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Durability and regeneration of activated carbon air-cathodes in long-term operated microbial fuel cells

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Abstract

The performance of activated carbon (AC) catalyst in air-cathodes was investigated in microbial fuel cells (MFCs) over one year operation. The maximum power of $1722 \pm 110 \text{ mW m}^{-2}$ was produced within the initial one-month MFC operation. AC air-cathodes could produce the maximum power $>1200 \text{ mW m}^{-2}$ within six months, but gradually evolved into a limiting factor for the power output in prolonged MFCs. The maximum power decreased by 55% when MFCs with AC air-cathodes were operated over one year. While salt/biofilm removal from one year cathodes increased limiting performance enhancement in cathodes, washing-drying-pressing could restore the cathode performance to original levels, but the performance restoration was temporary. Durable cathodes could be regenerated by re-pressing AC catalyst recovered from one year deteriorated air-cathodes with new gas diffusion layer, resulting in $\sim 1800 \text{ mW m}^{-2}$ of maximum power production. The present study indicated that AC was an effective catalyst in MFC cathodes, and could be recovered for reuse in long-term operated MFCs by simple methods.

Keywords:

Microbial fuel cells; Activated carbon; Air-cathode; Long-term operation; Regeneration of air-cathode

Highlights

- AC air-cathodes can produce power $>1722 \text{ mW m}^{-2}$ in long-term MFCs.
- AC in one-year deteriorated air-cathodes has performance as high as fresh AC.
- Durable air-cathodes can be regenerated with recovered AC by simple methods.

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1. Introduction

Microbial fuel cells (MFCs) have attracted increasing research attention due to the electricity harvest by exoelectrogenic bacteria while degrading the pollutions (Logan et al., 2015). Up to now, a variety of different configurations of MFCs, including double-chamber (Ali et al., 2015; Madani et al., 2015) and single-chamber assemblies (Ou et al., 2016; Sawasdee & Pisutpaisal, 2015), have been proposed for different applications. For wastewater treatments, single-chamber MFCs assembled with bioanodes and air-cathodes were believed to be one of the most practical configurations because they can be developed as long-term and continuously operated treating systems by passively using air-oxygen as electron acceptor at the cathode (Liu & Logan, 2004). However, the oxygen reduction reaction (ORR) kinetics is very slow, especially under MFC operating conditions (i.e. ambient temperature, atmospheric pressure and neutral pH), and ORR catalysts with high performance in terms of catalytic efficiency and durability were needed for air-cathode preparations. Varieties of ORR catalysts based on Pt (Cheng et al., 2006; Yang et al., 2011), graphene (Valipour et al., 2016), manganese oxide (Li et al., 2010; Liu et al., 2010) and manganese cobaltite/polypyrrole nanocomposite (Khilari et al., 2014) have been tested for air-cathode preparations. But several drawbacks of current catalysts for air-cathode preparation, including the cost and durability, are still bottle-neck for large-scale application of MFCs in practical wastewater treatments.

Cost-effective activated carbon (AC) has been shown to be promising catalysts alternative to expensive Pt for air-cathode preparation in single-chamber MFCs (Zhang et al., 2009). Inspired by this important work, AC, as the matrix composite material in air-cathode, subsequently attracted much attention in the fields of MFCs, mostly because of their promising electrocatalytic activity, low cost, environmental friendliness, and chemical stability. While varies of preparation protocols such as rolling, spreading and pressing methods were developed to construct air-cathodes using AC catalytic layer (CL) and gas diffusion layer (GDL) with different structures (Dong et al., 2012; Dong et al., 2013; Li et al., 2016; Yang et al., 2015), electrocatalytic performance of hybrid AC doped with multiple elements (e.g. Co, Cu, Ag, P, Fe, N) in air-cathode were also extensively investigated (Chen et al., 2014; Fu et al., 2015; Liu et al., 2016; Pan et al., 2016; Pu et al., 2014; Zhang et al., 2015). However, relatively few studies investigated the effects of long-term operation on the performance of AC air cathode in MFCs (Zhang et al., 2011), even though the durability of AC air-cathodes experiencing long-term operation is very important for practical wastewater treatments. The growth of cathode biofilms is a common phenomenon in single-chamber MFCs, and it was generally believed to be one of main factors for the deteriorating performance of air-cathodes (Liu et al., 2015; Yuan et al., 2013). However, removing the cathode biofilm only partially restored the performance of the cathode (Kiely et al., 2011; Zhang et al., 2011), indicating more factors should be investigated for understanding the cathode deterioration over time. Moreover, in practical applications, appropriate strategies for regeneration of air-cathodes are generally essential for the long-term operation of MFCs (Pasternak et al., 2016).

