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Sediment Microbial Fuel Cell with Double-Anode Arrangement for Enhanced Oxygen Reduction Reaction

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Biofilms formed on the cathodes of sediment microbial fuel cells (SMFCs) are mainly composed of heterotrophic bacteria that inevitably attach to cathode catalytic sites, inhibit the oxygen reduction reaction (ORR), and affect the practical performances of SMFCs. In the present work, a novel double-anode sediment microbial fuel cell (DA-SMFC) was designed and constructed with a commercial nitric acid-activated carbon felt set at sediment-water interface, and its electrical power generation performance and antibacterial mechanism were investigated. The voltage generation capacity of DA-SMFC reached up to 376 mV, higher than those of the sediment microbial fuel cell (SMFC) (332 mV) with the carbon felt put in sediment, due to the higher total organic carbon (TOC) removal efficiency. The electrochemical impedance spectroscopy, bacterium protein content, and SEM analyses indicated that the formation of biofilm on the cathode of DA-SMFC was significantly inhibited, resulting in significantly reduced protein contents on cathode, and decreased R_{ct} from 118.9 Ω to 91.6 Ω. This novel DA-SMFC system exhibited excellent antibacterial performances by inhibiting the migration of organic matters from the sediments to the cathode in overlying water, which would promote the application of SMFC.

Keywords: Sediment microbial fuel cell, Double-Anode, Oxygen reduction reaction, Biofilm, Electricity generation

1. INTRODUCTION

A sediment microbial fuel cell (SMFC) is a special bioelectrochemical system that can convert chemical energy of organic matters in sediment to electrical energy under the catalysis of bacteria [1-

4]. In an SMFC, microorganisms degrade the organic matters in aquatic sediment to generate electrons and protons. The protons flow from the sediment to the cathode, and the electrons are transferred to the cathode to reduce the terminal electron acceptors, such as nitrate, chlorate, and oxygen [5-7], forming an external circuit. Oxygen is a natural electron acceptor that can complete this circuit via oxygen reduction reaction (ORR) to constantly generate electric current with low maintenances [8-11]. SMFCs have been used as the power supplies of long-range or deep-sea sensors [12-15]. However, the low power generation efficiency of SMFCs limits their practical application of as an electrical power supply.

In a typical SMFC, the anode is inserted in the anaerobic sediment and cathode is soaked in the overlying water containing a higher level of dissolved oxygen to generate potentials with the naturally occurring oxygen gradient [16]. Therefore, the performance of cathode is the key factor affecting the efficiencies and performances of SMFCs [11, 17, 18]. An optimal cathode material [19, 20] and larger effective surface area of cathode [21] in a SMFC can effectively reduce O_2, and thus improve the power generation efficiency of the SMFC. However, a large amount of microorganisms from the air and water body can adsorb on the large surface area of cathode via accidental adsorption [22-24], and are complexly flora interwinded to form a biofilm [14,25,26] that uses organic matters as the carbon source [27]. The thick aerobic bacteria biofilm can competitively consume the oxygen in SMFC, and thus affect the ORR on cathode. Smaller effective surface areas of cathode lead to lower catalytic activities [6, 15, 28], and thus lowers the power generation efficiency of SMFC [22].

Great efforts have been made to reduce the biofilm colonization on cathode or increase the oxygen content in the cathode region of SMFC. Liu achieved high and stable electricity generations using enrofloxacin, a broad-spectrum fluoroquinolone antibiotic, to reduce the growth of cathode microorganisms [29]. Ma successfully improved the ORR kinetics on cathode by inhibiting the overgrowth of biofilm on cathode surface with nano silver/iron oxide/graphitic carbon as an antibacterial ORR catalyst [30]. Based on this discovery, they then prepared N-doped Ag/Fe/C catalysts to further improve the electrical conductivity and catalytic activity of cathode [19]. Similarly, Li obtained higher power densities using silver nanoparticles as an antimicrobial agent of cathode [18, 31]. Despite these contributions, studies have been rarely focused on the pathways to acquiring carbon sources for heterotrophic microorganisms [30, 32]. Exploring the carbon sources of cathode microorganisms would facilitate the method development for reducing cathode biofilms, improving cathode catalytic oxygen reduction, and promoting the application of SMFCs [19].

