

Work 8. Renewable Energy Production by Reverse Electrodialysis

I. Introduction

Salinity gradient energy, also called ‘blue energy’, can be produced by mixing two solutions of different salinity e.g. seawater and river water. It is a completely renewable and sustainable energy without any thermal or environmental pollution.

From a thermodynamic point of view, the Gibbs free energy of mixing (ΔG_{mix}) of two salt solutions at different concentration can be determined from the difference between the Gibbs free energy of the mixed solution (G_m) and Gibbs free energy of initial solutions:

$$\Delta G_{mix} = G_m - (G_c + G_d) \quad (1)$$

where subscripts ‘c’ and ‘d’ refer to concentrate and dilute solutions, respectively. From the definition of Gibbs free energy and chemical potential of solutions, ΔG_{mix} can be calculated as:

$$\Delta G_{mix} = \sum_i (c_{i,m} V_m RT \ln \gamma_{i,m} x_{i,m}) - (c_{i,c} RT \ln \gamma_{i,c} x_{i,c} + c_{i,d} V_d RT \ln \gamma_{i,d} x_{i,d}) \quad (2)$$

where c is the concentration of the solution (mol/m^3), V the volume of solutions (m^3), R universal gas constant (8.314 J/mol K), T the temperature (K), γ the activity coefficient of solute i and x the mole fraction of solute i .

Reverse electrodialysis (RED) is one of the promising membrane-based technologies used for salinity gradient power (SGP) generation. Figure 1 presents a schematic illustration of RED. In RED, cation exchange membranes (CEMs) and anion exchange membranes (AEMs) are alternately aligned to create a series of adjacent compartments: high concentration compartments (HCCs) and low concentration compartments (LCCs). When the compartments are filled with the respective feed solutions, an electrochemical potential is generated due to the salinity difference which initiates the selective transport of ions across the ion exchange membranes resulting in ionic flux that is converted into an electrical current through redox reaction over the electrodes. The total electromotive force generated in RED, termed as ‘Open Circuit Voltage (OCV)’, is the sum of the Nernst potential over each cell. Theoretically, OCV can be calculated by Nernst equation:

$$OCV \equiv \frac{NRT}{F} \left[\frac{\alpha_{CEM}}{z_{ct}} \ln \frac{\gamma_c c_c}{\gamma_d c_d} + \frac{\alpha_{AEM}}{z_{an}} \ln \frac{\gamma_c c_c}{\gamma_d c_d} \right] \quad (3)$$

where N is the number of membrane (cell) pairs, α the permselectivity of the ion exchange membrane, subscripts 'an' and 'ct' stand for 'anion' and 'cation', respectively. OCV is mainly dependent on the membrane permselectivity, concentration gradient and valence of transported ions. The membrane permselectivity represents the ability of the material to transport only counterions (i.e. cations in CEMs or anions in AEMs) and exclude co-ions (i.e. anions in CEMs or cations in AEMs).

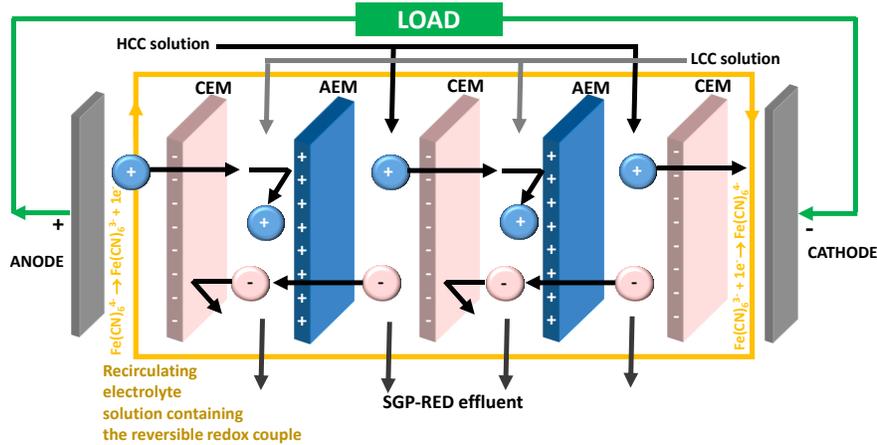


Figure 1. Scheme of a Reverse Electrodialysis system. CEM: Cation exchange membrane, AEM: Anion exchange membrane, HCC, High concentration compartment, LCC: Low concentration compartment.

Under a current flowing condition, according to Ohm's law, the voltage drop in the RED stack (V) is linearly related to the current flow (I) as:

$$V = OCV - R_i \cdot I$$

(4)

where R_i is the internal stack resistance. R_i can be obtained from the slope of V - I curves (Figure 2a). R_i is mainly constituted by Ohmic losses resulting from the resistance of membranes, the resistance of feed solutions, and to some extent, the resistance of the electrode system. The output power (P) is defined as:

$$P = VI$$

(5)

The power density (P_d) per cell pair can be expressed as:

$$P_d = \frac{P}{NA}$$

(6)

where A is the active area of a single membrane. For a RED stack loaded with a resistance of R_L , I can determine as:

$$I = \frac{P}{R_L}$$

(7)

Combining Eqs. 4, 7 and 8 results in:

$$P_d = \frac{1}{NA} \left(\frac{OCV}{R_i + R_L} \right)^2 R_L$$

(8)

