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Alkali production from bipolar membrane electrodialysis powered by microbial fuel cell and application for biogas upgrading

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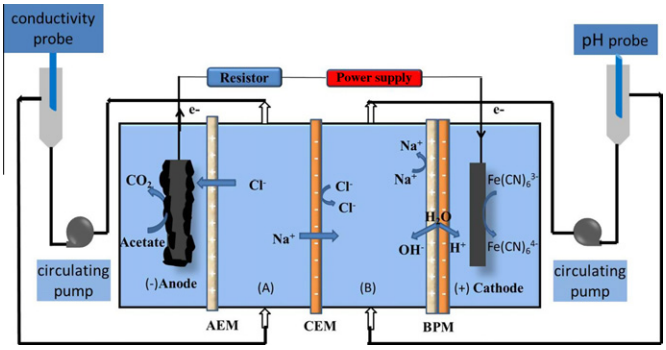
HIGHLIGHTS

- BPMED powered by MFC was proposed to utilize electricity *in situ* and produce NaOH.
- The maximum pH was about 11.6 with 0.5 V applied voltage.
- The produced NaOH was suitable for biogas upgrading and the final CH_4 reached 100%.
- The study provides an elegant and sustainable way to extend BPMED & MFC application.

GRAPHICAL ABSTRACT



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ABSTRACT

The biogas upgrading is necessary for its application, and alkali CO_2 adsorption is one efficient method. In this study, a coupled system, bipolar membrane electrodialysis (BPMED)–microbial fuel cell (MFC), was proposed for alkali production, which could also realize electricity *in situ* utilization. It was found that the pH in the alkali production chamber was 9.8. With higher NaCl concentration, bigger applied voltage and lower external resistance, the pH of the produced alkali solution also increased and the maximum value of which was 11.6. Meanwhile, our system also performed desalination. Furthermore, the produced alkali solution was utilized for biogas upgrading. The CO_2 content decreased notably in headspace, which even reached 0% at pH 11.6 of alkali solution. This study provides an elegant and sustainable way to extend BPMED and MFC application.

1. Introduction

The biogas, which could be maturely produced from renewable biomass and organic wastes in anaerobic digestion, is an alternative energy source for humans [1–3]. It normally consists of 40–75% methane, 25–60% carbon dioxide and other trace gases (for example, H_2S) [1,3]. The produced biogas should be upgraded for its utilization [4]. For example, as demonstrated by Deng and Hägg, upgrading methane concentration to 90% could not only efficiently increase its heating value but also notably reduce the acid gas corrosion [5]. The upgraded biogas (>98%) could be compressed and liquefied as vehicle fuel and produce heat and electricity [5]. Meanwhile, the existing natural gas grid could also be utilized for the upgraded biogas transportation. Thereby, the removal of CO_2 is a critical step to utilize biogas.

The common and commercialized methods for CO_2 removal include pressure swing adsorption (PSA), water scrubbing, chemical adsorption, membrane based gas separation, etc. [4,6,7]. Since the additional upgrading operation increases to the costs of biogas utilization, it is important to have an optimized process with low

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energy consumption and high efficiency. The chemical adsorption is one efficient way that is characterized of lower working pressure, smaller electricity consumption and higher operating capacity [4,8]. Moreover, the alkali adsorption (such as NaOH) could simultaneously reduce CO_2 and H_2S and avoid the pre-cleaning of H_2S in PSA and amine scrubber. However, the transporting cost of alkali is one of the issues for its utilization [8]. Therefore, it shall be much better if alkali can be produced on site. Bipolar membrane electrodialysis (BPMED) is an integrated technique of bipolar membrane (BPM) and traditional electrodialysis (ED), which has gained more attentions in the last two decades [9]. Bipolar membrane is a functional composite membrane comprising a cation exchange layer and an anion exchange layer, and can dissociate water into H^+ and OH^- simultaneously between the two layers under reverse bias direct current field [10,11]. Thus, BPMED can produce acid and alkali *in situ* (such as H_2SO_4 and NaOH production from Na_2SO_4), and significantly reduce the cost of acid and alkali [9,12]. Recently, BPMED was also reported to separate and enrich CO_2 by the *in situ* NaOH production [13]. However, similar to traditional electrodialysis, the investment cost of BPMED is also high [9,14]. Therefore, alkali production from BPMED would be an attractive technology for biogas upgrading if the energy cost could be reduced.

Microbial fuel cell (MFC) has been demonstrated as the novel biotechnology for energy recovery, wastewater treatment, bioremediation and valuable chemicals production [15,16]. In MFC, the bio-convertible substrates are consumed by exoelectrogenic bacteria in anodic chamber to generate proton and electron simultaneously. The proton migrates through proton/cation exchange membrane to the cathodic chamber. And the generated electron transfers through the external resistance to cathode and is consumed by electron acceptors in cathodic chamber [16]. Moreover, some new concepts are proposed to realize the *in situ* utilization of the generated electricity from MFC, such as microbial electrolysis cell, microbial desalination cell, and microbial electrosynthesis [15,17]. Hereby, why not power BPMED by MFC?

