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Effects of Fe, Ni, and Fe/Ni metallic nanoparticles on power production and biosurfactant production from used vegetable oil in the anode chamber of a microbial fuel cell

Jia Liu [a,b,*], Cumaraswamy Vipulanandan [b]

[a] Department of Civil and Environmental Engineering, College of Engineering, Southern Illinois University, 1230 Lincoln Dr., Carbondale, IL 62901, USA
[b] Department of Civil and Environmental Engineering, Cullen College of Engineering, University of Houston, 4800 Calhoun Rd., Houston, TX 77204, USA

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ABSTRACT

In this study, metallic nanoparticles (Fe, Ni, and Fe/Ni) were used as cathode catalysts to enhance power production and to improve the anode performance of a two-chambered microbial fuel cell (MFC). The metallic nanoparticles were rod-shaped and produced by the precipitation/co-precipitation method. A biosurfactant was produced in the anode chamber of the MFC from used vegetable oil by the bacteria *Serratia* sp. Overall cell voltage, power density, bacterial growth, and biosurfactant production were studied by applying different types of metallic nanoparticles to the cathode electrode. The influence of various types of nanoparticles on the impedance of the MFC was also investigated by electrochemical impedance spectroscopy (EIS), including analyses of anode impedance, cathode impedance, anode solution resistance, cathode solution resistance, and membrane resistance. The nanoparticles improved MFC performance in the following order: Fe > Ni > Fe/Ni. The addition of 1.5 mg/cm^2 Fe nanoparticles to the cathode surface enhanced power production by over 500% to 66.4 mW/m^3, promoted bacterial growth and biosurfactant production in the anode solution by 132.5% and 32.0%, respectively, and reduced anode impedance, cathode impedance, and membrane resistance by 26.8%, 81.6%, and 33.8% to 159.00 Ω, 7.69 Ω, and 261.09 Ω, respectively. For the first time, biosurfacant production in the anode chamber of the MFC was promoted by using the metallic nanoparticles as cathode catalysts. By improving the cathode properties, this study showed a new way to manipulated the performance of the anode chamber of the MFC.

1. Introduction

Transition metal nanoparticles are effective catalysts for chemical transformations owing to their large surface area and unique combination of reactivity, stability, and selectivity (Li and El-Sayed, 2001). The most widely used transition metals are Fe, Co, Ni, Cu, Rh, Pd, Ag, and Pt (Haruta, 2003). A catalyst layer on the electrode surface is crucial for the performance of microbial fuel cells (MFCs) (Birry et al., 2011; Morris et al., 2007). Different types of catalysts have been used for the cathode electrode of the MFC to accelerate the reaction rate on the electrode surface (Birry et al., 2011; Morris et al., 2007). The noble metal catalyst Pt is commonly used and has the highest activity toward the oxygen reduction reaction, but has a very high cost (Birry et al., 2011). Less expensive, non-noble metal catalysts have been studied, such as lead dioxide (Morris et al., 2007), Ni nanoparticles (Cheng et al., 2010), Fe_2O_3 nanoparticles (Peng et al., 2013), and PtFeNi and Pd-Fe nanoparticles (Li and Chan, 2013; Shao et al., 2006). Fe-aminoantipyrine, Fe phthalocyanine, and lead dioxide nanoparticles increase the power density of the MFC compared to that using Pt nanoparticles (Morris et al., 2007; Santoro et al., 2015; Yuan et al., 2011). Most of the nanoparticle cathode catalysts reported in the literature are spherical (Ramachandran et al., 2015). Cubic Au nanoparticles have also been adopted (Saravanakumar et al., 2016). Recently, rod shaped nanoparticles have been used as cathode catalyst to improve the performance of the MFC. For example, Fe_3O_4 nanorods were used as cathode catalyst for electricity generation from wastewater in a MFC (Kumar et al., 2016). Another type of Fe-based nanorods generated 3 times higher of the power density compared to Pt nanoparticle catalyst

* Corresponding author at: Southern Illinois University Carbondale, College of Engineering, 1230 Lincoln Dr., Carbondale, IL, USA.
E-mail address: jialiu@siu.edu (J. Liu).

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(Wen et al., 2012). Rod-shaped nanoparticles have larger specific surface areas compared to those of spherical or cubic nanoparticles, which increased the catalytic properties of the rod shaped nanoparticles. In this study, non-precious rod-shaped Fe, Ni, and bimetallic Fe/Ni nanoparticles were evaluated as cathode catalysts in the MFC, and their effects on MFC electricity production were studied.

Biosurfactant has been produced in the anode chamber of the MFC (Zheng et al., 2015). By endogenously manipulating the biosurfacant production, the power density of the MFC was enhanced (Zheng et al., 2015). Besides biosurfactant, alcohols (e.g., butanol) have also been generated from organic substrates in the anode chamber of the MFC during the oxidative process on the anode surface via fermentative bacteria or microalgae (Zhang et al., 2009; Lakaniemi et al., 2012). In addition, several types of chemical and bio- surfactants have been used as electron shuttles in the anode chambers of MFCs to improve bacterial extracellular electron transfer and the performance of MFCs (Shen et al., 2014; Wen et al., 2010; Song et al., 2015). Our previous studies have shown that the bacteria belonging to *Serratia* can utilize used vegetable oil in the anode chamber of the MFC to produce biosurfactant with oxygen supplied in the cathode chamber of the MFC (Fig. 1) (Liu et al., 2009; Prashanth et al., 2009). The electrons released during biosurfactant production in the anode chamber were captured by the anode and transferred to the cathode surface. The biosurfactant was produced by the following pathway. Firstly, fatty acids were formed by the hydrolysis of used vegetable oil. Then, the fatty acids reacted with water, the biosurfactant formed, and electrons were released. One typical reaction in the process is shown in Eq. (2). The molecular structure of the biosurfactant has been identified by mass spectroscopy (Freguia, 2007). A portion of the released electrons is transferred to the anode surface, while other electrons are retained within the product of the biosurfactant (Ren, 1998).

