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Bio-electrochemical reactors using AMI-7001S and CMI-7000S membranes as separators for silver recovery and power generation

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ABSTRACT

Bioelectrochemical reactors using AMI-7001S and CMI-7000S membranes were investigated for silver recovery and power generation. High silver removal (83.73–92.50%) and columbic efficiency (11.50–19.89%) were obtained in CMI-based reactor after 24 h, although, some diffusion of Ag^+ ions was observed. In contrast, substrate loss was found in AMI-based reactor, which caused low overall performance. At an initial Ag^+ concentration 2000 mg/L, a maximum power density of 5396 mW/m^3 and 3385 mW/m^3 were obtained in CMI and AMI-based reactor, respectively. Under SEM analysis, different morphologies of metallic silver deposits were detected on the cathode surfaces, and was confirmed by EDX and XRD technique. High diversity of anodic microbial communities were also found, in which *Firmulates*, *Proteobacteria*, and *Bateroidetes* were dominant phyla. *Geobacter* sp. and other exoelectrogens could be detected while no *Shewanella*-like sequences were retrieved. The study suggests that CMI-7000S showed better performance when compared to AMI-7001S at the same operational conditions.

1. Introduction

Recovery of precious metals from aqueous solution by using bioelectrochemical system (BES) technology has attracted more attention recently (Mathuriya and Yakhmi, 2014; Nancharaiah et al., 2015, 2016; Wang and Ren, 2014). Basically, a BES reactor consists of an anode and a cathode chamber, in which different oxidation and reduction processes occur. In principle, a BES employs microorganisms as exoelectrogens to convert organic matter during their anaerobic oxidation to produce electrons and protons (H^+) in the anode chamber. These electrons transport from the anode to the cathode through an electrical circuit to supply for the reduction of metal ions. The organic substrates as electron donors in the anolyte can be either simple organic molecules (e.g. acetate, glucose) or complex wastewaters (e.g. protein-rich wastewater), whereas metal ions in the catholyte are terminal electron acceptors (TEAs). As anode and cathode chambers are separately fed by different bulk liquids (i.e. substrate and metal-rich solution, respectively), a BES reactor requires a separator between them. The separator keeps the anolyte and catholyte separate from each other, preventing crossover processes, and eliminating metal toxicity. It also has to be conductive for ions, since one ion has to be transferred between the anode and cathode compartment to achieve the counterbalance for every negatively charged electron that crosses the external electric circuit (Krieg et al., 2014).

Most BES reactors, based on two-chamber microbial fuel cell (MFC) configuration, use polymer ion exchange membranes (IEMs) as separators. In a closed electrical circuit, to maintain the electro-neutrality, either negative charge equivalents (anions/hydroxide ions) travel from the cathode to the anode through anion exchange membrane (AEM) or positive charged ions (cations/protons) migrate from the anode to the cathode through cation exchange membrane (CEM). While proton exchange membranes (PEMs), such as Nafion 117 (Dupont Inc., USA) are used in most BES studies, CEMs such as CMI-7000S (Membranes Inc., USA), are also frequently used, as they are less expensive and often structurally stronger than Nafion 117 (Kim et al., 2007a). Due to the presence of negatively charged functional groups (i.e. sulfonate SO_3^-) attached to the fluorocarbon backbone ($-CF_2-CF_2$) of perfluorosulfonic acid membrane, Nafion shows high conductivity to various cations (Li et al., 2011). CMI-7000S is a strong acid polymer membrane with gel polystyrene and divinylbenzene (DVB) cross-linked structure, which also contains a lot of sulphonic acid groups ($R-SO_2OH$). According to Harnisch et al. (2008), a CEM exhibits comparable cation conductivity and mechanical durability, but generally has a higher ohmic resistance (R_Ω), as compared to Nafion. Specifically, the

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R_Ω of Ultrex CMI-7000 and Nafion 117 measured in the electrolyte as phosphate buffer solution (i.e. K_2HPO_4/KH_2PO_4 0.05 M at pH 7), was 45.1 and 9.2 Ω, respectively.

However, the biggest drawback of using Nafion or CEMs is the pH splitting problem during operation, as other cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), existing in the anolyte at higher concentration, compete with protons (H^+) to transfer from the anode to the cathode chamber through the membrane (Kokabian and Gude, 2015; Pandit et al., 2012). The anolyte gradually becomes more acidic and suppresses oxidation activity of bacteria in the anode chamber while the catholyte gradually becomes more alkaline and affects the soluble state of metal ions in the cathode chamber. Another drawback is the undesired diffusion of metal ions from the catholyte to the anolyte through CEMs. This diffusion is caused by the concentration gradient of electrolyte between the anode and cathode compartment and is not under the effect of an electrical field. Harnisch et al. (2008) reported that there are different ion transport mechanisms through the CEMs in biological fuel cells, in which the migrative fluxes refer to the transfer of ions in the electric field and the diffusive fluxes are related to the permeability of the electrolyte. Accordingly, when CEMs are used in a BES reactor for metal recovery, they may cause metal ion losses in the cathode chamber and further adverse effects on the microbial community in the anode chamber.

The AEMs, such as AMI-7001S (Membranes Inc., USA), have been considered to overcome the above disadvantages of Nafion and other CEMs. With positively charged quaternary ammonium group ($-NH_4^+$) attached to the polymer structure of the membrane, AEMs allow the migration of anions from the cathode to the anode chamber. Metal ions in the catholyte thus, cannot transport directly through AEMs, which presumably prevents any loss of metals. In addition, AEMs are found to facilitate proton transfer by using phosphate as the proton carrier and pH buffer solution, which produces a lower rate of pH splitting (Leong et al., 2013; Li et al., 2011). However, there is a possibility that few intermediate metabolites with a negative charge, such as acetate, butyrate, propionate etc., occurring during the biological oxidation in the anode chamber, percolate from the anode to the cathode chamber (Pandit et al., 2012). These diffusive fluxes through AEMs were also reported by Harnisch et al. (2008) and were attributed to the concentration gradient between the two chambers. This phenomenon leads to substrate loss which affects electron production and BES performance.