It was reported that, acidification (pH decreased from 7.0 to 5.4) in anodic solution and alkalization (pH increased from 7.0 to 9.5) in cathodic solution occur in MFC [18]. The pH changing significantly affected the electrode potential and decreases the voltage and power density of MFC [19]. Consequently, BPM was proposed as the separator in MFC to maintain neutral pH in anodic and cathodic chambers [20,21]. However, neutral pH was not maintained well because of low water dissociation efficiency of BPM (about 70%) [21,22]. Meanwhile, the high polarization resistance of BPM also led to lower voltage and power density of MFC, which was another drawback for BPM application [23].

Though BPM was not an ideal separator to maintain neutral pH, it can be a functional membrane to produce acid and alkali in MFC. Recently, as proposed by Chen et al. [24], BPM integrated with MFC was successfully used to produce acid and desalt. Therefore, in this study, BPMED was proposed to integrate with MFC to realize alkali production, and then the produced alkali was utilized for biogas upgrading. The parameters, including electrolyte concentration, external resistance, applied voltage and the system configuration, were investigated for alkali production. Then the produced alkali was applied to reduce CO_2 content in biogas.

2. Materials and methods

2.1. The setup of BPMED–MFC

As shown in Fig. 1, the whole reactor (AEM–CEM–BPM configuration; AEM, anion exchange membrane; CEM, cation exchange membrane) was separated to four chambers, including anodic chamber, desalination chamber, alkali production chamber and cathodic chamber. Three separators were arranged from left to right in MFC as follows, AEM (AMI-7001, Membranes International Inc., New Jersey), CEM (CMI-7000, Membranes International Inc., New Jersey) and BPM (BPM-1, Tingrun membrane technology development Co. Ltd., Beijing). For AEM–BPM configuration, as the CEM was not used between AEM and BPM, desalination and alkali production were in the same chamber. Hereinafter, the AEM–CEM–BPM configuration would be utilized throughout our study except the case of AEM–BPM configuration. The working area of three kinds of membrane were about 7 cm^2. The working volume of anodic, cathodic, alkali production and desalination chambers was 40, 40, 60 and 60 mL, respectively. The negative lead of the power supply (DF1731SD2A, Zhongce Electronics Co. Ltd., Ningbo) was connected to the cathode, and an external resistance (10 Ω) was connected between the positive lead of the power supply and the anode (Fig. 1). Liquid circulation was applied in desalination and alkali production chambers.

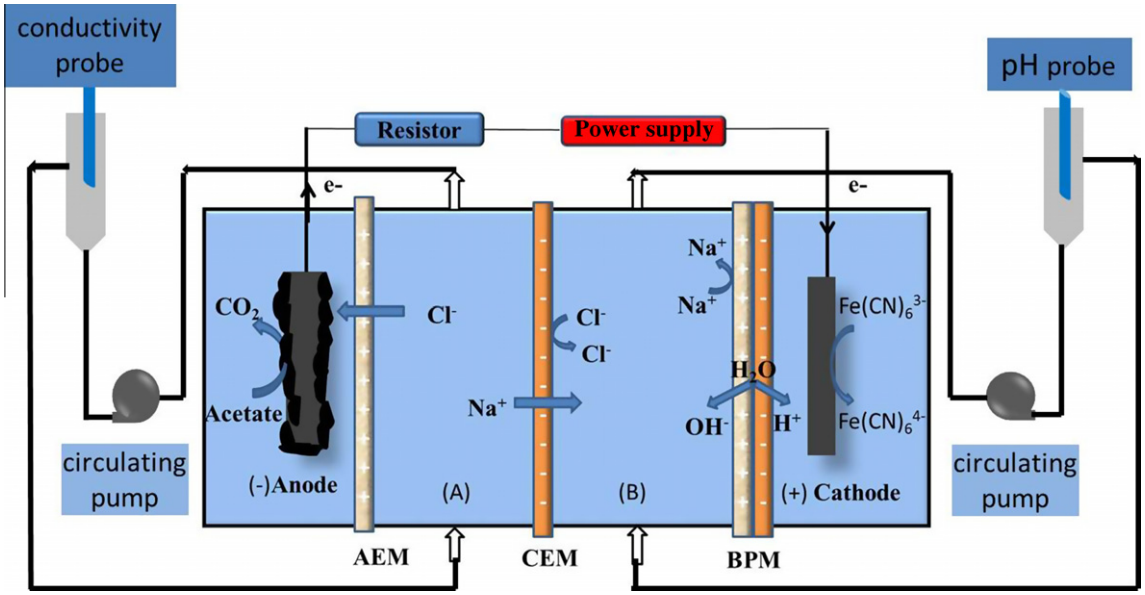

Fig. 1. The AEM–CEM–BPM setup of BPMED–MFC Notes: (A), desalination chamber and (B), alkali production chamber.