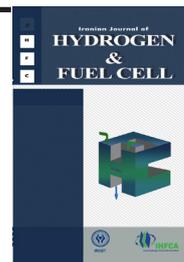


Iranian Journal of Hydrogen & Fuel Cell

IJHFC

Journal homepage://ijhfc.irostd.ir



A comparative study of three types of anode electrodes in a microfluidic microbial fuel cell

Maede Yahyanezhad Gele, Soheila Yaghmaei*, Mohammad Mahdi Mardanpour

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Azadi Avenue, P.O. Box 11365-9465, Tehran, Iran

Article Information

Article History:

Received:

04 Mar 2021

Received in revised form:

03 Apr 2021

Accepted:

12 Apr 2021

Keywords

Microfluidic microbial fuel cell

Anode

Nanomaterial

Oxalate

Shewanella oneidensis MR-1

Abstract

Microbial fuel cells (MFCs) are innovative bioelectrochemical approaches for the natural conversion of organic resources into energy based on the metabolic activities of inoculated bacteria that serve as biocatalysts. The main objective of the present study was to examine the effect of zinc foil modified with zinc oxide as a novel anode material to enhance power generation in a microfluidic MFC using oxalate as a substrate. X-ray diffraction and FE-SEM analyses were done for nanostructure confirmation and to understand the morphology of a zinc oxide-coated electrode. The microfluidic MFC performance was investigated and compared with a zinc foil and zinc foil linked stainless steel mesh through an external circuit. The experimental results expressed that the zinc foil, zinc foil externally linked stainless steel, and modified zinc foil as anode electrodes achieved the maximum power density of 2980 W m⁻³, 1080 W m⁻³, and 428 W m⁻³, respectively. The results demonstrated that the zinc oxide nanorods could not act as an effective avenue for improving the microfluidic MFC performance.

1. Introduction

Microbial Fuel Cells (MFCs) have been considered as a promising technology for the direct transformation of an organic substance into electricity using bacte-

rial biofilm as biocatalysts [1–3]. A microfluidic fuel cell, also called a co-laminar flow-based fuel cell, makes use of the liquid-liquid interface in place of a membrane for separation between the anolyte and catholyte [4–6]. Micro-scale MFC could be an interesting alternative power source for portable medical and electronic instruments [7]. Moreover, microfluidic

*Corresponding author. Phone number: +982166166430

E-mail address: yaghmaei@sharif.edu

doi: 10.22104/ijhfc.2021.4765.1217

fuel cells have the advantage of a high surface-to-volume-ratio, which is very beneficial in the performance of the cell due to the fact that electrochemical reactions are surface-based.

Since the application of micro-scale MFCs as a bio-energy generator for implantable medical devices (IMDs) includes bioelectricity [8], hydrogen as an effective antioxidant [9], and the presence of different hazardous organic sources in living organs, oxalate can be introduced as a potential substrate. Oxalate is the ionized form of oxalic acid mainly excreted through the kidney and is recognized as a toxic end-metabolite in the human body. Researches have shown that some diseases, like renal lithiasis, are caused by oxalate accumulation [10] and others are related to the amount of oxalate in the human body, such as chronic obstructive pulmonary diseases (COPDs) and asthma [11], autism [12], depression [13], coronary heart diseases (CHDs), and stroke [14].

Different factors influence the performance of MFC, for instance, equipment configuration and electrode material. Improving the above-mentioned agents would be very efficient in boosting the performance of an MFC. Among these, anodic materials are one of the most important factors affecting the execution of an MFC since they are the habitat of microorganisms, and the anode's characteristics influence the biofilm formation [15, 16]. Characteristics of an ideal anode are excellent electrical conductivity, high hydrophilicity, large surface area, and good biocompatibility, all of which are necessary for strong biofilm generation and better electrocatalytic activity [17–19]. Power generated by an MFC may not be sufficient for the continuous operation of a sensor or a transmitter. This is the main problem of using microbial fuel cells. Increasing the surface area of the electrodes can be a practical solution for this problem. A modified anode electrode could promote the performance of MFCs. In this regard, researchers in several studies have begun to adjust anodes using different nanoengineering techniques that have the ability to make electron transfer easier [20]. Also, different fabrication methods and modification styles involving nanomaterials have been carried out [21]. Modifying an anode with microstructures or coatings not only increases the surface area, which results in more current collection but also improves the adhesion ability of microbes to the electron surface [22, 23].

Our motivation in this work is to investigate zinc foil as a metal-based anode, the effects of an anode modi-

fied with ZnO nanostructures, and the role of providing excess surface for biofilm formation on improving the power generation in a micro-scale MFC.

