Enhancing the Performance of Sediment Microbial Fuel Cell using Graphene Oxide – Zeolite Modified Anode and V_2O_5 Catalyzed Cathode

Md. T. Noori, D. Paul, M. M. Ghangrekar, and C. K. Mukherjee

***Abstract*—Sediment microbial fuel cells (SMFCs) are the auspicious technology, which can recover energy from wastes in low-cost, but the low-level power recovery from these devices is great obstacle towards its community acceptance. The performance of SMFC could be prominently improved by using graphene oxide – Zeolite modified anode (GZMA) and application of V_2O_5/Vulcan XC composite catalyst on cathode. The SMFC with GZMA and V_2O_5/Vulcan XC composite catalyst (SMFC-4) was able to recover a power density of 15.2 mW/m^2 from fresh water aquaculture pond. This power density was found 2.49-times higher than the SMFC using GO modified anode (GMA) and without catalyzed cathode (SMFC-1). However, GMA and V_2O_5/Vulcan XC composite catalyzed cathode in SMFC-2, the power density of 6.02 mW/m^2 obtained from SMFC-1 could be enhanced to 10.6 mW/m^2 for SMFC-2, which was found slightly higher than the SMFC using GZMA and without catalyzed cathode (SMFC-3, 10 mW/m^2). The wastewater treatment efficiency in terms of chemical oxygen demand and total kjeldahl nitrogen from aquaculture water was found highest in SMFC-4 with a value of 89.5 ±1.9% and 64.2 ± 1.7%, respectively. In addition, at the end of each batch cycle i.e. after 15 days of continuous operation, all the SMFCs were found to be capable of reducing the ammonia nitrogen up to desired level (i.e. < 1 mg/L) for culture of India major carp.**

***Index Terms*—Indian major carp, power density, sediment microbial fuel cell, Water treatment.**

I. Introduction

Energy scarcity and ever-growing water pollution have become shattering problem for this world due to which the research focus on green energy has been shifted to develop sustainable technologies, capable of solving both the problems together [1]. Sediment microbial fuel cells (SMFCs) are newly developed device which can efficiently produce renewable energy from highly contaminated soil sediment with an additional feature of in-situ water and sediment treatment [2]. A SMFC comprises two electrodes viz. anode and cathode impeded 10 – 20 cm down the sediment-water interface and 5 – 10 cm below the air-water interface, respectively. Microorganisms in anode anaerobically oxidizes organic matter present in sediment by producing proton and electron. A natural voltage gradient, forces to move electrons via external circuit and protons via sediment to the cathode where redox cycle completes by reduction of oxygen with electron and proton. As a result, a usable voltage is developed between anode and cathode.

The bottom sediment and water in aquacultural pond becomes highly contaminated due to deposition of uneaten fish feed, dead biomass and fish excreta which eventually turns the water toxic for fish culture and thus needs quality in-situ treatment for making this water suitable for culture. The installation of SMFCs in aquacultural ponds can be promising approach for in-situ treatment of sediment and water [3], [4]. As for example, Sajana *et al*. (2013a) [2] was employed SMFC for in-situ remediation of aquaculture pond water and sediment. The results showed excellent removal efficiency for chemical oxygen demand (COD) and total Kjeldahl nitrogen (TKN) with a value of 79.4 % and 92.6 % respectively. In addition, the oxidizable organic matter in the sediment also reduced from 2.1 % to 0.64 % with recovery of specific power density (Pd) of 107.3 μW/m^2 normalized to anode surface area. Though the water treatment was found sufficient but this μW-level power cannot be used. Therefore, comprehensive strategies will be required to elevate the power recovery from SMFCs.

Power recovery can be enhanced by suitable enhancement in electrode reaction kinetics using electrochemical catalysts on cathode and incorporation of biocompatible materials on anode. The un-catalyzed cathode used in MFCs or SMFCs owes high overpotential which undesirably affects the oxygen reduction reaction (ORR), therefore hampering the performance. The novel metals as for example Pt, Pd, Ag etc. showed promising catalytic activity to diminish overpotential loss and enhanced the ORR and hence used widely as cathode catalyst for application in MFCs/SMFCs. However, the high cost of these catalyst forbids their use in such low-cost energy tapping solutions. As a solution, various low-cost non-platinized catalysts have been developed, for instance MnO_2 with graphene [5], V_2O_5 and MnO_2 with Vulcan XC [6], [7] showed excellent property for enhancing the ORR. A bare carbon anode possess higher degree of hydrophobicity and owns less site for microbial colonization which inhibits the biofilm formation, resulting in less power recovery. Recently, use of graphene for modification of anode and cathode showed excellent electrode kinetics and substantially ENHANCED THE POWER OUTPUT FROM MFCs [8]. In different studies, the stainless steel wire mesh anode modified with graphene enhanced the Pd by 18-times in MFC (2668 mW/m^2) as compared to the MFC using unmodified anode (159 mW/m^2) [9]; whereas the power density could be elevated from 85.4 mW/m^2 in MFC using unmodified anode to 215 mW/m^2 in MFC using zeolite modified anode due to

