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A comparison of mono- and multi-valent ions as stack feed solutions in microbial reverse-electrodialysis electrolysis cells and their effects on hydrogen generation

Syarif Hidayat, Young-Hyun Song, Joo-Yang Park*

Department of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul, 133-791, Republic of Korea

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ABSTRACT

Microbial reverse-electrodialysis cells (MRECs) are an emerging technology combining microbial electrolysis cells (MEC) with reverse electrodialysis (RED) for the production of hydrogen gas. In this study, the MREC system used monovalent ions (Na^+ and Cl^-) and a mixture of mono- and multi-valent ions (Mg^{2+} and SO_4^{2-}) as stack feed solutions, which were compared to determine the effect of the presence of multivalent ions on MREC performance. The MREC system operated under batch conditions using acetate as a substrate while the RED stack operated under continuous flow conditions using pure NaCl and a mixture with a 10% molar fraction of multivalent ions and a 90% molar fraction of monovalent ions as stack feed solutions (flow rate = 1.2 mL min^{-1}). When using 10% of $MgSO_4$ as a stack feed solution, the maximum current achieved for the MREC system decreased from 4.2 to 3.7 mA compared to the pure NaCl. Moreover, the quantity of hydrogen produced, the production rate, and yield also decreased by approximately 32, 35, and 23%, respectively. The results obtained from this study demonstrated that the presence of multivalent ions had an adverse effect on MREC performance.

1. Introduction

Currently, the greatest amount of energy consumption in the world is shared by fossil and nuclear fuels, resulting in severe environmental impacts such as: natural resource exhaustion, air and water pollution, soil contamination, and climate change (Ursua et al., 2012). With this regard, in order to ease the world energy crisis and deal with these environmental issues, a clean and renewable material-based energy system is highly desirable. Hydrogen gas is considered to be a clean fuel and is widely recommended as an alternative to fossil and nuclear fuels due to its potential for being produced from renewable materials, offering an important environmental benefit (Suwansaard et al., 2009). Water electrolysis and dark fermentation are the most common methods for hydrogen production among the available conventional technologies. Nevertheless, in its practical application, high electrical input energy (Chen et al., 2014) and a high concentration of end products in the effluent (Lee and Rittmann, 2010) are major obstacles possessed by these technologies. Therefore, to overcome these obstacles, an alternative technology is needed.

In recent years, the combined technology between microbial electrolysis cells (MEC) and reverse electrodialysis (RED), commonly referred to as microbial reverse-electrodialysis electrolysis cells (MREC), has been proposed as a new hydrogen gas production method (Kim and Logan, 2011; Nam et al., 2012; Luo et al., 2013; Watson et al., 2015). The major advantages of the MREC system compared to conventional technologies are that the MREC system can eliminate the required external energy for hydrogen generation and can also achieve relatively high hydrogen yield in addition to the efficient removal of organics. In the MREC system, the additional energy required to split water can be obtained from the small number of the RED stack. Kim and Logan (2011) reported that a five-cell paired RED stack could contribute approximately 0.5–0.6 V for hydrogen generation to the MREC system. A high hydrogen yield (3.4–3.5 mol-H_2 $mole^{-1}$-acetate) and efficient organic removal (87–94%) of the MREC system was demonstrated by Nam et al. (2012) and Luo et al. (2013) using 1.0 g L^{-1} sodium acetate as a substrate.

The stack feed solutions not only play an important role in providing necessary energy but also serve to create a

* Corresponding author.
E-mail addresses: syarif153@hanyang.ac.kr (S. Hidayat), yhsong86@hanyang.ac.kr (Y.-H. Song), jooypark@hanyang.ac.kr (J.-Y. Park).

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thermodynamically favorable reaction in the MREC system. Monovalent ions, particularly sodium (Na^{+}) and chloride (Cl^{-}), are commonly used to represent the characteristics ions found within river and sea water. However, in practice, the multivalent ions such as magnesium (Mg^{2+}), sulfate (SO_4^{2-}), and calcium (Ca^{2+}) are also present in both river and sea water in small quantities. In terms of the RED system, Post et al. (2009) and Vermaas et al. (2014) demonstrated that the presence of multivalent ions in stack feed solutions may have a reducing effect on the stack voltage and power density. In the bioelectrochemical systems, Nam et al. (2014) reported that $Mg(OH)_2$ precipitation occurred at the cathode surface and at the bottom of the cathode chamber due to a pH increase in the cathode.

In this study, the MREC system used monovalent ions and mixture of mono- and multi-valent ions as a stack feed solutions, which were compared to investigate the effects of multivalent ions on MREC performance. Mg^{2+} and SO_4^{2-} ions were used as multivalent ions because their concentrations are typically the highest after Na^{+} and Cl^{-} in both river and sea water (Vermaas et al., 2013). To evaluate MREC performance, the current generation, hydrogen production, production rate, yield, recoveries, and substrate removal were analyzed. Additionally, experiments with various concentrations of Na_2SO_4 were conducted to determine the inhibition effect of sulfate ions on the anode.