2. Experimental

2.1. Electrode fabrication

The modified zinc foil ($20 \times 20 \times 0.2$ mm, 99.9%) was pretreated according to the previously reported procedures [25] to achieve zinc oxide nanorods. In the first step, the zinc foil was first sonicated in ethanol for 5 min and then dried in a flow of dry nitrogen. In the succeeding step, clean zinc foil was submerged in a solution of ethylenediamine (11 mL) and water (24 mL) in a Teflon-lined stainless-steel autoclave (100 mL). The autoclave was heated at a constant temperature of 160°C for 24 h in an oven. After the hydrothermal treatment, the resulting zinc foil was taken out and washed with ethanol and the air-dried.

2.2. Electrode characterization

The crystal structure of the modified anode was analyzed by X-ray diffraction (XRD, PANalytical, PW3040/60 diffractometer). The morphology and composition of zinc foil modified with ZnO nanorods was characterized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7001F) and EDS.

2.3. Microfluidic assembly

The geometry of a microfluidic MFC was considered as a spiral microchannel cut by a laser beam with a thickness of $200 \mu\text{m}$ on polymethyl methacrylate (PMMA). The channel width and fluid passage length were $500\text{--}1000 \mu\text{m}$ and 11.03 cm, respectively. The total volume of the microfluidic MFC was $16.5 \mu\text{l}$. A zinc sheet was used as the anode of the cell. The thickness, width, and length were 0.2 mm, 2 cm, and 2 cm, respectively. The cathode electrode was fabricated with carbon cloth as a base material (2 cm in length and 2 cm in width) and covered by 0.5 mg cm^{-2} of platinum loading as reported in Cheng et al. [24]. It was glued to one side of the anodic compartment, and the cathode was placed in front of the zinc anode. Zinc

foil was coated with ZnO nanorods, as mentioned above. The zinc foil and zinc foil linked externally with stainless steel mesh (2 cm in length and 2 cm in width) were then applied as anodes in three separate operations of microfluidic MFCs.

2.4. Microfluidic MFC microbial culture

Shewanella oneidensis MR-1, obtained from the Biochemical and Bioenvironmental Engineering Center, Sharif University of Technology, Iran, was used as the biocatalyst of the microfluidic MFC. It was cultured in a tryptone soy broth (TSB) medium (5 g l⁻¹ NaCl, 2.5 g l⁻¹ K₂HPO₃, 17 g l⁻¹ tryptone, 3 g l⁻¹ soya peptone, and 2.5 g l⁻¹ glucose) under aerobic conditions at 30 °C. The medium was injected continuously using a syringe pump (New Era; NE-4000; USA) under an open-circuit condition. A steady cell potential peak was indication of successfully microbial enrichment and biocatalyst stabilization.

2.5. Analysis of microfluidic MFC

During the cell operation, its potential (V) was recorded in time intervals of 2 min using a multimeter data-

logger connected to a laptop. The current and power was obtained by Ohm's law ($I = V/R$) and the value of the external resistance in a closed-circuit condition. They were normalized using anodic section volume as mentioned in Logan et al. [25]. To polarize the microfluidic MFC, the variable external resistance, in the range of 0.1 to 250 kΩ, was used.

3. Results and Discussion

3.1. Characterization of modified electrode

X-ray diffraction analysis was employed to identify the crystalline structure of the synthesized sample. Figure 1 shows the XRD pattern of ZnO nanorods synthesized on zinc substrate. The diffraction peaks at $2\theta = 32.03, 34.69, 36.51, 47.77, 56.80, 63.07, 66.58, 68.15, 69.28, 72.91$ and 77.18 correspond to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes, respectively. All of these peaks are related to zinc oxide nanostructures.