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enhanced hydrophilicity [10]. Hence, as a remedy of low power out from SMFC, modification of anode by graphene oxide-zeolite and a suitable low-cost cathode catalyst could be a promising approach to enhance power recovery. The aim of this study was to evaluate the combined effect of V_2O_5/Vulcan XC catalyst on cathode and graphene oxide (GO) – zeolite (GZMA) composite or GO modified anode in SMFC. The performance of different combination of anode and cathode modification was assessed in terms of wastewater treatment, sediment treatment and power recovery.

II. Materials and Methods

A. Fabrication of Anode and Cathode

Modified Hummer's method was used to synthesize graphene oxide sheets [11], [12]. Composite solution of GO and zeolite (mass ratio 2:1) was prepared by dispersing required amount of GO (200 mg) and zeolite (100 mg) in 200 ml of deionized water using titanium horn probe sonicator (Piezo-U-Sonic, India). After 3 h of sonication, 5 ml of 5% polyvinyl alcohol (PVA) was mixed to the composite solution and sonicated for 30 min. The piece of carbon felts serving as anode having actual surface area of 200 cm (20 cm × 10 cm) was pretreated with 1 N HCl and cleaned under sonication for 30 min using deionized water to remove attached dust particles. Subsequently, rinsed repeatedly with deionized water and ethanol (35%) followed by heat treatment in muffle furnace for 30 min at 400 ℃. Treated carbon felts were then soaked in the above composite solution in a clean aluminum foil for 24 h at a temperature of 60 ℃ to obtain GO-zeolite modified anode (GZMA). A control GO modified carbon felt anode (GMA) was fabricated following the same procedure without presence of zeolite in the solution. The GZMA and GMA were further heat treated in a hot air-oven at 60 ^oC for 24 h and then stored in dehumidified container for further use in SMFC. Cathodes were fabricated using carbon felt current collector of dimension 20 cm × 10 cm. Current collectors were coated with V_2O_5/Vulcan XC composite catalyst and Vulcan XC base layer to fabricate high performance multilayered cathode as described earlier [6].

B. Test SMFCs

SMFCs were fabricated with PVC cylinder having an internal diameter of 11 cm and a length of 1.5 m as used in earlier studies [3]. Four identical SMFCs with different combination of anode and cathode were used in this study described as follows. The SMFC-1 contained GMA and bare carbon felt cathode, SMFC-2 had GMA and V_2O_5/Vulcan XC cathode, SMFC-3 had GZMA and bare carbon felt cathode and SMFC-4 had GZMA and V_2O_5/Vulcan XC. Anodes were placed vertically at a distance of 20 cm from the bottom, and the cathodes were positioned on the water column leaving a 5 cm distance from the surface of water. The end-to-end gap between anode and the cathode was 75 cm. After positioning the electrodes, PVC pipes were filled with sediment collected from an aquacultural pond containing Indian major carp (Silver Carp, Rohu, Catla and Mrigal) up to a height of 50 cm from the base. The schematic of SMFC is illustrated in Fig. 1. The experiments were carried out in batch mode using aquaculture water as substrate with a feeding cycle of 15 days. The chemical oxygen demand (COD) of 160-180 mg/L and ammonium nitrogen concentration of 3-4 mg/L were maintained by required amount of sucrose and NH_4Cl, respectively during feeding the SMFCs. Electrodes were connected externally with concealed copper wire using 330 Ω external resistance. Aeration was provided near the cathode by availing commercially available aquarium aerators at a depth of 25 cm from the top liquid level in all the SMFCs.

