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Optimization of membrane stack configuration for efficient hydrogen production in microbial reverse-electrodialysis electrolysis cells coupled with thermolytic solutions

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HIGHLIGHTS

- Membrane stack configuration was optimized for the MREC utilizing NH_4HCO_3 solutions.
- The optimum number of cell pairs was determined to be five.
- Increasing the number of cell pairs did not appreciably affect anode performance.
- Adding an LC chamber reduced ammonia crossover and improved hydrogen production.

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ABSTRACT

Waste heat can be captured as electrical energy to drive hydrogen evolution in microbial reverse-electrodialysis electrolysis cells (MRECs) by using thermolytic solutions such as ammonium bicarbonate. To determine the optimal membrane stack configuration for efficient hydrogen production in MRECs using ammonium bicarbonate solutions, different numbers of cell pairs and stack arrangements were tested. The optimum number of cell pairs was determined to be five based on MREC performance and a desire to minimize capital costs. The stack arrangement was altered by placing an extra low concentration chamber adjacent to anode chamber to reduce ammonia crossover. This additional chamber decreased ammonia nitrogen losses into anolyte by 60%, increased the coulombic efficiency to 83%, and improved the hydrogen yield to a maximum of 3.5 mol H_2/mol acetate, with an overall energy efficiency of 27%. These results improve the MREC process, making it a more efficient method for renewable hydrogen gas production.

1. Introduction

A microbial electrolysis cell (MEC) is a bio-electrochemical system which can achieve hydrogen production from various types of renewable biomass (Cheng and Logan, 2007). An applied voltage (>0.3 V in practice) is required to overcome the thermodynamic limit for hydrogen evolution at the cathode (Logan and Rabaey, 2012). To eliminate the need for electrical grid energy, a sustainable method for hydrogen production was recently proposed based on integrating a small reverse electrodialysis (RED) stack into the MEC, which was called a microbial reverse-electrodialysis electrolysis cell (MREC) (Kim and Logan, 2011a). A RED stack comprises an alternating series of anion (AEMs) and cation exchange membranes (CEMs) typically separated by porous spacers (Veerman et al., 2009; Vermaas et al., 2011a). When high concentration (HC) and low concentration (LC) solutions flow through alternating chambers in the stack, cations and anions in HC chamber migrate into the LC chamber through the membranes with opposing-charge functional groups due to concentration gradient, resulting in a potential difference across the membranes (Długołęcki et al., 2010; Vermaas et al., 2011b, 2013). Thus, renewable salinity gradient energy is converted to electrical energy to drive hydrogen evolution in an MREC, without the need for an external power source.

The use of RED stacks in MRECs can be limited to estuaries or coastal areas when river water and seawater are used for the HC and LC solutions. The use of these natural waters also requires substantial and energy intensive pre-treatment to minimize membrane fouling (McGinnis et al., 2007). To avoid these limitations,

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thermolytic solutions (Elimelech and Phillip, 2011) such as ammonium bicarbonate (NH_4HCO_3), have been proposed as the source of the salinity gradient energy for RED stacks (Cusick et al., 2012; Luo et al., 2012; Nam et al., 2012). With a thermolytic solution the ionic species can be volatilized and captured into HC solutions at temperatures below that needed to boil water. Heating ammonium bicarbonate solutions at ~60 °C and 1 atm, for example, volatilizes ammonia and carbon dioxide, which can be condensed to form the HC solution (McGinnis and Elimelech, 2007). NH_4HCO_3 solutions have been shown to work in MRECs (Nam et al., 2012), and the HC and LC solutions can be regenerated using waste heat and conventional distillation technologies. Thus, waste heat can be captured as electrical energy, enabling hydrogen evolution in an MREC.

The RED stack configuration and performance is critical to hydrogen production in an MREC. The number of cell pairs used can affect the electrochemical potential available to drive hydrogen production. Increasing cell pairs should improve the potential difference across the membrane stack (Długołęcki et al., 2009; Post et al., 2008), but adding cell pairs can increase the internal resistance through the addition of extra HC and LC chambers (Veerman et al., 2008, 2010). In addition, the use of more cell pairs can increase capital costs as the cost of the stack is dominated by cost of the ion exchange membranes (Post et al., 2010; Ramon et al., 2011; Turek and Bandura, 2007). Thus, it is essential to ascertain an optimum number of cell pairs for balancing cost and MREC performance. In addition, the application of higher potentials could adversely affect electrochemical performance by changing the anode potentials to values unfavorable for microbial oxidation of substrate.

