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Short communication

Improved interfacial oxygen reduction by ethylenediamine tetraacetic acid in the cathode of microbial fuel cell

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ABSTRACT

In this study, ethylenediamine tetraacetic acid (EDTA) was investigated as a new kind of non-polymeric catalyst binder to improve interfacial oxygen reduction reaction (ORR) for the cathode of microbial fuel cell (MFC). The electrochemical analysis and MFC tests show negative correlation between ORR activity and molar concentration of EDTA applied during electrode preparation. In particular, the 0.02 mol/L-EDTA yields higher ORR activity than other binder materials like Nafion, water, 0.1 mol/L-EDTA and 0.2 mol/L-EDTA, as indicated by the strongest response of ORR current and the smallest charge-transfer resistance. Accordingly, the MFC with cathode of 0.02 mol/L-EDTA produced a maximum power density of 722 mW/m^2, accounting for a value approximately 42% higher than that of commercial Nafion binder (5 wt%, 507 mW/m^2). The improved ORR activity should be attributed to the enhanced proton transfer from phosphate ions to EDTA-involved three-phase boundary as a result of dipole ion bonds on nitrogen atoms having unshared pair of electrons in EDTA molecule.

1. Introduction

Microbial fuel cell (MFC) has been drawing a drastically growing research attention because it shows great promise for its potential in recovering electrical energy during wastewater treatment (Logan et al., 2006). However, there remain several challenges for scale-up applications of MFC technology in the near future. Recently, the significance of cathode performance arises because the power production of MFC was believed to be limited by the properties of three-phase boundary layer where oxygen reduction reaction (ORR) occurs, which essentially relies on electrocatalyzing activity, oxygen diffusion and solubility, electron conductivity, as well as proton availability (Cheng et al., 2006; You et al., 2011). As has been widely adopted in proton exchange membrane (PEM) fuel cells, it is common practice to use perfluorosulfonic acid (*i.e.*, Nafion, 5 wt%) ionomer as standard binder to enable three-phase contact between gaseous oxygen, protons and electrocatalyst in MFC cathode (Aelterman et al., 2009). However, the commercial Nafion binder may be problematic in terms of not only high cost, but also inducing large liquid–liquid junction overpotential caused by adsorption of sulfonate groups to active sites, and thus hindering proton migration to the electrocatalytic surface. This gives priority to the exploitation of inexpensive and more efficient binder materials for MFC applications.

There have been several previous studies addressing the feasibility of using non-Nafion binder for the cathode of MFC. For example, Huang et al. (2010) fabricated the catalytic electrode using only water rather than Nafion as binder, achieving comparable power output with that using Nafion binder in MFC. Besides, the mixed binder made from Nafion (67 wt%) and polytetrafluoroetylene (PTFE) was reported by Wang et al. (2010) who found that the maximum power density was only decreased by approximately 20% in comparison with that using 100 wt% Nafion binder. Additionally, efforts are also emerged to develop more economically viable binder materials such as sulfonated, non-sulfonated poly (-sulfone) (Saito et al., 2010), polystyrene-b-poly (ethylene oxide) (Saito et al., 2011), as well as cationic fluorinate polymer (Chen et al., 2012), so as to improve the overall performances of MFC. Yu et al. (2012) demonstrated the increased power production using hydrophilic anion exchange ionomer (QDPSU), and they attributed the enhanced interfacial transfer of hydroxyl ions to the improvement of interactions between ionomer and oxygen. However, these polymeric materials still suffer from problems of high cost and sensitivity to temperature.

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Ethylenediamine tetraacetic acid (EDTA) is a common and inexpensive chemical, which is used as hexadentate chelating agent to sequester transition metals. By virtue of this nature, EDTA was adopted to synthesize platinum-free ORR electrocatalysts for MFC (Aelterman et al., 2009; Wang et al., 2011; Xia et al., 2013). However, there appears to be few studies on EDTA serving as binder to improve interfacial proton transfer. In reality, EDTA is a very hydrophilic aminopolycarboxylic acid with various protonated forms depending on pH of the solution. Under near pH-neutral electrolyte (MFC condition), the EDTA exists mostly in the form of H_2Y^{2-}/HY^{3-} species with two dipole ion bonds on nitrogen atoms (pKa=6.20, 25 °C) (Serjeant and Dempsey, 1979), making it capable of accepting protons to mediate proton transfer between electrolyte and three-phase boundary of ORR electrode.

This study focuses on examination of EDTA as non-polymeric binder for the establishment of three-phase boundary on ORR electrode, and investigating its performances of promoting interfacial proton transfer and power generation in MFC.

2. Materials and methods

2.1. Preparation of binder layer and cathode

To prepare binder layer and cathode, soluble disodium salt of EDTA was dissolved in deionized water (DI-water) to obtain 0.02 mol/L, 0.2 mol/L, 0.1 mol/L EDTA solution, followed by mixing for 2 h by magnetic stirring at room temperature. To prepare catalyst ink, the required amount of Pt/C powders (0.5 mgPt/cm^2) was added to the binder solution (450 μL), and then dispersed uniformly under sonication for 30 min. The as-prepared slurry was cast immediately on electrolyte-facing side of the well-fabricated stainless steel mesh-made gas diffusion electrode as described in our previous work (You et al., 2011). The electrodes were denoted as EDTA-0.2, EDTA-0.1 and EDTA-0.02. For comparison, the electrodes were also made by using commercial Nafion solution (5 wt%) and DI-water as binder according to the same procedures.

