Reducing pumping energy by using different flow rates of high and low concentration solutions in reverse electrodialysis cells

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ABSTRACT

Energy use for pumping affects both net energy recovery and operational costs of reverse electrodialysis (RED) systems. In order to reduce the energy needed for pumping, electrical performance and hydrodynamic power losses in a RED stack were investigated by simultaneously (2–140 mL/min) or independently varying the flow rates of the high concentration (HC, 35 g/L NaCl) and low concentration (LC, 0.35 g/L NaCl) solutions. Power was not consistently reduced at lower flow rates due to trade-offs between increases in diffusion boundary layer resistance and decreases in solution resistance of the LC channels. The maximum net power output ($\sim$0.04 W) was obtained with both LC and HC flow rates at $\sim$20 mL/min. Separately varying the flow rates of the HC and LC solutions indicated that the optimum flow rate of the HC solution (10 mL/min) was much lower than that of the LC solution (20 mL/min) due to the more substantial impact of the LC channel on power production. The use of these two optimized flow rates minimized hydrodynamic power losses (pumping energy) while producing comparable power to that achieved with the two higher flow rates (50 mL/min of both HC and LC solutions).

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1. Introduction

Reverse electrodialysis (RED) is a sustainable energy technology that can be used to convert salinity gradient energy into electricity [1–3]. Salinity gradients that naturally exist between seawater and river water can be harnessed using RED to provide a large and renewable source of electricity. In theory, the global power production from salinity gradients could be as much as $1.4-2.6$ TW, which is sufficient to meet the current worldwide demand for electrical power ($\sim$2 TW) [4,5]. A RED stack consists of alternating cation (CEMs) and anion exchange membranes (AEMs). When solutions with different salinities flow on either side of these ion exchange membranes, Donnan potentials are created that drive cations from high concentration (HC) to low concentration (LC) channels through CEMs, and anions from HC to LC compartments through AEMs [6–8]. A large number of pairs of CEMs and AEMs are stacked together to increase the total potential [9,10]. At both ends of the stack, electrodes are used to convert the ionic flux into an electrical current, typically using a reversible redox reaction or by water splitting [11,12].

The power output of a RED stack depends on the electromotive force (the total potential over the stack) and internal resistance that consists of both ohmic and non-ohmic resistances [13–15]. The ohmic resistance is produced by the membrane resistance and the LC and HC solution resistances. The main ohmic resistance is usually the solution resistance of the LC channels [9,16]. The non-ohmic resistance consists of the electrical double layer and diffusion boundary layer resistances. Ion exchange membranes contain a high concentration of fixed charged groups attached to the polymer back bone, which attract counter ions with an opposite charge from the solution, and form an electrical double layer over the membrane surface [16,17]. The electrical double layer resistance arises from the interfacial ionic charge transfer in the solution phase through the electrical double layer to the membrane. When a current is applied, charge is transported through the membrane by counter ions (positive or negative), carried by both positive and negative ions in the bulk solution. The difference in ion transport number between the bulk solution and the membrane results in the formation of a diffusion boundary layer at the membrane surface [16,18]. Because the thickness of diffusion boundary layer (micrometers) is much larger than that of electrical double layer (nanometers), the diffusion boundary layer resistance is usually the dominant non-ohmic resistance [16,19,20].

The improvement in electrical power by a RED stack that is obtained at higher flow rates is usually attributed to a decrease of diffusion boundary layer resistance [7,9,10,19]. However, the solution resistance in LC channels can also have a large contribution to the internal resistance of a RED stack. At lower flow rates, the

solution conductivity in the LC channels will rapidly increase due to accumulated transport of more ions from the HC into the LC channels, which will reduce the ohmic resistance of the RED stack [13,19]. Therefore, it is possible that similar or better performance of the stack can be obtained at lower flow rates due to the trade-off between the increase of diffusion boundary layer resistance and the decrease of solution resistance in LC channels. Moreover, the flow rates not only affect the electrical performance of a RED process, but they also impact energy required to pump the HC and LC solutions through the RED stack. The pumping energy is an important part of the costs for RED operation, but it can be reduced by pumping at lower flow rates [14,21,22]. Many studies have noted energy losses due to pressure drops in RED stacks [13,14,19]. However, using high flow rates of HC and LC solutions additionally impacts net energy production due to the energy needed to transport these solutions from the source to the RED stack site. Therefore, to make RED a commercially attractive renewable energy source, the electrical performance of the RED stack needs to be maximized while minimizing the flow rates of feed waters, in order to reduce energy losses due to both pressure drops in the stack and energy losses for pumping water to the site.

The flow rates of the HC and LC solutions fed to a RED stack are usually set to be the same [3,23,24]. However, the optimum flow rates of LC and HC solutions should be different due to the larger impact of solution and diffusion boundary layer resistances for the LC solution. Thus, it is likely that performance can be maintained at lower flow rates of HC solution than those of the LC solution. The reduction in the flow rate of the HC solution could reduce energy needed for pumping. Different flow rates of HC and LC solutions would create different pressures in adjacent channels, but pressure regulators can be used to adjust these pressures to avoid damage to the membranes.

