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Reverse electrodialysis: Performance of a stack with 50 cells on the mixing of sea and river water

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ABSTRACT

The purpose of reverse electrodialysis (RED) is to produce electricity upon the mixing of two solutions. We studied the power density (W/m^2) and the energy efficiency (the amount of energy produced from specified volumes of river and sea water in relation to the thermodynamic maximum). With a stack of 50 cells (of 10 cm × 10 cm), a power density of 0.93 W/m^2 was obtained with artificial river water (1 g NaCl/L) and artificial sea water (30 g NaCl/L), which is the highest practical value reported for RED. This value is achieved due to an optimized cell design using a systematic measurement protocol.

The main factor in the power density is the cell resistance. With the used membranes (Fumasep FAD and FKD) and a spacer thickness of 200 μm, a cell resistance of 0.345 Ω is measured under RED conditions. This is about one and a half times the value as expected from the contribution of the individual components. This high value is probably caused by the shielding effect of the spacers. The largest contribution to this resistance (about 45%) is from the river water compartment.

The hydrodynamic loss resulted in a maximal net power density of about 0.8 W/m^2 at a flow rate of 400 mL/min. At this optimum the consumed power for pumping is 25% of the total generated energy. The majority of the pump power is lost in the manifolds.

Multistage experiments were performed at maximal power conditions (a current density of about $-30\ A/m^2$ and at a flow rate of 300 mL/min). At these conditions the theoretical energy efficiency is maximal 50%. In practice however, the energy efficiency of a single stack is 9%. The effluent concentrations of the so operated stack are used for a second experiment and so on, simulating a multistage operation. With 3 stages a cumulative energy efficiency of 18% is achieved. A fourth stage did not increase this value. The power density of the 3 stages together was 50% of the power density of the first stage, indicating that energy efficiency and power density are counteracting.

Further increase of power density and energy efficiency can be obtained with a better spacer and manifold design. A more open spacer is beneficial for RED in two ways: less shielding and lower pressure drop. Less shielding decreases the electrical resistance of the cell. A lower pressure drop permits the use of thinner water compartments, resulting again in a decreased electrical resistance of the cell and an improvement of the power density.

1. Introduction

In 1954 Pattle [1] wrote: *The osmotic pressure of sea-water is about 20 atmospheres, so that when a river mixes with the sea, free energy equal to that obtainable from a waterfall 680 ft high is lost. There thus exists an untapped source of power which has (so far as I know) been unmentioned in the literature.* This ‘salinity power’ is in principle clean and sustainable and gives no thermal pollution and no CO_2 exhaust. The energy that theoretically can be generated per m^3 river water is 2.5 MJ when mixed with a large surplus of sea water or 1.7 MJ when mixed with 1 m^3 sea water (Table 1). Wick and Schmitt [2] estimated the total global salinity power to be 2.6 TW, which is sufficient to supply the global electricity demand (2 TW) or 16% of the total present energy consumption [3]. There are different methods to extract energy from the mixing of sea and river water. Described techniques are reverse electrodialysis (RED) [1,4,5], pressure retarded osmosis (PRO) [6,7], vapor pressure difference utilization [8], mechanochemical methods [9], the so called ‘hydrocratic generators’ [10], membrane-less hydro-voltaic cells [11] and cryoscopic techniques like freezing temperature difference utilization [12]. RED as well as PRO are promising techniques for the generation of energy from a salinity gradient. Post et al. [13]

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Table 1
Gibbs free energy from mixing V_R (m^3) river water (S_R = 0 kg NaCl/m^3) with V_S (m^3) sea water (S_S = 30 kg/m^3) at 298 K.

V_R (m^3)	V_S (m^3)	V_R/V_S	ΔG_{RED} (MJ)
∞	1	∞	∞
10	1	10	6.1
2	1	2	2.8
1	1	1	1.76
1.26	*0.74*	*1.72*	*1.87*
1	2	0.5	2.06
1	10	0.1	2.43
1	∞	0	2.55

showed that in the case of sea water with river water, RED is very promising.

In principle, RED is a seemingly simple technique. Nevertheless, only 8 groups have published in scientific journals on their experimental results with RED operating on sea and river water [1,4,5,12,14–20] during a period encompassing more than 50 years. In these papers RED has been proven on lab scale. However, the reported power densities were relatively low and the efficiency of the process (energy efficiency) was not taken into account. Meanwhile, the knowledge of ion exchange membranes has increased and many ion exchange membranes with good properties have been developed. Furthermore, energy demand, and therewith also the problems concerning chemical and thermal pollution as well as greenhouse problems caused by CO_2 exhaust, has grown enormously. The investigation of this technique using state of the art membranes and the improvement of the operational properties of the process is aimed at providing a solution to these problems.

