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Microwave Preparation of Catalyst Layer for Enhancing the Oxygen Reduction of Air Cathode in Microbial Fuel Cells

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A novel microwave irradiation method was used to prepare the catalyst layer (CL) of activated carbon air cathodes (ACACs) in microbial fuel cells (MFCs) instead of conventional heating processes. Microwave preparation resulted in a more homogenous distribution of polytetrafluoroethylene (PTFE) in CLs and slightly reduced the hydrophobicity of CLs. These physicochemical characteristics improved the three-phase interfaces (TPIs) for the oxygen reduction reaction (ORR), by increasing the catalytic area of activated carbon and facilitating the diffusion of oxygen gas and H^+/OH^- ions. Compared to the conventional ACACs, the charge transfer resistance and the diffusion resistance of the microwave prepared ACACs decreased by 17.6%~35.6% and 18.4%~66.2% respectively. As a result, the maximum power density of MFCs increased by 23.3% (from 1237±84 mW/m^2 to 1525±19 mW/m^2), 15.6% (from 1370±36 mW/m^2 to 1584±9 mW/m^2) and 9.2% (from 1296±17 mW/m^2 to 1415±81mW/m^2) respectively at activated carbon/PTFE mass ratios of 4, 6 and 8. This novel preparation method has a promising future as an application in MFCs.

Keywords: microbial fuel cell; air cathode; catalyst layer; microwave; power generation

1. INTRODUCTION

Microbial fuel cells (MFCs) are a novel biotechnology for simultaneous energy recovery and wastewater treatment based on the catalytic capability of exoelectrogenic bacteria [1-3]. At present the power generation and capital cost of MFCs are primarily limited by the cathodes [4-6], hence development of cathodes that are highly efficient, low cost and easily scalable is critical for the commercialization of MFCs. Activated carbon air cathodes (ACACs) are considered as a most promising cathode type for practical applications in real MFCs, due to their high power output, relatively low cost and needless of energy consumption [7-10]. The catalyst layer (CL) of ACACs provides gas-liquid-solid three-phase-interfaces (TPIs) for the oxygen reduction reaction (ORR), thus is critical for the performance of an air cathode. The preparation approach (including the electrode fabrication method, catalyst/binder mass ratio, heating temperature, applied pressure, etc.) directly affects the microstructure, hydrophilic-hydrophobic property and distribution of catalyst and binder materials in CL, thus has a great influence on the TPIs and the ORR activity of ACACs.

To improve the TPIs of CL for ACACs, several processing parameters for electrode preparation have been optimized. For the electrode fabrication method, CLs and ACACs can be produced by an improved pressing [4, 11, 12] or rolling method [13, 14] instead of the traditional brushing method [15, 16] which is coarse and labor-consuming. In the study by Dong et al [13], optimizing the catalyst/binder mass ratio to be 6:1 resulted in an optimal TPIs based on the high ORR exchange current and maximum electricity production capacity of ACACs. In another study, Dong et al. [14] observed that heating the CL at 80^{o}C resulted in higher porosity and lower hydrophobicity than that heated at 340^{o}C. The improved TPIs facilitated the aqueous ionic transfer within the CL and increased the power generation of MFCs by 35%. Santoro et al. [12] optimized the heating temperature (150~200^{o}C) and applied pressure (1400 psi) for the fabrication of an air cathode. The CL featured a low electrode contact resistance, uniformly-distributed mesopores of 200-800 nm, and high content of carbon oxides for favorable ORR activity. These previous studies provide useful guidance for optimizing the TPIs of CL. However, in all current studies the conventional heating processes using furnace, water-bath or drying oven are employed for CL drying or sintering. These methods heat materials based on the principles of heat conduction, convection and radiation, which transmit thermal energy from the external to the internal of the material. Thus, there exists a temperature gradient within CLs, hindering the formation of uniform TPIs.

In this report, a novel microwave irradiation method was proposed to prepare the catalyst layer of ACACs instead of the conventional heating process, in order to optimize the TPIs. The microwave irradiation technique has been widely used for chemical analysis, sintering of ceramic materials, and synthesizing organic/inorganic materials. It heats materials through inducing internal friction heat by the high frequency rotation/vibration of electric dipoles inside the material. Thus, the internal and external of the material are heated simultaneously, and a homogenous temperature distribution within the material can be achieved [17]. This technique has distinctive advantages of simplicity, rapidity, uniformity and energy saving compared with the conventional heating treatment [18-20]. Up to now, preparation of CL of ACACs by microwave irradiation had not been investigated in MFCs. It is expected that preparation of CL with microwave heating would shorten the preparation time and improve the TPIs, so as to improve the ORR activity of air cathodes. In order to elucidate the effect of microwave preparation on the TPIs of CLs, the physicochemical characteristics (i.e. surface morphology, hydrophobic/hydrophilic property and surface chemical composition) of the CLs prepared with both microwave irradiation and conventional heating process were examined. The ORR activity of different air cathodes and the power generation of MFCs were also evaluated.