In the present study, the durability of AC air-cathodes over one year operation was investigated. In addition to biofilms, more factors were explored to understand the reasons for deterioration of the cathode. It was found that deteriorated AC air-cathodes could momentarily restore performance by salt/biofilm removal. However, re-generated cathodes with AC recovered from deteriorating cathodes experiencing one-year MFC operation exhibited performance as high as cathodes prepared with fresh AC.

2. Materials and Methods

2.1. Electrode preparation

AC air-cathodes consisted of current collector, AC catalytic layer and GDL. Commercial stainless steel mesh (316L, 0.3 mm wire diameter, 0.55 mm×0.55 mm mesh) was used as current collector without further treatment after series of washing with acetone and deionized water. Commercial polytetrafluoroethylene (PTFE) microporous filtering film was used as GDL without any treatments. To prepare the AC catalytic layer, AC (specific area $\sim 1100 \text{ m}^2 \text{ g}^{-1}$, Xinshen Carbon, Fujian) and PTFE (60% suspension, Hesentech, Shanghai) were first mixed by a weight ratio of 7/3 in ethanol. Following well mixed, the dough-like AC-PTFE mixture was laminated into 1.0 mm sheet on a glass plate by rolling operation. After drying at 85°C for 60 min to remove the residual ethanol, the AC/PTFE sheet was cut into circular slices with 65 mm diameter which would be used as CL in air-cathode. Finally, the stainless steel mesh and PTFE microporous filtering film were pressed on both sides of AC-PTFE sheet in a stainless steel pattern die under 17 MPa pressure for 5 min to obtain the prepared AC air-cathode. Anodes were assembled with three pieces of carbon felt (diameter 4.5 cm, thickness 1.0 cm) and stainless steel (316L) bolt and nuts. Details of the electrode preparation and the MFC setup are provided in Fig. S1.

2.2. MFC operation

MFC chambers were made of plexiglass with a total empty volume of 118 mL (cylinder with 5.0 cm diameter and 6.0 cm length). Assembled single-chamber MFC had an effective solution volume of $\sim 60 \text{ mL}$, and the AC air-cathode in the MFCs had an effective exposure area of 19.6 cm^2 to air. MFC duplicates were operated in parallel for reproducibility. MFCs were initially activated by inoculating mixing culture taken from a separately operated (long-term running) MFC anode chamber which was inoculated with anaerobic activated sludge (sampled from the waste treatment plant in Yangzhou brewery) and was operated using acetate as electron donor. Long-term operation of MFCs was carried out by feeding artificial growth medium (AGM) in batch mode. The AGM, of pH 7.0, was prepared with the following constituents (in grams per liter of deionized water): NaAc, 1.6; NaHCO_3 , 2.5; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1; KCl, 0.1; NH_4Cl , 1.5; $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 0.6; NaCl, 0.1; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.1; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.005; $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$, 0.001; yeast extract 0.05. The initial pH of AGM was adjusted to 7.0 using HCl and NaOH solution. Unless otherwise stated, an external resistance of 100Ω was connected across the bioanode and the air-cathode in all MFCs for long-term operation.