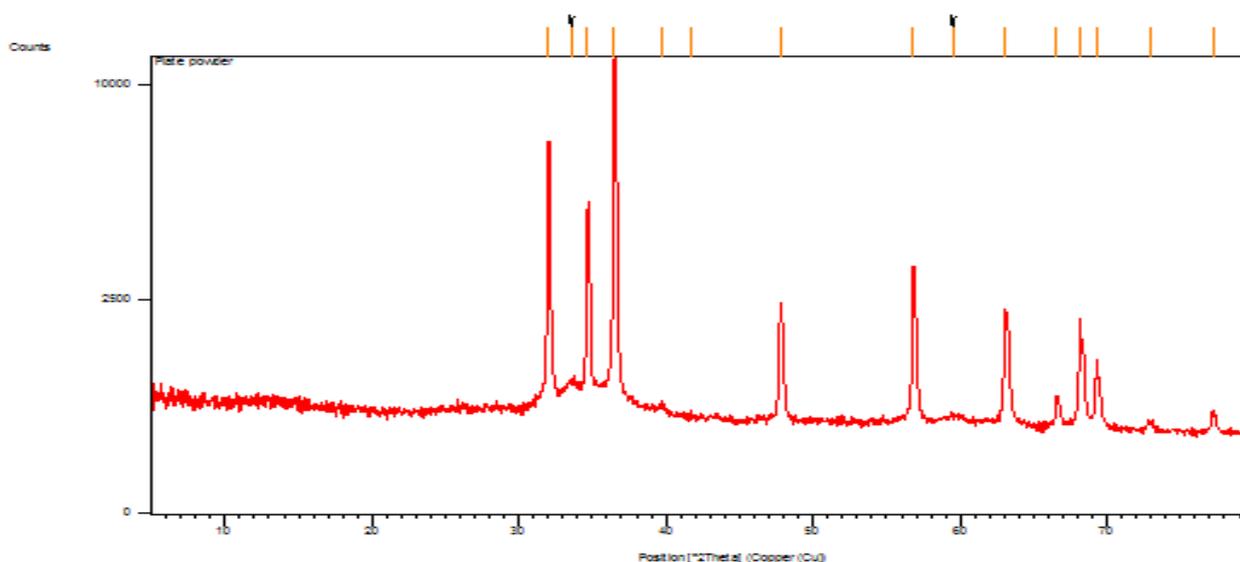


Fig. 1. The XRD pattern of the prepared anode electrode.

Field-emission scanning electron microscopy (FE-SEM) was utilized to determine the shape, particle size, and morphology of the synthesized material. As

can be observed from Figures 2a and b, the ZnO nanostructure possesses a nanorod shape. ZnO nanorods have a uniform distribution size of 30-50 nm.

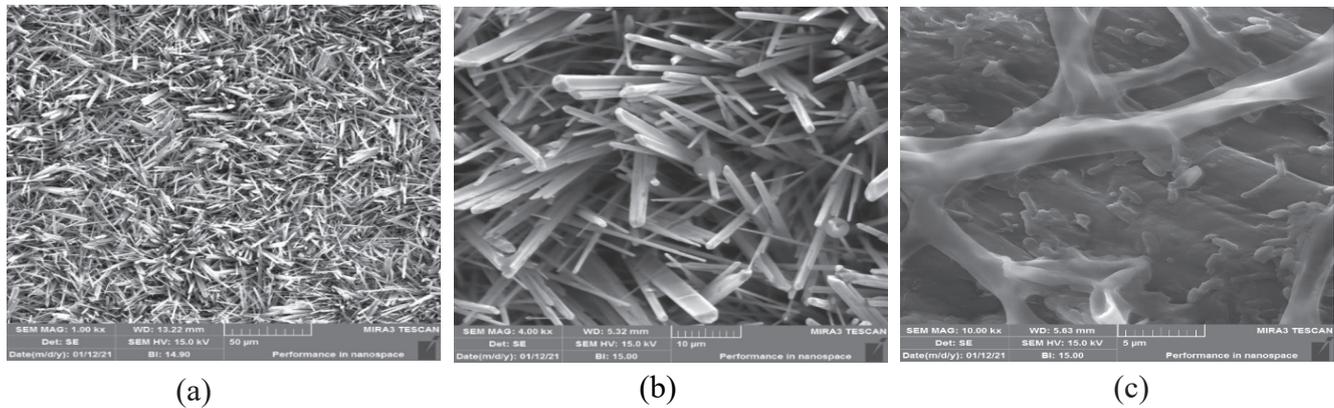


Fig.2. FE-SEM images: the ZnO nanorods synthesized on zinc substrate at (a) 1000 and (b) 4000 magnification, respectively, and (c) the biofilm layer on the zinc foil anode after inoculation.

In addition, elemental analysis was performed, and the results are illustrated in Figure 3. The final modified electrode includes the related pieces and is in good agreement with the formation of the synthesized

nanostructure. As shown in the inset, the EDS spectrum could help determine the weight percentages and quantity of each element.

