REVIEW ARTIKEL: TECHNOLOGY REVERSE ELECTRODIALYSIS MEMBRANE

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Abstract. *The level of world energy consumption is increasing continuously, so that environmental impacts such as CO_2 emissions are increasing. The renewable energy source that has great potential in the world is the Salinity Gradient Power, which utilizes energy from mixing sea water and river water. Reverse Electrodialysis is one of the most promising methods to capture salinity gradient power to solve energy demands in the future due to being environmentally-friendly in producing no emission pollutant gases and producing a high density of energy, which generates power via the transport of the positive and negative ions in the water through selective ion-exchange membranes.Ion-exchange membranes are used in environmental and energy technologies of electrodialysis desalination and reverse electrodialysis power generation, respectively. Recent studies reported empirical evidence that the conductivity and permselectivity of IEMs are bound by a tradeoff relationship, where an increase in ionic conductivity is accompanied by a decrease in counterion selectivity over co-ion. The analysis revealed the mechanism for the tradeoff induced by bulk solution concentration: a higher salinity suppresses IEM charge-exclusion, thus lowering permselectivity, but elevates mobile ion concentration within the membrane matrix to improve conductivity. As such, IEM applications are practically confined to sub-seawater salinities, i.e., RED using hypersaline streams will not be efficient. In another tradeoff driven by IEM water sorption, increasing membrane swelling enhances effective on diffusivity to raise conductivity, but diminishes permselectivity due to dilution of fixed charges.*

Keyword : CO_2, IEM, reverse electrodialysis, salinity

1. Introduction

The development of renewable and environmentally friendly energy is very important in reducing dependence on the use of fossil fuels. This is because the level of world energy consumption increases continuously, so that environmental impacts such as CO_2 emissions are increasing [1-4,14-17]. Salinity Gradient Power is a renewable energy source with great potential in the world, namely utilizing energy from mixing seawater and river water. Approximately 0.70-0.75 kWh of energy is released when 1 m^3 of river water mixes with 1 m^3 of seawater. SGP is a promising renewable energy that does not cause emissions so that it can be categorized as clean energy [9-11,22-25]. The two most promising methods of applying Salinity Gradient Power are Pressured Retarded Osmosis and Reverse Electrodialysis. The Reverse

Electrodialysis method generates electrical energy using ion flow which is induced when salt water and fresh water are mixed through Ion Exchange Membranes. One of the important factors to increase the efficiency of the Reverse Electrodialysis process is the improvement of the transport properties of the Cation Exchange Membrane [12].

The development of a Cation Exchange Membrane with special characteristics, such as selectivity, ionic conductivity, permeability and high chemical, thermal and mechanical resistance is desirable. So it must be considered in the selection of ion exchange membranes that have long lasting properties chemically and mechanically [15]. investigated the preparation of Cation Exchange Membrans magnetic matrices by inserting cobalt ferrite nanoparticles into a PVC membrane [4,6]. The addition of $CoFe_2O_4$ nanoparticles in the membrane matrix caused an increase in membrane conductivity and surface hydrophility, but the addition of $CoFe_2O_4$ that was too high caused a decrease in the permeability and properties of the membrane [5,6].

GO has a specific surface area and high mechanical strength, flexibility, and atomic level thickness so that the addition of GO to polymer membranes can improve membrane performance, such as hydrophility, conductivity, and membrane permeability [32-35]. Unused battery waste can be utilized graphite rods for membrane additives. Renewable energy sources have received significant attention due to limited fossil fuel sources and global warming . The oceans represent a vast and largely untapped source of energy [31].

One of the forms is the salinity gradients. RED is one of the most promising methods to capture salinity gradient power to solve energy demands in the future due to being environmentally-friendly in producing no emission pollutant gases and producing a high density of energy , which generates power via the transport of the positive and negative ions in the water through selective ion-exchange membranes [30,42-44] . Ion-exchange membranes are charged polymeric films that allow the selective transport of oppositely-charged species , while retaining the like-charged ions and water . IEMs are employed in environmental and energy technologies, such as desalination, fuel cells, and salinity gradient power generation , and also chemical production by the chloralkali process [45] .