2.3. Measurements and calculations

The voltage produced by MFCs, and electrode potentials relative to a double salt-bridge

saturated calomel electrode (SCE, Leici-217, Shanghai) were continuously measured using a multiple-channel high-impedance voltmeter (Keithley 2700). Polarization curves of MFCs were measured using a battery testing system (Neware CT-3008W, Shenzhen, China) in the mode of constant current discharge. During polarization measurements, the bioanode and air-cathode of the tested MFC were connected to the negative terminal and positive terminal of the battery testing system, respectively. By selecting the mode of constant current discharge in the battery testing system, the tested MFC was controlled to discharge at constant current. The discharge current was increased from 0 mA (open circuit state) step by step with a typical current step of 1 mA until voltage output close to zero. At each constant current level, stable voltage output of MFC was measured to calculate the power output (Power = Current×Voltage), and the electrode potentials (vs. SCE) were measured to describe the polarization behaviors of the bioanode and the air-cathode. Linear sweep voltammetry (LSV) measurements for AC cathodes was performed from open circuit potentials to -0.3 V (vs. SCE) using a potentiostat (CHI 660c, Shanghai, China) with SCE and the bioanode as reference electrode and counter electrode, respectively. For polarization and LSV measurements, MFCs were first disconnected from the circuit until the open circuit voltage plateaued before measurements. Current density and power density were normalized to the effective exposure area of the air-cathode.

2.4. Microbial analysis

Microbial communities in biofilms formed on the anode and the air-cathode were investigated using 16S rDNA gene amplicon sequencing (MiSeq system, Illumina, USA). The DNA was extracted from 250 mg samples using the MoBio PowerSoil DNA extraction kit (MO BIO Laboratories, Loker Ave West, Carlsbad, CA, USA) following the manufacturer's instructions. DNA concentration and purity was checked by running the samples on 1.0% agarose gels. V4-V5 region of the 16S rDNA was amplified by PCR amplifications, and the sequencing was subsequently determined on an Illumina MiSeq platform by TynyGene (Shanghai, China). Details of PCR amplifications and sequence data analysis were performed as described in previous study (Zhang et al., 2016).

2.5. Regeneration of AC air-cathodes

Generally, four steps, biofilm removing, washing, drying and pressing, were involved in regenerating AC air-cathodes from deteriorated cathodes. Cathodes were taken down from the assembled MFCs, and the cathode-attached salt/biofilm was carefully scraped off using a paper knife. Generally, the washing was performed by repeatedly soaking the salt/biofilm removed cathodes in 100 ml deionized water until the final conductivity of the washing solution was detected below 200 $\mu\text{S cm}^{-1}$ (Fig. S2). For comparison, individual biofilm-removed cathodes were alternatively washed in 0.1 N HCl or 0.1 N NaOH over 24 hours prior to washing by deionized water. After drying at 110 °C, the treated AC cathodes were re-pressed under 17 MPa pressure for 5 min in pattern die. Finally, the regenerated AC air-cathodes were re-installed in original MFCs for further MFC experiments.

3. Results and Discussion

3.1. Electricity production during long-term operation

Fig. 1

Typical voltage produced by MFCs with external resistance of $100\ \Omega$ over one year cycling operation.

Stable electricity production could be achieved when MFCs were initially operated by feeding AGM with inoculum for several days. Stable voltage produced by MFCs with $100\ \Omega$ external resistance was initially $0.487 \pm 0.015\ \text{V}$ (Fig. 1), resulting in $1210\ \text{mW m}^{-2}$ stable power production. The maximum power was $1481 \pm 75\ \text{mW m}^{-2}$ (6 duplicates, 3 operation cycles) in the initially activated MFCs. However, the maximum power was observed to increase to $1722 \pm 110\ \text{mW m}^{-2}$ when the MFCs were operated over one month (Fig. 2A). Electricity production, in terms stable voltage output (Fig. 1) and the maximum power density (Fig. 2A), was found to decrease when the MFCs were continuously operated over six months. The significant reduction in voltage and power production was found to occur until nine-month operation. The measured stable voltage and maximum power density in the 9th month were $0.265 \pm 0.017\ \text{V}$ and $943 \pm 41\ \text{mW m}^{-2}$, respectively. Further operation beyond nine months produced slower reduction in electricity production, resulting in $0.236 \pm 0.011\ \text{V}$ of stable voltage and $777 \pm 19\ \text{mW m}^{-2}$ of the maximum power density over one year operation (Fig. 1 & 2A).

