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Proof-of-concept experiments of an acid-base junction flow battery by reverse bipolar electrodialysis for an energy conversion system

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ABSTRACT

The acid-base junction potential can be used to generate electricity instead of the reduction-oxidation potential, which is often used for energy conversion between chemical energy and electricity. In this study, reverse bipolar electrodialysis was designed for energy conversion between acid-base solutions and electricity. Operating a flow battery with various HCl/NaOH concentrations, or an ABJFB, the current-voltage relationships showed typical polarization curves that were similar to those obtained in power generation from a fuel cell. We further demonstrated that the cell can be operated in a charge/discharge cyclic mode in a single cell. To the best of our knowledge, this study is the first report on a proof-of-concept experiment demonstrating the cyclic operation of an ABJFB.

1. Introduction

Most often, energy conversion between chemical energy and electricity occurs through redox reactions at the electrodes. For example, a fuel cell generates electricity by oxidizing fuel and reducing oxidants at the anodes and cathodes, respectively [1,2]. Lithium ions in a lithium battery move between electrodes with redox reactions [3,4]. A redox flow battery employs a redox couple for energy conversion [5–7].

Similar to the electric potential occurring at electrodes due to redox reactions, a difference in the concentrations of ionic species across an ion exchange membrane can create a membrane potential. That can be used to generate electricity when the potential is appropriately combined with electrode reactions. RED is a representative application of the concentration potential, in which sea water and river water are put into contact across ion exchange membranes [8,9]. In RED, cationic concentration differences across a CEM and anionic concentration differences across an AEM result in a membrane potential [10,11]. The diffusion of corresponding ions through ion exchange membranes leads to the flow of electric current.

An ABJFB system is a form of the modified RED or RBED by introducing a BPM, which consists of a CEL and an AEL having opposite charges (Fig. 1 (a)) [12,13]. Due to the bias property of a BPM, protons and hydroxyl ions permeate through the CEL and the AEL respectively. The BPM is used to split water molecules into protons and hydroxyl ions under an electric field; accordingly, salt is converted to an acid and a base, as shown in Fig. 1 (a).

In this case, the membrane process is called bipolar membrane electrodialysis, or water splitting electrodialysis. As RED generates electricity from the membrane potential between high and low salt concentrations, the RBED may generate electricity from the membrane potential between acid and base solutions since the JP occurs with acid and base solutions through a CEL and an AEL of a BPM, respectively (Fig. 1 (b)). In addition, the ABJFB can be connected to multi-cells, which may generate electric power for practical application at a higher voltage (Fig. 1 (c)) [16].

Previously, an acid-base electrochemical cell was reported as a secondary battery powered by forced ionization [14]. However, it was suggested that palladium foil may be used as a depolarizing electrode instead of a BPM. Later, an acid-base concentration cell for electric power generation was patented using depolarizing electrodes [15]. It was found that the energy efficiency of this cell was significantly lower than the theoretical value because of the low permselectivity of the membranes. Other drawbacks of the systems previously studied are their use of hydrogen gas for electrode reactions and their

Abbreviations: Acid-base junction flow battery, *ABJFB*; Anion exchange membrane, *AEM*; Anion exchange layer, *AEL*; Bipolar membrane, *BPM*; Cation exchange layer, *CEL*; Cation exchange membrane, *CEM*; Junction potential, *JP*; Reduction oxidation, *Redox*; Reverse electrodialysis, *RED*; Reverse bipolar electrodialysis, *RBED*; Coulombic efficiency, *CE*; Voltage efficiency, *VE*; Energy efficiency, *EE*; Activity coefficient, γ; Equilibrium constant of water, K_w; Gas constant, R; Absolute temperature, T; Faraday constant, F; Number of electrons, n; Charging time, t_c; Charging voltage, V_c; Discharging time, t_d; Discharging voltage, V_d.