2.2. Electrochemical measurements

The electrochemical measurements of the electrodes were carried out under open-to-air mode in a typical three-electrode cell containing 50 mM phosphate buffer solution (PBS) at room temperature (25 °C). Linear sweep voltammetry (LSV, scan rate of 1 mV/s) and electrochemical impedance spectroscopy (EIS, open-circuit mode, frequency range of 10^5–0.005 Hz with sinusoidal perturbation of 10 mV) characterizations were performed on an electrochemical system (CHI750D, Chenhua Co. Ltd., China) using the saturated calomel electrode (SCE) as reference electrode and a platinum plate (1.0 cm^2) as counter electrode (Saito et al., 2011). The obtained EIS data were fitted to predetermined equivalent electrical circuit using ZSimpwin 3.10 software (Echem. US).

2.3. MFC construction and operation

The MFC experiments were performed in a single-chamber MFC at batch-fed operation. The MFC reactor was made of Plexiglas tube (28 mL) having a distance of 4 cm between the anode and cathode, which were connected with anti-corrosion titanium wires across given resistor (1000 Ω). The carbon cloth without water-proof was used as anode (7.0 cm^2), and the prepared gas diffusion electrode was used as cathode (7.0 cm^2). The activated sludge collected from the secondary sedimentation tank of local wastewater treatment plant was used for enriching electrochemically active microorganisms of the MFC. The electrolyte (per liter of DI water) contained 50 mM PBS (K_2HPO_3, KH_2PO_3), NH_4Cl (0.93 g), KCl (0.31 g) amended with pretreated wastewater and 1 g/L glucose substrate (You et al., 2011). Cell voltage was recorded every 2 min by using data acquisition system (PISO-813, ICP-DAS, Co. Ltd., Taiwan) connected to a personal computer *via* PCI interface. Voltage obtained was then converted to power density (P, mW m^{-2}) according to $P=V^2/(R_{EX}A_{anode})$, where $V(V)$ is the voltage across given external resistor (Ω) and A_{anode} (m^2) the anode surface area. The polarization and power curves were obtained by recording peak stable cell voltage with respect to step-wise change of external resistances (50–10000 Ω). The electrode potentials were recorded versus SCE reference.

3. Result and discussion

The as-prepared Pt/C-coated cathodes immobilized with different binders were tested by using LSV and EIS characterization in electrochemical cell in 50 mM PBS. As is shown in Fig. 1A, the ORR current was negatively correlated to the molar concentration of EDTA applied to the cathode, and the EDTA-0.02 film amounted to higher oxygen reduction current than that with Nafion, water, EDTA-0.1 and EDTA-0.2. Remarkably, the positive shift of onset potential (38 mV) was observed for EDTA-0.02 compared with that for Nafion, indicating less ORR activity for Pt with Nafion. Likewise, as is revealed from the semicircles in high frequency range in EIS

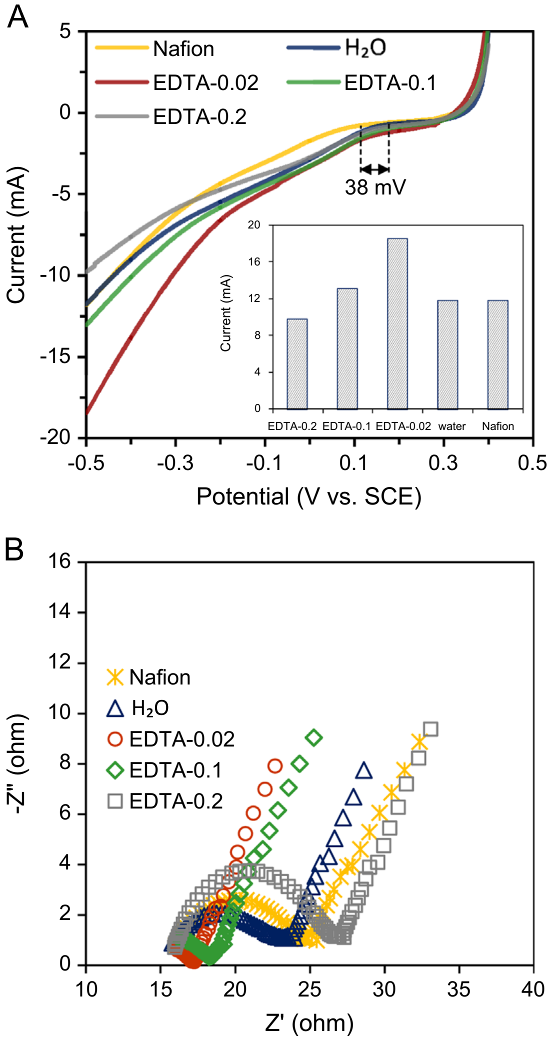

Fig. 1. (A) LSV and (B) EIS for cathodes with different binders, *i.e.*, Nafion, water and different molar concentrations (0.01, 0.1, 0.2 mo/L) of EDTA (50 mM PBS, 25 °C).