Reverse electrodialysis , the power generation analog of ED, converts the chemical potential energy stored in salinity gradients to useful electrical work by the directional permeation of ions across the charge-selective membranes [49] . Demonstrated that the use of hot and highly concentrated brine discharged from MD could improve the RED efficiency by increasing the salinity gradient and decreasing the electrical resistance. One important factor for increasing the efficiencies of the mentioned processes is improvement in transport properties of cation exchange membranes such as ion exchange capacity, ionic conductivity and permselectivity [47,50]. Selecting chemically and mechanically durable ion exchange membranes for applying in their harsh environments is necessary. Polyvinyl chloride is one of the most extensive thermoplastic materials in the world due to its valuable properties, wide applications, high chemical resistance, barrier properties and low cost [2,4,6] . However, PVC has a low ion exchange and conductivity.

This study analyzes ion transport across IEMs to elucidate the dependence of key performance parameters, ionic conductivity and charge selectivity, on intrinsic membrane chemical and structural properties. Firstly, the working principles of ion-exchange membranes, electrodialysis, and reverse electrodialysis are described. The underpinning phenomena relating operating conditions and membrane properties to IEMs performance are highlighted and the principal factors governing the observed

conductivity-permselectivity tradeoff are elucidated [32]. Lastly, the implications for ED desalination, RED salinity gradient power generation, and membrane development are discussed.

2. Principles of ion-exchange membranes and IEM processes

2.1. Electrochemical membrane processes

Fig. 1 provides a useful overview of the relationship between electrodialysis (ED), RED, short-circuit reverse electrodialysis (SRED), voltage assisted reverse electrodialysis (VARED), and diffusion dialysis (DD). ED is a well-established desalination method, where an external electrical voltage is applied to overcome the electromotive force (in addition to any overpotential at the electrodes) such that ions migrate against their respective concentration gradient to obtain desalted water. In contrast, the electrical voltage in RED is lower than the electromotive force such that ions move under the concentration gradient to generate an ionic current that has opposite direction to the electrical field. Whereas ED consumes electricity, its reverse process RED produces electricity from salinity gradient; their power density is given by the product of the electrical voltage output and the corresponding current density. Under the special condition where the electrical voltage output is 0 (close-circuit condition), electricity is neither produced nor consumed. In this case, ions can diffuse under their respective concentration gradients at rates faster than the corresponding ones under RED conditions; this process is referred as SRED in this paper. To further enhance the rates of transport of ions, an external voltage can be applied in the same direction to the ionic current. This configuration, referred as VARED, accelerates the ion removal from the high concentration stream at the expense of additional energy consumption compared to SRED. Both SRED and VARED can have potential applications in desalination by removing salts from the high concentration solution at accelerated rates.