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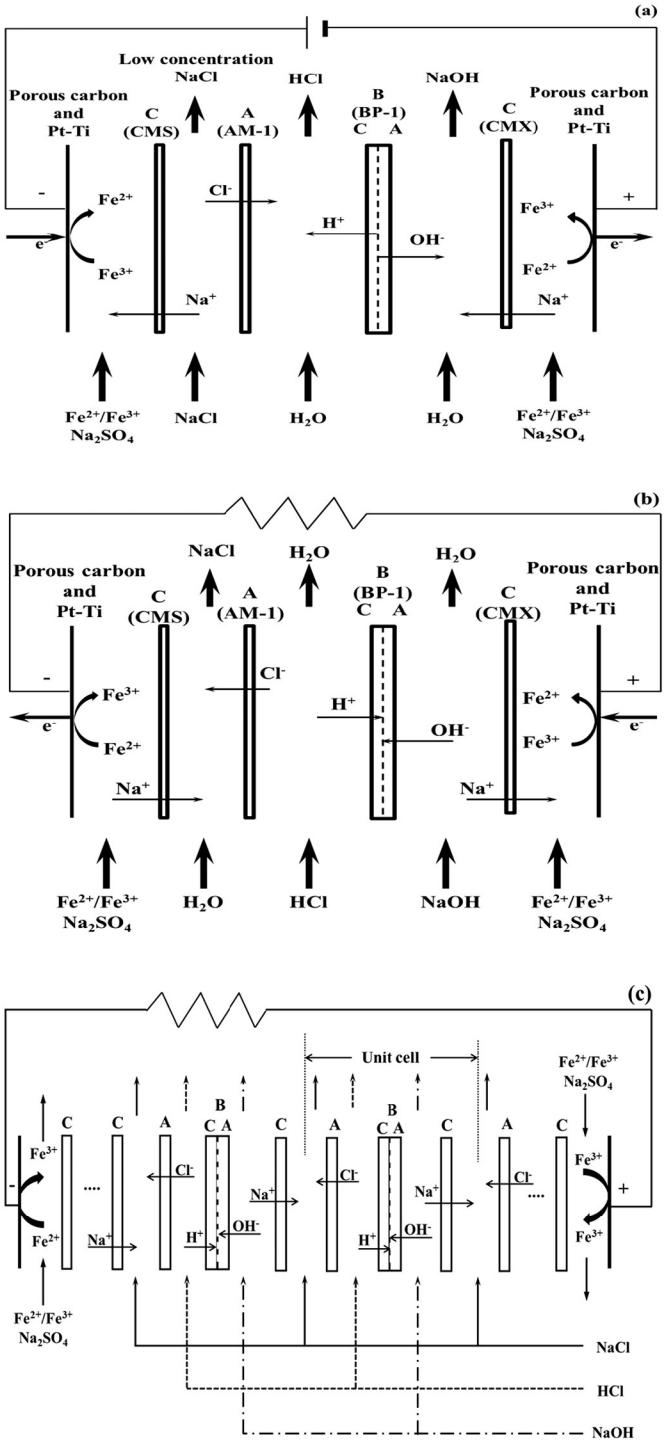

Fig. 1. (a) Acid and base generation by bipolar membrane electrodialysis for a charge process, (b) Electricity generation by reverse bipolar electrodialysis for a discharge process, (c) A multi-cell scheme for energy generation in an ABJFB (C: CEM, A: AEM, B: BPM).

complicated cell structure to complete the electrode reactions, often employed in the electrolysis process.

In the present study, based on Walther's patent [16], reverse bipolar membrane electrodialysis is combined with redox electrolyte to avoid gas generation at the electrodes. Typically, an Fe^{2+}/Fe^{3+} electrolyte is used in a RED system to generate an electrode reaction without electrolysis. Therefore, electricity can be generated in a single cell using metal redox electrolytes instead of gases, as shown in Fig. 1 (b). Fig. 1 (a) and (b) depict the charge and discharge processes, respectively.