2. MATERIALS AND METHODS

2.1. Air cathode fabrication

Activated carbon air cathodes (ACACs) were prepared by pressing a catalyst layer (CL) and a gas diffusion layer (GDL) on both sides of a stainless steel mesh current collector. The GDLs of each cathode were prepared in parallel as follows: XC-72 carbon black (CB, Wuxi Sophie Roland International Trading Co. Ltd, China), polytetrafluoroethylene (PTFE, 60 wt%, Yilida Power Source Co., Ltd, China) (mass ratio CB:PTFE=3:7) and an appropriate amount of isopropanol were mixed thoroughly under ultrasonic agitation for 30 min. The mixture was then stirred and dried at 80^{o}C in a water bath to form a dough like paste, which was then pressed to be a gas diffusion film of 0.5 mm thickness using a press machine (7 MPa, 1.5 min). Afterwards, the film was pressed onto one side of a stainless steel mesh (40×40 mesh, type SUS304, Shanghai Xingan mesh Co. Ltd, China) and sintered at 340^{o}C for 40 min to form a hydrophobic thee-D porous structure for gas transport.

The CL was made of super-capacitive activated carbon (AC, Shanghai Heda Carbon Materials Co., Ltd, China), XC-72 carbon black, PTFE (10% wt) and isopropanol with three AC/CB/PTFE mass ratios of 4:0.1:1, 6:0.1:1 and 8:0.1:1. CL films of 0.5 mm thickness were prepared using the same fabrication procedure as GDL. They were heated at 200^{o}C for 60 min in a drying oven, and then pressed on the other side of stainless steel mesh to reach a final thickness of 0.8 mm. The products were referred to as ACACs. For microwave preparation of CL, the water bath heating step for the mixture of activated carbon, carbon black and PTFE was replaced by microwave treatment. The mixture was placed into a microwave oven (Galanz, 50Hz, 700 W) and intermittently heated in a pattern of 10 s irradiation on and 60 s irradiation off, repeated for 5 times. Repeating the irradiation pattern for more than 5 times would make the material too dry to be compressible. The sintering step at 200^{o}C in a drying oven was also preplaced by microwave treatment for 3 irradiation on-off cycles. The cathode samples were referred to as AC-4, AC-6, AC-8, AC-M4, AC-M6 and AC-M8 with the numbers indicating the mass ratio of AC/PTFE and M indicating microwave treatment of CL.

2.2. CL characterizations and electrochemical analysis

The morphology of the cut section of different CLs was observed using a field emission scanning electron microscope (SEM; Utral 55, CorlzeisD, Germany). The wettability of the CLs was determined by the contact angle (CA) using a Dataphysics OCA20 contact angle system at room temperature. A droplet of distilled water with droplet size of 5.0 μL was used for measurement. Six different positions for the same sample were measured to obtain the average CA value. The elemental composition of the CLs was examined using X-ray photoelectron spectroscopy (XPS; Escalab 250Xi, Thermo Scientific, USA) with an Mg Kα X-ray source. All binding energies were referenced to the C 1s peak at 284.6 eV to compensate for the surface charging effects. The relative contents of different atoms and functional group species were calculated from the ratio of the peak areas after correcting with the sensitivity factors.

The electrochemical behaviors of the abiotic cathodes with different CLs were determined by a potentiostat (CHI 660D, ChenHua Instruments Co., Ltd., Shanghai, China) in an electrochemical cell as previously described [15, 21]. All tests were performed in 50 mM PBS with the air cathode (surface area of 7 cm^2) as the working electrode, a platinum sheet of 1 cm^2 as the counter electrode and an Ag/AgCl (0.197 V vs. SHE) close to the cathode as the reference electrode. Before each test, the cathode was soaked in 50 mM PBS for 24 h and the electrolyte was bubbled with nitrogen gas for 30 min to remove oxygen from the solution. Electrochemical impedance spectroscopy (EIS) measurement was performed at the open circuit potential of each cathode over a frequency range from 100 KHz to 5 mHz with an AC signal amplitude of 10 mV. Individual resistances were estimated by fitting the impedance data with an equivalent circuit model using the ZView 3.1 software with errors of fit of ≤5%.

Tafel plots (log|current density|, A/cm^2 versus |overpotential|, V) were measured by sweeping the overpotential ($|\eta|$) from 0 mV to 100 mV at a scan rate of 1 mV/s [22]. $\eta = 0$ is defined as the open circuit potential (OCP) of the cathode versus the reference electrode [23]. The exchange current density (j_0) can be calculated from the linear region of Tafel plots through the equation [23] :

$$\lg|j| = \lg j_0 + (\beta nF/2.303RT)\,|\eta| \qquad (1)$$

where j is the current density, β is a system factor which is dependent with pH, n is the electron transfer number during ORR; F, R, and T represent faraday constant, gas constant and absolute temperature respectively.

2.3. MFC tests

Single-chambered cubic MFCs with a working volume of 28 mL and reactor length of 4 cm were constructed as previously described [24]. The anodes were heat-treated (450°C for 30 min) graphite fiber brushes (2 cm in outer diameter and 2.5 cm in length). Anodes were pre-acclimated and operated at 1000 Ω for over 3 months before the cathode was replaced by one of the tested cathodes (projected area of 7 cm^2). The nutrient medium contained 1 g/L sodium acetate and 50 mM PBS ($Na_2HPO_4{\cdot}12H_2O$, 11.466 g/L; $NaH_2PO_4{\cdot}2H_2O$, 2.75 g/L; KCl, 0.31 g/L; NH_4Cl, 0.13 g/L; trace minerals 12.5 mL/L) [24]. MFCs were operated under 1000 Ω of external resistance in a fed-batch mode. Polarization curves were measured according to the method as previously described [15, 25]. All the tests were performed in duplicate in a constant temperature room at 30°C.