In the present study, the relationship between the carbon source required for the growth of cathode bacteria and the organic matters in sediment was investigated in an SMFC with a carbon felt set at the sediment-water interface as the second anode. By comparing the voltages, TOCs, cathode electrochemical impedance spectroscopy (EIS) data, total protein contents, and SEM images of the SMFC devices with or without the interfacial carbon felt, the properties of SMFC with controlled carbon source were determined. The results suggest that the kinetics of ORR and application of SMFC can be promoted with optimal cathode carbon sources.

2. EXPERIMENTAL SECTION

2.1 Sediment sampling

Sediment samples were collected from the Dacheng River near the Qilu University of Technology, Shandong Academy of Sciences (35°33’9”N, 116°48’34”E), Jinan, China. The river is a typical eutrophic water body rich in natural vegetation. Sediments were sampled from the sludge deposition approximately 5 cm below the sediment-water interface, and passed through a 0.5 cm sieve to remove coarse debris.

2.2 Construction of SMFC and DA-SMFC

Each SMFC was operated in a 2 L plastic measuring cylinder (8 cm in inner diameter and 48 cm in height) containing 600 mL anaerobic sediment sample and 1800 mL overlying water from the Dacheng River.

Carbon felts (7 cm inner diameter and 100-200μm aperture) were pretreated with 5% nitric acid as described by Erable [33], and used as electrodes. SMFC was constructed with anode I (0.5cm thick), anode II (1 cm thick), and one cathode (0.5 cm thick), where anode I and anode II were put 8 cm and 4 cm below the sediment surface, respectively, and the cathode was placed at 30 cm above the sediment-water interface (**Fig. 6 A)**. In the DA-SMFC, the anode I and cathode were located at positions similar to those in SMFC, and anode II was placed at the sediment-water interface **(Fig. 1)**. All electrodes were connected with insulated titanium wires to an external resistance of 1000 Ω.

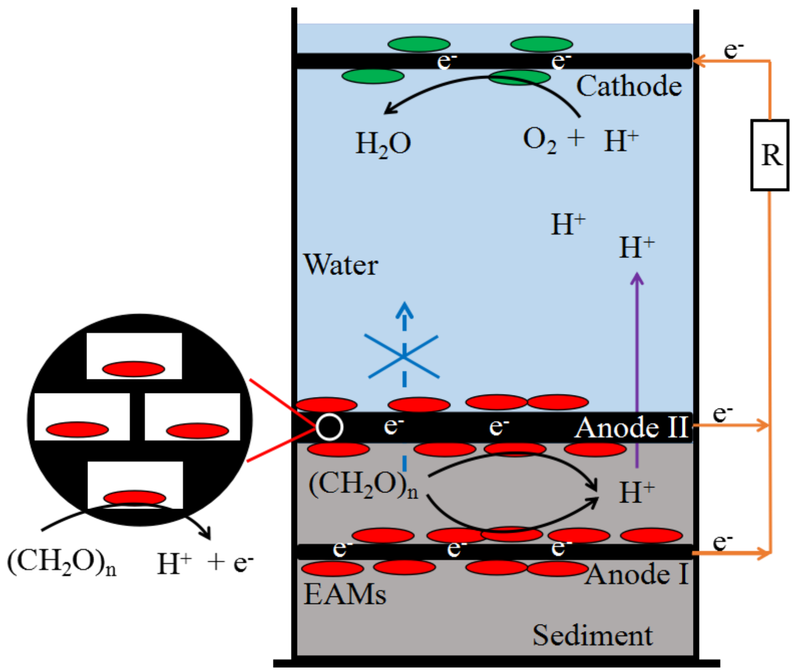

Figure 1. Schematic diagram of DA-SMFC. Anode II was put at the sediment-water interface of SMFC to inhibit the migration of organic matters from sediment to water. EAMs, electrochemically active microorganisms.

