Reverse electrodialysis for Power Generation

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Abstract- **The use of reverse electrodialysis, to derive energy from the difference between the chemical potentials of concentrated and dilute salt solutions is reviewed. The process employ the flows of brine and dilute solutions through alternating cells bounded by cation- and anion-exchange membranes in a stack placed between two electrodes to generate a voltage by the passage of salt through the membranes. Potential sources of brine include the salt domes of oil and gas wells, salt water lakes, and geothermal brines. This paper also reviews a range of membrane properties of the commercially available membranes.**

Keywords: **Power generation, Reverse electrodialysis, membranes for RED.**

1. INTRODUCTION

Renewable and sustainable energy sources are playing an important role in the 21st century and are becoming increasingly important due to environmental problems, such as global pollution phenomena and global warming. Membrane technology provides an opportunity to gain renewable and sustainable energy from salinity gradients via, e.g. pressure retarded osmosis and reverse electrodialysis. The latter method seems more attractive for power generation using sea and river water. Reverse electrodialysis (RED) is a non-polluting, sustainable method for energy generation by mixing fresh and salt water. RED converts the free energy generated by mixing the two aqueous solutions into electrical power and the system can be applied wherever two solutions of different salinity are mixed, e.g. where river water flows into the sea. The principle of RED was first proven by Pattle, who with his pioneering work in this field was the first one that generated power using RED. In the 70s, Weinstein and Leitz investigated the effect of solution composition on power output and the main conclusion of this work was that large-scale energy conversion by RED may become practical, but only with major advances in the manufacturing of ion exchange membranes and with careful optimization of the operating conditions. In the early 1980s, Lacey conducted a comprehensive investigation on RED. Conclusion of his work was that to make RED commercially available it is necessary to minimize the internal stack resistance of the RED cells and to maximize the net power output from the cell. Lacey concluded that membranes for RED should have a low electrical resistance and a high selectivity combined with a long service life time, acceptable strength, dimensional stability and low-cost. In the mid 1980s, Jagur-Grodzinski investigated membrane spacer modifications and different salt solution streams in order to generate more energy. In 2007, Turek and Bandura studied the effect of solution velocity on cell power output and process

economy. Turek, mentioned that the main bottleneck for a successful RED system seems to be the membrane price. Despite that remark, the focus of most of the earlier work on RED was on stack design, solution flow and solution composition, but not on membrane characterization and membrane performance. Most scientists used electrodialysis membranes to study the RED process. The ion exchange membranes are the key elements in the RED system. The most important membrane properties for RED are ion exchange capacity, swelling degree, and of course the membrane resistance and its selectivity (the ability of the membrane to distinguish between cations and anions), because of their direct effect on the overall RED performance. Up to now, it is still not known which membrane parameter is the dominant factor with respect to power generation in RED. It is essential to identify the key membrane parameters for RED in order to further improve the power output of RED. The data available in the existing literature do not offer sufficient information on membrane properties relevant to RED to enable proper mutual comparison of the different commercially available membranes. Currently, no complete overview is available with respect to the application of ion exchange membranes in RED which covers the full range of membrane types.

This review presents an overview of reverse electrodialysis. It investigates a range of membrane properties of commercially available membranes that are important with respect to application in RED. The objective of this study is to analyze the membrane properties under equivalent conditions to enable a fair comparison of the results and a proper evaluation for application in RED.

2. Theoretical background

2.1. Principle of reverse electrodialysis

In RED, a concentrated salt solution and a less concentrated salt solution are brought into contact through an alternating series of anion exchange membranes (AEM) and cation exchange membranes (CEM) (Fig. 1,1.1).