In this study, the influences of different HC and LC flow rates were examined on electrical performance of a commercial RED stack as well as pumping energy. Initially, the effects were examined with the flow rates of HC and LC solutions simultaneously reduced from 140 mL/min to 2 mL/min to identify the region where there could be a trade-off between power output and pumping energy consumption. Then, the optimum flow rates of HC and LC solutions were determined by separately changing the flow rates of HC or LC solutions.

2. Materials and methods

2.1. Reverse electrodialysis stack

A commercial 10 cell pair RED cell (ED 64002-020, PCCell GmbH, Heusweiler, Germany) was used for all experiments. Both the anode and the cathode were titanium mesh coated with platinum and iridium (Ti/Pt–Ir), with a projected area of 64 cm² (8 cm × 8 cm). The membrane stack was assembled with 11 cation exchange membranes (PC-SK) and 10 anion exchange membranes (PC-SA) provided by the manufacturer. The active membrane area was 64 cm² (8 cm × 8 cm) per membrane, for a total active membrane area of 0.13 m². The thickness of spacers was 0.5 mm with a volume of porosity around 70%. The anolyte and catholyte (1 L, 35 g/L NaCl) were mixed and recycled at 100 mL/min to avoid large changes in pH. The HC (35 g/L NaCl) and LC (0.35 g/L NaCl) solutions flowed separately through the HC and LC channels of the stack in a single pass mode, at the indicated flow rates. Digital pressure gauges (DG25, Ashcroft, Inc., Stratford, CT) were installed at the inlets and outlets of the HC and LC channels to monitor pressure changes. Pressure regulators (Hoffman open jaw screw compressor clamp, Humboldt Scientific, Inc., Raleigh, NC) were added at the outlets of the HC and LC channels to adjust and obtain similar average pressures in the HC and LC channels in order to avoid membrane damage.

2.2. Performance tests

The open circuit voltages, maximum power densities, and maximum currents produced by the RED stack were obtained by conducting polarization tests. Galvanostatic polarization was performed using a multi-channel potentiostat (model 1470E, Solatron Analytical, Hampshire, England), with current scanned from 0 to the maximum (when the voltage of the RED stack became reversed) at a rate of 0.2 mA/s. Ag/AgCl reference electrodes (BASi, West Lafayette, IN) were placed on either side of the membrane stack in the anolyte and catholyte to record the stack voltages. At least three polarization curves were recorded for each set condition. The open circuit voltage was determined from the vertical axis intercept of the polarization curves and the maximum current was obtained from the horizontal axis intercept of the polarization curves. The power density of the RED stack, which excluded electrode overpotentials, is calculated as [25]

$$P_{stack} = \frac{U_{stack} \cdot I_{stack}}{A_{mem}} \qquad (1)$$

where P_{stack} is the power density of the RED stack (W/m² membrane), U_{stack} is the voltage of the membrane stack (V), I_{stack} is the scanned current (A), and A_{mem} is the total active membrane area of the stack (m²).

The ohmic and non-ohmic resistances were distinguished using chronopotentiometry [13,19,22]. When a sudden change in electrical current is induced, the ohmic resistance causes a rapid change in stack voltage, while the response of the non-ohmic resistance is much slower and results in a gradual, time-dependent, change in stack voltage [22]. Therefore, the ohmic resistance was determined here from the sudden jump in voltage when an electrical current (50 mA and 100 mA) was interrupted, while the non-ohmic resistance was calculated based on the remaining, time-dependent voltage change during the current interruption for about 2 min [13,19]. The solution resistances in HC and LC channels are calculated as

$$R_{HC/LC} = \frac{nl}{\sigma A} \qquad (2)$$

where n is the number of HC or LC channels ($n = 10$), l is the thickness of HC or LC channels (0.05 cm), σ is the averaged inlet and outlet conductivities (in S/cm), A is the effective area available for charge transport (~44 cm²) that was corrected for the spacer shadow effect by subtracting the projected area of the spacers (~20 cm²) from the maximal membrane area available for charge transport (64 cm²). The membrane resistance was obtained by subtracting HC and LC solution resistances from the ohmic resistance.

2.3. Energy calculations

Electrical power output of the stack (P_{ele}, in W) is calculated by $P_{ele} = P_{max}A_{mem}$, where P_{max} is the maximum power density of the stack obtained by polarization tests (W/m² membrane) and A_{mem} is the total active membrane area of the stack (m²). Hydrodynamic power losses (P_{hydro}, in W) when HC and LC solutions flowed through the stack at different flow rates are calculated based on the pressure drops according to [7,9]

$$P_{hydro} = Q_{HC}\Delta p_{HC} + Q_{LC}\Delta p_{LC} \qquad (3)$$

where Q_{HC} and Q_{LC} are the flow rates of HC and LC solutions (m³/s), and Δp_{HC} and Δp_{LC} are the pressure drops of the HC and LC channels (Pa). The net power produced by the stack (P_{net}, in W) was obtained by subtracting the hydrodynamic power loss from the electrical power ($P_{net} = P_{ele} - P_{hydro}$).

Pumping energy was also consumed to transport HC and LC solutions from the source to the RED stack. It is desirable to