2.3 Measurement of voltages generated by SMFCs

The voltages generated by SMFCs were measured with a portable digital multimeter (UT71D, Fengxiang technology Co., Ltd., Beijing, China) and recorded at the 24-hour intervals.

2.4 Chemical analysis

The total organic carbon (TOC) content in overlying water was measured using a TOC analyzer (TOC-V CPH, Shimadzu 5000-A, Japan).

2.5 Electrochemical impedance spectroscopy (EIS) of cathode

To determine the electrochemical properties of the SMFCs, EIS was conducted on an electrochemical workstation consisting of a typical three-electrode testing system (CHI 660E, Chen Hua instrument Co., Ltd., Shanghai, China), where a saturated calomel electrode acted as the reference electrode and a platinum wire was used as the counter electrode. Impedance spectra on cathodes were recorded in the frequency range from 5 mHz to 100 KHz at the 10 mV amplitude sinusoidal perturbation. Nyquist curves were drawn from the real parts (Z_{re}) and imaginary parts (Z_{im}) of cathodes.

2.6 Protein contents of the biofilms formed on SMFC cathodes

The protein contents of biofilms formed on cathodes were determined according to a method reported in literature [34]. Cathodes at operation day 5, 25, and 60 were rinsed with phosphate buffer solution (PBS, pH=7.2, 0.27 g KH_2PO_4/L, 1.42 g $NaHPO_4$/L, 8 g NaCl/L, 0.2 g KCl/L), and heated in 0.2 M NaOH at 100 °C for 5 mins to break bacterial cells. The solution was then cooled to room temperature, and centrifuged at 13400 rpm for 10 min. The supernatant was collected for protein content analysis using a Bradford protein assay kit (Shanghai Biotech Co.,Ltd., Shanghai, China).

2.7 SEM imaging of biofilms on cathode

Carbon felt cathodes (3×5 mm) were immersed in 2.5% glutaraldehyde at 4 °C for 10 hours, washed with PBS six times for 20 mins, sequentially immersed in 30%, 50%, 70%, 90%, and 100% ethanol for 20 min, freeze-dried for 2 hrs, and imaged under a scanning electron microscope (SEM, Quanta200F, FEI Company).

