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Electric field induced salt precipitation into activated carbon air-cathode causes power decay in microbial fuel cells

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ABSTRACT

As a promising design for the real application of microbial fuel cells (MFCs) in wastewater treatment, activated carbon (AC) air-cathode is suffering from a serious power decay after long-term operation. However, the decay mechanism is still not clear because of the complex nature of contaminations. Different from previous reports, we found that local alkalinization and natural evaporation had an ignorable effect on cathode performance (~2% decay on current densities), while electric field induced salt precipitation (~53%) and biofouling (~37%) were dominant according to the charge transfer resistance, which decreased power desities by 36% from 1286 ± 30 to 822 ± 23 mW m^{-2} in 6 months. Biofouling can be removed by scrapping, however, electric field induced salt precipitation under biofilm still clogged 37% of specific area in catalyst layer, which was even seen to penetrate through the gas diffusion layer. Our findings provided a new insight of AC air-cathode performance decay, providing important information for the improvement of cathodic longevity in the future.

1. Introduction

Microbial fuel cell (MFC) is a promising and environmentally friendly technology because it generates electricity from wastewater directly using electroactive microorganisms (Logan et al., 2006), which turns energy-consuming process (such as active sludge process) into energy-saving process (Hou et al., 2016; Ren and Umble, 2016). As recognized in recent years, the most critical bottleneck for the application of MFCs is the cathode because the very high overpotential of oxygen reduction reaction mainly limited the cathode potential and therefore the power density (Logan et al., 2015). Although several chemicals such as oxygen, ferric iron, manganese, and nitrobenzene had been used as cathodic electron acceptors (Li et al., 2010; Rhoads et al., 2005; Ter Heijne et al., 2006), oxygen is the best choice for application because of its relatively high oxidation potential, availability, and environmental sustainability (Liu and Logan, 2004). Air-cathode is one of the most promising designs since it utilizes ambient oxygen as electron acceptor through the passive air diffusion instead of energy-consuming aeration. Although the Pt catalyst with Nafion as the binder provided attractive current densities, the high capital cost hampered its application in wastewater treatment plant.

Pt catalyzed oxygen reduction reaction (ORR) through an efficient four-electron pathway. However, AC provided more active sites (three phase interfaces) by its abundant micro/meso pores when it is pressed with polytetrafluoroethylene as a 3D catalyst layer. In recent years, activated carbon (AC) air-cathode is found to produce comparable or even higher power density than Pt/C, which is a promising substitute of Pt in MFCs due to its high power output, simple structure, and relatively low cost. The power density of AC air-cathode reached 1220 mW m^{-2} comparing to 1060 mW m^{-2} obtained by Pt loaded carbon cloth, while the cost of AC air-cathode was only 50–70 \$ m^{-2} (3.5–5% of Pt/C-Nafion cathode) (Zhang et al., 2009). The invasion of the catalyst layer into current collectors further enhanced the power density to 2503 ± 61 mW m^{-2}, and the addition of OH^- transport channels in AC by quaternary ammonium compounds achieved a maximum of 2781 ± 36 mW m^{-2} (Dong et al., 2013; Wang et al., 2014; Zhang et al., 2014b). The loading of chemical catalysts on AC can also enhance the power output. For example, the immobilization of Fe-N-C cocatalyst on AC produced 2600 ± 50 mW m^{-2} in 50 mM phosphate buffer (Yang and Logan, 2016).

However, the above reported maximum power densities are not sustainable when MFCs were operated more than one month. As a

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sustainable water infrastructure, MFCs should perform stably in complex mixtures of organic pollutants and bacteria. Single chambered reactors usually suffer from both the increase of internal resistance and the decrease of Coulombic efficiency because of the forming of aerobic microorganism biofilm on the surface of air-cathode. The undesired biofouling could obstruct the oxygen and hydroxide transport along micropores and channels of reaction sites (Chen et al., 2012; Li et al., 2016a; Zhang et al., 2012). These contaminations decrease the exposure of reaction sites which could further lower the catalytic activity of AC air-cathode (Dong et al., 2012a; Wang et al., 2014). In order to improve the longevity of AC air-cathode, for example, to avoid the growth of cathode biofilm, additional chemicals such as silver nanoparticles, quaternary ammonium compounds or enrofloxacin, had been applied. However, these extra treatments incurred an increase in cathode cost (An et al., 2011; Li et al., 2014; Liu et al., 2015). It was further revealed that the contamination of AC cathode was a mixture of biofilm and salt precipitation after 17 months of operation, and the cleaning with weak hydrochloric acid recovered power density by 14–29% (Zhang et al., 2014a).

Although some of previous researches had hypothesized reasons for their power decay, however, the exact mechanism of how cathodic contamination formed is still not clear. In our opinion, the possible reasons of this contamination were due to: natural evaporation and local alkalinization, biofilm, and electric field induced ion transfer. Electrolyte evaporated through the porous air-cathode. This may incur a deposition of soluble salts into cathode after a long time. Ions of salts are also moved by the electric field of MFCs, so we define this as electric field induced ion transfer. It had been reported that the local cathodic pH of both single and dual chambered MFCs was alkaline (Yuan et al., 2013). This is another factor that potentially affect cathode performance. Here we operated AC air-cathodes in different systems to identify the three reasons, including soaking in an abiotic alkaline catholyte, the use of membrane to separate biofilm and the usual condition. The chemical oxygen demand (COD) was set at domestic wastewater level (~400 mg L^{-1}). It should be noted that the COD concentration has a critical effect on cathodic biofilm because the aerobic growth of planktonic bacteria as well as cathodic biofilm in MFCs need sufficient substrate. Relatively high COD (800–1000 mg L^{-1}) in previous test may incur a fast growth of cathodic biofilm. These cathodes were operated for 6 months, and then evaluated using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), etc. The change of anodic bacterial communities was also investigated (supporting information).

