater [8]. However, owing to the weak mechanical strength of ACNF, their application in BFMC systems has not yet been tested.

To utilize BMFCs as the source of long-term stable power supply for underwater devices, power management systems (PMS) must be employed to help convert and boost the fluctuating and insufficient loading to a stable applicable voltage output. Typically, DC–DC converters were used to boost the voltage output [10,11,16,17,30,31], and a capacitor was placed before the converter for energy storage [12,17]. However, these

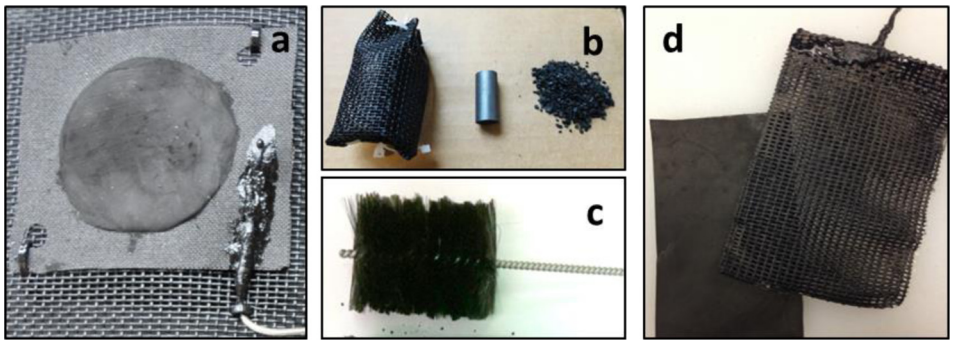

Fig. 1 – Electrode materials employed in the BMFC systems. (a) Activated Carbon (AC) Cathode; (b) Granular Activated Carbon (GAC) anode; (c) Carbon Brush (CB) anode; (d) Activated Carbon Nanofibers (ACNF) anode.

circuits were not always successful, since the PMS itself consumed power and the MFC voltage was only high enough to charge the capacitor but not to operate the converter. To address this problem, a charge pump that a required low input voltage (0.3 V) was implemented to boost the voltage high enough to transfer energy to the converter [16]. Furthermore, most PMS systems developed insofar were neither self-charging nor tested with BMFC systems [12,14,15].

For real world application, BMFCs are required to be durable and cost effective for maintaining long-term stability and robustness under adverse conditions. This necessitates more effort to optimize reactor configuration, enhance electrode materials, and integrate with PMS [32,33].The objective of this study was to develop cost-effective cathode and PMS for long-term stable operation of BMFCs. First, the performance of AC cathodes with different sizes and polymer hydrophobic binder loadings were compared in batch-mode BMFC systems. Second, GAC, CB, and ACNF were compared as the anodes materials in batch-mode BMFCs in terms of power generation and durability for long-term benthic operations. Third, novel Caged BMFC system was developed and tested by integrating multiple pairs of AC cathodes and GAC anodes for high stability and robustness. Fourth, a PMS with low power requirement was constructed and coupled with BMFCs. The stability of BMFCs with multi-anodes was examined by deliberately decoupling multiple electrode arrays to simulate bioturbation in underwater environment.

Materials and methods

Cathode materials

Activate carbon (AC) cathodes was prepared by thoroughly mixing 10 g of AC and 3.35 g of 60% wt. polytetrafluoroethylene (PTFE), and homogenized for the even distribution of PTFE [24]. PTFE has been widely used as a binding matrix and as well to increase the durability of cathodes in single chamber MFCs [13,21]. Using a hydraulic press and round punch die set, the AC mixture was compressed at 14 kPa (2 psi) onto 30% Teflon coated carbon cloth (CC), resulting in an AC cathode. The AC cathode was then heated for 1 h at 200 °C to ensure the AC mixture stayed intact on the CC and has the best performances [24].After being cooled, the AC cathodes were connected to the insulated standard electrical copper wires using conductive epoxy and electrical tape glue, as shown in Fig. 1a.

Two sizes of AC cathodes (Diameters: 2.5 cm and 5.0 cm) were examined in the batch-mode BMFC systems (volume: 500 mL) (Fig. 2a). Carbon cloth (CC, non-wet proofed, Fuel Cell Earth; geometric area: 16 cm^2) was used as the anode material.