3. RESULTS AND DISCUSSION

3.1Comparison between the voltages generated by SMFC and DA-SMFC

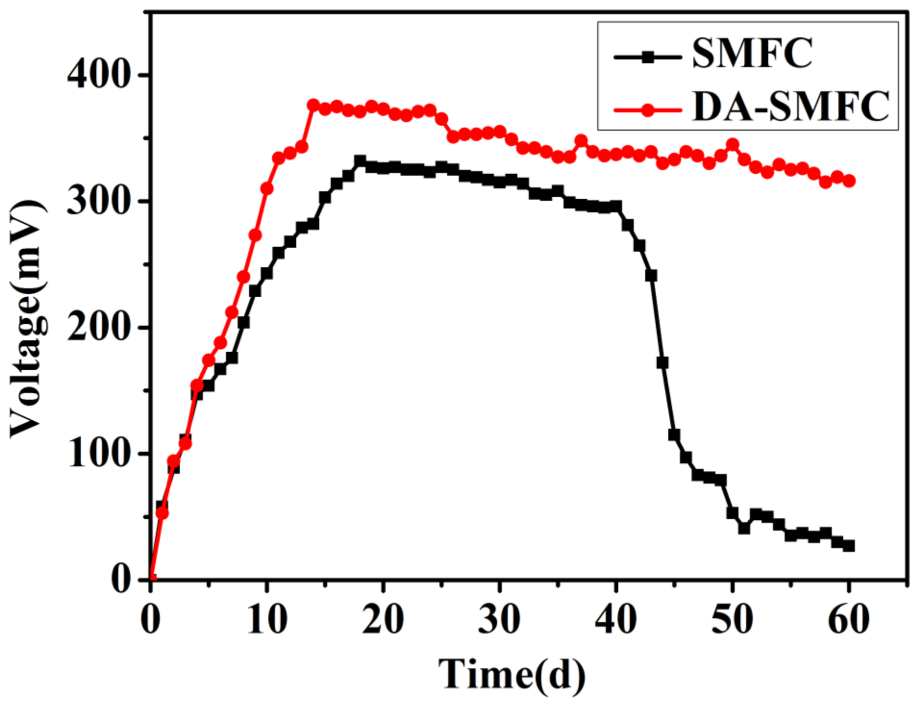

Figure 2. Voltages generated by SMFC and DA-SMFC during the operation (R_{ex}=1000Ω).

Fig. 2 shows the voltages generated by SMFC and DA-SMFC during a 60-day operation. Their voltage generations exhibited similar increasing trends initially. Both SMFC and DA-SMFC output powers at day 2, and the voltage generated by DA-SMFC became higher than that generated by SMFC at day 5. The highest voltage was observed at day 14 in DA-SMFC and at day 18 in SMFC, and the former is (376 mV) is 13.3% higher than the latter (332 mV). Once the highest voltage reached, the voltage of SMFC gradually decreased and that of DA-SMFC remained at a high level (over 300 mV) during the rest of operation. These results suggest that DA-SMFC can generate higher and more stable voltages than SMFC, consistent with the results reported in literature [18, 19, 29-31].

The oxygen reduction kinetics on a cathode is affected by the effective surface area of the cathode where oxygen accepts electrons and protons to form water [27]. The voltage of DA-SMFC rapidly reached the maximum and remained constant with no significant changes in 60 days, probably because the dual anode system was able to directly contact with the electron acceptor, oxygen, and make a plenty of electrons continuously with the rich organic matters in sediment, forming a stable electron flow from anode to cathode. Therefore, the carbon felt at the sediment-water interface of SMFC was able to improve the electricity generation.

3.2 Total organic carbon (TOC)

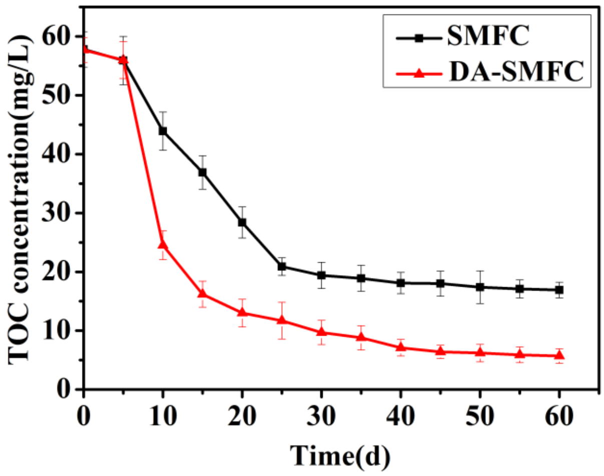

Figure 3. TOC contents in the cathode chambers of SMFC and DA-SMFC.

The total organic carbon (TOC) in overlying water is mainly the organic matters diffused from sediment [35]. The effects of DA-SMFC on the migration of organic matters from sediment to overlying water were then determined to further explore its influences on the development of heterotrophic aerobic bacteria on cathode surface. Fig. 3 shows the TOC contents in the cathode chambers of SMFC and DA-SMFC during a 60-day operation. It is clear that the TOC content in the cathode chamber of DA-SMFC (5.7±1.25 mg/L) is lower than that of SMFC (16.9±1.34mg/L). The TOC removal efficiency was determined to be 90.12% for DA-SMFC and 70.76% for SMFC. Heterotrophic bacteria on the biofilm formed on SMFC cathode [32] can consume organic matters in overlying water, resulting in decreased TOC in the SMFC. Theoretically, that there are less microorganisms attached on the DA-SMFC cathode than SMFC (Fig. 5) and the ability of DA-SMFC to reduce TOC content is lower. However, the experimental results revealed that DA-SMFC was able to more effectively reduce TOC than SMFC. It can be explained that the anode II in DA-SMFC could inhibit the diffusion of organic matters from sediment to overlying water [32], and, in addition to the cathode bacteria, the biofilms on the anode II absorbed and degraded the organic matters in overlying water [36]. Based on these results, it can be concluded that the carbon felt at the sediment-water interface significantly improved the TOC removal efficiency of DA-SMFC.