3. RESULTS AND DISCUSSION

3.1. Characterization of the TPIs of CLs

As seen from the SEM images of the cut section of the CLs (Fig. 1), large aggregates likely to be the binding compounds of PTFE and activated carbon/carbon black existed in the CLs prepared with conventional heating process. However, in the microwave prepared CLs the aggregates were smaller and uniformly distributed around the activated carbon catalysts, indicating that the microwave irradiation resulted in a more scattered and homogenous distribution of PTFE within the CL. This is probably due to the high-frequency reciprocating motion of the PTFE/activated carbon/carbon black molecules under the microwave irradiation and a homogeneous temperature distribution throughout the CL material [17, 20]. The homogenous distribution of hydrophobic PTFE and hydrophilic activated carbon/carbon black within the CL may increase the catalytic area of activated carbon and facilitate the diffusion of both oxygen gas and H^+/OH^- ions [13, 26].

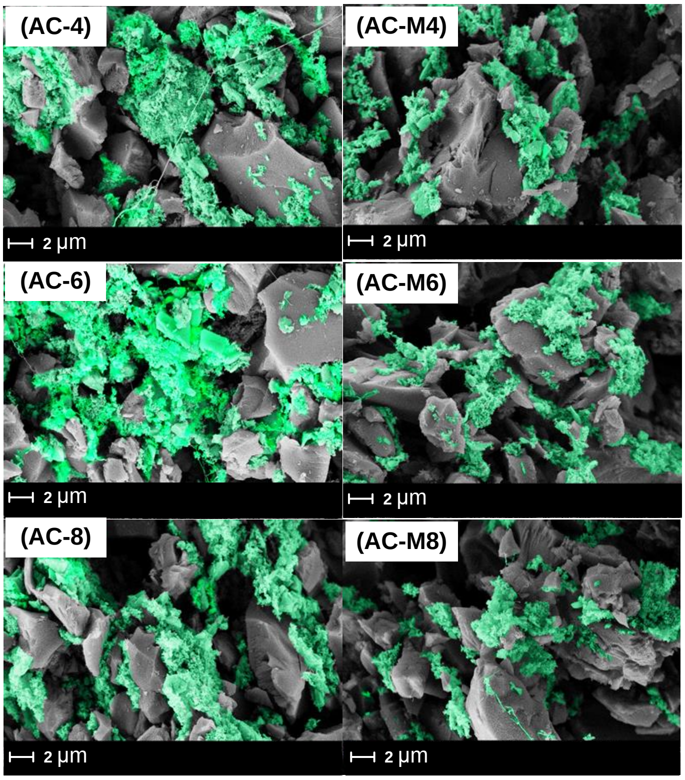

Figure 1. SEM images of the cut section of different CLs (10000X). The aggregates of PTFE and activated carbon/carbon black are marked by green shadows.

The contact angle represents the hydrophobic/hydrophilic property of a solid surface [27, 28]. The CA values were 134±4°, 126±1° and 122±2° respectively for AC-4, AC-6 and AC-8 (Fig. S1 in Electronic Supplementary Information). Compared to the plain CLs, the CAs of the microwave prepared CLs decreased to 121±1° for AC-M4, 116±3° for AC-M6, and 102±2° for AC-M8. This suggests that microwave preparation slightly reduced the hydrophobicity of the CLs [28]. The slight decrease in hydrophobicity is expected to be favorable for the diffusive transport of H^+ and OH^- species within the CLs, while does not evidently block the diffusion of oxygen gas. This may improve the gas-liquid-solid TPIs and accelerate the oxygen reduction kinetics.

XPS analyses of AC-6 and AC-M6 indicated that only C, F, O and N atoms existed on the CLs (Fig. 2a). As compared to AC-6, the F atom content on AC-M6 decreased from 17.29% to 12.96% (F/C ratio decreased from 22.61% to 16.36%) (Table 1). Detailed deconvolution of F1s spectra revealed the presence of two types of fluorine functionalities (Fig. 2b), i.e. partially fluorinated carbons at 689.45±0.05 eV and fully fluorinated carbons at 690.25±0.15 eV [12]. The decrement of F content primarily originated from the decrease of partially fluorinated carbons with microwave preparation. High resolution O1s spectra revealed that AC-6 contained two types of oxygen functionalities, i.e. the C-OH or C-O-C groups (532.7 eV) and oxygenated tetrafluoroethylene (536.4 eV). However, the oxygenated tetrafluoroethylene disappeared in AC-M6. The lower F content in AC-M6 would result in a lower degree of hydrophobicity of CL [12], which was most likely the reason for the lower CA of AC-M6 than the plain cathode.