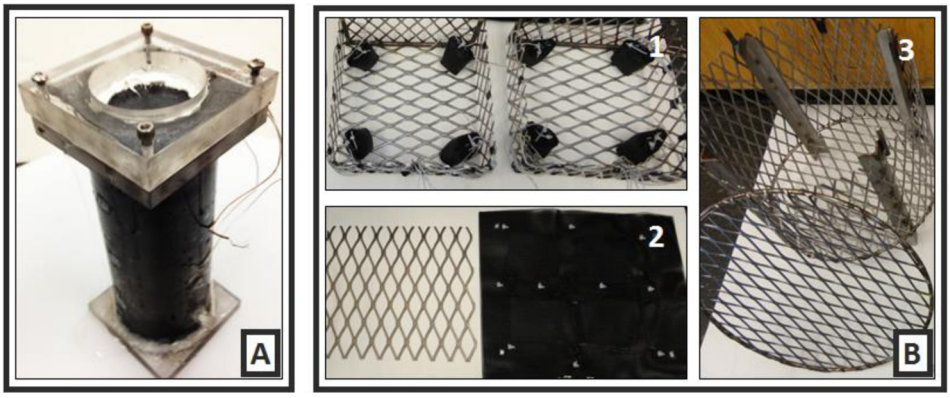

Fig. 2 – BMFC Systems: (A) Batch BMFC for activated carbon (AC) cathode and carbon-anode tests; (B) Caged BMFC system setup and components-(1) Two layers of GAC anodes, where four anodes are placed in the corners of each box; (2) Four activated carbon (AC) cathode mesh and support base; (3) Exterior cage with four protruding rods and cover.

The loading of AC [0.12 mg/cm^2] on the cathode surface was kept the same for the two sizes of AC cathodes by mixing AC and PTFE in the proportional to the cathode area. Contrary to previous MFC studies, where PTFE solution was used as hydrophobic coating on cathodes to prevent water evaporation [15], it was used to bind AC onto the CC in this study and create a defined three phase interface. Two weight percentages (% wt.) of PTFE, 20% and 60% were tested on AC cathodes with the diameter of 2.5 cm to determine the optimal PTFE loadings. Previous studies of MFCs treating wastewater correlated the MFC performance with PTFE loadings and optimized the PTFE percentage at 20% [24]. For an AC mixture with 20% wt. PTFE, 1.12 g of 60% wt. PTFE was mixed and blended with 10 g of AC. For an AC mixture with 60% wt. PTFE, 3.35 g of 60% wt. PTFE was blended with 10 g of AC.

Anode materials

Three carbon-based anode materials with large surface area and high conductivity were examined in the batch mode BMFC system (volume: 500 mL) (Fig. 2a): granular active carbon (GAC), carbon brush (CB), and activated carbon nanofiber (ACNF). GAC (diameter: 0.5–2 mm, mesh size: 8 × 30, Specific surface area: 843 m^2/g [9], General Carbon, Paterson) was packed into a polypropylene mesh bag (length: 2.5 cm; width: 2.25 cm) and then inserted into sediment (Fig. 1b). CB (Mill Rose Inc., OH; fiber stack diameter: 3.8 cm; and fiber stack height: 6.25 cm) was directly placed into the sediment (Fig. 1c). ACNF (geometric area: 16 cm^2, Specific surface area: 1159 m^2/g [9]) was fabricated by heat-treatment of electrospun polyacrylonitrile precursor and steam activation to produce carbon nanofibers in a nonwoven architecture [8]. In order to maintain its mechanic integrity, ACNFs were sandwiched in a polypropylene mesh bag with dimensions proportional to their geometric area and then embedded into sediments (Fig. 1d).

Benthic MFC systems

Two types of BMFC systems were used in this study. The first type was batch mode BMFC system (effective working volume: 500 mL, inner diameter: 7.5 cm, and length: 15 cm) made from plexiglass cylinders (Fig. 2a) to investigate the performance of (i) different AC cathodes and, (ii) three carbon-based anodes. The anodes were placed inside the plexiglass cylinder and buried in sediments to support the growth of microorganisms and collect the electrons generated. AC cathodes were secured onto the Plexiglas cylinder and immersed in water to utilize the dissolved oxygen as the electron acceptor. Total water depth was 12 cm, and the AC cathodes were positioned parallel to the benthic surface at a distance of 4 cm. Organic soil sediments collected from the Mirror Lake at University of Connecticut with diverse microbes and organics were used as inocula. The superior of the two AC cathodes tried was used as working cathode for the anode tests. Sodium acetate was initially added as an additional carbon source to enhance the inoculation of anaerobic electrogenic bacteria, and then filled with 200 mM phosphate buffer solution (PBS, pH 7.0). All analysis was conducted in duplicates and operated at room temperature of 21 °C.