3.3 Comparison between the electrochemical resistances of SMFC and DA-SMFC

Electrochemical impedance spectroscopy (EIS) is the most powerful technique to determine the charge transfer resistances between electrodes and the electrolyte interface. In the present work, EIS was conducted to determine the effects of the anode II in DA-SMFC on the kinetic activity on cathode. Fig. 4 shows the Nyquist curves produced from the electrochemical impedance data of SMFC and DA-SMFC cathodes. A Nyquist curve is usually consisted of a semicircle loop in the high frequency region and a vertical line in the low frequency region [37]. The diameter of semicircle loop, R_{ct}, reflects the kinetic activity on cathode [38]. The R_{ct} of the DA-SMFC cathode was determined to be ~91.6 Ω, lower than that of SMFC (~118.9 Ω). Smaller R_{ct} allows faster electron-transfers between the electrode and electrolyte [38]. Therefore, the cathode of DA-SMFC can more effectively catalyze oxygen reduction reactions.

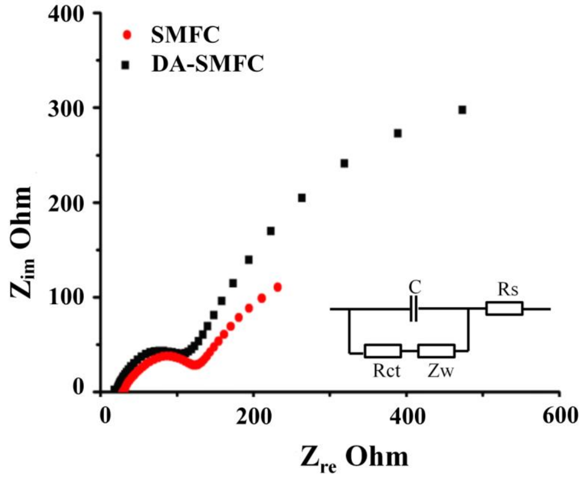

Figure 4. Nyquist curves for the cathodes in SMFC and DA-SMFC.
The inset shows the equivalent circuit of the electrochemical interface, where
R_s represents the ohmic resistance,
R_{ct} represents the charge transfer resistance,
Z_w represents the Warburg impedance,and
C is the double layer capacitance.

3.4 Protein contents of biofilms on SMFC cathodes

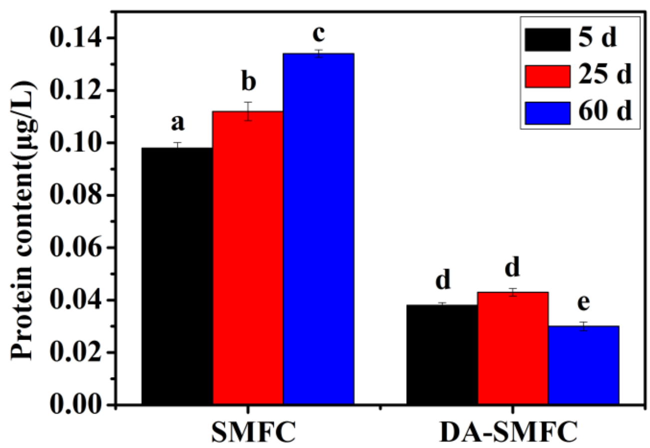

Figure 5. Protein contents of the biofilms formed on SMFC and DA-SMFC cathodes at operation day 5, 25, and 60. The a, b, c, d and e represent the significant difference between the samples (Tuskey's HSD test, $P < 0.05$).