The electrochemical membrane processes ED, RED, SRED, and VARED are analogous to their pressure/ osmotic-pressure-driven counterparts reverse osmosis, pressure retarded osmosis, forward osmosis, and pressure-assisted forward osmosis, respectively [35]. DD is a process similar to SRED in that no external voltage is applied. However, instead of using both AEMs and CEMs in an alternative sequence in SRED, only one type of membrane is used in DD. DD processes using AEMs are commonly applied for recovering acids [30–34]. In these applications, the transport of anions (e.g., Cl^-, SO_4^{2-} or NO_3^-) under their concentration gradient across an AEM is accompanied by H+ as a counter-ion due to its small size and high mobility; electroneutrality is maintained during the transport of ions such as no net electric current is produced [45]. For this reason, DD is located at the origin of the plot in Fig. 1a,b. In a similar manner, DD processes using CEMs can be used for separating base containing solutions [45]. To further accelerate the ions migration in DD, a voltage assisted diffusion dialysis (VADD) can be used by applying an external electric field in the same direction as the concentration gradient [46].
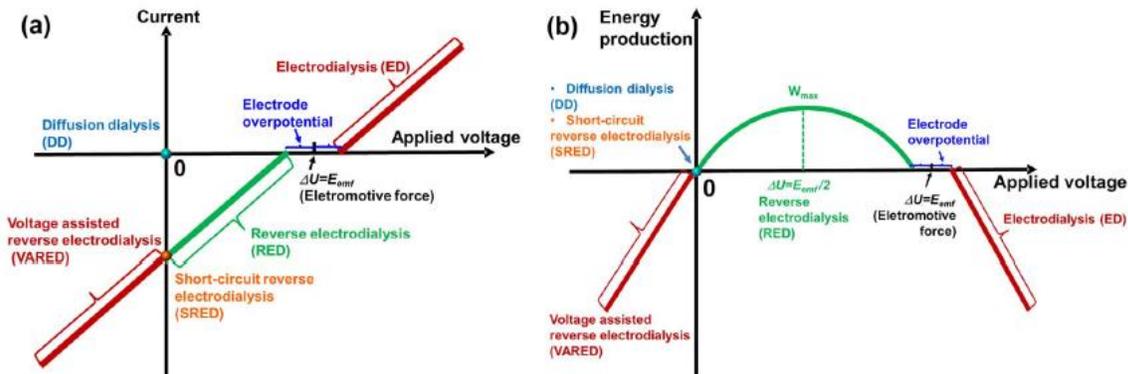
Fig. 1. (a) Current as a function of applied voltage in ED, RED, SRED, VARED, and DD; (b) energy output as a function of applied voltage in ED, RED, SRED, VARED, and DD. ED process where electrical energy is consumed to drive ionic transport against the concentration gradient; RED process where electricity is generated from ionic current along the concentration gradient; VARED process where electricity is consumed to further enhance the ionic transport from the concentrated solution to dilute solution; SRED and DD processes where electricity is neither consumed nor generated.[28]

2.2. Working principles of ion-exchange membranes

Ion-exchange membranes are water-swollen polymeric films of typically 50-200 m thickness, with a high density of charged ionic functional groups fixed to the backbone chains [1, 30, 31]. The selective transport of IEMs is achieved by the charge exclusion principle: the fixed functional groups exclude like-charged co-ions and the membrane preserves electroneutrality by having a high concentration of counterions (opposite charge to fixed moieties). Ion transport is driven by electrochemical potential, and the comparatively greater concentration results in a larger flux of counterions than co-ions. Hence, IEMs allow the preferential permeation of counterions over co-ions, but because co-ions are not completely excluded from the membrane matrix, the charge selectivity of IEMs is imperfect. Cation exchange membranes (CEMs) with fixed negatively charged functional groups, such as, sulfonic acid, phosphoric acid, and derivatives of sulfonamide and azole, selectively favor cations permeation; whereas anion exchange membranes (AEMs) possess cationic functional groups, e.g., quaternary ammonium, to
facilitate transport of anions over cations [32, 33].

2.3. Electrodialysis desalination

Electrodialysis (ED) is an IEM-based desalination technology that utilizes an electric current to separate charged ions from a saline stream and produce freshwater [2, 7]. In ED, an external electric potential is applied across a stack comprising repeating pairs of CEM and AEM. Saline feed stream flows through each compartment channel between the membranes. The external electric potential drives the permeation of cations towards the cathode and the anions towards the anode. As the IEMs selectively allow the permeation of counterions and retain co-ions, cations and anions permeate into the concentrate compartment from the abutting diluate streams, across the CEM and AEM, respectively, but ions in the concentrate stream are hindered from crossing into the diluate compartment (Fig. 2).
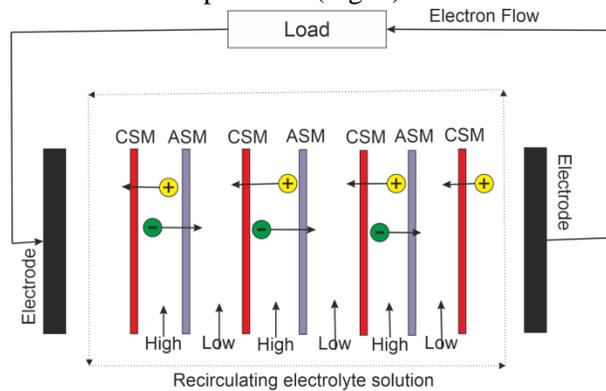

Fig 2. Reverse Electrodialysis (RED) - CEM: cation exchange membrane; AEM: anion exchange membrane.