The second type was caged BMFC (Fig. 2b, volume: 10 L) developed in this study to protect the BMFC system from marine life intrusion and undulating water in aquatic environment. The cylinder cage was made of stainless steel (316 ¾ #16 Flattened, height: 30 cm diameter: 34 cm) to prevent corrosion or rust by the elements, and the electrodes were securely tied to the cage. The cage had four protruding rods to support the anode cage (Fig. 2b. Image 1) and cathode layer (Fig. 2b. Image 2). The BMFC system had four pairs of anodes/cathodes, with four cathodes and eight anodes (1 cathode was connected to 2 anodes in each pair). This multi-pair anode/cathode configuration was expected to secure stable and robust power output even if certain pairs were malfunctioned. Inside the cylinder cage (Fig. 2b. Image3), two layers of square anode cages (Fig. 2b. Image 1) (length: 5 cm), were placed at the bottom, and a layer of AC cathodes (Fig. 2b. Image 2) was placed on the upper part of the cage, and strapped securely onto a plastic mesh using cable ties and rested on support base. To complete the setup, a meshed cover was installed on top of the cage after all the parts were installed inside the cage (Fig. 2b. Image 3). The assembled BMFC system was then put into a fiberglass container (volume: 150 L), with the two layers of anodes being buried in sediments (total sediment depth: 31 cm) and the AC cathodes layer immersed in water (total water depth: 12 cm). Sodium acetate was added as a source of additional nutrients for bacteria to accelerate the acclimation process, and rest of the container was filled with 100 mM Phosphate Buffer Saline (PBS) (pH 7). The distance between AC cathodes and sediments surface was maintained at 5 cm.

Electrochemical measurements

The voltage over an external resistance (R_{ext}) of 100 Ω was continuously recorded using a data log system (Keithley Instruments Inc.) every two hours. The power curves, an estimate of the power density, were plotted from the voltage and current densities using variable resistors (15–2500 Ω). The open circuit potential (OCP) is the actual cell potential measured in the absence of current. The power and current were normalized to the cathode surface area (/m^2) to evaluate the AC cathode performance for different sizes and PTFE loading, while the power and current normalized to BMFC volume (/m^3) were used to evaluate the anode performance (GAC, CB, and ACNF).

Power management system (PMS)

A power management system (PMS) capable of stabilizing the power output of BMFCs was developed (Fig. 3). The major components of the PMS were a multi-anode decoupling circuit, a super capacitor, a switch, and a DC–DC converter. The anode decoupling circuit consisted of charge pumps to negate the effects of a defective anode. Following the charge pump, a super capacitor was placed to accumulate the energy from the pump discharges. A switch unit was incorporated to prevent excess current drawn from the super capacitor when connected to a DC–DC converter, hence enabling the circuit to boost the voltage output.

A pair of electrode consisting of multiple anodes and one cathode was the input of the decoupling circuit in this study.

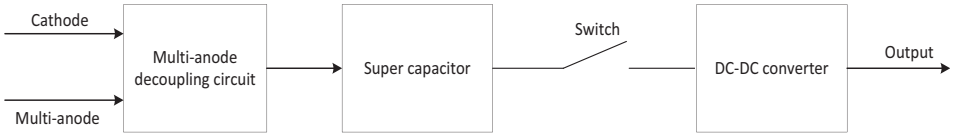

Fig. 3 – PMS circuit and block diagram.

The multi-anode decoupling circuit was composed of charge pumps S-882 and capacitors (Seiko Instruments), the number used was contingent on the extent of anode employed in the BMFC system. This configuration ensures that if one anode was impaired due to bioturbation, the voltage across the electrode would drop to zero, and the input voltage of the charge pump become zero or less than the required minimum voltage. Because the minimum required input voltage was not met, the charge pump would not start. However, the other charge pumps still continued their operation. Thereby, the defective anode was disconnected from the system. The circuit was self-starting and designed to automatically detect whether or not an anode was impaired. A minimum output voltage of 3.3 V is required to power most underwater devices [9,10,16].

The output of the decoupling circuit was connected to a super capacitor, which was used as a storage element. The super capacitor could be selected based on the energy and time demand for the load. This can vary from a few seconds to a few minutes [34]. In this PMS, the super capacitor capacity was 50 mF. If the DC–DC converter started to draw current from the super capacitor, the capacitor's voltage dropped quickly below the level required to start up the DC–DC converter. Consequently, the DC–DC converter will stop working. A switch unit was applied to control this energy transfer process between the super capacitor and the DC–DC converter. It enabled the energy transfer when the voltage on the super capacitor is high enough (>1.44 V) and disabled this process when the voltage on the super capacity dropped below a threshold (1.12 V). For the switch, a P-type metal-oxide-semiconductor logic (PMOS) was used in this design, and the DC–DC converter (L6920DB, ST Microelectronics) was used as an amplifier to boost the output voltage to an operating level. The inherent efficiency of the PMS is directly dependent on the efficiency of the components (e.g. charge pumps, converter) used, and was estimated according to Eq. (1).

$$\eta_{overall} = \eta_1 \eta_2 \quad (1)$$

where, $\eta_1$is the efficiency from the MFC to super capacitor, and η_2 is the efficiency of the DC–DC converter.