The objective was to study the behavior of a RED stack with commercially available membranes with respect to two operational important parameters: energy efficiency (the gained power in relation to maximal thermodynamic value) and power density (the power generated per m^2 membrane). These two response factors are dependent on membrane properties (conductivity, selectivity, osmotic behavior), cell properties (compartment thickness, spacer type), stack design parameters (way of feed, electrode system), operating conditions (flow rates, electrical load) and water quality (salt content, impurities, temperature, polyvalent ions). These parameters are conflicting in many ways. This article focuses on the main parameters affecting power density and energy efficiency: (i) current density, (ii) membrane and spacer resistance, and (iii) feed flow rate. In order to obtain a maximal power density we used commercial membranes with a low resistance. Experiments were performed with a custom made RED stack with a variable number of cells. The largest stack consisted of 50 cells with a total effective membrane area of 1 m^2, generating a power output of 0.93 W which is the highest power density ever reported for RED operating on river and sea water.

2. Theory

2.1. Reverse electrodialysis

A typical RED system consists of a variable number of alternating cation and anion exchange membranes in a stack. Fig. 1 shows such a system with only one cell. Every cell consists of a cation exchange membrane (CEM), a salt water compartment, an anion exchange membrane (AEM) and a sweet water compartment. Positive ions from the sea water diffuse through the CEMs to the river water compartment and build up a positive potential on one side of the stack. The negative ions from the sea water diffuse through the AEMs to the river water compartment on the other side and cause a negative potential in this location. The potential difference between the two solutions can be calculated using the Nernst equation. If sea water is considered as a solution of 30 kg NaCl/m^3 and river water as a solution of 1 kg NaCl/m^3, this potential difference is 140–160 mV per cell. If there is an external circuit connected to the end electrodes, electrical power can be extracted from the system. The ionic current in the cells is then converted to an external electron current via redox reactions at the electrodes.

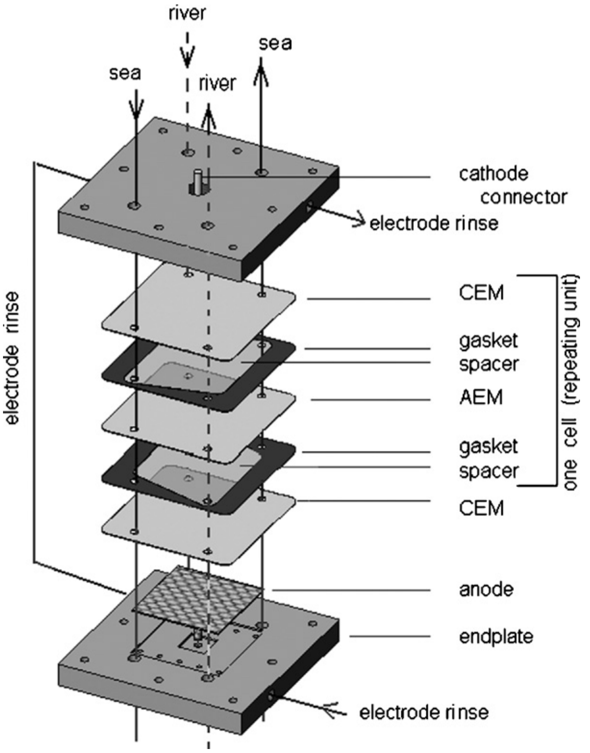

Fig. 1. A reverse electrodialysis stack with one cell.

2.2. Power density determination

The theory about reverse electrodialysis was formulated by Weinstein and Leitz [14], Clampitt and Kiviat [21], Jagur-Grodzinski, and Kramer [17] and Lacey [22] and is summarized by Veerman et al. [20]. Key parameters of a RED cell are the electromotive force, internal resistance and delivered power. The voltage across a 100% selective membrane can be calculated if pure NaCl solutions of 1 and 30 g/L at 298 K are used, giving values of 0.080 V for a CEM and 0.078 V for an AEM, or together E_{cell} = 0.158 V for a cell.

The power efficiency (η_P) is the fraction of total power that is delivered to an external power consumer with resistance R_u:

$$\eta_P = \frac{I^2 R_u}{I^2 R_i + I^2 R_u} = \frac{R_u}{R_i + R_u} \tag{1}$$

At the condition of maximal power output ($R_u = R_i$), the power efficiency is not higher than 50%. A higher efficiency can be achieved (by taking $R_u > R_i$) at the cost of a decreased power output.

The power density P_d of a RED system is defined as the external power per membrane area (W/m^2) and is maximal under the condition of $R_u = R_i$:

$$\begin{aligned} P_d &= \frac{P_u}{2A} = \frac{I^2 R_u}{2A} = \left(\frac{E_{cell}}{R_i + R_u}\right)^2 \frac{R_u}{2A} \\ &= \frac{E_{cell}^2}{8AR_i} = \frac{E_{cell}^2}{8A(R_{AEM} + R_{CEM} + R_{river} + R_{sea})} \end{aligned} \tag{2}$$

where A stands for the active cell area and $2A$ for the total membrane area (AEM and CEM) in a cell. R_{AEM}, R_{CEM}, R_{river} and R_{sea} are