In this study, different numbers of cell pairs and stack arrangements were tested to determine the optimum membrane stack configuration for an MREC utilizing NH_4HCO_3 solutions. The number of cell pairs was optimized based on measuring current and hydrogen production rates, and calculating energy recoveries and efficiencies. Anode, cathode and stack performance were evaluated by galvanostatic polarization during variation of numbers of cell pairs. The stack arrangement was also changed to minimize ammonia crossover into the anode chamber. Previous studies used an AEM in the stack adjacent to the anode chamber (Kim and Logan, 2011a; Nam et al., 2012). This configuration minimized internal resistance by having a HC chamber adjacent to the anode chamber, but it resulted in high rates of ammonia transfer into the anolyte. In one series of tests, as much as 540 mg/L of total ammonia nitrogen (TAN) was transferred into the anode chamber over a single cycle (initial conductivity of the HC NH_4HCO_3 solution of 103 mS/cm) (Nam et al., 2012), which could inhibit current generation by the anode microorganisms (Nam et al., 2010) and therefore hydrogen gas production. To avoid this situation, the effect of adding an LC chamber adjacent to the anode chamber was examined to reduce TAN crossover.

2. Methods

2.1. MREC construction

The MREC was composed of an anode chamber, a cathode chamber, and a RED membrane stack (Fig. 1). Two cubic Lexan blocks with a cylindrical cavity were used as the anode and cathode chamber (30 mL liquid volume each). A glass tube was glued to the top of cathode chamber for hydrogen collection (Mehanna et al., 2010). The anode was a heat treated graphite fiber brush (25 mm diameter × 25 mm length; fiber type: PANEX 33 160 K, ZOLTEK). The cathode was stainless steel mesh (projected area: 7 cm^2; Type 304, #60 mesh, McMaster-Carr) coated with platinum catalyst layer (5 mg/cm^2 10% Pt on carbon black) on the side facing membrane stack, and carbon black layer (5 mg/cm^2) on the other side.

A RED stack with up to 7 cell pairs was sandwiched between the anode and cathode chambers (Fig. 1). One cell pair consisted of a pair of HC and LC chambers, and a pair of AEM and CEM (Selemion AMV and CMV, Asashi glass, Japan). Except as noted otherwise, one additional AEM was used to close the last chamber at the end of the stack next to the electrode. The effective area of each membrane was 8 cm^2 (4 cm × 2 cm). Membranes were separated by polyethylene woven spacers and silicone gaskets with a thickness of 1.3 mm.

2.2. Solutions

The anolyte was 1 g/L sodium acetate in a nutrient buffer solution containing 8.4 g/L $NaHCO_3$, 0.31 g/L NH_4Cl, 0.13 g/L KCl, 0.05 g/L Na_2HPO_4, 0.03 g/L $NaH_2PO_4{\cdot}H_2O$, trace elements and minerals. A 1 M $NaHCO_3$ solution was used as catholyte (Nam et al., 2012). Based on the solubility of NH_4HCO_3 at room temperature (approx. 2 M), a NH_4HCO_3 solution of 1.7 M was used (conductivity of 103 mS/cm) as the HC solution. The LC solution was prepared by dilution of the HC solution with distilled water to produce a salinity ratio of 75 (Luo et al., 2012).

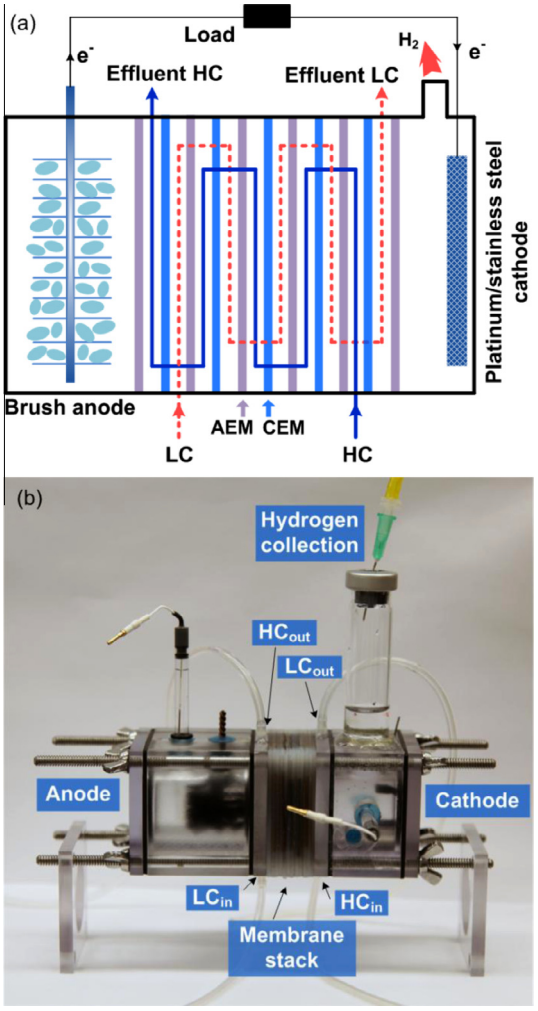

Fig. 1. (a) Schematic and (b) photograph of microbial reverse-electrodialysis electrolysis cell (CEM, cation exchange membrane; AEM, anion exchange membrane; HC_{in}, high concentration solution inlet; HC_{out}, high concentration solution outlet; LC_{in}, low concentration solution inlet; LC_{out}, low concentration solution outlet).