Results and discussions

AC cathodes performance in batch-mode BMFC systems

Two diameters of AC cathodes (diameter: 2.5 cm and 5.0 cm) were examined in the batch-mode BMFC system as biocathodes to improve oxygen reduction reaction (ORR) [35]. Cathodes with diameters of 1–5 cm have been used widely in MFCs [36–38], and hence similar sizes were used in this study. The performance of 5.0 cm cathode with 20% wt. PTFE was better than that with 60% wt. PTFE (Table 1). Larger cathode diameter (2.5 cm–5.0 cm) improved the OCP by about 14.2%, even though the surface area increased by 75.0%. The OCP, which is the maximum voltage generated at infinite resistance (open circuit), was 618–633 mV for 5.0 cm ACCs, and 587 mV for 2.5 cm ACCs (Table 1). The OCP of AC cathodes with 60% wt. PTFE dropped by 15–20% after 2 weeks of operation, and fell below 100 mV after 4 weeks, while the ones with 20% PTFE only dropped 6% and stabilized at around 200 mV. The decrease in OCP and the final stabilization could be attributed to the biofouling (Fig. 4), which may have initially hindered the abiotic ORR,nevertheless enabled biotic ORR. Previous studies on non-catalyzed cathodes have found similar trends [39–43].

The SEM images showed the morphological structure of AC cathodes. The clean AC cathodes with 20% and 60% wt. PTFE had uniform structure (Fig. 4a and b), while the AC cathodes after 4 weeks of operation had extensive biofilms growing on ACC surface (20% wt. PTFE) (Fig. 4c). The loosely structured characteristic of AC enabled accessibility for enhanced microbial interactions, and resulted in widespread biofilm formation. Since cathodes are always installed in aerobic environment to effectively react with oxygen, protons, and electrons, PTFE hydrophobic loading is a key element for the performance of cathode [21,42]. An optimal PTFE loading helps to bind the AC and improve electrical conductivity of AC by bridging the pores for long-term operation in underwater environment [44,45]. However, high PTFE loading was found to prevent biofilm attachment, penetration into the cathode, and increase ohmic resistance [21]. Earlier studies demonstrated the correlation between PTFE content and fouling [43].This was further associated with the variation in OCP and the performance of AC cathodes. The optimal PTFE loading for AC cathodes was established in our earlier studies (20% PTFE (wt.)) [23,24,42,43]. Cathode biofilms proved to be detrimental in single chamber MFC systems treating wastewater (air cathodes) by decreasing proton mass transport and causing catalyst fouling [21,23,24]. But for AC cathodes in water (the BMFC in this study), the biofilms growing on AC (Fig. 4c) were

Table 1 – The average OCP (mV) for new and used (2 and 4 weeks) AC cathodes of different diameters and PTFE dilutions (% wt.).

OCP (mV)	2.5 cm 60% wt. PTFE	5.0 cm 60% wt. PTFE	5.0 cm 20% wt. PTFE
New cathodes	587 ± 19.1	618 ± 16.4	633 ± 15.5
Cathodes after 2 weeks	504 ± 2.2	509 ± 6.6	583 ± 5.3
Cathodes after 4 weeks	39 ± 6.3	98 ± 1.2	196 ± 6.4

