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Enhanced catalytic activity and inhibited biofouling of cathode in microbial fuel cells through controlling hydrophilic property

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HIGHLIGHTS

- Hydrophilicity increased by addition of LA132 binder.
- Optimal hydrophilicity enhanced electrochemical activities of cathode.
- The maximum power density was enhanced by 14% with proper hydrophilicity.
- Biofilm was inhibited due to hydrophilic and electronegative catalyst layer.

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ABSTRACT

The hydrophilicity of activated carbon cathode directly determines the distribution of three-phase interfaces where oxygen reduction occurs. In this study, activated carbon cathodes are fabricated by using hydrophobic polytetrafluoroethylene (PTFE) and amphiphilic LA132 at various weight ratio to investigate the effect of hydrophilic property on cathode performance. Contact angle tests confirm the positive impact of LA132 content on hydrophilicity. Cathode with 67 wt% LA132 content shows the highest electrochemical activity as exchange current density increases by 71% and charge transfer resistance declines by 44.6% compared to that of PTFE cathode, probably due to the extended reaction interfaces by optimal hydrophilicity of cathode so that oxygen reduction is facilitated. As a result, the highest power density of 1171 ± 71 mW m^{-2} is obtained which is 14% higher than PTFE cathode. In addition to the hydrophilicity, this cathode had more negative charged surface of catalyst layer, therefore the protein content of cathodic biofilm decreased by 47.5%, indicating the effective bacterial inhibition when 67 wt% LA132 is used. This study shows that the catalytic activity of cathode is improved by controlling proper hydrophilicity of cathode, and that biofilm can be reduced by increasing hydrophilicity and lowering the surface potential.

1. Introduction

Microbial fuel cells (MFCs) have attracted intense attention over the past decade as promising technology to extract energy from wastewater [1–3]. Air cathode MFCs are considered as more practical configuration because readily oxygen from air serves as electron acceptor. For carbon based cathode, oxygen reduction reaction (ORR) occurs at three-phase interfaces which closely relate to property of catalyst layer [4]. Generally, these properties of catalyst layer in terms of hydrophilicity, wettability, and mass transport largely depend on binder materials.

During cathode preparation, binder is used not only holding catalysts together but also conveying oxygen or ions to the reaction sites [5,6]. Nafion is usually used as catalyst binder due to its high proton conductivity benefited from hydrophilic and sulfonated property [5], but the expensive cost always limits its further application. Therefore, many researchers have focused on alternative binders to replace the expensive Nafion binder. Hydrophobic binders, such as polytetrafluoroethylene (PTFE) [7], poly(-dimethylsiloxane) (PDMS) [8] and poly(sulfone) RADEL [9] have been tested in cathode preparation and acquired comparable power densities to that of Nafion based cathode. The main reason for

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the better electrochemical activity is attributed to protect the cathode from suffering water flooding which will deteriorate oxygen transport [10]. However, the affinity with oxygen due to hydrophobicity inhibits the protons accessibility of the reaction sites, therefore restrains cathode performance. Generally, there is a proper hydrophobicity for both better catalytic activity and reactant transport of air cathode. When the PTFE was mixed with Nafion binder, power density increased linearly with the Nafion percentage, indicating appropriately increased hydrophilic property favored cathode reaction [10]. It was also reported that the increased hydrophilicity of polystyrene-*b*-poly(ethylene oxide) binder based cathode enhanced proton flux to reaction surface by higher water uptake [11]. Therefore, the inexpensive and neutral hydrophilic cathode binder is in desperate need.

Biofouling is another problem for air cathode in single chamber MFCs [12–14]. Biofilm within the catalyst layer would not only obstruct the oxygen and hydroxide transport along microenvironment of reaction sites [15–18], but also decrease the exposure of reaction sites which further lowered the catalytic activity of cathode [12]. The undesired biofouling is usually inhibited by incorporation antibacterial chemicals into catalysts during cathode preparation such as silver nanoparticles [19], quaternary ammonium [20], vanillin (4-hydroxy-3-methoxybenzaldehyde) [21], and enrofloxacin [22]. However, these processes either enhance cathode cost due to chemicals addition, or complicate the preparation process. One alternative method to reduce biofouling relates to the surface hydrophilicity, charge and surface energy which are usually studied in membrane process [23], and all these surface characterizations are effectively changed by binder species. Based on these analysis, binder provides promising way to reduce biofouling without additional bacteriostat while increasing cathode performance.

In order to better understand the effect of hydrophilicity on cathode performance, the amphiphilic LA132 binder (a viscous and aqueous emulsion) was introduced and mixed with PTFE at different mass ratio to fabricate activated carbon cathode with various hydrophilicity. The catalytic activity was investigated by integrating catalytic kinetics with the hydrophilic property. By comparison the protein content of biofilm on cathode, the effect of hydrophilicity, surface energy, and charge property on cathodic antibacterial activity was evaluated.