Fig. 2

Power density (A) and electrode potentials (B) measured in MFCs operated at different stages.

Table 1 Maximum power production in reported MFCs with AC air-cathodes

Cathode	Anode*	medium	P _{max} (mW m ⁻²)	Ref.
P-doped AC	CF	acetate	1096±33	(Chen et al., 2014)
Silver on AC	CF	acetate	1080±60	(Pu et al., 2014)
Iron–nitrogen–AC	CF	acetate	2437±55	(Pan et al., 2016)
n-type Cu ₂ O doped AC	CF	acetate	1390±76	(Zhang et al., 2015)
Pore former decorated AC	CFB	glucose	892±8	(Li et al., 2016)
cobalt decorated AC	CF	acetate	1421±54	(Liu et al., 2016)
nano Fe ₃ O ₄ in AC	CF	acetate	1430	(Fu et al., 2015)
AC-based cathodes	CC	acetate	682	(Santoro et al., 2014)
AC	CC	acetate	1720	(Janicek et al., 2015)
AC	CM	acetate	1086±8	(Dong et al., 2013)
AC	CFB	acetate	1214±123	(Zhang et al., 2011)
AC	CFB	acetate	1055±31	(Liu et al., 2015)
AC	CF	acetate	1722±110	This study

*Carbon-fiber brush (CFB), Carbon felt (CF), Carbon cloth (CC), Carbon mesh (CM)

Compared with most reported single-chamber MFCs with AC air-cathodes (Table 1), the present MFCs produced higher power density except for MFCs with air-cathodes prepared with AC doped with iron and nitrogen (Pan et al., 2016). High power production (>1200 mW m⁻²) could be maintained for initial six-month operation. However, the present MFCs exhibited much greater power reduction (55%) than previously reported MFCs with AC air-cathodes (22% power reduction for cathodes with 30% porous GDL and 40% reduction for cathodes with 70 % porous GDL)(Zhang et al., 2011) over one-year operation, probably due to the use of thin PTFE microporous filtering film as GDL. Newly prepared AC cathodes had more porous structure in GDL (Fig. S3) which would favor more oxygen diffusion into gas-liquid-solid three-phase boundary to increase the cathode performance, but would increase water percolation in prolonged MFC operation, lowering the cathode performance. Polarization measurements showed that AC cathodes gradually evolved into the main limiting factor of power output when the MFCs were operated beyond half a year (Fig. 2B). Apart from the initial operation phase, the polarization performance of the bio-anode was almost identical over a one-year operating period. In contrast, the potentials of AC air-cathodes were significantly shifted to negative direction with running time, indicating that the observed power reduction could attribute to the deteriorating performance of AC air-cathodes over long-time running. The deterioration of performance in air-cathodes was a common phenomenon even in relatively short-term (< four months) operated MFCs probably due to biofilm formation, salt formation and/or corrosion of current collector in air-cathodes (Janicek et al., 2015; Li et al., 2016; Liu et al., 2015; Pasternak et al., 2016; Zhang et al., 2011). The cathode deterioration in the present MFCs could not be fully explained by the above factors (see the following sections).

3.2. Appearance feature and microbial communities in deteriorated cathodes

Fig. 3

Photographs of AC air-cathodes showing salt/biofilm formation of both sides. (A) medium-facing side at half-month operation; (B) medium-facing side at one-year operation; (C and D) duplicate air-facing medium sides at one-year operation.

