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Modeling of power generation with thermolytic reverse electrodialysis for low-grade waste heat recovery

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HIGHLIGHTS

- This work is the first attempt to develop an NH_4HCO_3-RED model for power generation.
- The activity and molar conductivity can be described with electrical conductivity.
- Actual permselectivity plays a critical role to estimate the RED performance.
- The model fits well to the experimental results with parametric variations.
- The optimal operating conditions can be achieved by the validated model.

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ABSTRACT

Significant attention has been paid to closed-loop reverse electrodialysis (RED) systems using a thermolytic solution for low-grade waste heat energy recovery. They have several cost benefits when compared with open-loop RED with seawater and river water, such as no need of repetitive pretreatment and removal of locational constraints. This study presents the model of RED using ammonium bicarbonate (NH_4HCO_3), one of the promising solutes for the closed-loop RED, whose ionization has not been clarified. Because of the unclarified electrochemical information of NH_4HCO_3 electrolyte, the Planck-Henderson equation was used to approximate the membrane potential based on conductivity measurements, and the solution resistance was experimentally computed. Furthermore, the experimentally obtained permselectivity of the membrane was applied for a more precise estimate of the membrane potential. We found that the developed NH_4HCO_3-RED model was in good agreement with the experimental results under various operating conditions. We also characterized the net power density, which considers the pumping loss, by using our model. In our system, the maximum net power density of 0.84 W/m^2 was obtained with an intermembrane distance of 0.1 mm, a flow rate of 3 mL/min, and a concentration ratio of 200 (2 M/0.01 M) as optimum conditions. We expect that this study will improve our understanding of the NH_4HCO_3-RED system and contribute to relevant modeling studies, using NH_4HCO_3 or some other compounds, for generating higher energy densities.

1. Introduction

As the world energy consumption is growing, demand on fossil fuel is also dramatically increasing. The increase in fossil fuel consumption causes various problems such as global warming and climate change. The voices of the world have recently gathered in the Paris climate conference to prevent bigger disasters. Many researches have been conducted to lessen and replace the consumption of fossil fuel. One of the emerging sources is waste heat, which is a cause of heat pollution, but can also be one of the sources for a different way of generating electricity [1,2]. There are several techniques to harness waste heat, such as the Organic Rankine Cycle (ORC) and the thermoelectric power. However, to recover energy using these techniques has clear downsides, such as environmentally harmful refrigerants and limitation of downsizing in ORC, and low efficiency and poor form factor in thermoelectric element [3–9].

A closed-loop reverse electrodialysis (RED) system that combines RED with thermal separation can harness the waste heat by utilizing the Salinity Gradient Energy (SGE) [10]. RED is a power generation technique based on SGE by controlling a mixing of

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Nomenclature

C	concentration (M)
D	diffusion coefficient (m^2/s)
F	Faraday constant (96,485 C/mol)
I	current (A)
J	molar flux (mol/m^2 s)
L	length (m)
P	power (W)
Q	volumetric flow rate (mL/min)
R	resistance (Ω)
R_g	universal gas constant (8.314 J/mol K)
T	ambient temperature (K)
V	voltage (V)
V_w	molar volume of water (mol/m^3)
W	width (m)
d_h	hydraulic diameter (m)
h	membrane thickness (m)
t_i	transport number of ion species i (–)
i	current density (A/m^2)
n	porosity (–)
p	power density (W/m^2)
t	residence time (s)
z_i	valence number of ion species i (–)
Greek symbols	
Δp	pressure drop (Pa)
Λ	molar conductivity($S{\cdot}m^2/mol$)
α	permselectivity (–)
β	open ratio (–)
γ	activity coefficient (–)
δ	intermembrane distance (m)
ε	permittivity (F/m)
η_{pump}	pump efficiency (–)
μ	viscosity (Pa s)
Subscripts	
H	high concentration solution
L	low concentration solution
CEM	cation exchange membrane
AEM	anion exchange membrane

