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Application of Co-naphthalocyanine (CoNPc) as alternative cathode catalyst and support structure for microbial fuel cells

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ABSTRACT

Co-naphthalocyanine (CoNPc) was prepared by heat treatment for cathode catalysts to be used in microbial fuel cells (MFCs). Four different catalysts (Carbon black, NPc/C, CoNPc/C, Pt/C) were compared and characterized using XPS, EDAX and TEM. The electrochemical characteristics of oxygen reduction reaction (ORR) were compared by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The Co-macrocyclic complex improves the catalyst dispersion and oxygen reduction reaction of CoNPc/C. The maximum power of CoNPc/C was 64.7 mW/m^2 at 0.25 mA as compared with 81.3 mW/m^2 of Pt/C, 29.7 mW/m^2 of NPc/C and 9.3 mW/m^2 of carbon black when the cathodes were implemented in H-type MFCs. The steady state cell, cathode and anode potential of MFC with using CoNPc/C were comparable to those of Pt/C.

1. Introduction

A microbial fuel cell (MFC) is a novel bioprocess which employs exoelectrogenic biofilms as a biocatalyst for electricity generation (Logan, 2008; Logan, 2009; Lovely, 2008; Rabaey and Verstraete, 2005; Rozendal et al., 2008). Biofilms that oxidize various biodegradable substrates transfer electrons to the anode electrode and are phylogenetically and functionally diverse in bacterial species. A naturally developed biofilm in MFC can be obtained from inocula such as sediment and sludge digester; therefore, it can generate electricity without the novel catalysts (e.g. Pt of chemical fuel cells) and significantly reduces the cost of anodes.

The cathode catalysts, however, have been relatively limited by costly precious metals such as platinum or non-sustainable catholytes such as ferricyanide (Logan, 2008). Although Pt has been known to be the best catalyst for oxygen reduction reaction (ORR), the cost is estimated at around 50% of the total capital cost of the system (Rozendal et al., 2008). Moreover, the effectiveness of Pt as ORR catalyst would be far diminished due to the lower power density than fuel cells, and contamination from biological process (Tartakovsky and Guiot, 2006). Alternatively, several Pt-free non-noble transition metals such as Co, Fe and Mn and their supporting structures have been studied in the form of iron(III) phthalocyanine (FePc) and Cobalt tetramethoxyphenylporphyrin (CoTMPP) for oxygen reduction reaction (ORR) (Cheng et al., 2006; Duteanu et al., 2010; Lefebvre et al., 2009; You et al., 2006; Zhao et al., 2005). Recently, stainless steel alloy and NiMo have been used for alternative low cost catalysts in microbial fuel cells (Selembo et al., 2009).

The structure of supporting material for the active site significantly affects the performance of the ORR as well as the metal catalyst (Bezerra et al., 2007; Lee et al., 2009; Zhang et al., 2006). Research studies on fuel cells show macrocyclic complexes containing nitrogen atoms produce active catalytic properties. The high catalytic activity has been attributed to its large surface area and homogeneous catalyst particle distribution on the electrode. The enhanced electron transfer rate and stability between the active site and electrode can also contribute to the improved catalyst performance using polymeric structure. It has been shown that various non-Pt (e.g. Fe and Co) macrocyclic complexes such as $N_4^-, N_2O_2^-, N_2S_2^-, O_4^-$andS$_4^-$ systems produced a certain level of catalytic activity for ORR (Wiesener et al., 1989; Zhang et al., 2006). Heat treatment and pyrolysis of supporting material have also been reported to increase ORR performance by improving particle size and dispersion of catalyst, surface morphology, and stability (Bezerra et al., 2007). Formation of nitrogen containing macrocyclic complexes by heat treatment might act as bridge for electron transfer, while protecting the catalytic active site from byproducts. For MFCs, polymer based materials such as Nafion and PTFE (poly-

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tetrafluorethylene) suspension for binding catalyst on electrode have been used (Cheng et al., 2006). The chemical structure of binder and its mechanism for electron transfer between the catalytic active site and the electrodes in MFCs have not been studied extensively.

In this paper, we have studied how to improve the surface morphology of carbon using naphthalocyanine (NPc) by a heat treatment method (Lee et al., 2009). It has been reported that NPc has different redox properties because of the substitution of benzenic groups in the macrocyclic structure (Isaacs et al., 1998). To the authors' knowledge, this is the first work to apply NPc to MFC cathode and to study morphological and electrochemical properties of the catalyst. Four different cathode catalysts (Carbon black (C), NPc on carbon black (NPc/C), Co-NPc on carbon black (CoNPc/C), Pt on carbon black (Pt/C)) were characterized using X-ray photoelectron spectroscopy (XPS), Energy-Dispersive X-ray Spectroscopy (EDAX) and transmission electron microscopy (TEM). The electrochemical characteristics of ORR were compared using CV and LSV. These cathode catalysts were finally implemented into MFC reactors and were also compared for cell potential and power output.