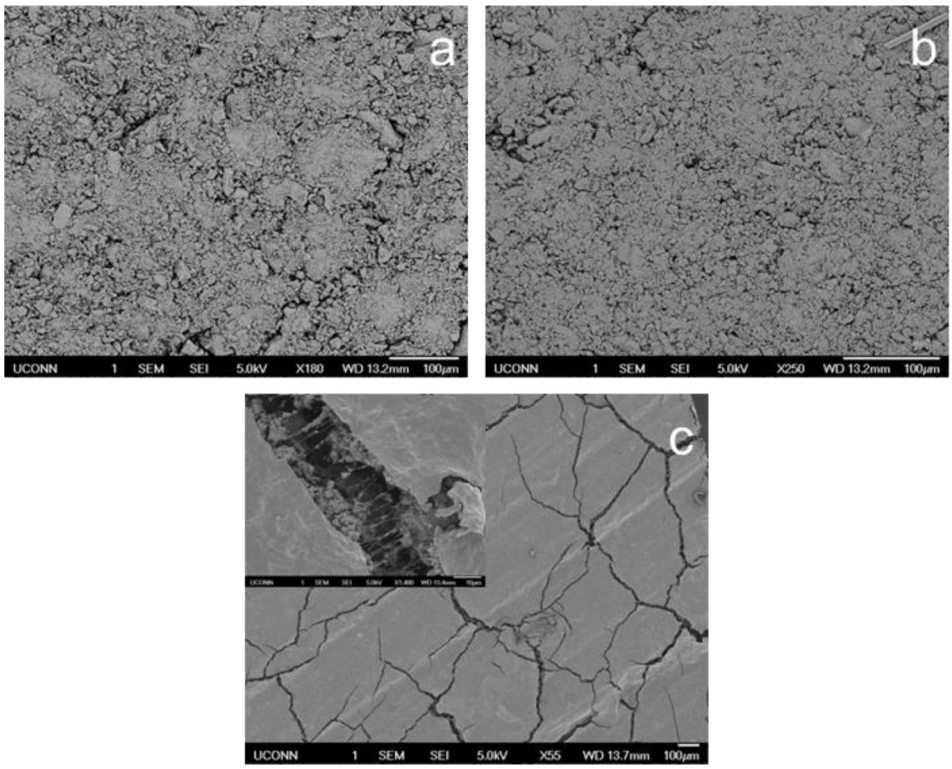

Fig. 4 – Scanning electron microscope (SEM) images of AC cathode materials: (a) Clean 20% wt. PTFE (100 μm, 200×); (b) Clean 60% wt. PTFE (100 μm, 200×); (c) 20% wt. PTFE with biofouling (100 μm, 50×), Inset (10 μm, 1500×).

able to maintain stable biotic ORR, and had more stable OCP over the entire operational period (Table 1).

The power density and polarization curves of the 5.0 cm AC cathode with 20% and 60% (wt.) PTFE were compared over 6 weeks of operational period in batch mode BMFC systems after an initial incubation time (Fig. 5). The power densities normalized to cathode area showed that AC cathodes with 20% wt. PTFE had higher power density (0.045 W/m^2) than that of AC cathodes with 60% wt. PTFE (0.0175 W/m^2) (Fig. 5a). Polarization curves were used to indicate the stability of voltage when the external resistance (R_{ext}) was increased from 15 to 2500 Ω (Fig. 5b). The lower PTFE loading (20%) was able to sustain stable current generation over higher PTFE loading (60%), which this could be attributed to the higher porosity of 20% PTFE (wt.) cathode enabling a better and faster growth of aerobic bacteria and higher ORR [24]. Previous studies also found that higher biofilm activity on the cathode enhanced chemical oxygen demand (COD) degradation, which resulted from higher diversity of aerobic bacteria growing and higher ORR [39,40,43]. As the anode conditions were strictly anaerobic in all the tests, the overall performance of the BMFC system was governed by the performance of the cathode and significantly improved over time for AC cathodes with 20% wt. PTFE.

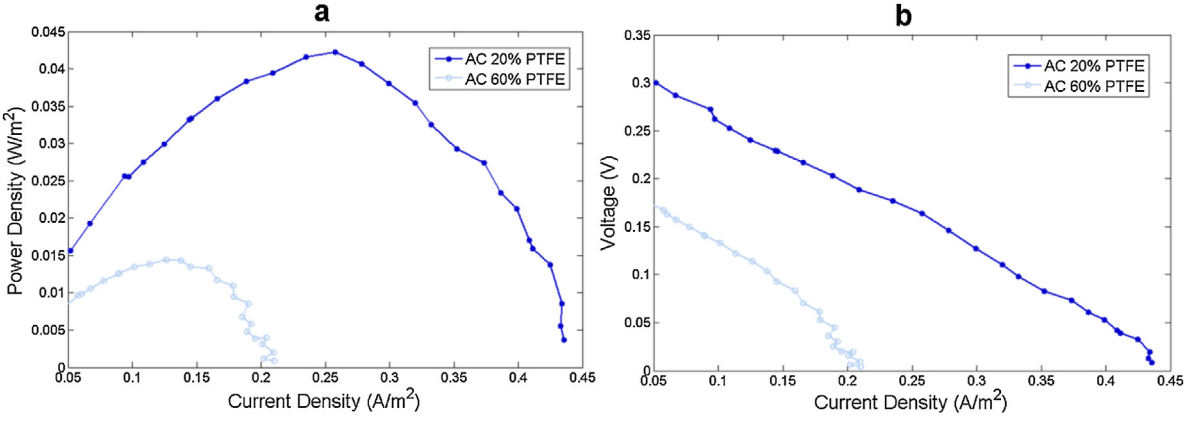

Fig. 5 – Power generation (a) and Polarization curve (b) for the batch-mode BMFC systems with 5.0 cm AC cathode of different PTFE percentages. (All data were represented as an average of duplicate reactors data sets).