(a) Charge: NaCl + HOH + electricity → HCl + NaOH.

(b) Discharge: HCl + NaOH → NaCl + HOH + electricity.

2. Experimental

The JP of BPM (BP-1, Tokuyama, Japan) was measured by connecting two Ag/AgCl electrodes and a multi-meter (DMM4020, Tektronix) at various HCl and NaOH concentrations from 0.01 to 1.0 M in a 2-compartment cell. CEL and AELs in the BPM were placed between the acid and base electrolytes, respectively. To maintain the uniform concentration in each chamber, the electrolytes were stirred during measurement and the membrane responded to the equilibrium potential within 30 min.

In reversed bipolar membrane electrodialysis, polarization curves were obtained using a single cell (effective area: 9 × 5 cm^2) that consisted of two electrodes (porous carbon felt, Nippon Carbon Co., Japan) with platinum-coated titanium, a mono selective CEM (CMS), an AEM (AM-1), BP-1, and a CEM (CMX) as shown Fig. 1(b). All membranes were purchased from the Tokuyama Corporation. Each electrolyte flowed from the inlet to the outlet except for the circulated redox couple (a mixture redox solution of 0.1 M iron (II) sulfate heptahydrate and iron (III) sulfate hydrate with 0.1 M Na_2SO_4). A low concentration of 0.01 M NaCl flowed between the CMS and AM-1 compartment. HCl and NaOH solutions at equal concentrations from 0.1 to 0.7 M were used at 0.1 M interval in the CEL and AELs, respectively. All electrolytes were pumped at a flow rate of 30 ml min^{-1}. A DC load (Model ESL-300Z, E.L.P. TEK, Korea) was connected to both current collectors to measure the current-voltage relations.

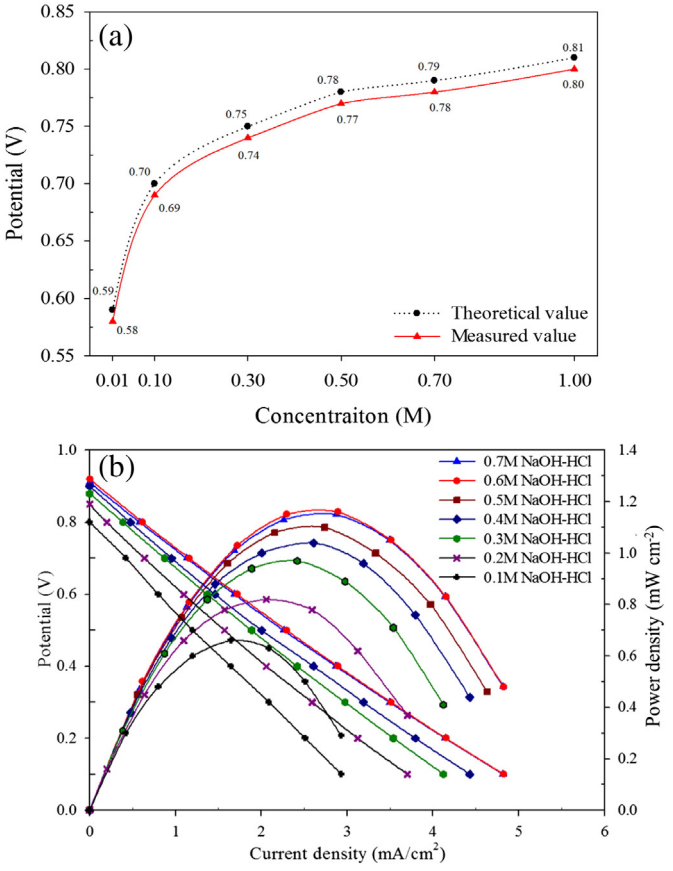

Fig. 2. (a) Measurement of the JP and (b) power generation according to different concentrations of acid and base electrolytes in a single cell.