two different salinity solutions with ion exchange membranes (IEM). It has the advantage of not emitting environmentally harmful gas and unlimited free fuel supply in the vicinity of places where sea and river water meet. On the other hand, accessibility to these natural resources limits its locational options. Moreover, one of the barriers for commercializing RED systems is the high maintenance cost of the IEMs, which need to be either replaced with new ones or recovered when affected by different types of fouling [11,12]. These downsides of RED can be overcome by adding a thermal separation process, due to its closed-loop characteristic [13–16]. The different salinity solutions can keep electromotive force by separating the increased solute from the diluted side and recapturing it in the concentrated side, without any fresh solution supply, and hence the process can be operated as a closed-loop system. The closed-loop system mitigates the geographical limitations since there is no need of a continuous supply of fresh seawater and river water, thus preventing the danger of membrane fouling as well as saving in pre-treatment costs.

A thermolytic solution that can be easily separated at a relatively low temperature is necessary for this process. Ammonium bicarbonate (NH_4HCO_3) electrolyte is the one of the promising thermolytic solutions, due to its low decomposition temperature of around 60 °C at 1 atm, high solubility in water, and relatively low molecular weight [17,18]. Initially, Luo et al. performed RED experiments using NH_4HCO_3 with various inlet conditions such as flow rate and feed solution concentration [10]. A maximum power density of 0.33 W/m^2 was obtained with an intermembrane distance of 0.5 mm, when the concentrated and diluted solution are 1.5 and 0.02 M, respectively. Kwon et al. added quantitative characterizations of other parameters, such as IEM types and intermembrane distances [19]. They obtained 0.77 W/m^2 with an intermembrane distance 0.2 mm, when the concentrated and diluted solution are 1.5 and 0.01 M, respectively. Subsequently, Bevacqua et al. has recently performed a parametric study for the better performance. As of now, they obtained the largest power density of 0.89 W/m^2 with an intermembrane distance 0.3 mm and the concentrated and diluted solutions are 2 and 0.02 M each [20]. In their series of studies, Geise et al. provided great insight into transport phenomena of NH_4HCO_3 through IEMs [21–24]. They analyzed the relationship among the membrane resistance, permselectivity, membrane structure, functional groups fixed on several kinds of IEMs, and individual ion species of NH_4HCO_3 electrolyte.

Meanwhile, literature has been published since 2011 on RED numerical simulations. Veerman et al. developed a one-dimensional numerical model for a unit cell [25]. Tedesco et al. improved the model in respect to the previously neglected non-ideal phenomena, such as concentration polarization (CP), and validated a wider concentration range and temperature variation [26]. Kwon et al. modified several thermodynamic properties of the model, such as viscosity and dielectric constant, and considered the CP phenomena with empirical equations for a more precise computation up to a high concentration range [27]. However, the challenge of numerical simulation with NH_4HCO_3 has not been faced, owing to the complexity of expressing its extensive electrochemical information, compared to that of the NaCl binary electrolyte.

The main issue for the simulation is to estimate the membrane potential and internal resistance. Unlike NaCl, which is the conventional electrolyte for the RED process, the electrochemical information of NH_4HCO_3 required to estimate the membrane potential and internal resistance, such as transport number and activity, is not only unclarified but also unavailable in the literature. However, there was a recent study estimating the membrane potential based on electrical conductivity measurements [28]. Moreover, the solution resistance could be experimentally computed in the range of concentration of our interest, according to the definition of molar conductivity.

In this study, we conducted a numerical simulation for RED power generation replacing all the solution and membrane properties related to NaCl with the properties related to NH_4HCO_3, and validated it through our experimental results. The permselectivity of the IEM was not just assumed as in previous researches [25,26,29], but measured by an experiment in order to more precisely predict the RED performance. After the model validation, the optimum operating conditions were characterized with different settings in terms of intermembrane distance, flow rate and concentration ratio.