2. Materials and methods

2.1. Reactor setup

Construction of the MREC reactor was similar to the reactor reported by Kim and Logan (2011) with a modification of the inlet and outlet on the RED stack (Fig. 1). Two cube-shaped chambers (3.0 cm diameter × 4.0 cm length) made from acrylic were used for the anode and cathode with Tedlar® bags (EvergreenTop Co., Ltd, South Korea) attached to the top of cathode chamber to collect hydrogen. A graphite fiber brush (2.5 cm diameter × 3.0 cm length, T700 SC-12000, Toray, Japan) with heat pretreatment at 450 °C within a furnace for 30 min and a titanium mesh coated with platinum catalyst (0.5 mg/cm^2, 2.8 cm diameter) were used as the anode and cathode electrode respectively. The small number of the RED, which stacked alternately between the anode and cathode chambers, were comprises of silicon gaskets (3.5 cm × 2.5 cm), non-conductive spacer (3.25 cm × 2.25 cm) and seven pairs of anion- and cation-exchange membranes (3.5 cm × 2.5 cm, Selemion CMV and AMV, Asahi glass, Japan).

To determine the effect of the presence of multivalent ions on MREC performance, different compositions of high concentration (HC) and low concentration (LC) solutions were used as stack feed solutions. The solutions were made from pure NaCl as a standard solution and a mixture of dissolved NaCl and/or $MgSO_4$, $MgCl_2$, or Na_2SO_4 as a comparison. The calculations to determine the molar fraction of the mono- and multi-valent ions and the mixture were obtained from the previous research (Vermaas et al., 2014). The total molar concentration of the HC and LC were always 0.517 and 0.010 M, respectively. In other words, to keep the molarity of feed solution constant, compared to pure NaCl solution, part of NaCl was replaced by multivalent ions. The molar fraction of the mixtures between NaCl and/or $MgSO_4$, $MgCl_2$ or Na_2SO_4 was 10% (0.052 M) and 90% (0.465 M), 10% of the dissolved salts were $MgSO_4$ (HC = 6.2 g L^{-1}; LC = 0.12 g L^{-1}), $MgCl_2$ (HC = 4.91 g L^{-1}; LC = 0.10 g L^{-1}) or Na_2SO_4 (HC = 7.34 g L^{-1}; LC = 0.14 g L^{-1}) and the remaining 90% was NaCl (HC = 27.0 g L^{-1}; LC = 0.52 g L^{-1}). The sulfate ion could be presented in anode chamber due to ion transport via AEM. Furthermore to investigate whether the presence of sulfate ion in anode chamber has an effect or not on the MREC performance, further experiments were conducted with various concentrations of sulfate ions (25% and 50% of Na_2SO_4).

2.2. Reactor operation

The anodes were inoculated with sludge and biofilm taken from an existing microbial fuel cell (MFC) reactor. For pre-acclimation, the anodes were enriched with a solution containing 1.0 g L^{-1} sodium acetate and a 100 mM phosphate buffer solution (PBS) (Junsei Chemical Co., Ltd, Japan) in the single chamber of the MFC. The same medium (1.0 g L^{-1} and 100 mM PBS solution consisted of (per liter) NH_4Cl, 0.31 g; KCl, 0.13 g; $NaH_2PO_4 \cdot H_2O$, 6.6 g; Na_2HPO_4, 8.19 g; and mineral 12.5 mL and vitamin 1.25 mL solutions) which used for pre-acclimation were also used as an anolyte. In the cathode chamber, 0.517 M of sodium chloride (NaCl) and a solution mixture of NaCl and $MgSO_4$ were used as the catholyte and were degassed for 30 min. The anolyte were consist of the medium and PBS solution consisted of stack feed solutions were continuously fed to the RED at a flow rate of 1.2 mL min^{-1} while the MREC reactor operated in a fed-batch mode via connection to a fixed external resistance of 10 Ω.

2.3. Experimental analysis and calculations

2.3.1. Analysis

The cell voltages were measured every 5.0 min using a voltage recorder (VR-71, T&D Corporation) connected to a computer. The

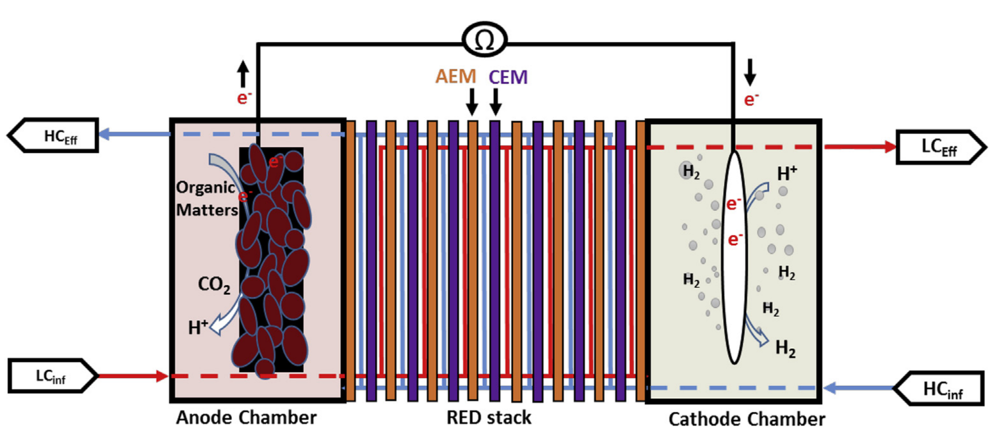

Fig. 1. Schematic diagram representation of a microbial reverse-electrodialysis electrolysis cell (MREC).