2.4. Reverse electrodialysis energy production

Reverse electrodialysis (RED) produces useful work from salinity gradients by inverting the operating principles of ED separation [9, 34]. Instead of supplying external electrical energy, RED generates power

from the controlled mixing of high and low concentration solutions. A similar membrane stack configuration as ED is utilized: a repeating cell consists of, in spatial order, a CEM, a high concentration (HC) solution compartment, an AEM, and a low concentration (LC) solution compartment (which is bordered by the CEM of the next cell). This alternating structure enables the series addition of Nernst potentials arising from the concentration difference across the IEMs. Selective transport of anions and cations in the HC solution, across the AEM and CEM, respectively, to the adjacent LC chambers produces a net charged ion flux. Like ED, a reversible redox couple is circulated between the two end electrode chambers to transform ionic current in the stack to an electric current that powers the load in the external circuit.

2.5. Ion exchange capacity
The ion exchange capacity (IEC) of cation exchange membranes was measured by acid-base titration method. Membrane samples were immersed into excess 1 M HCl solution for 24 hours to saturate all the fixed charged groups with H+; then the samples were washed with demi-water until the surface water was completely removed. Following this, the samples were immersed into 40 ml of 2 M NaCl solution to exchange H+ with Na+ and to release H+ into solution. This step was repeated 3 times for a complete exchange. Finally, the immersed solutions were collected into a beaker and titrated with 0.01 M NaOH. The titration was continued until the pH of the collected solution reached the pH of the initial 2 M NaCl solution [35]. The pH values were monitored with a pH meter (WTW Inolab Terminal Level 3, Germany).

2.6. IEC (Ion Exchange Capacity) Analysis
The cation exchange membrane was immersed in 1M HCl for 15 hours, and then immersed using deionized water for 1 hour to be free from chloride. Then the membrane was immersed in 1 M NaCl solution for 6 hours. The hydrogen ions removed from the membrane were then titrated with 0.01 M NaOH solution and used the phenolphtalein indicator. The IEC is calculated using the following equation [19]:

$$IEC = \frac{Cx\,V}{W}$$

with:
IEC = ion exchange capacity (meq / g)
C = molar concentration of the titrant (M)
V = volume of titrant (ml)
W = dry membrane sample weight (grams)

2.7 Porosity

The porosity test was carried out to determine the amount of membrane porosity [52]. The pore structure affects the ion conductivity. Porosity was measured by weighing the dry weight of the membrane, then immersing the membrane in demin water for 24 hours. Then weigh the membrane wet weight. The porosity can be calculate with equation [51]:

$$Porosity = \frac{m_{wet}x\,m_{dry}}{AL\rho_w}$$

with:
m $_{wet}$ = wet weight (g)
m $_{dry}$ = dry weight (g)
A = membrane area (cm)

L = membrane thickness (cm)

ρ_w = density of water (gram / ml)

3. Performance parameters for ED and RED

3.1. Current efficiency

Current efficiency, CE, is a measure of ionic current utilization in ED and RED for separation and energy production, respectively:

$$CE_{ED} = \frac{z_{ct}J_{ct}}{z_{co}J_{co}+z_{ct}J_{ct}} \qquad (1)$$

$$CE_{RED} = \frac{z_{co}J_{co}+z_{ct}J_{ct}}{z_{ct}J_{ct}} \qquad (2)$$

where z is the ion valence, J is the ion flux, and subscripts ct and co denote counter- and co-ions, respectively. Note that z and J can be positive or negative, depending on charge and direction, and the product zJ gives the ionic current. In ED desalination, the electric current drives counterand co-ion fluxes. These two ion fluxes flow in opposite directions and are of different charge, with only the counterion flux performing the desired function of desalinating the saline feed, whereas co-ion flux is an unwanted leakage of ions to the diluate stream that actually compromise desalination performance[24,27,38]. Current efficiency for ED desalination is, thus, the ratio of the current due to counterion flux to the total ionic current, Eq. 1. Conversely, the aim of RED is to generate an ion flux that can then be used to drive an external circuit and, hence, CERED is defined differently from ED desalination. Because both fluxes are in the same direction the current from counterion flux is partly negated by co-ion flux. The RED current efficiency, Eq. 2, is the net ionic current divided by the current due to counterion flux. Note that equation for CERED is the reciprocal of CEED. Current efficiency of ED and RED is analogous to the Faradaic efficiency of electrochemical processes, which quantifies the percentage of charge utilized for the desired electrochemical reaction[12].

3.2. Permselectivity

Permselectivity describes the selectivity for counterion transport and is defined as the ionic current carried by counterion flux less the current from co-ion flux, normalized by the total ionic current [1, 31]:

$$\alpha = \frac{|z_{ct}J_{ct}|-|z_{co}J_{co}|}{\sum|z_iJ_i|} = t_{ct} - t_{co} \qquad (3)$$

Note that the sign conventions of z and J are neglected and only the magnitude of the ionic currents are used to calculate . Further, the fraction of total ionic current carried by species i is the transport number, t_i, and, hence, permselectivity is also the counterion transport number less the co-ion transport number (Eq. 3) [1]. An IEM with perfect charge selectivity is only permeable to counterions but not co-ions and, therefore, permselectivity equals to one. Experimentally characterized measurements are commonly reported in literature, but those values are more accurately termed "apparent permselectivity", and is the ratio of measured open-circuit voltage (OCV) to theoretical Nernst potential [1]. Because of the ease of experimental characterization (one electrochemical reading instead of tracking counter- and coion concentration changes), apparent permselectivity is often used as a proxy parameter to approximate the fraction of ionic current carried by counter- and co-ions during actual ED and RED operation even though

it deviates from the definition of Eq. 3. Comparison between apparent and real permselectivities are discussed later in Section 5.

3.3. Area specific resistance

Area specific resistance, ASR, is defined in Eq. 17 as the slope of Vm with respect to the net current density, i_{tot} F $(z_{co}$ J_{co} $z_{ct}J_{ct})$, i.e., differential resistance:

$$ASR = \frac{d\Delta V^m}{di_{tot}} \qquad (4)$$

Because the contribution of IEM to total internal resistance is significant in ED and RED [17], the membrane ASR should be small to suppress undesired resistive losses. In IEM processes, steady state current-voltage response can be described by one of the three regimes: ohmic (or under-limiting), plateau (or limiting), and overlimiting [49]. The current analysis will focus on simulating ion-exchange membranes working within the ohmic regime, which is the common operating conditions for ED and RED. In this relatively low current regime, i.e., under-limiting the relation between current density and imposed voltage is linear; ion depletion in the concentration polarization boundary layer is not dominant and a limiting current is not reached (i.e., before plateau regime).

3.4. Conductivity

Conductivity is the reciprocal of resistivity, and describes the ability of the IEM to conduct ionic currents:

$$\sigma = ASC \; x \; l = \rho^{-1} \qquad (5)$$

where ASC is the area specific conductance of membrane, which is equal to the multiplicative inverse of ASR, and l is the ion-exchange membrane thickness. It is instructive to note that conductivity and resistivity are intensive properties, i.e., independent of membrane physical dimensions, whereas ASC and ASR are extensive properties. Introducing and ASC enables the relationship between conductivity and permselectivity to be examined in an analytical framework akin to permeability-selectivity of gas separation and salt-rejecting membranes [10, 11].

4. Conclusion

The power of the salinity gradient can be converted directly to electricity using RED technology. This review summarizes the RED system of processes and items used. Innovations in RED stack components and system design are important aspects to improve RED power output performance. To date, several low IEMs adapted to high resistance and high permselectivity have appeared suitable for RED applications.

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