2. Materials and methods

2.1. Air-cathode materials and fabrication

Rolling pressed AC air-cathodes consisted of a catalyst layer (CL), a current collector and a gas diffusion layer (GDL) were fabricated according to the procedure previously reported by our group (Dong et al., 2012b; Li et al., 2017). The catalyst layer was made of activated carbon (Xinsen Carbon Co. Ltd., Fujian, China) and polytetrafluoroethylene (PTFE) emulsion (60 wt%, Hesen, Shanghai, China) with an optimized mass ratio of 6:1. The gas diffusion layer was made of carbon black (CB, 30 nm, Vulcan XC-72R, Cabot Corporation, US) and PTFE with an optimized mass ratio of 4:9 (Li et al., 2016b), with stainless steel meshes (Type 304N, 60 meshes, Detiannuo Commercial Trade Co., Ltd., Tianjin, China) as the current collector.

2.2. MFC configuration and operation

Single chambered cubic MFCs (4 cm in length with an inner cylindrical chamber of 3 cm in diameter, a total volume of 28 mL) were constructed as described previously (Li et al., 2016b). The anode was a graphite fiber brush (2.5 cm in diameter and 5 cm in length) with a Ti wire core. The cathode was placed on the other side of the reactor. The medium was 0.5 g L^{-1} sodium acetate amended with 5 mL L^{-1} vitamins and 12.5 mL L^{-1} trace minerals in phosphate buffer solution (50 mM PBS; NH_4Cl 0.31 g L^{-1}, KCl 0.13 g L^{-1}, NaH_2PO_4 $2H_2O$ 2.772 g L^{-1},Na_2HPO_4 4.576 g L^{-1}) (Dong et al., 2012b). All the MFCs were operated in fed batch mode when the voltage decreased to <30 mV, forming a complete cycle. The external resistor was fixed at 1 kΩ except as noted (25 ± 1 °C).

Our hypothesis is that the cathodic contamination in MFCs is mainly from natural evaporation and local alkalinizetion, biofilm, electric field induced ion transfer. In order to systematically investigate the mechanism, three groups of reactors were operated: 1) abiotic single chambered reactors with alkaline electrolyte (natural evaporation and local alkalinization); 2) dual chambered MFCs (natural evaporation and local alkalinization + electric field induced salt precipitation) and 3) single chambered MFCs (natural evaporation and local alkalinization + biofilm + electric field induced ion transfer). Three reactors were operated for each group as repeats. For abiotic alkaline reactors, they were assembled with identical cathodes filling 50 mM PBS without acetate, and the pH of electrolyte was adjusted to 9.0 by KOH. We set this pH because: 1) the local pH of air-cathode in single chambered MFCs was reported as 9 ± 1 (Yuan et al., 2013); 2) the pH of catholyte stabilized at 9.0 ± 0.2 in dual chambered MFCs according to our pre-experiment. For dual chambered MFCs, the anode and cathode chambers were 28 mL and 14 mL (3 cm in diameter and 2 cm in length), separated by a cation exchange membrane (CEM, Ultrex CMI-7000, Membranes International Inc., Glen Rock, NJ, USA). For single chambered MFCs, their cathodes directly contacted the medium with acetate. Anodes were preacclimated under 1 kΩ for over six months in AC air-cathode MFCs before installed into single and dual chambered MFCs.

Voltages across an external resistor were recorded every 30 min by a data acquisition system (PISO-813, ICP DAS Co., Ltd, China). Polarization and power density curves were measured every month by varying the external resistance from 1 kΩ to 50 Ω, with a time interval of 30 min to stabilize the voltage. Error bars (±SD, standard deviation) were calculated based on measurements in triplicate reactors. Both anode and cathode potentials were recorded simultaneously versus an Ag/AgCl reference electrode (+197 mV, 3.5 M KCl, versus a standard hydrogen electrode) except as indicated. The Coulomb efficiency (CE) was calculated according to equation (1):

$$CE = \frac{8\int_0^{t_b} Idt}{FV\Delta COD} \times 100\% \quad (1)$$

where 8 is a constant for COD calculation. I is the current (A) over time t (s), V is the volume (L) of the anode chamber, F is Faraday's constant (9.65×10^4 C/mol).

2.3. Electrochemical tests and analysis

Electrochemical analysis of fresh, used and cleaned cathodes were conducted in an abiotic reactor in a 50 mM PBS medium. For the cleaning process, cathodes were washed twice with acetone and deionized water to remove organic substances after 6 months (samples were marked as C_{SC-R}). LSVs were tested by a potentiostat (Autolab PGSTAT 302N, Metrohm, Switzerland) at a scan rate of