Rearrangement of Eq. 4 and 8 enable the fitting of variations in P_d with current density i (A/m^2) to a parabolic trend:

$$P_d = -a \cdot i^2 + b \cdot i \quad (9)$$

where a and b are fitting parameters. It's possible to determine the maximum power density $P_{d,max}$ and the corresponding current density (i_{max}) from the peak values of the parabolic curve as (Figure 2b):

$$\left(P_{d,max} = \frac{b^2}{4a}, i_{max} = \frac{b}{2a} \right)$$

(10)

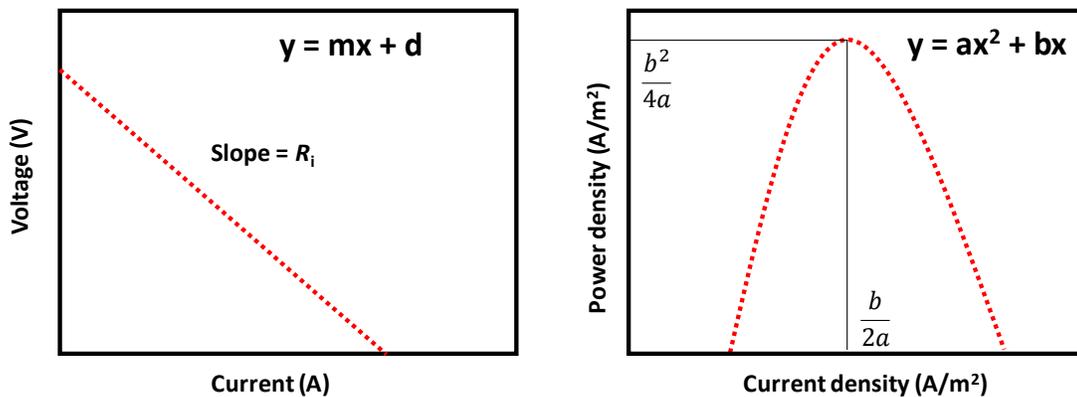


Figure 2. Typical plots of V vs I and P_d vs I for a RED.

Aim of the work: Determination of the OCV, $P_{d,max}$ and R_i of a RED system under varying operating conditions

Safety precautions: Wear safety glasses and laboratory coat all the time in the laboratory. Wear gloves when using any hazardous or toxic agent.

II. Experimental

Apparatuses

- ◆ RED stack
- ◆ External test load
- ◆ Digital multimeter
- ◆ Conductivity meter

Chemicals

- ◆ **Electrolyte:** 0.3 M $K_4Fe(CN)_6$, 0.3 M $K_3Fe(CN)_6$ and 2.5 M NaCl
- ◆ **Feed solutions**
 - Brine (5 M NaCl)/river water (0.017 M NaCl)
 - Sea water (0.5 M NaCl)/river water (0.017 M NaCl)
 - Brine (5 M NaCl)/seawater (0.5 M NaCl)

Procedure

1. Prepare the electrolyte and feed solutions according to the specified concentrations. Record the conductivity of all solutions.
2. Assemble the RED stack as shown in the circuit diagram below: Figure 3.
3. Connect the feed and electrolyte tubings to the respective RED inlet and outlet appropriately
4. Run the pumping of all solutions into the RED stack
5. Record the OCV after a stable signal is observed.
6. Start loading the RED stack and record the V and I within the experimental range
7. Record the conductivity of feed outlet solutions at a controlled time interval
8. Repeat steps 5 and 6 at a varying flow velocity and temperature of feed solutions

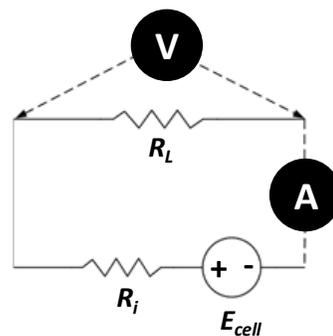


Figure 3. Electric circuit diagram of the experimental RED set-up.

III. Results and discussion

- ◆ Plote V and I curves: compare and discuss results items of variations of OCV, R_i and ionic shortcut for the different experimental conditions

- ◆ Plot P_d vs i curves: compare and discuss the results items of $P_{d,max}$ and $I_{d,max}$ for the different experimental conditions

IV. Home checklists

1. Considering 100% permselective membranes, calculate the theoretical potential that can be generated from a pair of IEM in RED stack by mixing 1 m³ of:
 - a. sea water (0.5 M NaCl)/river water (0.017 M NaCl)
 - b. sea water (0.5 M NaCl)/brackish water (0.1 M NaCl)
 - c. brine (5 M NaCl)/seawater (0.5 M NaCl)
 - d. brine (5 M NaCl)/brackish water (0.1 M NaCl)
 - e. brine (5 M NaCl)/river water (0.017 M NaCl)
2. For the above cases (1a-e), calculate:
 - a. the theoretical output power. Derive a simplified version of Eq. 2 to calculate this
 - b. based on the results 2a, estimate the energy efficiency of RED under the investigated experimental conditions
3. From the values of feed conductivity and compartment thickness:
 - a. calculate the resistance of the HCC and LCC solutions (Assume 20 % spacer-filled volume)
 - b. estimate % contributions of feed compartment resistances to the total internal resistance of the RED stack