2. Methods

2.1. MFC configuration and operation

Two-chamber H-type MFCs were used with an aqueous-cathode in order to assess the performance of different catalysts (Oh et al., 2009). The two bottles were connected with a glass tube (inner diameter: 3.5 cm^2) with a proton exchange membrane (NafionTM 117, Dupont Co., Delaware, USA) held by a clamp in the middle of the tube. The distance between the electrodes was approximately 16 cm. The anode electrodes (2.5 × 4.0 cm each, projected area of 20 cm^2) were made of carbon paper (E-Tek, USA) and connected via an external resistor (1000 Ω, except as noted) to the cathode (2.5 × 4.0 cm each, catalyst coated project area of 10 cm^2). Anaerobic digester sludge samples from the Wastewater Treatment Plant in Chuncheon, Korea (10 ml) were used as inoculum with bacterial media containing phosphate buffer (50 mM, pH 7.0), and minerals and vitamins (Kim et al., 2007). The anode and cathode reactor liquid volumes were 250 ml, respectively. Four H-type MFC reactors were set up for the experiments. During the enrichment period, Pt cathode was used as a cathode with external resistance (1000 Ω) in phosphate buffer solution (50 mM, pH 7). Once the voltage increased and stabilized at around 290 mV (with 1000 Ω), Pt cathode was replaced with the prepared different cathode materials. Current–voltage response and power density curves were analyzed by the IviumStat electrochemical analyzer (IVIUM Technology, The Netherlands). The current was increased from 0 to 0.4 mA in series. At each level of current, the voltage response was recorded after stabilization in 600–1200 s The cell, anode, and cathode potential were also monitored with a Ag/AgCl reference electrode (BAS Inc. Japan). The reference electrode was placed to the cathode chamber as close as possible to the electrode in order to reduce IR loss.

2.2. Preparation of catalysts on naphthalocyanine (NPc)

Naphthalocyanine modified carbon (NPc/C) was prepared by the following method: 5,9,14,18,23,27,32,36-octabutoxy-2,3-naphthalocyanine (NPc, Sigma–Aldrich, MO) (0.044 g) was dissolved into 17.2 ml of acetic acid (99.7%, Sigma Aldrich) for 1 h. The solution was added into 50 ml of acetone (99.5%, Samchun chemicals, Korea) which contained 0.4 g of carbon black (Vulcan XC-72R, Cabot) as dispersion. The mixture was stirred at room temperature and evaporated at 70 °C, subsequently, the obtained powder was heat treated at 700 °C in N_2 atmosphere. The Co-impregnated carbon (CoNPc/C) catalyst was prepared by the same method with the above except from using 2,3-naphthalocyanine cobalt(II) (0.044 g, Sigma–Aldrich, MO) instead of NPc.

2.3. Preparation of cathode electrode based on naphthalocyanine (NPc)

Alternative catalysts (NPc/C or CoNPc/C, 10 mg) were dissolved into 57.2 μl of 2-propanol (99%, Samchun chemicals, Korea), 114.4 μl of distilled water, and 57.2 μl of nafion perfluorinated ion-exchange resin (Sigma Aldrich, MO), then dispersed into the carbon mixture. Each catalyst paste was obtained by sonication (130 W) for 1 h at 25 °C. NPc/C or CoNPc/C was pasted onto carbon paper (TGPH-090 Naracell Tech, Korea) by brush. The catalyst loading of the prepared counter electrodes for MFCs were NPc (1.33 mg/cm^2) and CoNPc (1.72 mg/cm^2), respectively.

2.4. Analyses of catalytic property

The compositional analysis of the CoNPc/C was conducted by Energy-Dispersive X-ray Spectroscopy (EDAX) (ELIONIX ERA-8800FE, Japan). In order to identify the morphological properties, the catalysts were characterized by field emission transmission electron microscopy (FETEM, JSM-6700F) using a Philips CM20T/STEM Electron Microscope system at 200 kV. The FETEM sample was prepared by placing a drop of the catalyst suspension with ethanol on a carbon-coated copper grid. X-ray photoelectron spectrometry (XPS) study was carried out with the Al K_α X-ray source of 1486.6 eV (the chamber pressure below 5×10^{-9} Pa). The C1s electron binding energy was referenced at 284.6 eV and a nonlinear least-squares curve-fitting program was employed with a Gaussian–Lorentzian production function.

Cathodic oxygen reduction reaction test was carried out by analyzing the cyclic voltammetry (CV) and Linear sweep voltammetry (LSV) using a potentiostat (700C Series, CH Instruments Inc., USA) with the C, NPc/C, CoNPc/C, and Pt/C (E-Tek) working electrode (WE), a Pt-foiled counter electrode (CE) and an Ag/AgCl reference electrode placed in the same buffer solution with the anode as described in the above section. LSV was conducted with the rotating ring disk electrode (RRDE) (CH Instruments Inc., USA) with a rotation rate of 1600 rpm in an oxygen saturated buffer solution as described in the above section. The reaction electron number (n) on the disk electrode was calculated by the following equations (Liu et al., 2007).

$$n = \frac{4i_d}{i_d + i_r/N} \qquad (1)$$

where N is the collection efficiency, i_r is the ring current density, and i_d is the disk current density respectively.

3. Results and discussion

3.1. Morphology of NPc/C and CoNPc/C

The morphological investigation of NPc/C and CoNPc/C by FESEM shows homogeneous distribution of Co particle on carbon supporting structure on the electrode (data not shown). This result indicates that the Co catalyst was completely absorbed onto carbon support; therefore, the observed morphology with and without Co looks similar. The mesoporous carbon structure supporting catalysts are forming homogeneous spherical particles with a diameter of 100 nm. The high surface area of the carbon structure impregnating catalyst may improve electrochemical activity of catalysts for oxygen reduction of the cathode. The