The membranes separate the concentrated solution from the diluted solution and only ions can pass through the ion selective membranes. Anion exchange membranes contain fixed positive charges which allow anions to permeate through the AEM towards the anode and cation exchange membranes contain fixed negative charges which allow cations to be transported through the CEM towards the cathode. The difference in chemical potential between both solutions is the driving force for this process. At the electrodes a redox couple is used to mitigate the transfer of electrons. The chemical potential difference generates a voltage difference over each membrane.
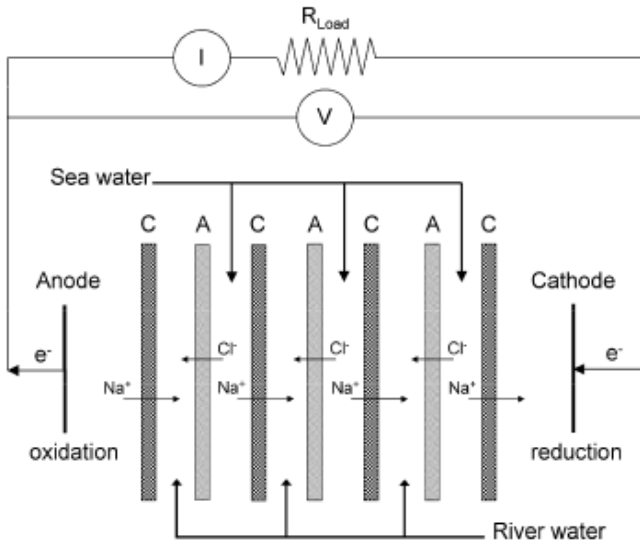
Fig. 1. Schematic representation of reverse electrodialysis: A is an anion exchange membrane, C a cation exchange membrane, V is the potential difference over the applied external load (V), I is the electrical current (A) and R_load is the resistance of the external load (Ω). A redox couple is used at the electrodes to mitigate the transfer of electrons.
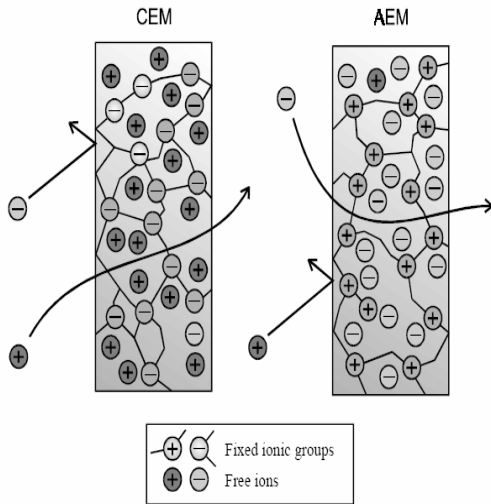
Figure 1.1: The two types of (mono polar) electrodialysis membranes. On the left: cation-exchange membrane, on the right anion-exchange membrane.

The theoretical value of the potential over the membrane for an aqueous monovalent electrolyte (e.g. NaCl) can be calculated using the Nerst equation (Eq.(1)):

$$\Delta V_{theo} = \frac{RT}{zF} \ln \frac{a_c}{a_d} \qquad (1)$$

where ΔV_{theo} is the theoretical membrane potential for a 100% selective membrane (V), R is the gas constant (8.314J/(mol K)), T is the absolute temperature (K), z is the electrochemical valence, F is the Faraday constant (96,485 C/mol), a_c is the activity of the concentrated solution (mol/l) and a_d is the activity of the diluted solution (mol/l). For fresh water (0.017 M NaCl, $y_\pm$ = 0.878) and sea water (0.5 M NaCl, $y_\pm$ = 0.686), the theoretical voltage difference per membrane is 80.3 mV. The overall potential of the system is the sum of the potential differences over each pair of membranes.

2.2. Ion exchange membrane properties

Ion exchange membranes are membranes with fixed anionic or cationic exchange groups that are able to transport cations or anions. The specific properties of ion exchange membranes are all related to the presence of these charged groups. Amount, type and distribution of ion exchange groups determine the most important membrane properties. Based on the type of fixed charge group, ion exchange membranes can be classified as strong acid and strong base, or weak acid and weak base membranes. Strong acid cation exchange membranes contain sulfon groups as charged group. In weak acid membranes, carboxylic acid is the fixed charged group. Quaternary and tertiary amines are the fixed positive-charged groups in strong and weak base anion exchange membranes, respectively.

2.2.1. Ion exchange capacity

The ion exchange capacity (IEC) is the number of fixed charges inside the ion exchange membrane per unit weight of dry polymer. The ion exchange capacity is a crucial parameter which affects almost all other membrane properties. The IEC is expressed in milli equivalent of fixed groups per gram of dry membrane (mequiv./g membrane).

2.2.2. Fixed charge density

Ion exchange membranes contain fixed-charged groups attached to the polymer backbone. In cation exchange membranes, the fixed negative charges are in electrical equilibrium with the mobile cations (counter-ions). The opposite relation exists in anion exchange membranes. The fixed charge density, expressed in milli equivalent of fixed groups per volume of water in the membrane (mequiv./l) strongly depends on the IEC and the swelling degree of the membrane: in the swollen state, the distance between the ion exchange groups increases thus reducing the fixed charge density. The transport of counter ions through the membrane is determined by the fixed charge density in the membrane and the difference between the concentrations of the electrolyte solution in contact with that membrane. The concentration and type of the fixed ionic charges determine the permselectivity and the electrical resistance of the membrane.

2.2.3. Permselectivity

When an ion exchange membrane is in a contact with an electrolyte (salt solution), ions with the same charge (co-ions) as the fixed ions are excluded and cannot pass through the membrane, while the oppositely charged ions (counter ions) can pass freely through the membrane. This effect is known as Donnan exclusion [14]. The permselectivity of a membrane describes the charge selectivity of the ion exchange membrane. It reflects the ability of the membrane to discriminate between ions of opposite charge.