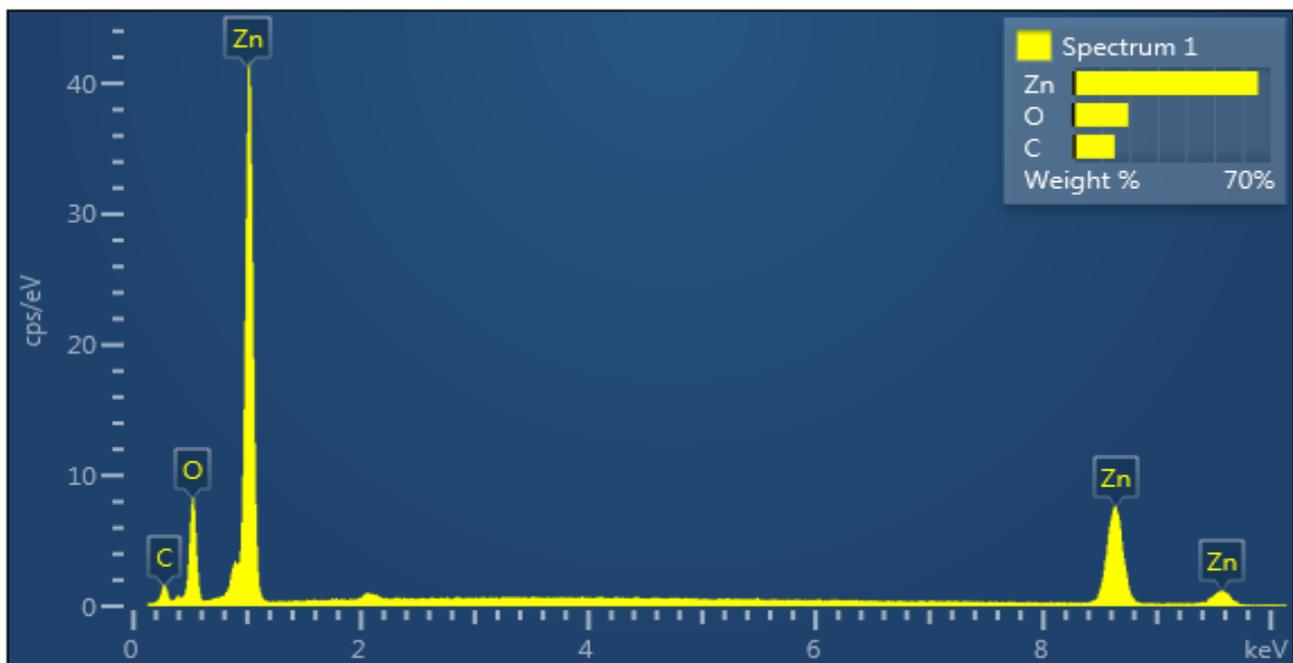


Fig. 3. EDS spectrum of the synthesized ZnO nanorods on zinc substrate.

3.2. Effect of different substrate flow rate on the microfluidic MFC performance

In order to evaluate oxalate biodegradation conditions and select an appropriate feed injection rate, the current evolution of microfluidic MFC at 10 k Ω external resistance, as a power supply, was monitored at a concentration of 156 mg l⁻¹ the normal amount of oxalate in urine. The sustained current density at an anolyte flow rate of 100 μ l h⁻¹ and 200 μ l h⁻¹ was 2010 A m⁻³

and 4250 A m⁻³, respectively. As shown in Figure 4, the output current density for microfluidic MFC at an anolyte flow rate of 200 μ l h⁻¹ was greater than at 100 μ l h⁻¹. Increasing the substrate flow rate to 500 μ l h⁻¹ resulted in a decrease in the current density to 3850 A m⁻³. The increase in the substrate flow rate brings about distraction in the bioelectrochemical activity of the microorganism; this might be the cause of low current density at higher substrate flow rates.