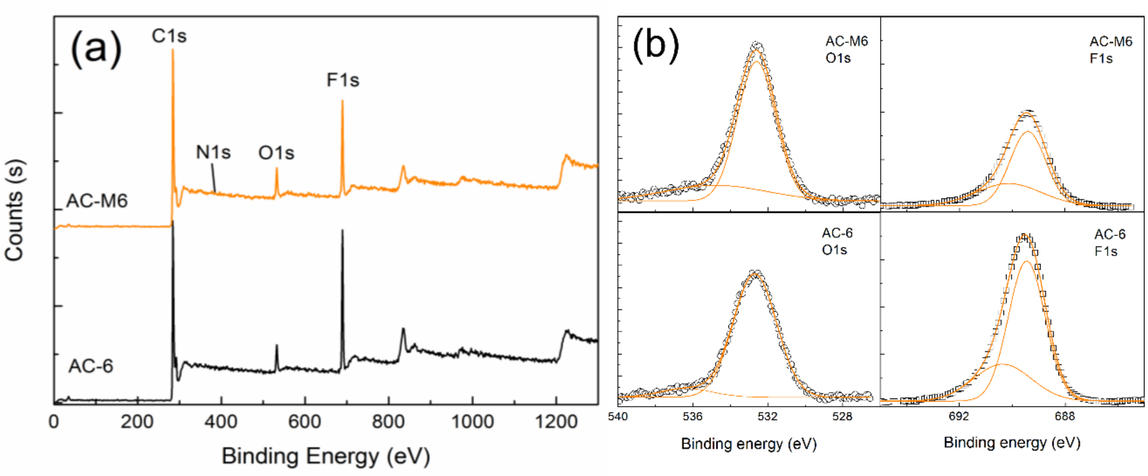

Figure 2. XPS spectra of the CLs of the AC-6 and AC-M6 cathodes: (a) whole spectra, (b) high-resolution spectra of O1s and F1s; baseline substracted.

Table 1. Elemental contents, atomic ratios of O/C and F/C, and functional group contents of different catalyst layers as determined by XPS

Elemental contents	AC-6	AC-M6
C (%)	76.47	79.23
F (%)	17.29	12.96
O (%)	5.41	7.04
N (%)	0.83	0.77
F/C (%)	22.61	16.36
partially fluorinated carbons	12.22	8.40
fully fluorinated carbons	5.07	4.56
O/C (%)	7.07	8.88
C-OH and/or C-O-C	4.99	5.41
chemisorbed oxygen	----	1.63
oxygenated tetrafluoroethylene	0.42	----

3.2. Tafel analysis

The exchange current density (j_0) describes the rate of charge transfer reaction between the reactant and the electrode at the equilibrium potential [29]. According to the Tafel plots in Fig. 3, j_0 (A/cm^2) values of the air cathodes with different CLs were calculated and listed in Table S1 over the linear region where the overpotential ranged from 80 mV to 100 mV [30]. Increasing j_0 values were obtained from AC-4 (1.71×10^{-4} A/cm^2), to AC-6 (1.85×10^{-4} A/cm^2) and AC-8 (1.95×10^{-4} A/cm^2), which was probably due to the increased electrochemical active surface for ORR with the increased content of activated carbon in CL. Similar results have been reported in previous literature [13]. Microwave preparation of CL improved the exchange current density of air cathodes at all AC/PTFE ratios, suggesting an enhanced ORR catalytic activity [31]. AC-M8 exhibited the highest j_0 value of 2.26×10^{-4} A/cm^2, followed by AC-M6 (2.24×10^{-4} A/cm^2) and AC-M4 (2.02×10^{-4} A/cm^2). These values were 15.9%, 21.1% and 18.1% higher respectively than the untreated cathodes with the same AC/PTFE ratio. The reason for the increased j_0 of the microwave prepared CLs was possibly that the active catalytic surface of activated carbon was increased due to the well-distribution of PTFE [12, 30, 31].

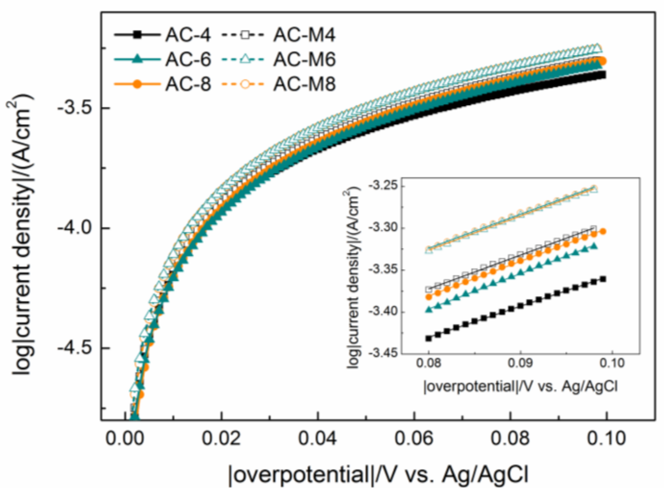

Figure 3. Tafel plots of air cathodes with different CLs recorded in 50 mM PBS (pH=7) at the scan rate of 1 mV/s. Insert is the linear fit for the Tafel plots of the overpotential from 80 to 100 mV.