2.2.4. Electrical resistance

The electrical resistance of the membrane is an important property of ion exchange membranes, because it is directly related to the maximum power output in reverse electrodialysis and the energy consumption in electrodialysis processes. The membrane resistance is determined by the ion exchange capacity and the mobility of the ions within the membrane matrix. The electrical

resistance is dependent on temperature and decreases with increasing temperature. The specific membrane resistance is in principle reported in Ω cm. However, more useful and most often reported in literature is the membrane resistance in Ω cm^2.

2.2.5. Heterogeneous and homogenous ion exchange membranes

Ion exchange membranes can be divided with respect to their structure and preparation procedure into two categories: homogeneous and heterogeneous membranes. In homogenous ion exchange membranes the fixed charge groups are evenly distributed over the entire membrane matrix. Homogenous membranes can be manufactured via polymerization and poly-condensation of functional monomers (e.g. fenylosulfonic acid with formaldehyde) or via functionalization of a polymer by for example dissolving the polymer in a suitable solvent and subsequent functionalization by, e.g. post-sulfonation. Heterogeneous membranes have distinct macroscopic uncharged polymer domains of ion exchange resins in the membrane matrix. This type of membranes can be produced by melting and pressing of a dry ion exchange resin with a granulated polymer (e.g. polyvinylochloride). Another method to prepare heterogeneous membranes is dispersion of the ion exchange resin in a polymer solution. The distinct difference between homogenous and heterogeneous ion exchange membranes also influences the properties of the specific membrane.

2.3. RED membrane model

To predict the relative contribution of the different components in a RED stack, a theoretical model was used. The relationship between the salt concentration (activity) in the two compartments (diluted and concentrated), the process temperature and the selectivity of the membrane is shown in the following equation:

$$V^o = N \frac{2\alpha_{av}RT}{zF} \ln \frac{a_c}{a_d} \tag{2}$$

where V^o is the open circuit potential of the membrane stack (V), α_{av} is the average membrane permselectivity of an anion and a cation exchange membrane pair, N is the number of membrane pairs, R is the gas constant (8.314J/(mol K)), T is the absolute temperature (K), z is the electrochemical valence, F is the Faraday constant (96,485 C/mol), a_c is the activity of the concentrated salt solution (mol/l) and a_d is the activity of the diluted salt solution (mol/l).

The stack resistance can be defined as the sum of the resistances of the individual stack components as shown in the following equation:

$$R_{stack} = \frac{N}{A} \left(R_{aem} + R_{cem} + \frac{d_c}{\kappa_c} + \frac{d_d}{\kappa_d} \right) + R_{el} \tag{3}$$

where N is the number of membrane pairs, A is the effective membrane area (m^2), R_{aem} is the anion exchange membrane resistance (Ω m^2), R_{cem} is the cation exchange membrane resistance (Ω m^2), d_c is the thickness of the concentrated compartment (m), d_d is the thickness of the diluted compartment (m), K_c is the concentrated compartment conductivity (S/m), K_d is the diluted compartment conductivity (S/m) and R_{el} is the electrode resistance (Ω).

The final stack power output of the RED stack can be found from Kirchhoff's law and is defined as

$$W = I^2 R_{load} = \frac{(V^o)^2 R_{load}}{(R_{stack} + R_{load})^2} \tag{4}$$

Here I is the current (A), R_{load} is the load resistance (Ω), R_{stack} is the stack resistance (Ω) and V^o is the stack open circuit potential (V).

To generate a maximum power output (W_{max}), R_{load} needs to be equal to R_{stack}.

In that case, Eq. (4) changes into Eq. (5) which shows the relationship between the open circuit potential, the maximum power output and the stack resistance.

$$W_{max} = \frac{(V^o)^2}{4R_{stack}} \tag{5}$$

Combination of Eq. (5) with Eqs. (2) and (3) finally yields Eq. (6) which relates the maximum power output of the RED stack to the individual contributions of each component. More specifically, it relates the maximum power output of the system (W_{max}) to the average membrane selectivity (α_{av}) and the membrane resistance (R_{aem} and R_{cem}).

$$W_{max} = NA \frac{[\alpha_{av}RT/F \ln(a_c/a_d)]^2}{R_{aem} + R_{cem} + (d_c/\kappa_c) + (d_d/\kappa_d)} \tag{6}$$

where N is the number of membrane pairs, α_{av} is the average membrane pair permselectivity, R is the gas constant (8.314J/(mol K)), T is the absolute temperature (K), F is the Faraday constant (96,485 C/mol), a_c is the concentrated solution activity (mol/l), a_d is the diluted solution activity (mol/l), R_{aem} is the anion exchange membrane resistance (Ω m^2), R_{cem} is the cation exchange membrane resistance (Ω m^2), A is the effective membrane area (m^2), d_c is the thickness of the concentrated compartment (m), d_d is the thickness of the diluted compartment (m), K_c is the concentrated (0.5 M NaCl) compartment conductivity (4.648 S/m) and K_d is the diluted (0.05 M NaCl) compartment conductivity (0.551 S/m).