The appearance feature of AC air-cathodes changed remarkably on both sides when MFCs were operated over long-time. Visual biofilms could be observed to form on the medium-facing side of the air-cathodes in MFCs experiencing half-month operation by the naked eyes (Fig. 3A), and the biofilms eventually grew to be deep colour with the thickness of >2 mm at the end of one-year operation (Fig. 3B). Microbial community analysis indicated that *Proteiniphilum* (13.18%) and *Pseudomonas* (12.42%) were the dominant bacterial genera in the cathodic biofilms formed over one year whereas *Geobacter* (27.37%) and *Flavobacterium* (10.59%) were most enriched in anodic biofilms (Table 2). *Pseudomonas* were well known to be exoelectrogenic genus, and the species from *Pseudomonas* were commonly enriched in anodic biofilms (Nor et al., 2015) and cathodic biofilms (Sun et al., 2016). *Proteiniphilum* genus was reported to be dominant in the anodic bacterial community in a methane-producing microbial electrolysis cell (Zeppilli et al., 2015), but was found to be the most enriched genus in the present cathodic biofilms. Other highly enriched genus in the current cathodic biofilms, such as *Alkaliflexus* (7.87%), was also reported in other cathodic community (Sun et al., 2016). On the outer sides (air-facing sides) in cathodes, no obvious feature change could be observed by naked eyes within three-month operation. Prolonged MFC running would see colour change and salt formation on the outer sides of air-cathodes. However, there was greater variation in extrinsic outer side features between cathodes in duplicate MFCs experiencing one-year operation, from white salt formation without noticeable biofilms formation (Fig. 3C) to salt formation with deep-colour mould-like biofilm (Fig. 3D). Different salt/biofilm formation pattern on the outer side of air-cathodes might affect the rate of air-oxygen diffusion into the catalytic layer, probably affecting the cathode performance. However, compared with initial cathodes without salt/biofilm formation, the diversity of salt/biofilm in duplicate cathodes experiencing one-year operation did not generate more divergence in cathode performance although the electrochemical performance in one-year operated air-cathodes

Table 1

Difference in relative abundance of the bacterial genera between anodic biofilms and cathode biofilms in MFCs operated over one year

Taxonomy		Abundance (%)	
Phyla	Genera*	Anodic biofilm	Cathode biofilm
Proteobacteria	<i>Pseudomonas</i>	3.42	12.42
	<i>Parapusillimonas</i>	0.06	1.89
	<i>Devosia</i>	0.04	1.72
	<i>Brevundimonas</i>	0.13	1.65
	<i>Nitrincola</i>	0.00	1.50
	<i>Aquamicrobium</i>	0.15	1.48
	<i>Nitrateductor</i>	0.03	1.08
	<i>Arenimonas</i>	5.01	1.04
	<i>Alcaligenes</i>	0.03	0.88
	<i>Bordetella</i>	0.03	0.87
	<i>Azoarcus</i>	1.63	0.77
	<i>Advenella</i>	0.50	0.51
	<i>Acinetobacter</i>	2.80	0.13
	<i>Geobacter</i>	27.37	0.06
Bacteroidetes	<i>Proteiniphilum</i>	3.94	13.18
	<i>Alkaliflexus</i>	0.00	7.87
	<i>Flavobacterium</i>	10.59	1.24
	<i>Myroides</i>	0.53	0.90
	<i>Taibaiella</i>	1.03	0.70
	<i>Petrimonas</i>	2.81	0.63
Firmicutes	<i>Sedimentibacter</i>	0.15	0.75
	<i>Erysipelothrix</i>	0.04	2.39
	<i>Fusibacter</i>	0.00	1.29
Spirochaetae	<i>Sphaerochaeta</i>	2.15	1.27
	<i>Fluviicola</i>	1.80	0.22
Tenericutes	<i>Acholeplasma</i>	0.01	4.08
Chloroflexi	<i>Leptolinea</i>	2.61	0.03
Actinobacteria	<i>Cellulosimicrobium</i>	0.00	1.11

*Only established genera were shown.