Anode performance in batch-mode BMFC systems

Three anode materials (GAC, CB, and ACNF) with high surface area for biofilm growth and electron transfer [18,36] were examined in the batch-mode BMFCs for 6 weeks. AC cathodes (diameter: 5 cm) with 20% wt. PTFE were used as the cathode electrodes in these tests. The volumetric power density (Fig. 6a)and polarization curves (Fig. 6b) showed that the BMFCs with CB and ACNF had high power densities (1.81 ± 0.19 W/m^3 and 1.25 ± 0.11 W/m^3 respectively, and maintained stable OCP values between 0.5 and 0.6 V, while those with GAC had a lower power density of 0.4 ± 0.09 W/m^3 and the OCP value of about 0.45 V. The correlation of voltage and current exhibited a steep drop for GAC, but sustained a moderate drop for CB and ACNF. Earlier studies demonstrated a good performance for GAC due to its relatively high surface areas and conductivities [7], but it did not perform well in the batch-mode BMFC systems. Furthermore, the redox characteristics and physical property of sediments, along with the dynamics of underwater environment in BMFC systems were very different from traditional MFC systems treating wastewater [5]. The GAC tested in this study was packaged as a column in polypropylene nets and embedded into sediments (Fig. 1b), this could have clogged the pores substantially, thereby increasing the mass transfer resistance and limiting the GAC anode performance.

The interaction of biofilms with the anode surface is critical for power generation in MFC systems [6,7]. An optimal biofilm growth on the anode leads to the prominence of electrogenic bacteria and enhances electron transport to the anode electrode [46,47]. CB and ACNF have a significant advantage of providing a higher interfacial bioavailable surface area, and hence act as an effective anode surface. In addition, high interconnectivity and conductivity between carbon fibers permitted extensive biofilm growth and contributed to the good performance of CB and ACNF anodes. Previous studies of BMFCs indicated that anode electrode could be the limiting factor due to the high mass transfer resistance in sediment [5,11,18]. Hence employing anodes with high interfacial surface and porous areas could minimize the mass transfer diffusional limitation. It should be noted that even though CB and ACNF have higher power density than GAC, their fragile structures and low mechanic strength might require extra maintenance when being embedded into sediments, and their stability for long-term operation needs to be examined in further investigations.

Caged BMFC performance

The caged BMFC system with multiple pairs of GAC anodes and AC cathodes of 5.0 cm with 20% PTFE (wt.) was tested over 12 weeks of setup. The reason for selecting GAC as anode was that GAC had much higher mechanic strength and was easier to assemble and install in sediments CB and ACNF anodes. While, AC cathode of 5.0 cm with 20% PTFE had the highest power density among the AC cathodes tested in the batch-mode BMFC (Fig. 5). The unique advantage of the multiple-electrode configuration was to minimize internal losses, enhance robustness, and allow malfunctioned anodes (due to potential bioturbation) to be isolated [18]. The caged BMFC system had four AC cathodes and eight GAC anodes, with each AC cathode being connected in parallel to two GAC anodes (termed as 1 array pair), so that there were total 4 array pairs (Fig. 2b). The anodes/cathodes experienced acclimatization period of 1–2 weeks, during which the reactants/products in sediment transported to GAC anodes and biofilms started to grow on AC cathodes in water [5,19]. The average OCP for the electrode pairs exhibited a steady increase from 0.13 V initially and stabilized at 0.45 V after 2 weeks (data not shown here). The moderate voltage output and fluctuations among pairs were pertinent to the dynamic fluctuations in the BMFC system.

The overall performance of the BMFC electrode pairs was evaluated based on the power-current and voltage–current curves (Fig. 7). To specifically characterize the robustness of the multi-electrode pattern, power and current outputs were estimated as a function of the performing pairs. The pair numbers (1–4 array pairs) indicated number of functional electrode pair arrangements to represent bioturbation in natural environment [18]. For example, 1 array pair represented only 1 array pair was functional and the remaining 3 array pairs did not perform. Under the best case of all

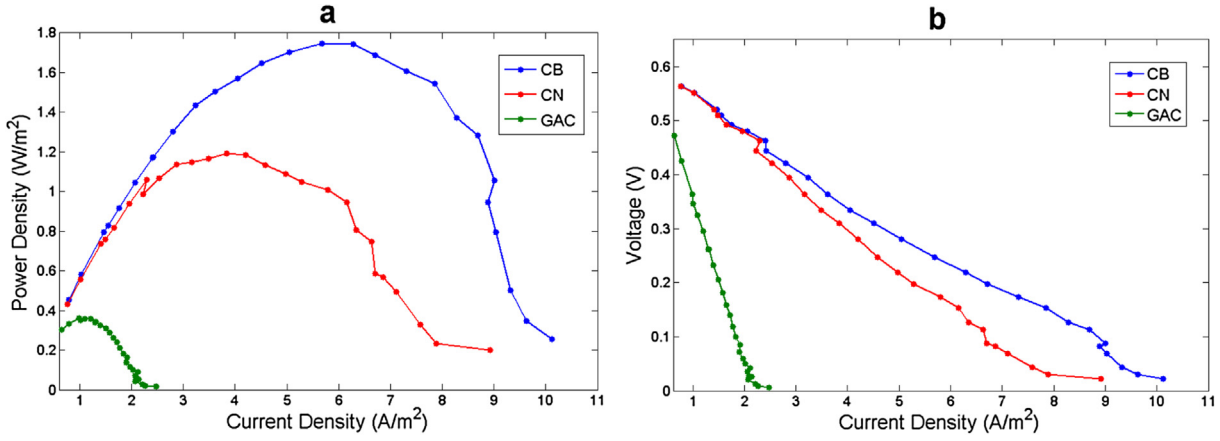

Fig. 6 – Power generation (a) and Polarization curve (b) for the batch-mode BMFC systems with different anode materials (GAC, CB, and ACNF). (All data were represented as an average of duplicate data sets).