3.3. EIS analysis

Nyquist plots of all cathodes displayed similar shapes which contained a depressed semicircle over high frequency range followed by a straight line with an angle of approximately 45^{o} to the real axis over the low frequency range (Fig. 4 a~ c). Accordingly, an equivalent circuit model consisted of an ohmic resistance, a charge transfer resistance and a diffusion element was employed to fit the impedance data (Fig. 4c insert) [21, 32]. As shown in Fig. 4d, the ohmic resistance (R_{ohm}) of all cathodes had a similar value of 15.1±0.2 Ω, due to the use of the same cell, fixed reference electrode and the same configuration of air cathode. The charge transfer resistance (R_{ct}) decreased from AC-4 (8.7 Ω) to AC-6 (7.1 Ω) and AC-8 (3.4 Ω), indicating an increased oxygen reduction kinetics with the increased content of activated carbon in CL [13, 33]. Microwave preparation of CL led to a decrease in R_{ct} at all AC/PTFE ratios, with values decreased by 35.6%, 31.0% and 17.6% respectively for AC-M4 (5.6 Ω), AC-M6 (4.9 Ω), and AC-M8 (2.8 Ω). This result indicates that microwave irradiation improved the catalytic activity of CL on ORR [30], probably due to the reduced PTFE content and increased catalytic area of activated carbon in CL.

The diffusion resistance (R_d) is related with the diffusion of oxygen gas and aqueous H^+ or OH^- ions within the CL [34, 35]. Microwave preparation of CL substantially reduced the R_d of cathodes at all AC/PTFE ratios. AC-M6 had the smallest R_d of 11.5 Ω, which was 18.4% lower than that of AC-6 (14.1 Ω). The R_d values of AC-M4 (12.4 Ω) and AC-M8 (15.7 Ω) were 66.2% and 45.3% lower than that of AC-4 (36.7 Ω) and AC-8 (28.7 Ω) respectively. The reduced R_d of the microwave treated cathodes was probably attributed to the slightly improved hydrophilicity of CL and the homogenous distribution of hydrophobic phase and hydrophilic phase within the CL, which facilitated the diffusion of both oxygen gas and H^+/OH^- ions [12, 14, 36]. Overall, the total internal resistance (R_{ohm}+R_{ct}+R_d) of the cathodes decreased in the order: AC-M6 (31.4 Ω) < AC-M4 (33.2 Ω) < AC-M8 (33.8 Ω) < AC-6 (36.4 Ω) < AC-8 (47.2 Ω) < AC-4 (60.4 Ω), as a result of their differences in both the charge transfer and diffusion resistances.

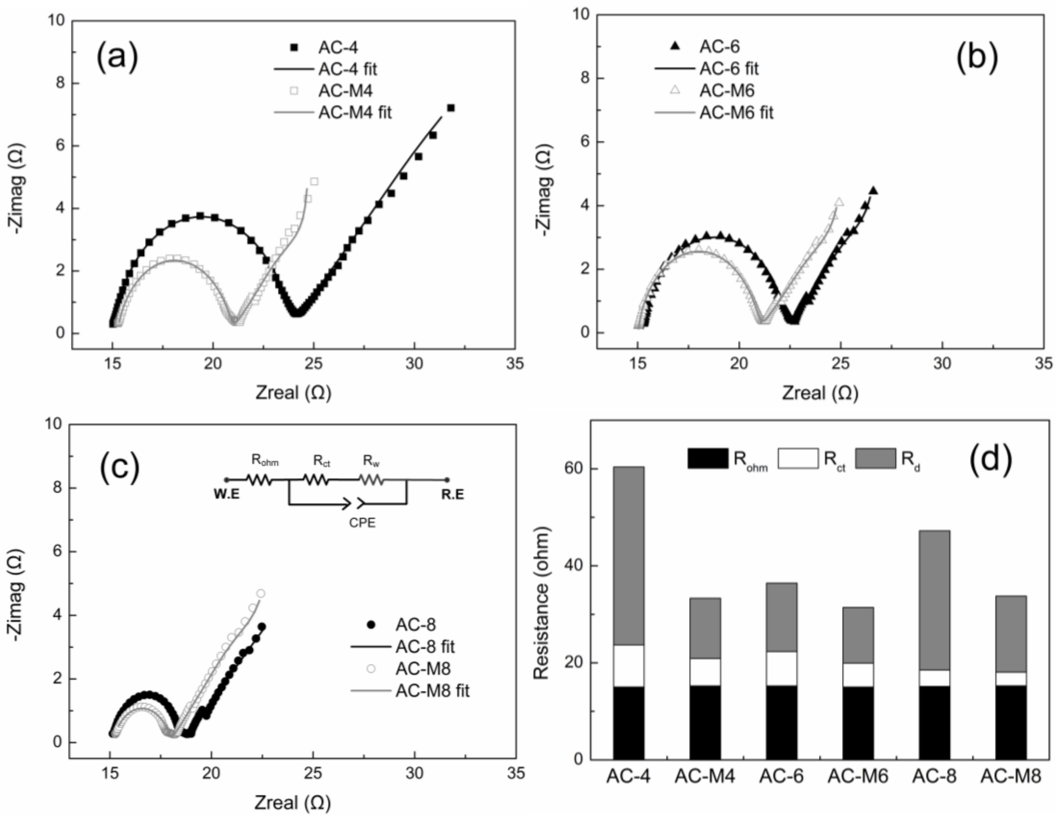

Figure 4. (a~c) Nyquist plots of EIS for different cathodes in 50 mM PBS of pH=7; points are experimental data, lines are fitted curves using the equivalent circuit modal inserted in (c). (d) fitted resistance values using the equivalent circuit modal.