**The darker background indicating higher abundance (%).

decreased significantly (Fig. 4). Steel mesh corrosion, which was previously reported to be severe within 30 days of operation, and was suggested to be the main reason for the decreasing performance of AC air-cathodes (Janicek et al., 2015), was not observed in the present AC air-cathodes even in MFCs experiencing one-year operation. The discrepancy observed in the present study with those reported in the literature might be attributed to differences in the stainless steel type employed in different experiments because separated experiments demonstrated that stainless steel 304, a type stainless steel with less corrosion resistance, could be quickly corroded in AC air-cathodes within several days of operation (data not shown).

Fig. 4
LSV measurements for duplicate AC air-cathodes in initial activated MFCs and one-year operated MFCs (scan rate 1 mV s^{-1}).

3.3. Regeneration of AC air-cathodes

Fig. 5
Comparison of maximum power density produced by MFCs with different types of cathodes. Type I-AC-C: cathodes with salt/biofilm experiencing one-year operation; type II-AC-C: salt/biofilm scraped cathodes experiencing one-year operation; type III-AC-C: regenerated cathodes through removing salt/biofilm, washing (0.1 M NaOH , deionized water), drying and pressing procedures; type IV-AC-C: regenerated cathodes through removing salt/biofilm, washing (ionized water), drying and pressing procedures; type V-AC-C: regenerated cathodes through removing salt/biofilm, washing (0.1 M HCl , deionized water), drying and pressing procedures.

Fig. 6

Power density (A) and electrode potentials (B) measured at different operation stages in MFCs with cathodes repressed using new GDL and recovered AC catalyst from one-year deteriorated cathodes.

Different strategies were employed to regenerate the AC air-cathodes from deteriorated AC air-cathodes experiencing one-year MFC operation. It was found that biofilm removal by scraping method could partially restore the performance, but very limiting. Compared with salt/biofilm attached air-cathodes (type I-AC-C in Fig. 5), maximum power by salt/biofilm scraped air-cathodes (type II-AC-C in Fig. 5) increased by 7.3% from $777 \pm 19 mW m^{-2}$ to $834 \pm 41 mW m^{-2}$, less than those in previous reports (Kiely et al., 2011; Zhang et al., 2011). When salt/biofilm

scraped AC cathodes were further treated to remove potential minerals deposited in the activated carbon layers by washing-drying-pressing procedures, the cathode performance could be significantly restored to higher levels. Compared with cathodes soaked with 0.1 M NaOH and deionized water (type III-AC-C and type IV-AC-C in Fig. 5), cathodes first soaked with 0.1 M HCl for 24 h following repeatedly washing with deionized water exhibited the most performance increase (type V-AC-C in Fig. 5), enhancing power density by 95% from $777 \pm 19 \text{ mW m}^{-2}$ in deteriorating state to $1518 \pm 38 \text{ mW m}^{-2}$ in regenerated state. However, the power restoration in these cathodes regenerated by washing-drying-pressing procedures was temporary. The performance in all types of cathodes regenerated by washing-drying-pressing procedures was found to quickly decrease with time, resulting in much lower power generation within dozens of hours. The maximum power for cathodes regenerated with 0.1 M HCl washing decreased by 43% to $873 \pm 56 \text{ mW m}^{-2}$ within 2 days operation, similar to the 40% decrease to $710 \pm 44 \text{ mW m}^{-2}$ for cathodes regenerated by deionized water washing (type IV-AC-C and type V-AC-C in Fig. 5). For cathodes regenerated by 0.1 M NaOH washing, two days operation reduced the maximum power by 22% to $856 \pm 25 \text{ mW m}^{-2}$ (type III-AC-C Fig. 5). Polarization measurements showed that the fast power reduction in MFCs could be attributed to the performance reduction in regenerated cathodes (Fig. S4). Although all cathodes were compacted by repressing under 17 MPa, the outer surface were found to gradually became moist in the course of fast power drop, suggesting that fast power drop might be due to destruction of the gas-liquid-solid three-phase boundary in regenerated cathodes. Although cathodes regenerated by washing-drying-pressing procedures exhibited similar appearance feature on both side with newly prepared AC air-cathodes (Fig. S5), the water resistance of PTFE GDL decreased probably due to aging or potential surface modification by salt/biofilm formation during long-term operation over one year. This speculation was supported by additional experiments with AC cathodes re-pressed with new PTFE filtering film.