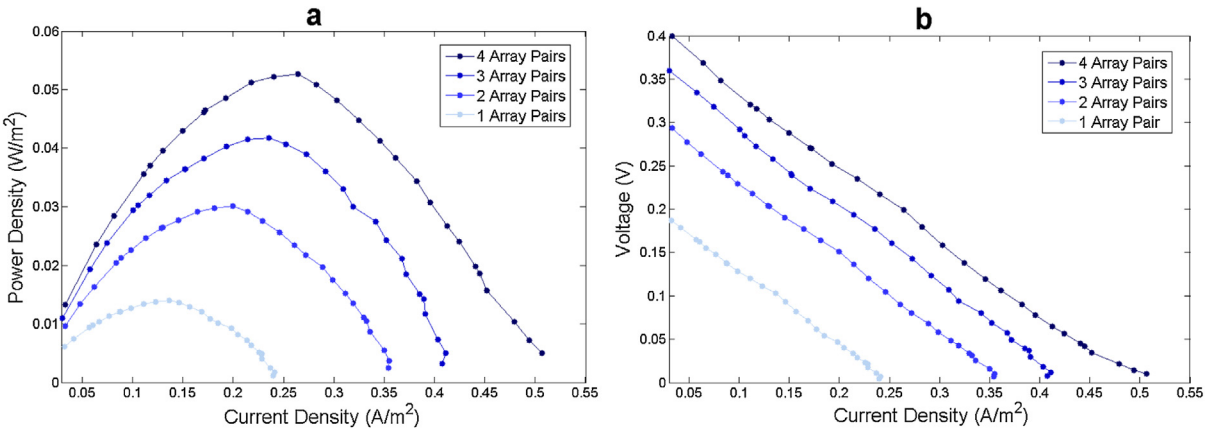

Fig. 7 – Power generation (a) and Polarization curve (b) for the caged BMFC system with different pairs of anodes/cathodes. (All data were represented as an average of duplicate data sets).

functional pairs (4 array pairs), the BMFC system had a peak power density of 0.56 W/m^2 (Fig. 7a) at a current density of 0.25 A/m^2 (Fig. 7b). From 1 pair to 4 array pairs, there was a fourfold increase in power and two fold increase in current output. The concerns of natural variability and dynamics of real environmental systems would be appropriately addressed by employing a multi-electrode distributed BMFC system with biocathodes.

AC cathode of 5.0 cm with 20% PTFE wt. used in the caged BMFC system was different from traditional abiotic cathodes that always required costly metal catalysts (e.g. Pt) [6,19]. Long-term stability of Pt-loaded cathodes is a critical problem for BMFC operations in underwater environments. Earlier studies have demonstrated that for biocathodes utilizing oxygen as the terminal electron acceptor, electron mediators (e.g. iron and manganese) were first reduced by the cathode (abiotically) and then re-oxidized by microbial fouling on the cathodes [20,22,25]. Biocathodes with mature biofilms would potentially reduce the mass transfer resistance losses and thereby enhance ORR over long-term operations. Increasing electrode area alone would not proportionally increase power output of BMFCs [12,39]. This investigation was the first successful demonstration of BMFC system employing biocathodes capable of sustaining stable power generation. The overall performance of the system was much higher than earlier studies using single-electrode arrays [5,13], with peak power densities in the range of 0.03–0.06 W/m^2 and current densities of 0.05–0.1 A/m^2. This further validated the premise that long-term stability and performance of BMFCs can be optimized by the use of durable, cost-effective and distributed electrode design.

PMS performance in BMFCs

The PMS was connected to a lab-scale BMFC system (Fig. 2a, volume: 500 mL with 3 GAC anodes and 1 AC cathode 20% wt. PTFE) and a working external load ($R_{ext\text{-}w}$, e.g. pressure/temperature sensor) to simulate real time energy harvesting performance. The output voltage of the $R_{ext\text{-}w}$ and voltage of the super capacitor were recorded using an oscilloscope over time, as shown in (Fig. 8). The expected values were obtained for three conditions: 1 anode working and 2 deliberately impaired, 2 working and 1 deliberately impaired, and all 3 anodes working. The results showed that the boosted output voltages were the same in all the three conditions, but exhibited different duration periods of charging/discharging for the charge pump connected to the super capacitor (Table 2).