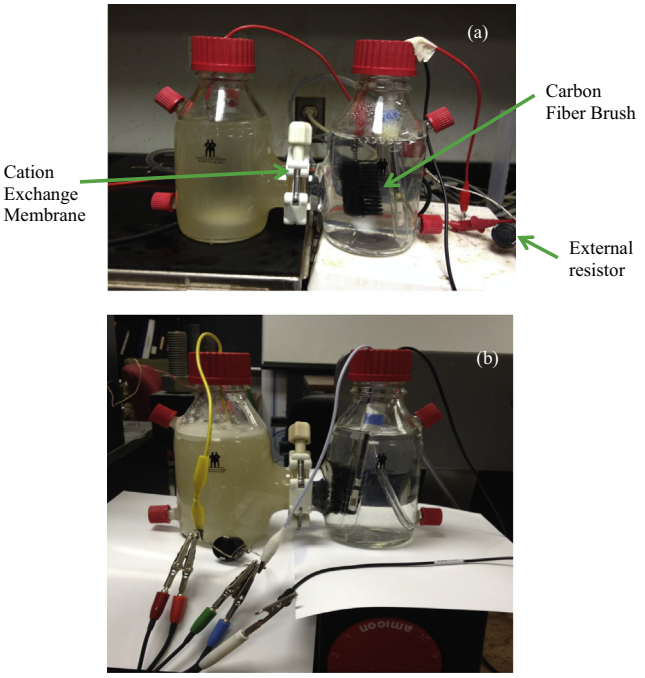
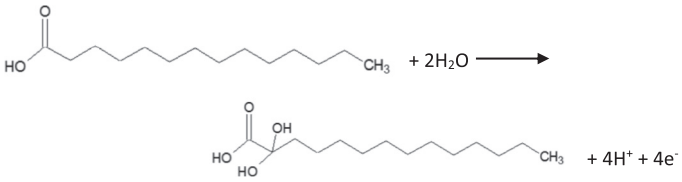


Fig. 1. Configuration of (a) the microbial fuel cell and (b) electrochemical impedance spectroscopy measurements of the microbial fuel cell.



In the cathode chamber, oxygen combines with the generated electrons and protons to form water. The reaction is summarized in Eq. (3).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

Accordingly, it is of interest to study the effect of cathode nanoparticle catalysts on biosurfactant production and bacterial growth in the anode chamber of the MFC.

High inner resistance impedes a high power density of the MFC (Fan et al., 2008). Using catalysts on the electrode surface, the inner resistance of the MFC can be reduced with an increase in power density (Zhang et al., 2015). The effects of the nanoparticles used in this study were also quantified by their influence on the inner resistance of the MFC, characterized by both electrochemical impedance spectroscopy (EIS) and the power density peak method.

To sum up, in a MFC producing biosurfactant, effects of different cathode catalysts were studied for the first time on its performance. In particular, the effects of Fe, Ni, and Fe/Ni nanoparticles were investigated on the overall cell potential, power density, inner resistance, and anode performance based on biological activities in the anode chamber of the MFC.

2. Materials and methods

2.1. Production and characterization of metallic nanoparticles

Metallic nanoparticles in this study were produced in foamed liquid (Srinivasan, 2007). For Fe nanoparticles, 1.2 g of $FeSO_4{\cdot}7H_2O$ was mixed with 0.79 g of cetyltrimethylammonium bromide (CTAB) cationic surfactant in deionized (DI) water. Then, 0.33 g of $NaBH_4$ was added to precipitate the Fe nanoparticles. To produce Fe/Ni nanoparticles, 1.5 g of $FeSO_4{\cdot}7H_2O$ was initially mixed with 1.3 g of $NiCl_2{\cdot}6H_2O$ and 0.5 g of CTAB in DI water, and 0.71 g of $NaBH_4$ was then added to precipitate the bimetallic Fe/Ni nanoparticles. To produce Ni nanoparticles, 1.3 g of $NiCl_2{\cdot}6H_2O$ was initially mixed with 0.25 g of CTAB in DI water, and 0.3 g of $NaBH_4$ was then added to precipitate the Ni nanoparticles.

After adding $NaBH_4$, the solution foamed. The entire reaction was conducted under a nitrogen environment. After the reaction, the nanoparticles were allowed to settle down without stirring. The nanoparticles were then collected and washed with acetone at least 6–7 times. The chemical reactions for nanoparticle formation are shown in Eqs. (4) and (5). The nanoparticles were stored in acetone in the nitrogen environment and dried in the nitrogen environment before use.

$$FeSO_4 + 2NaBH_4 + 6H_2O \rightarrow Fe\downarrow + 7H_2\uparrow + 2B(OH)_3 + Na_2SO_4 \quad (3)$$

$$NiCl_2 + 2NaBH_4 + 6H_2O \rightarrow Ni\downarrow + 7H_2\uparrow + 2B(OH)_3 + 2NaCl \quad (4)$$

For the microscopic analysis, the nanoparticle powders were suspended in ethanol solution and sonicated for 30 min. A piece of 400 mesh Cu grid on a carbon tape was used to hold the sample for scanning electron microscopy (SEM) (LEO 1525; LEO Electron Microscopy Inc, Thornwood, NY, USA). Energy-dispersive

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