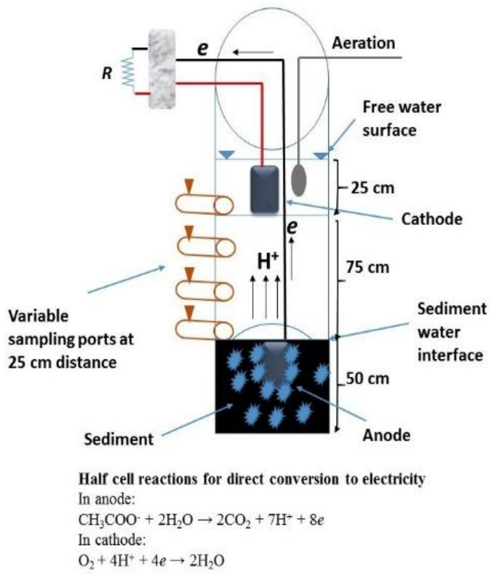

Fig. 1. Schematic diagram of test SMFC.

C. Analysis and Calculations

The pH of the aquaculture water was measured with digital pH meter (Kusam meco, India). Ammonium nitrogen (NH4+-N) of the samples were determined by using ion selective probes (Thermo Fisher Scientific, USA). Total Kjeldahl Nitrogen (TKN) and COD of water and sediment samples were estimated by using standard protocol as suggested by APHA (1998) [13]. The percent weight of organic carbon in sediment was determined by the loss on ignition (LOI) method, which is based on sequential heating of the samples in a muffle furnace [14].

The daily observation of voltage (V) and current (I) were noted using a digital multimeter (RISH Multi 15S, India). Polarization studies were carried out by varying the external resistance from 40,000 Ω to 30 Ω using resistance box (GEC 05 R Decade Resistance Box, India) after allowing the circuit to stabilize for 30 minutes at each resistance and corresponding voltages were recorded. The current density (Id) and power density (Pd) were calculated according to Id (mA/m^2) = V/RA where, V is voltage at corresponding to the resistance (R) and A is the projected anode surface area (m^2) and Pd (mW/m^2) = $V \times Id$. Internal resistance of the SMFCs were measured from the slope of the line from the plot of voltage versus current.

III. Results and Discussion

A. Water and Sediment Treatment

Aquaculture used water and in-situ sediment treatment is one of the foremost advantage of SMFC [2]. The effluent aquaculture water quality from all the SMFCs was monitored for COD, nitrogen content in the form of TKN and ammonium-nitrogen (NH_4^+-N) concentration in influent and effluent. The COD concentrations of water in all three SMFCs were observed in 5 days interval and at the end of the first batch cycle, it was found to reduce from 160-180 mg/L to 20-30 mg/L in SMFC-2, 3 and 4. SMFC-1 showed comparatively higher concentration of COD in the range of 30-40 mg/L in effluent water. The trend was found almost similar for all batch cycle for 60 days of operation (Fig. 2a). In contrast to the all batch cycle, the highest average COD removal efficiency of 89.5 ± 1.9% was observed in SMFC-4 followed by SMFC-2 (85 ± 1%), SMFC-3 (83.4 ± 1.2%), and SMFC-1 (79 ± 2%). The result indicates that the enhanced reaction kinetics of anode and cathode offered synergetic effect on organic matter degradation, resulting in higher COD removal efficiency in SMFC-4 which was expected to have better electrode kinetics due to anodic modification with GZMA and catalyst layer on cathode. In addition, enhanced ORR in SMFC-4 and SMFC-2 using V_2O_5/Vulcan XC cathode helped to balance microenvironment inside anode which tended the anodofile to utilize more substrate, therefore enhanced COD removal efficiency was observed [15]. However, the increased biocompatibility of anode offered by zeolite also had significant effect on the COD removal efficiency due to which the SMFC-3 revealed almost similar removal efficiency as compared to the SMFC-2. Following similar trend of COD, the effluent TKN concentration of 1.37 mg/L in SMFC-4 was the lowest followed by SMFC-3 (1.75 mg/L), SMFC-2 (1.7 mg/L) and SMFC-1 (2 mg/L) after completion of first batch cycle (15 days) when the substrate contained initial TKN concentration of 4.1 mg/L, 4.31 mg/L, 4.23 m/L, and 4 mg/L in SMFC-1, SMFC-2, SMFC-3 and SMFC-4, respectively (Fig. 2b). The average TKN removal efficiency of 52.9 ± 1.6%, 59.6 ± 2.1%, 59.2 ± 1.2% and 64.2 ± 1.7% was achieved in SMFC-1, SMFC-2, SMFC-3 and SMFC-4, respectively during observation period of 60 days (4 batch cycle).