Eq. (6) predicts the theoretical membrane stack power output and relates the maximum power output of the system to the individual membrane characteristics, it can be used as a tool to compare different anion and cation exchange membranes with respect to their performance in a RED stack. If Eq. (6) is used to predict the power output obtainable with only a cation exchange membrane, then the average membrane pair permselectivity (α_{av}) is replaced by the individual membrane selectivity (α). The resistance of the anion exchange membrane term will be removed in that case and the concentrated and diluted compartment thickness (d) will be divided by two. The same procedure is applicable for anion exchange membranes. This calculated power output for only one type of the membrane is used to compare the different anion or cation exchange membranes with each other.

In the model a few assumptions were made: (i) concentration polarization phenomena near the membrane surface are negligible due to the small current densities obtained through the membranes. This phenomenon can be minimized with well designed fluid dynamics between the membranes, (ii) the resistance of the electrodes is assumed to be negligible compared to the membrane resistance. This assumption is allowed when a large number of membrane cell pairs is used, (iii) the feed solution does not change in concentration along the channels. This assumption has a strong relationship with the feed channel design and in a well-designed system this effect can be neglected.

In order to compare commercially available membranes with each other it is more desirable to convert the power output into power density by normalizing it for the membrane area (W/m^2). Power density per square meter of membrane can be easily calculated from the maximum power output:

$$w_{\max} = \frac{W_{\max}}{AN_{\mathrm{m}}} \qquad (7)$$

where $w_{\max}$ is the maximum power density (W/m^2), $W_{\max}$ is maximum power output (W), A is the effective membrane area (m^2) and N_{m} is the number of membranes.

Obtained power output per type the membrane (anion or cation exchange membrane) is used only to benchmark membranes with each other.

5. Conclusion

This paper evaluates the potential of commercially available anion and cation exchange membranes for application in RED. Different membrane properties and characterization methods are discussed and a theoretical membrane model for RED was used to allow fair comparison of the characterization results for application in RED. Literature shows that the charge density has a strong influence on the permselectivity and the membrane resistance, but that there does not exist a straight forward relationship between these properties. In general cation exchange membranes have a higher charge density and a corresponding higher permselectivity than anion exchange membranes. Heterogeneous ion exchange membranes have a relatively low charge density compared to homogeneous membranes and a much higher resistance due to the membrane structure and the separation of charged domains in an

uncharged polymer matrix. This makes RED a potentially attractive alternative for energy production.

Nomenclature

a_{c}	concentrated solution activity (mol/l)
a_{d}	diluted solution activity (mol/l)
A	membrane area (m^2)
c_{fix}	fixed charge (mol/l)
F	Faraday constant (96,485 C/mol)
i	current density (A/m)
I	current (A)
N	number of cell pairs
N_{m}	number of membranes
R	gas constant (8.314 J/(mol K))
R_{aem}	anion exchange membrane resistance ($\Omega\,\mathrm{m}^2$)
R_{cem}	cation exchange membrane resistance ($\Omega\,\mathrm{m}^2$)
R_{c}	concentrated solution resistance (Ω)
R_{d}	diluted solution resistance (Ω)
R_{el}	electrode resistance (Ω)
R_{load}	load resistance (Ω)
R_{stack}	resistance of the stack (Ω)
T	absolute temperature (K)
V^{o}	stack open circuit potential (V)
w	power density (W/m^2)
$W_{\max}$	maximum power output (W)

Greek symbols

α	permselectivity of the membrane
α_{av}	average permselectivity of an anion and a cation membrane pair
$\gamma_{\pm}$	mean activity coefficient
ΔV_{meas}	measured membrane potential (V)
ΔV_{theo}	theoretical membrane potential (V)

REFERENCES

[1]. R.E. Lacey, Energy by reverse electrodialysis, Ocean Eng., 7 (1980) 1–47

[2]. J. Weinstein and B. Leitz, Electric power from differences in salinity: the dialytic battery, Science, 191 (1976) 557–559.

[3]. http://www.wetsus.nl/eng/Themes5b.htm.

[4]. M. Turek, Cost-effective electrodialytic seawater desalination, Desalination, 153 (2002) 371–376.

[5]. Piotr Długołęcki, Kitty Nymeijer, Sybrand Metz and Matthias Wessling, Current status of ion exchange membranes for power generation from salinity gradients, Journal of Membrane science, 319,July 2008, Pages 214-222 .