3.4. Power generation of MFCs

The MFCs with the AC-6 cathode output the maximum power density (Pmax) of 1370±36 mW/m^2 (Fig. 5a), which was 5.7% and 10.8% higher than that of the AC-8 (1296±17 mW/m^2) and

AC-4 (1237±84 mW/m^2) MFCs. Microwave preparation of CL substantially improved the Pmax of AC-6 by 15.6% to 1584±9 mW/m^2 for AC-M6. For the cathodes with AC/FTFE ratio of 4:1, the Pmax value was increased by 23.3% to 1525±19 mW/m^2 (AC-M4) due to the microwave treatment of CL. For the cathodes with AC/FTFE ratio of 8:1, the Pmax value was also improved by 9.2% to 1415±81mW/m^2 (AC-M8). Based on the electrode polarization curves (Fig. 5 b and c), the anode potentials in all MFCs were nearly identical, indicating that the difference in power generation of MFCs was attributed to the cathode performance. The cathodes with microwave prepared CLs exhibited higher potentials than those with untreated CLs at the same current density. This was attributed to their decreased internal resistances arising from the improved ORR catalytic property and accelerated reactants diffusion in CLs.

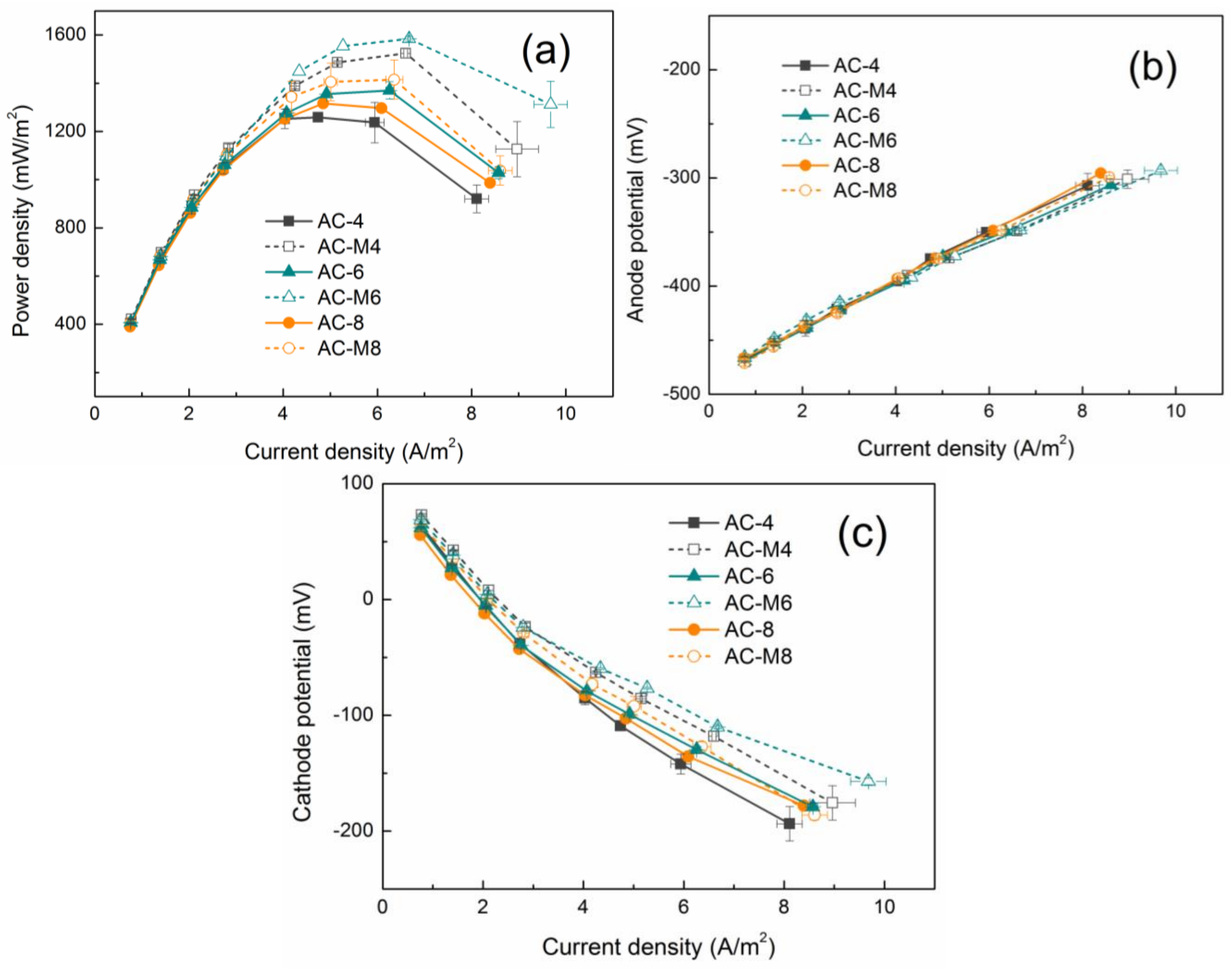

Figure 5. Power density (a), anode polarization (b) and cathode polarization (c) curves of MFCs with different air cathodes. Data are means ± standard deviations of duplicates.