The protein content on cathode reflects the amount of biofilm on a microbial fuel cell electrode [39, 40]. The protein contents on the SMFC cathodes at operation day 5, day 25, and day 60 were measured to quantify the corresponding biofilms. As shown in Fig. 5, the protein content on cathode surface in DA-SMFC is significantly lower than that of SMFC ($P < 0.05$). The protein content on the SMFC cathode increased dramatically from 0.098 μg/L at day 5 to 0.134 μg/L at day 60. In contrast, that on DA-SMFC cathode remained constant in the first 25 days, and remarkably decreased to 0.03 μg/L at day 60 ($P < 0.05$), indicating that the amount of biofilm on DA-SMFC cathode was effectively reduced by the anode II. The proteins on cathode mainly originate from the colonization of heterotrophic bacteria on cathode surface. Increasing the hydrophilicity of cathode surface [39] or adding antibiotics to the cathode [40] can inhibit the formation of biofilm on the SMFC cathode. Our method using a carbon felt set at the sediment-water interface is easier to operate and more environment friendly.

Table 1. Correlation analyses of protein content and TOC content in SMFC and DA-SMFC.

Setup	Correlation coefficient
SMFC	-0.738*
DA- SMFC	0.109

* significance of correlation at $P < 0.05$

Statistics analyses [41] revealed a significant negative relation between the protein content on cathode and the TOC content (p= -0.738, significance of correlation at $P < 0.05$) in SMFC, but no significant relation between them in DA-SMFC (p=0.109) (Table 1). These results indicate that the amount of microorganism attached on cathode surface is closely related to the content of organic matters in overlying water. The carbon felt at the sediment-water interface in DA-SMFC was able to reduce the organic matters migrated to the cathode, leading to the depletion of organic matters in the cathode chamber of DA-SMFC that slowed the development of biofilm at the initial operation stage, and caused rapid apoptosis of biofilm during operation.

3.5 Development of biofilms on SMFC and DA-SMFC cathodes

Fig. 6 shows the SEM images of the biofilms formed at operation day 1, 5, 25, and 60 on SMFC and DA-SMFC cathodes. It is clear that the biofilms formed on SMFC cathode are denser than those on DA-SMFC cathode. In SMFC, a biofilm was rapidly formed and attached on the carbon felt cathode surface, and became thicker as the operation prolonged (Fig. 6 A). In contrast, the development of the biofilm on DA-SMFC cathode was rather slow. It is worth noting that the biofilm on DA-SMFC cathode at operation day 60 is less than that at day 25, suggesting that the morphologic change of biofilm was caused by cell apoptosis. A thick biofilm of heterotrophic aerobic bacteria formed on the cathode surface of SMFC [32] can cover the pores in the catalytic layer, and thus interferes with the oxygen diffusion [42]. The organic matters in cathode chamber (overlying water) are the important carbon source for the growth of heterotrophic bacteria on cathode surface. Our results suggest that the colonization of heterotrophic bacteria on the DA-SMFC cathode was successfully inhibited. It can be explained that the anode II at the sediment-water interface was able to reduce the migration of organic matters from sediment to overlying water, and thus inhibited the development of biofilm on cathode, consistent with the results of protein content analysis (Fig. 5). The inhibition of biofilm on SMFC cathode can promote the reaction between the cathode electrons and oxygen, and thus improve the reaction kinetics.