2. Materials and methods

2.1. Cathode preparation

Air cathodes were prepared by rolling press method as described [7]. Briefly, catalyst layer and gas diffusion layer were placed on each side of stainless steel mesh (60-mesh), then pressed with steel mesh successively to be sandwich-like cathode. Catalyst layers were prepared by activated carbon powder (Carbosino Material Co., Ltd, Shanghai, China) and mixed binders (PTFE and LA132) with a mass ratio of 6:1. In order to investigate the effect of hydrophilicity on cathode performance, the content of LA132 in mixed binders varied as 0 wt% (only PTFE, control), 33 wt% (denoted as M33), 67 wt% (M67) and 75 wt% (M75). Because both increasing LA132 and lowering PTFE binder could enhance the hydrophilicity of catalyst layer, to illustrate the contribution of LA132 binder on hydrophilicity, cathodes with only PTFE binder were prepared, but the dosage was equal to that in M33 and M67, which were remarked as P67 and P33, respectively. Gas diffusion layer was firstly prepared by carbon black (Hesen Electrical Co., Ltd, Shanghai, China) and PTFE (60 wt %, Hesen, Electrical Co., Ltd, Shanghai, China) with a mass ratio of 3:7, followed by sintering at 340 °C for 25 min. Finally, all cathodes were cut into circles with 4 cm diameter for use.

2.2. MFCs configuration and operation

The single chamber MFCs were constructed with cube-shaped cylindrical chamber with 4 cm in length by 3 cm in diameter as previously described [24]. Carbon fiber brush pretreated by heating 30 min at 450 °C was employed as anode [25]. The prepared electrodes with different LA132 contents were used as cathodes while only PTFE contained was used as control. All MFCs were inoculated with the effluent of MFCs operated over 1 year and medium which contained glucose (1 g L^{-1}), 50 mM phosphate buffer solution, vitamins (5 mL L^{-1}) and minerals (12.5 mL L^{-1}) prepared as described [26]. All reactors were operated in triplicate in fed-batch mode at 30 °C with external resistance of 1000 Ω.

2.3. Protein content of biofilm

The antibacterial performance of cathode was evaluate by protein content which was determined by the bicinchoninic acid (BCA) method against a bovine serum albumin standard in 0.1 N NaOH [27]. To extract the protein from electrodes, the surface biofilm of cathode was firstly removed and placed into centrifuge tube with 10 mL of 0.2 N NaOH, the remaining cathode was then cut into pieces and placed into this tube. The tube was finally stored at 4 °C for 1 h during which the tube was vibrated every 15 min for 1 min. After transferring the extracted liquid, the electrode fragments were further rinsed with 10 mL of deionized water to remove the residues, which was then mixed with the collected liquid to obtain the final concentration of 0.1 N NaOH. Later, the obtained liquid was completely extracted via three freeze-thaw cycles (frozen at −20 °C for 2 h followed by thawing at 90 °C for 10 min). Finally, the sample of protein extract was measured by BCA method.

2.4. Structural and electrochemical characterization

The functional groups of LA132 were examined by Fourier transform infrared (FTIR) spectroscopy (Spectrum One B, PerkinElmer, USA) with the attenuated total reflection (ATR) method, and the FTIR spectra of the LA132 film was scanned from 650 cm^{-1} to 4000 cm^{-1}. The constituent elements for LA132, PTFE, and the mixed binder were evaluated by X-ray photoelectron spectroscopy (XPS) with employing a monochromatic Al Kα radiation at 1486.6 eV (XPS, PH1-5700 ESCA system, US). Contact angle measurements were carried out in a Digidrop goniometer under ambient conditions, and the contact angle of water drop was measured using the Digidrop software. Based on the contact angles, the equation-of-state approach was used to calculate the surface energy as follows [28]:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_s}{\gamma_l}}e[-\beta(\gamma_l - \gamma_s)]^2$$

where θ is the contact angle; β is the constant equal to 0.0001247 (m^2 mJ^{-1})^2, γ_s and γ_l are surface energy of solid and tested liquid.

Zeta potential of cathode was measured suing a SurPASS Electrokinetic Analyser (Anton Paar GmbH, Austria) based on streaming potential test. The test was carried out using the clamping cell apparatus and 10 mM KCl (Ph 7.0) as electrolyte.

The electrochemical activities of cathodes were tested in an abiotic electrochemical cell which was filled with 50 mM phosphate buffer solution. The abiotic electrochemical system was composed of prepared air cathode (working electrode), Pt sheet (counter electrode), and Ag/AgCl referenced electrode (saturated KCl, +197 mV versus standard hydrogen electrode; SHE). All