4. CONCLUSIONS

This work develops a novel microwave irradiation approach to prepare the catalyst layer of ACACs in microbial fuel cells. This preparation method improved the TPIs for ORR by providing a more homogenous distribution of PTFE and a slightly reduced hydrophobicity of CLs. As a result, the microwave prepared ACACs exhibited much lower charge transfer and diffusion resistances than the conventional cathodes. Consequently, the maximum power density of the MFCs with the microwave prepared ACACs increased by 9.2%~23.3%. Compared to the conventional heating process, the microwave irradiation approach described in this study is time-saving, easy to implement, and effective in optimizing the TPIs of CL and improving the ORR of ACACs. Therefore, it has a great potential to be used for the fabrication of high-performance electrodes in MFCs.

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SUPPLEMENTARY DATA:

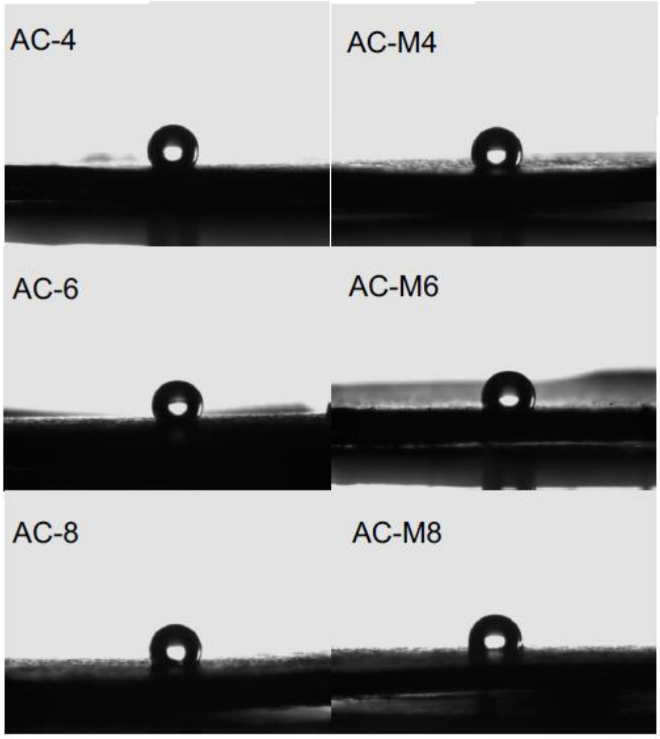
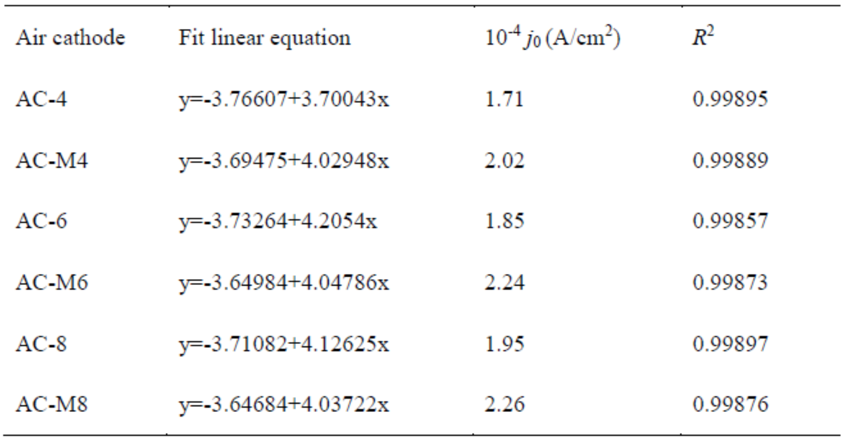


Figure S1. Contact angles of deionized water droplets on different CL surfaces of air cathodes.

Table S1. Linear fit equations and exchange current densities calculated from the linear region of the Tafel plots.



Air cathode	Fit linear equation	$10^{-4}\ j_0$ (A/cm^2)	R^2
AC-4	y=-3.76607+3.70043x	1.71	0.99895
AC-M4	y=-3.69475+4.02948x	2.02	0.99889
AC-6	y=-3.73264+4.2054x	1.85	0.99857
AC-M6	y=-3.64984+4.04786x	2.24	0.99873
AC-8	y=-3.71082+4.12625x	1.95	0.99897
AC-M8	y=-3.64684+4.03722x	2.26	0.99876