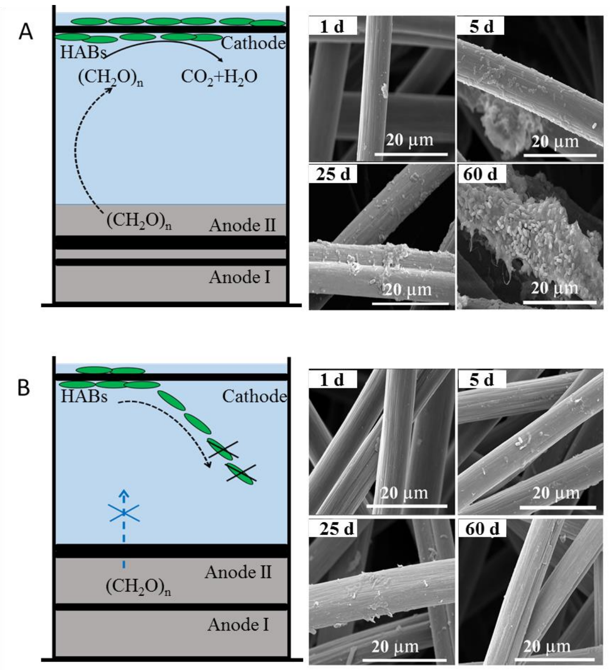

Figure 6. Mechanism maps and scanning electron microscope (SEM) images of the biofilms formed on SMFC (A) and DA-SMFC (B) cathodes. HABs, heterotrophic aerobic bacteria.

3.6 Functional mechanism of carbon felt at the sediment-water interface of SMFC

Sediments are rich in nutrients [43] and a variety of nutrient exchanges take place at the sediment–water interface [35, 43-45]. The nutrient flux across sediment-water interface from the sediment plays an important role in nutrient balance of water [35]. The porous structure of carbon felt with a high specific area can adsorb large amounts of impurities [46, 47], and thus minimize the diffusion of organic matters from the sediment to overlying water. The microorganisms attached at the interface carbon felt anode can also degrade the organic matters in overlying water [48, 49]. In addition, the carbon felt used in the present work was treated with nitric acid [33], which increased the surface area of anode and the amount of biofilm on the anode. Therefore, the carbon felt anode II at the sediment-water interface improved the electricity generation performance of DA-SMFC by inhibiting the migration of organic matters from sediment to overlying water (Fig. 6B).

Due to the depletion of organic matters in the cathode chamber of DA-SMFC, only a small amount of heterotrophic bacteria were attached on the cathode surface at the initial stage. The biofilm gradually vanished with the prolongation of operation time due to lack of organic substrates. In other words, the formation and development of biofilm on DA-SMFC cathode was inhibited due to the reduced influx of organic matters [32]. A surface biofilm imposes an additional resistance on the oxygen reduction reaction with protons, causing overpotentials on cathode and reduced cathodic reactions [8]. The larger effective area of DA-SMFC cathode could promote the kinetic activity of cathode. In all, the carbon felt at the sediment-water interface of DA-SMFC can inhibit the migration of organic matters to the cathode, reduce the formation and development of biofilm on cathode surface, and thus improve the voltage generation performance of SMFC.

An increased the amount of dissolved oxygen (DO) and current of MFC by inhibiting the growth of heterotrophic aerobic bacteria with silver nanoparticles as a cathode catalyst [28]. Similar results were also demonstrated by other researchers [31, 50]. A high R_{ct} of cathode indicates a higher overpotential for oxygen to be transferred from water to electrode surface. Our results suggest that DA-SMFC might be able to obtain more DO than SMFC, which contributed to the higher kinetic activity of cathode and its excellent voltage generation performance.

4. CONCLUSION

A double-anode sediment microbial fuel cell (DA-SMFC) with the ability to effectively inhibit the colonization of heterotrophic bacterium has been rationally designed and constructed. Compared with conventional SMFCs, the DA-SMFC was able to dramatically inhibit the growth of cathode bacteria and lower the R_{ct} of cathode from 118.9 Ω to 91.6 Ω. The reduction in the amount of cathode bacteria significantly enhanced the kinetic activity of cathode, increased the voltage generation of SMFC up to 376 mV, and improved the stability of SMFC. The barrier carbon was felt via physical adsorption onto anode II, which was used to control the carbon source, e.g. the organic matters in the sediment, of cathode bacteria. In conclusion, the simple design of DA-SMFC with a carbon felt at the sediment-water interface was able to control the carbon source of cathode heterotrophic aerobic bacteria, and optimize the kinetics of ORR, and would promote the application of SMFC.

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