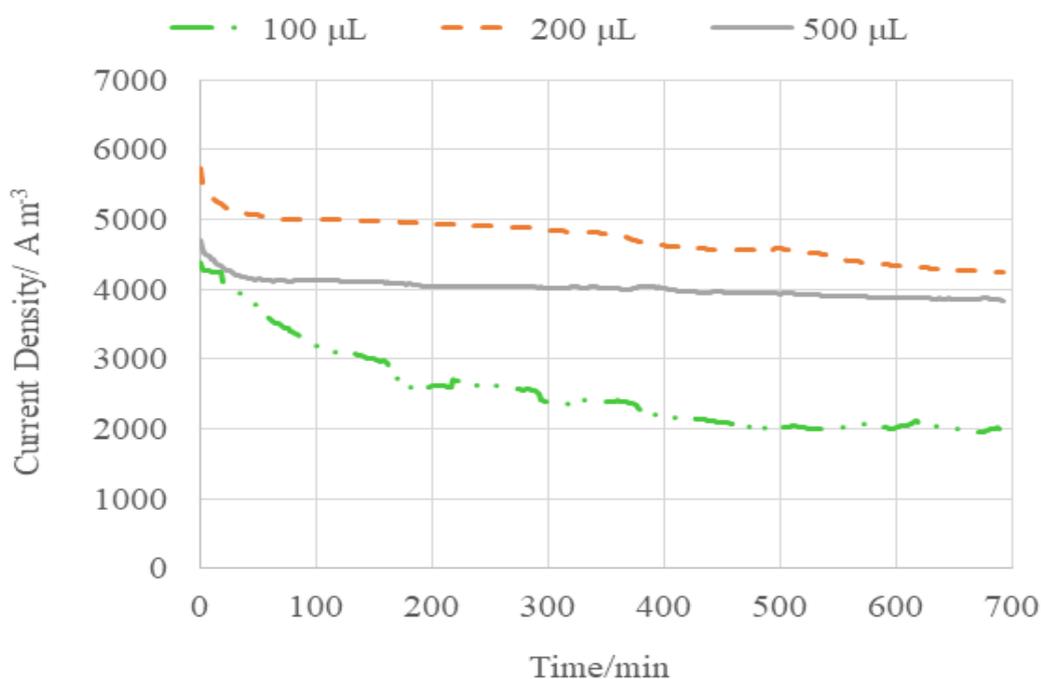


Fig.4. Current evolution of microfluidic MFC at an external resistance of 10 k Ω .

3.3. Open Circuit Potential (OCP)

Microfluidic MFC operation was under an open circuit potential (OCP) condition at the optimum anolyte flow rate of 200 μ l h⁻¹ for all three anode materials. For the zinc foil anode, the beginning OCP of the microfluidic MFC was 1591 mV; after 1050 min, it sustained the constant maximum amount of 1251 mV. Since the externally linked stainless steel mesh provided more space for biofilm formation than the zinc foil solely, it was expected that a higher cell potential would be observed; but as shown in Figure 5, the maximum po-

tential decreased to 1210 mV (about 3% lower than the zinc sheet). In the succeeding step, the zinc foil modified with ZnO nanorods was used to assess the effect of the increased area provided by these nanostructures. As can be observed in Figure 5, the cell potential not only did not increase but decreased about 6% lower than the unmodified zinc foil. As reported in previous studies [26–28], nano-decoration can improve the adhesion of biofilm and electrochemical performance of MFC, but in this work, we observed ZnO nanorods are the exception. Hence, they are not a good alternative for modifying anode to enhance the performance of MFCs.

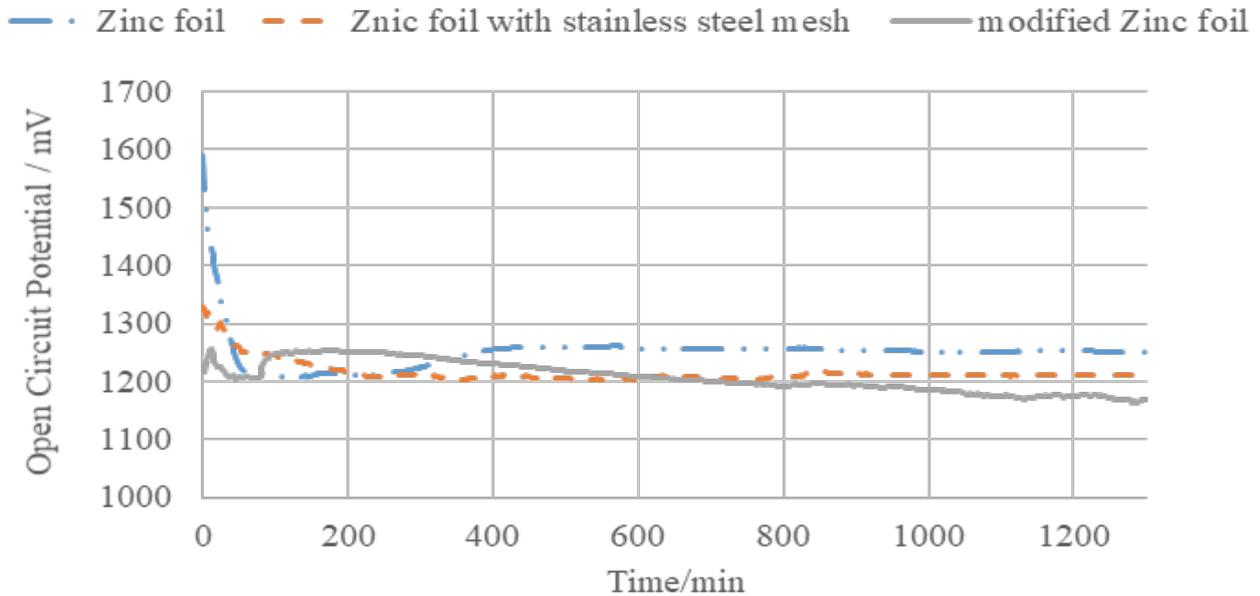


Fig. 5. Open circuit potential of different anode material at a flow rate of $200 \mu\text{l h}^{-1}$ and an oxalate concentration of 156 mg l^{-1} .