TABLE I: AVERAGE (±SD) IN-SITU POLLUTANT REMOVAL EFFICIENCY BY USING DIFFERENT SMFCS

SMFC	Water treatment			*Sediment treatment	
	COD, %	TKN, %	NH4+, %	COD, %	TKN, %
SMFC-1	79 ±2%	52.9 ±1.6%	73.4 ±1.7	37%	35.8%
SMFC-2	85 ±1%	59.6 ±2.1%	74.3 ±1.2	46%	42.9%
SMFC-3	83.4 ±12%	59.2 ±1.2%	73.7 ±2	48.2%	46%
SMFC-4	89.5 ±1%	64.2 ±1.7%	81.4 ±1.6	52.1%	49.4%

* After completion of the experiment (60 days).

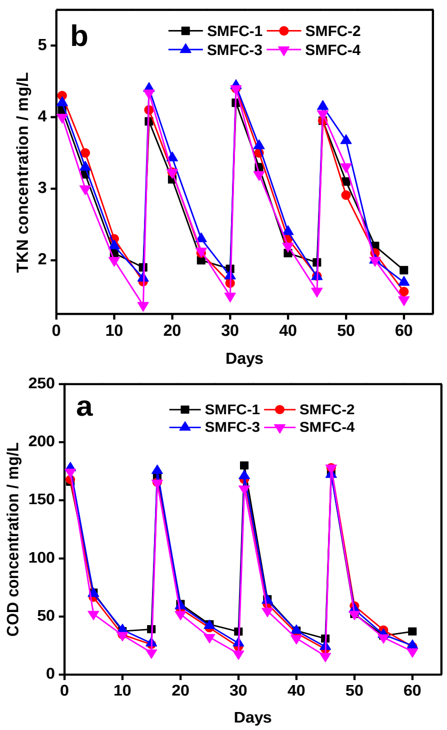

Fig. 2. (a) COD and (b) TKN concentration profile in the function of operation day.

The presence of excess of NH_4^+-N concentration in aquaculture water can cause serious health issues to the fish. Based on the several studies the NH_4^+-N concentration more than 1 mg/L was found lethal for various species of fish and aquatic animal including IMC [16]. The concentration of NH_4^+-N of 3-4 mg/L was maintained in pond water to evaluate the nitrification ability of SMFCs. During first batch cycle, the NH_4^+-N concentration was observed below 1 mg/L with removal efficiency of 71% for SMFC-1, 72.7% for SMFC-2, 74% for SMFC-3 and 82% for SMFC-4. At the end of the each batch cycle, consecutively for 4 batch cycles, the ammonium-nitrogen concentration in the effluent water was found to be < 1 mg/L which can be considered healthy for optimum growth of IMC [16] and hence revealing SMFCs as an excellent device for in-situ ammonia nitrogen treatment from aquaculture pond. The overall treatment performance of different SMFCs is shown in Table I.

The initial concentration of organic matter in the sediment was found to be 5.72%. After 60 days of operation, it was reduced to 3.5%, 3.01%, 2.9% and 2.68% in SMFC-1, SMFC-2, SMFC-3, SMFC-4, respectively. In contrast, higher organic matter removal efficiency of 52.1% was observed in SMFC-4 followed by SMFC-3 (48.2%), SMFC-2 (46%) and SMFC-1 (37%). Similarly, the initial TKN concentration of the sediment was estimated as17 mg/g and after 60 days of SMFC employment, the TKN values of the sediment were reduced to 10.9 mg/g, 9.7 mg/g, 9.1 mg/g and 8.6 mg/g for SMFC-1, SMFC-2, SMFC-3 and SMFC-4, respectively which is in terms of removal efficiency can be calculated as 35.8% for SMFC-1, 42.9% for SMFC-2, 46% for SMFC-3 and 49.4% for SMFC-4. These results indicate that the organic matter in the sediment was oxidized by the bacteria on the anodes and the enhanced biocompatibility of anode modified with GZMA facilitated favorable environment to degrade higher amount of organics as compared to the other anode in SMFC. Moreover, the oxidized layer at the sediment surface layer prevents diffusion of toxic compounds into pond water, favoring better water quality suitable for fish growth [4].