AC in deteriorated air-cathodes experiencing one-year MFC operation was collected by scraping method after washing and drying. The collected AC powder were directly used to re-generate cathodes with new PTFE filter as GDL by pressing method under 17 MPa without any additional treatments. The collected AC powders themselves had adhesivity and ductibility, thus no adhesion PTFE was added during the cathode regeneration. Experiments showed that cathodes re-pressed with AC recovered from long-term deteriorated air-cathodes showed high performance in prolonged MFC operation. Maximum power production in MFCs with re-pressed cathodes was $>1800 \text{ mW m}^{-2}$ during initial one-month operation (Fig. 6), similar to fresh AC cathodes (Fig. 2A). Based on the observations that biofilms removal could not fully restore the performance of long-term AC air-cathodes, degradation of the AC catalyst performance was previously suggested to be responsible for performance reduction in long-term AC air-cathodes (Zhang et al., 2011). However, the data in this study illustrated that AC experiencing even one-year MFC operation still had electrocatalytic performance in cathodes as high as fresh AC material, suggesting that more factors rather than degradation of the AC catalyst performance should be considered to understand the performance deterioration of long-term AC air-cathodes. Compared with cathodes regenerated through washing-drying-pressing procedures (Fig. 5), durability of cathodes was entirely restored by re-pressing recovered AC with new PTFE GDL (Fig. 6), suggesting that the mechanical structure and the effectiveness of the GDL were important to the performance stability of the air cathode. Compared with reported catalysts such as Pt (Cheng et al., 2006; Kiely et al., 2011; Yang

et al., 2011), AC catalyst can be easily recovered from long-term deteriorated air-cathodes for recycling. Moreover, AC-based cathodes can be regenerated by simple pressing method to obtain good mechanical structure, which is of great significance to practical MFC application in wastewater treatment.

4. Conclusion

AC air-cathodes could produce maximum power density of 1722 mW m^{-2} within initial one-month MFC operation, but showing significant power reduction by 55% in one year operation. In addition to salt/biofilm formation, destruction of the gas-liquid-solid three-phase boundary caused by invalid GDL was the main reason for the cathode deterioration in MFCs operated over one year. The AC catalyst recovered from long-term deteriorated air-cathodes exhibited performance as high as fresh AC catalyst, resulting in $>1800 \text{ mW m}^{-2}$ of maximum power production. The results in the present study illustrated that AC catalyst could be recycled for reuse in long-term MFCs.

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Supporting materials

Durability and regeneration of activated carbon air-cathodes in long-term operated microbial fuel cells

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Fig. S1 Electrode preparation and single-chamber MFC setup. (A) current collector, activated carbon catalytic layer and PTFE gas diffusion layer; (B) air-facing surface of the cathode; (C) medium-facing surface of the cathode; (D) assembled carbon felt anode; (E) assembled single-chamber MFC.

Fig. S2 Conductivity during salt/biofilm removed cathodes washing repeatedly with 100 ml deionized water

Fig. S3 SEM observation of medium-facing surface (A) and air-facing surface (B).

Figure S4 Power production and electrode potentials in MFCs assembled with regenerated cathodes through different washing-drying-pressing procedures.

Figure S5 Cathodes re-generated from deteriorated AC air-cathodes experiencing one-year MFC operation through salt/biofilm scrapping-washing-drying-pressing procedures. (A) air-facing surface; (B) medium-facing surface.