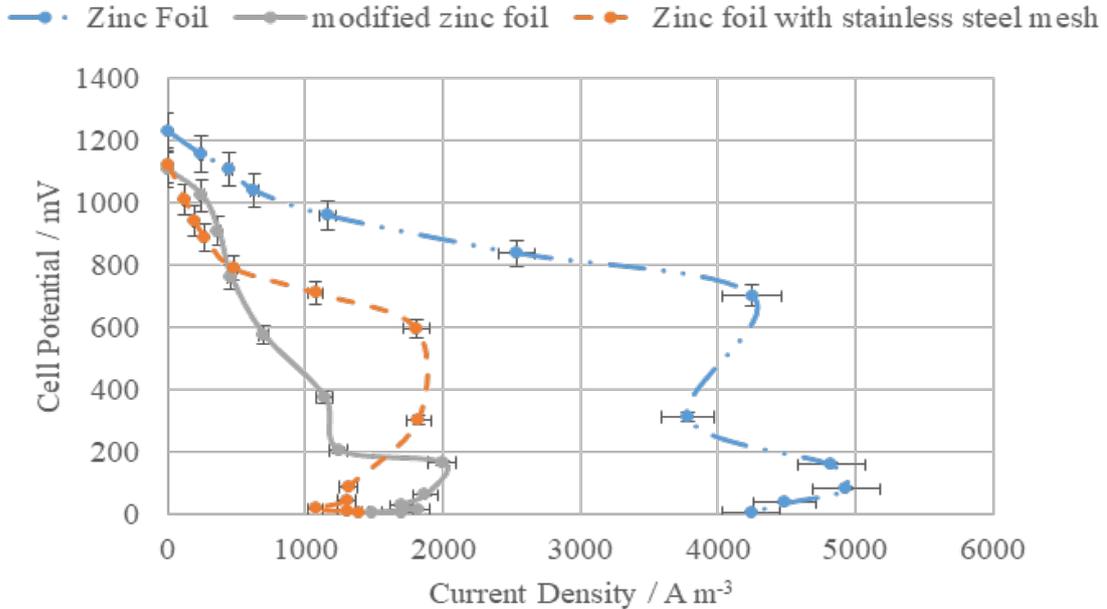
3.4. Bioelectricity generation from oxalate

The difference in the response of microfluidic MFCs to changes in the external resistance under different conditions for anode materials is better elucidated by the polarization and power density curves as shown in Figures 6a and b, respectively. Internal resistance was determined using the current interrupt method. A maximum power density of 2980 Wm^{-3} was achieved for oxalate oxidation in the microfluidic MFC using a zinc foil anode electrode. The maximum power density for the microfluidic MFC providing more surface for the growth of bacterial by linking stainless steel mesh through an external circuit to the zinc foil was observed at 1080 Wm^{-3} . Modifying zinc foil with ZnO nanorods to increase the specific surface area to improve the performance of the microfluidic MFC resulted in a power density of 428 Wm^{-3} , which was a significant decrease from the amount of the power obtained from the unmodified anode. The maximum

power densities obtained from the different anode materials confirm that ZnO nanorods cannot be useful to improve the performance of MFCs.

The internal resistance is principally resistance to electron transfer between microorganisms and electron acceptors. This parameter for an oxalate-fed microfluidic MFC at flow rates of $200 \mu\text{l h}^{-1}$ was about $50 \text{ k}\Omega$ for the modified zinc foil as the anode. The value of the other anode materials, zinc foil with stainless steel wire mesh and unmodified zinc foil, was about $10 \text{ k}\Omega$. The internal resistance of the oxalate-fed microfluidic MFC with a modified anode was 5-fold greater than the other two conditions for the anode, indicating that using ZnO nanorods on an anode surface had an opposing influence on the generation of bioelectricity by oxalate. *Shewanella oneidensis MR-1* exchanges electrons through conductive nanowires to electron acceptors. It should be noted that the electron transfer of *S.oneidensis MR-1* biofilm is based on both direct electron transfer (DET) and mediated electron transfer (MET).