Some small-scaled BES reactors (i.e. 50–100 mL of working volume for each chamber), operated in a short time duration (i.e. 8–10 h), were studied to recover silver from different Ag(I)-containing solutions, including silver nitrate $AgNO_3$ containing free Ag^+ ions (Choi and Cui, 2012; Lim et al., 2015; Tao et al., 2012), silver thio-sulphite complex $[AgS_2O_3]^-$ (Tao et al., 2012), and ammonia-chelated silver $Ag(NH_3)_2^+$ (Wang et al., 2013). In the above studies, either Nafion 117, AMI-7001S, or bipolar membrane (BPM-I, Beijing Ting Run Co., China (Wang et al., 2013)) was used as a separator in dual-chamber BES reactors. Due to the difference in ion transfer mechanism through these membranes, the BES performance, characterized by silver recovery and power generation efficiency, may be affected. The current intensity and electrochemical reaction rate, thus, may have an impact on the formation and growth of silver deposits on the cathode surface. Small size reactors employed in the above studies for shorter duration may not clearly indicate the influence of membrane and transport phenomenon. Therefore, it is important to scale-up BES reactors and run for longer duration to understand the effects of the membrane on BES performance.

In addition, BES performance also depends on the microbial community, substrate conversion rate, and extracellular electron transfer (EET) in the anode chamber. Most BES studies normally use anaerobic sludge from the digesters or sedimentation tanks of wastewater treatment plants to inoculate the bio-anodes. Compared to single strains, mixed cultures have attracted more attention due to their higher adaptability, stability, and productivity (Mathuriya, 2013; Patil et al., 2009). The bacterial characterization of several MFC systems with different operational conditions (e.g. inoculum sources, substrate types), showed very different and diverse microbial communities (Bond et al., 2002; Choo et al., 2006; Holmes et al., 2004; Kim et al., 2004, 2007b; Liu et al., 2007; Logan et al., 2005; Phung et al., 2004; Rabaey et al., 2004). Electrochemically active bacteria (EAB), participating in electricity generation have been reported frequently as iron-reducing bacteria (i.e. *Geobacter* sp. and *Shewanella* sp.) and phototrophic bacteria (i.e. *Rhodopseudomonas* sp.) due to their prominent roles in most BES studies. However, there may be other unknown species, contributing to electricity generation through a variety of mechanisms, which need to be identified.

Therefore, this study was conducted in BES reactors (2.0 L) for 24 h to evaluate the effect of different separators (i.e. AMI-7001S, CMI-7000S) on BES performance which was characterized in terms of power generation, substrate removal, silver removal efficiency, and characteristics of electrodeposits on the cathode surface. The crossover of the substrate and Ag^+ ions through AMI-7001S and CMI-7000, and the formation of precipitants on membrane surfaces were also considered, in order to clarify the difference in ions transfer mechanism between these separators. From the authors' understanding, this aspect still has not been considered by previous studies. The anodic microbial community was also characterized to identify the dominant species, and the presence of exoelectrogens contributing to electron transfers in the anode biofilm.

2. Materials and methods

2.1. BES reactors fabrication

Cubic-shape BES reactors (i.e. R1 and R2), made from acrylic plates, were used in this study. Each reactor consisted of an anode and a cathode chamber (1.0 L working volume for each chamber), which were separated by an ion exchange membrane (i.e. AMI-7001S for R1 and CMI-7000S for R2) (Fig. 1). Membrane sheets (264 cm^2 surface area/sheet) were pre-treated by immersing in 5% NaCl solution for 12 h to allow for membrane hydration and expansion. In both reactors, carbon brush (15 cm × 6 cm), prepared by twisting carbon fiber (Thai Carbonfiber Co., Thailand) with Ti wire of 1.0 mm in diameter (Prolog Titanium Co., Ltd), served as an anode, while the cathode was a graphite plate (90 cm^2, Fujian, China). Before making the electrical connection with Ti wire, the carbon brush was first cleaned by soaking in pure acetone overnight. After that, it was acid treated by soaking in a mixture of ammonium peroxydisulfate (200 g/L) and concentrated sulfuric acid (100 mL/L) for 15 min. The anode was then heat-treated in a muffle furnace at 450 °C for 30 min and finally washed three times with distilled water. The graphite plate cathode was immersed more than 24 h in 2 mM potassium permanganate solution ($KMnO_4$) before assembling. Two BES reactors were connected to a computer equipped with a data logger (Grant Instruments, Cambridge Co., Ltd), to record cell voltage progression during experiments.

2.2. Start-up and operation

The experiments were conducted under batch fed conditions and room temperature (20–25 °C). All chemicals used are analytical grade and obtained from Fisher Scientific (UK) and Wako Pure Chemical Industries, Ltd. (Japan). The solutions and reagents were prepared by using Milli-Q water.

(1) Start-up: Anode chambers were inoculated by anaerobic sludge (100 mL), collected from the digester of a domestic wastewater treatment plant (Tokyo, Japan). For the anolyte (900 mL), the following medium was used (all per liter): $C_6H_{12}O_6$ (0.935 g) as electron donor, Na_2HPO_4 (3.55 g), K_2HPO_4 (3.4 g), NH_4OH (0.2 g),