References

1. B.E. Logan, *Nat. Rev. Micro.*, 7(2009) 375-381.
2. W. Liu and S. Cheng, *J. Zhejiang Univ. Sci. A*, 15 (2014) 841-861.
3. R. Ramachandran, S.M. Chen and G.P.G. Kumar, *Int. J. Electrochem. Sci.*, 10 (2015) 7111-7137.
4. X. Zhang, D. Pant, F. Zhang, J. Liu, W. He and B.E. Logan, *ChemElectroChem*, 1 (2014) 1859-1866.
5. V.J. Watson, C. Nieto Delgado and B.E. Logan, *Environ. Sci. Technol.*, 47 (2013) 6704-6710.
6. N.W. Zhu, J.J. Huang, W.H. Shen, L.X. Tu, P.X. Wu and H.Q. Ma, *Int. J. Electrochem. Sci.*, 10 (2015) 2634-2645.
7. X. Zhang, H. Sun, P. Liang, X. Huang, X. Chen and B.E. Logan, *Biosens. Bioelectron.*, 30 (2011) 267-271.
8. S. Cheng, H. Liu and B.E. Logan, *Environ. Sci. Technol.*, 40 (2006) 2426-2432.
9. X.J. Li, X. Wang, Y.Y. Zhang, N.S. Gao, D.S. Li and Q.X. Zhou, *Int. J. Electrochem. Sci.*, 10 (2015) 5086-5100.
10. H.R. Yuan, L.F. Deng, Y.J. Qi, N. Kobayashi and M. Hasatani, *Int. J. Electrochem. Sci.*, 10 (2015) 3693-3706.
11. F. Zhang, S. Cheng, D. Pant, G.V. Bogaert and B.E. Logan, *Electrochem. Commun.*, 11 (2009) 2177-2179.
12. C. Santoro, K. Artyushkova, S. Babanova, P. Atanassov, I. Ieropoulos, M. Grattieri, P. Cristiani, S. Trasatti, B. Li and A.J. Schuler, *Bioresour. Technol.*, 163 (2014) 54-63.
13. H. Dong, H. Yu, X. Wang, Q. Zhou and J. Feng, *Water Res.*, 46 (2012) 5777-5787.
14. H. Dong, H. Yu, H. Yu, N. Gao and X. Wang, *J. Power Sources*, 232 (2013) 132-138.
15. S. Cheng, H. Liu and B.E. Logan, *Electrochem. Commun.*, 8 (2006) 489-494.
16. S. Cheng, H. Liu and B.E. Logan, *Environ. Sci. Technol.*, 40 (2006) 364-369.
17. W. Chen, J. Zhao, J.Y. Lee and Z. Liu, *Mater. Chem. Phys.*, 91 (2005) 124-129.
18. Z.Q. Tian, S.P. Jiang, Y.M. Liang and P.K. Shen, *J. Phys. Chem. B,* 110 (2006) 5343-5350.
19. S. Harish, S. Baranton, C. Coutanceau and J. Joseph, *J. Power Sources*, 214 (2012) 33-39.
20. Y. Huang, J. Cai and Y. Guo, *Appl. Catal. B,* 129 (2013) 549-555.
21. S. Cheng, W. Liu, J. Guo, D. Sun, B. Pan, Y. Ye, W. Ding, H. Huang and F. Li, *Biosens. Bioelectron.*, 56 (2014) 264-270.
22. D.A. Lowy, L.M. Tender, J.G. Zeikus, D.H. Park and D.R. Lovley, *Biosens. Bioelectron.*, 21 (2006) 2058-2063.
23. H. Dong, H. Yu, X. Wang, Q. Zhou and J. Sun, *J. Chem. Technol. Biot.*, 88 (2013) 774-778.
24. B. Logan, S. Cheng, V. Watson and G. Estadt, *Environ. Sci. Technol.*, 41 (2007) 3341-3346.
25. S. Cheng and J. Wu, *Bioelectrochemistry*, 92 (2013) 22-26.
26. L. Nie, J. Liu, Y. Zhang and M. Liu, *J. Power Sources*, 196 (2011) 9975-9979.

27. M. Ahn, Y.H. Cho, Y.H. Cho, J. Kim, N. Jung and Y.E. Sung, *Electrochim. Acta,* 56 (2011) 2450-2457.
28. A.V. Shevade, S. Jiang and K.E. Gubbins, *J. Chem. Phys*, 113 (2000) 6933-6942.
29. C.H.H. Hamann and W. Vielstich, *Electrochemistry*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (2008).
30. H. Dong, H. Yu and X. Wang, *Environ. Sci. Technol.*, 46 (2012) 13009-13015.
31. D. Li, Y. Qu, J. Liu, W. He, H. Wang and Y. Feng, *J. Power Sources*, 272 (2014) 909-914.
32. F. Zhang, M.D. Merrill, J.C. Tokash, T. Saito, S. Cheng, M.A. Hickne r and B.E. Logan, *J. Power Sources*, 196 (2011) 1097-1102.
33. Y. Zhang, X. Wang, X. Li, N. Gao, L. Wan, C. Feng and Q. Zhou, *RSC Advances,* 4 (2014) 42577-42580.
34. X. Li, X. Wang, Y. Zhang, N. Ding and Q. Zhou, *Appl. Energy*, 123 (2014) 13-18.
35. X.Y. Wang, J. Yan, H.T. Yuan, Y.S. Zhang and D.Y. Song, *Int. J. Hydrogen Energy*, 24 (1999) 973-980.
36. Z.Q. Tian, X.L. Wang, H.M. Zhang, B.L. Yi and S.P. Jiang, *Electrochem. Commun.*, 8 (2006) 1158-1162.