(a)



(b)

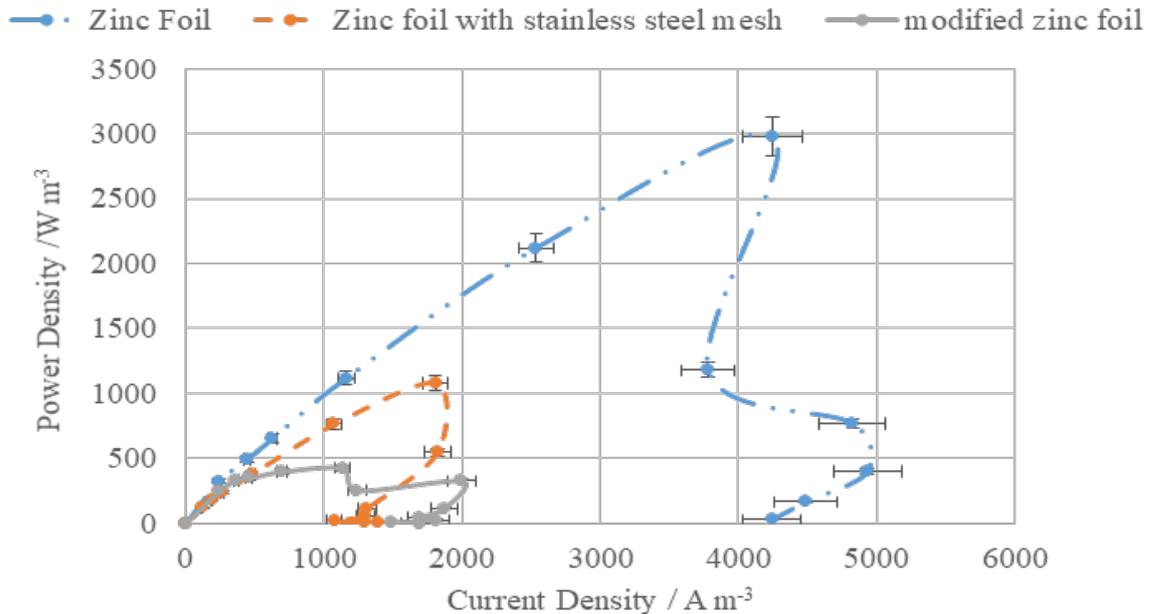


Fig. 6. a) Polarization curves for the different anode materials at a flow rate of $200 \mu\text{l h}^{-1}$ and oxalate concentration of 156 mg l^{-1} . b) Power density curves for the different anode materials at a flow rate of $200 \mu\text{l h}^{-1}$ and oxalate concentration of 156 mg l^{-1} .

4. Conclusions

The anode electrode is the most critical component in MFC performance, and modifying it can be one of the most efficient ways to increase the surface and gener-

ate more bioelectricity. In this work, modified anode electrodes have been developed to enhance the bacteria adhesion and power generation in microfluidic microbial fuel cells. The power density (428 W m^{-3}) achieved for an anode modified with ZnO nanorods was about 7 folds lower as compared to the unmodified zinc foil anode. Using an anode electrode of stain-

less steel mesh with the zinc to provide more surface area resulted in a 2.7 fold decrease in the output power density.