The decoupling circuit had two time parameters for charging/discharging voltage loads, t1 and t2 (in hours, h), respectively (Table 2). The t1 was the time when the super capacitor started charging from 0 V initially to reach the maximum charge voltage, 1.44 V (V_d, discharge start voltage), while t2 was the time when the super capacitor started charging from the voltage 1.12 V (V_c, charge start voltage) to V_d. When the super capacitor voltage exceeded V_d, the switch unit connected the super capacitor and the DC–DC converter. The output voltage of the DC–DC converter and the $R_{ext\text{-}w}$ were observed via the oscilloscope and the output was 3.3 V (as the sharp peak line in blue curves in Fig. 8). When the super capacitor voltage decreased to V_d, the switch unit

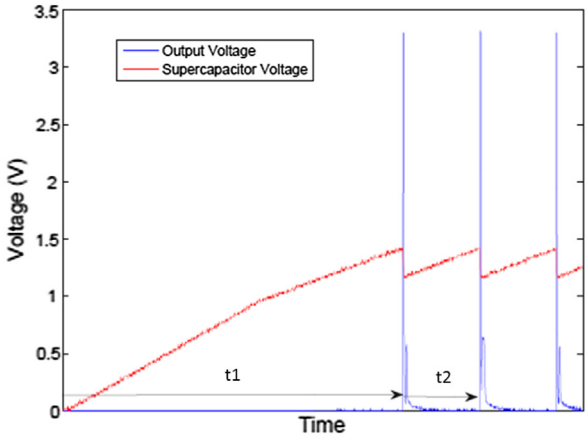

Fig. 8 – Super capacitor and output voltages with the corresponding charging/discharging times for the charge pumps (Time in hours (h)).

Table 2 – The charging/discharging times for the charge pump connected to the super capacitor. (The number of charge pumps is representative of the number of working anode electrodes.)

Number of charge pumps	t1 (h)	t2 (h)
1	3.13	0.58
2	1.93	0.35
3	1.58	0.3

disconnected the super capacitor and the DC–DC converter, and then the output dropped to 0 V. The overall efficiency ($\eta_{overall}$) of the PMS estimated by Eq. (1) was 22.54% for one anode, 34.72% for two anodes, and 37.80% for three anodes, indicating the overall efficiency is proportional to the number of active anodes in the BMFC system. Overall efficiencies were notably higher than the reported values (i.e. efficiencies derived from charge pump and converter) ranging between 14 and 22% [48,49].The results showed that increasing the anode numbers in the BMFC system shortened the time required for the super capacitor to power the converter and the R_{ext}. In other words, the multi-anode system can be powered to the external working load within a short timeframe.

The PMS system developed has the unique advantage of lower startup voltage, incorporation of charge pumps and super capacitor with large storage to exclude the effects of a defective anode(s) in the event of bioturbation [9,10,16]. The PMS design is complementary to the multi-electrode BMFC system, where the charging/discharging duration for the super capacitor is substantially reduced, and the system continued to operate even if a section of the BFMC system failed. As BMFCs typically generate a low voltage output that is not sufficient to directly power underwater sensor networks [2,11,50,51], an interface circuit is needed to boost the output voltage high enough to operate devices. The prospect of employing a PMS is the most efficient technique for managing the energy pool to provide long-term and stable power outputs. Further deployment and waterproofing of PMS and other electronic components for the working loads (e.g. sensors and relay network, power stations) is equally vital to provide a complete functional BMFC system solution in the ocean environment.

Conclusions

Novel AC-based multi-electrode and PMS were developed for high stability and improved long-term power generation in caged BMFCs. The electrode materials and PMS were evaluated in lab-scale BMFCs for over 12-week operational period. The major conclusions drawn from this study:

1. AC cathodes were successfully fabricated as alternative Pt-free biocathodes. AC cathode of 5.0 cm with 20% PTFE wt. showed the best performance.
2. The caged BMFC system with multiple pairs of anodes/cathodes achieved peak power density of 0.56 W/m^2 at a current density of 0.25 A/m^2.
3. ACNF and CB had better performance over GAC as anode materials in BMFC systems, but the mechanic strength and fragile structures can be an issue of concern for long-term operations in benthic systems.
4. A PMS system developed for the BMFC system can generate peak output of 3.3 V necessary for the working load.

Acknowledgments

This study was funded by the Office of Naval Research (ONR) Microbial Fuel Cell (MFC) Program (N000141210345). Eri Muto was supported by the National Science Foundation grant OCI-1156859 (REU Site). Mike Kölln was supported by the NSF REU Program. The authors thank Dr. Jeff McCutcheon for providing the ACNF materials.

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