A. *Power Production*

Electricity generation reached at stable state after first feed-batch cycles in all three SMFCs. As shown in Fig. 3a, SMFC-4 produced maximum operating voltage (OV) of 319 mV with maximum sustainable power density of 15 mW/m^2 followed by SMFC-2 (225 mV and 7.6 mW/m^2), SMFC-3 (210 mV and 6.7 mW/m^2) and SMFC-1 (159 mV and 3.8 mW/m^2). This higher OV and sustainable power density in SMFC-4 among other tested SMFCs was due to enhanced redox kinetics regulated by GO-zeolite composite in anode and V_2O_5/Vulcan XC catalyst in cathode. The results also infer that the cathode kinetics had vital effect on the performance due to which SMFC-2 performed better as compared to SMFC-3 and SMFC-1, though having GZMA and GMA, respectively. In addition, the voltage drop in all the SMFCs can be seen at the end of the each batch cycle possibly due to limited availability of organic matter in the substrate.

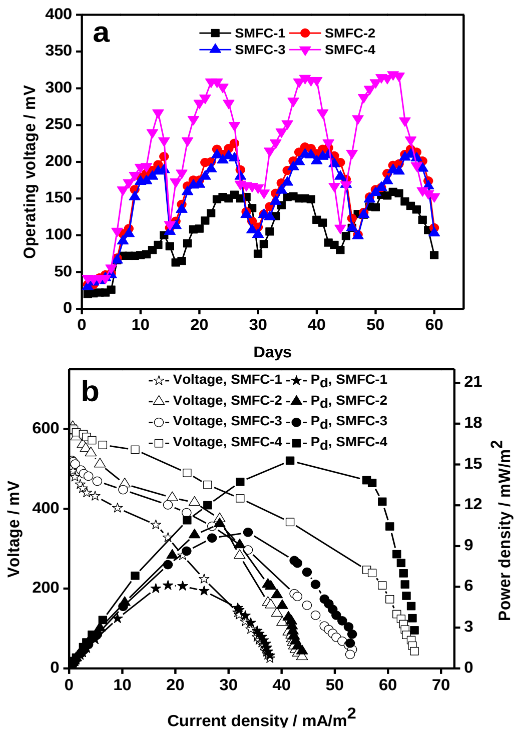

Fig. 3. (a) Daily observation of voltage output from SMFCs and (b) Polarization plots.

Polarization studies were performed to obtain optimum power density normalized to the actual surface area of anode. A lower power density of 6.09 mW/m^2 was obtained in SMFC-1 with unmodified anode and without catalyzed cathode, in contrast with highest power production of 15.2 mW/m^2 in SMFC-4 followed by 10.6 mW/m^2 in SMFC-2 and 10 mW/m^2 in SMFC-3 (Fig. 3b). The calculated internal resistance of 326 Ω was lowest in SMFC-4, resulting in highest maximum current density of 65 mA/m^2 followed by SMFC-2 (432 Ω), SMFC-3 (485 Ω) and SMFC-1 (668 Ω). The voltage vs. current density plot as shown in Fig. 3b, also reveals higher overpotential loss including activation loss, ohmic loss and concentration loss in SMFC-1 as compared to other SMFCs and hence supported lowest current density of 37 mA/m^2. SMFC-4 had lowermost voltage drop in high, moderate and low current range, revealing less overpotential loss due to improved anode and cathode kinetics [17]. Due to presence of V_2O_5/Vulcan XC in SMFC-2, however fetched significant improvement on power density as compared to SMFC-3 (only anode was modified) but at higher current density a significant drop in voltage was occurred. This sudden voltage drop can be attributed to the concentration overpotential which resulted in less current density in SMFC-2 as compared to SMFC-3 (43.8 mA/m^2 vs. 53 mA/m^2).

IV. Conclusion

The present study demonstrated the effect of GZMA and V_2O_5/Vulcan XC catalyzed cathode on the performance of freshwater SMFC. Synergetic effect of anode and cathode modification with GO-zeolite and V_2O_5/Vulcan XC, respectively in SMFC (SMFC-4) showed 1.5 and 2.49-times higher power as compared to the SMFC using GZMA and without catalyzed cathode (SMFC-3) and SMFC using GMA without catalyzed cathode (SMFC-1), respectively. The SMFC-4 also demonstrated superior water/sediment treatment as compared to other tested SMFCs. In addition, all the SMFCs offered adequate water treatment at the end of the batch cycle. The present modification technique of anode and cathode for SMFC will be beneficial for scaling-up this technology to obtain renewable energy from aquaculture ponds as well as to improve the in-situ treatment efficiency of SMFCs.

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