References

- [1] Rabaey K, Keller J. "Microbial fuel cell cathodes: From bottleneck to prime opportunity?" *Water Sci Technol* 2008;57:655–9.
- [2] Qiao Y, Bao SJ, Li CM. "Electrocatalysis in microbial fuel cells - From electrode material to direct electrochemistry". *Energy Environ Sci* 2010;3:544–53.
- [3] Li M, Zhou M, Tian X, Tan C, McDaniel CT, Hassett DJ, et al. "Microbial fuel cell (MFC) power performance improvement through enhanced microbial electrogenicity." *Biotechnol Adv* 2018;36:1316–27
- [4] Kjeang E, Djilali N, Sinton D. "Microfluidic fuel cells: A review. *J Power Sources* 2009;186:353–69.
- [5] Nasharudin MN, Kamarudin SK, Hasran UA, Masdar MS. "Mass transfer and performance of membrane-less micro fuel cell: A review." *Int J Hydrogen Energy* 2014;39:1039–55.
- [6] Mousavi Shaegh SA, Nguyen NT, Chan SH. "A review on membraneless laminar flow-based fuel cells." *Int J Hydrogen Energy* 2011;36:5675–94.
- [7] Ren H, Lee HS, Chae J. "Miniaturizing microbial fuel cells for potential portable power sources: Promises and challenges." *Microfluid Nanofluidics* 2012;13:353–81.
- [8] Mardanpour MM, Yaghmaei S. "Characterization of a microfluidic microbial fuel cell as a power generator based on a nickel electrode." *Biosens Bioelectron* 2016;79:327–33.
- [9] Fadakar A, Mardanpour MM, Yaghmaei S. "The coupled microfluidic microbial electrochemical cell as a self-powered biohydrogen generator." *J Power Sources* 2020;451:227817.
- [10] González AF, Pieters L, Hernández RD. "Effectiveness of herbal medicine in renal lithiasis: A review." *Siriraj Med J* 2020;72:188–94.
- [11] Kartha GK, Li I, Comhair S, Erzurum SC, Monga M. "Co-occurrence of asthma and nephrolithiasis in children." *PLoS One* 2017;12:1–8.
- [12] Mahajan P V., Salvi PS, Mahajan S, Subramanian S. "A Mini Review of Gastrointestinal Pathology and Nutrition in Autism Spectrum Disorder." *J Adv Med Med Res* 2019;29:1–8.
- [13] Zhang J, An S, Tang M, Wan Y, Liu Q. "Preventive strategies for patients with both heart disease and depression." *Eur J Prev Cardiol* 2018;25:1678.
- [14] Arafa A, Eshak ES, Iso H. "Oxalates, urinary stones and risk of cardiovascular diseases." *Med Hypotheses* 2020;137:109570.
- [15] Liu JL, Lowy DA, Baumann RG, Tender LM. "Influence of anode pretreatment on its microbial colonization." *J Appl Microbiol* 2007;102:177–83.
- [16] Lowy DA, Tender LM, Zeikus JG, Park DH, Lovley DR. "Harvesting energy from the marine sediment-water interface II. Kinetic activity of anode materials." *Biosens Bioelectron* 2006;21:2058–63.
- [17] Xu H, Wang L, Wen Q, Chen Y, Qi L, Huang J, et al. "A 3D porous NCNT sponge anode modified with chitosan and Polyaniline for high-performance microbial fuel cell." *Bioelectrochemistry* 2019;129:144–53.
- [18] Cui D, Wang YQ, Xing LD, Li WS. "Which determines power generation of microbial fuel cell based on carbon anode, surface morphology or oxygen-containing group?" *Int J Hydrogen Energy* 2014;39:15081–7.

- [19] Zhang P, Liu J, Qu Y, Zhang J, Zhong Y, Feng Y. "Enhanced performance of microbial fuel cell with a bacteria/multi-walled carbon nanotube hybrid bio-film." *J Power Sources* 2017;361:318–25.
- [20] Scott K, Rimbu GA, Katuri KP, Prasad KK, Head IM. "Application of modified carbon anodes in microbial fuel cells." *Process Saf Environ Prot* 2007;85:481–8.
- [21] Zhou M, Chi M, Luo J, He H, Jin T. "An overview of electrode materials in microbial fuel cells." *J Power Sources* 2011;196:4427–35.
- [22] Crittenden SR, Sund CJ, Sumner JJ. "Mediating electron transfer from bacteria to a gold electrode via a self-assembled monolayer." *Langmuir* 2006;22:9473–6.
- [23] Siu CPB, Chiao M. "A microfabricated PDMS microbial fuel cell." *J Microelectromechanical Syst* 2008;17:1329–41.
- [24] Cheng S, Liu H, Logan BE. "Increased performance of single-chamber microbial fuel cells using an improved cathode structure." *Electrochem Commun* 2006;8:489–94.
- [25] Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, et al. "Microbial fuel cells: Methodology and technology." *Environ Sci Technol* 2006;40:5181–92.
- [26] Liang Y, Zhai H, Liu B, Ji M, Li J. "Carbon nano-material-modified graphite felt as an anode enhanced the power production and polycyclic aromatic hydrocarbon removal in sediment microbial fuel cells." *Sci Total Environ* 2020;713:136483.
- [27] Naina Mohamed S, Thomas N, Tamilmani J, Boobalan T, Matheswaran M, Kalaichelvi P, et al. "Bioelectricity generation using iron(II) molybdate nanocatalyst coated anode during treatment of sugar wastewater in microbial fuel cell." *Fuel* 2020;277:118119.
- [28] Liu Y, Zhang X, Zhang Q, Li C. "Microbial Fuel Cells: Nanomaterials Based on Anode and Their Application." *Energy Technol* 2020;8.