The Role of Membrane, Feed Characteristic and Process Parameters on RED Power Generation

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Abstract. Reverse electrodialysis (RED) is a renewable energy-generating SGE technique using energy from salinity gradients. This research investigates the effect of membrane and feed characteristics on reverse electrodialysis (RED) power generation. Some investigations on the process parameters effect for the complement of the main study were also conducted. The generated power of RED was measured using power density analysis. The experiments were performed using artificial seawater varied from 0 to 1 g/L NaCl for diluted salt water and from 0 to 40 g/L NaCl for concentrated salt water. In a study of ions type, NaCl non-pa is used to represent monovalent ions, and MgSO4 represents divalent ions. The results showed that the highest voltage generation is 2.004 Volts by 14 cells number of the RED membrane utilizing a RED self-made laboratory scale. The power density was enhanced by raising the flow rate (0.10 L/min), concentration difference (40 g/L), and the presence of electrode rinse solution. Further, the ion type (monovalent, divalent, and multivalent) influenced the resulting RED power density, where the divalent ion (MgSO4)’s power density was greater than that of the monovalent ion (NaCl). The resistance and selectivity of the membrane were the major keys for the power generation of RED.

Keywords: Reverse electrodialysis, power density, salinity gradient energy, Gibb free energy

Introduction

Releasing renewable energy for conventional energy will help reduce CO2 emissions (Topal et al. 2014). Salinity gradient energy (SGE) offers enormous potential as a sustainable and environmentally friendly energy source. SGE’s fundamental concept uses Gibbs energy produced by mixing two solutions with a difference in salinity or salt concentration (Simoes et al. 2022). This energy is able to be developed in the area where many meeting estuaries are available. In a theory, mixing 1 m² of river water and 1 m² of seawater will generate a Gibbs energy of 1.4 MJ (Post et al. 2009). However, the total discharge of rivers into seas is used to calculate the theoretical global SGE potential, which is estimated to be between 1.4 and 2.6 TW (Mei and Tang, 2018; Ortiz-Imedio et al., 2019).

Reverse electrodialysis (RED) is a renewable energy-generating SGE technique using energy from salinity gradients. It also involves the use of electrodes for power generation. Handaja et al. (2021) In RED, diluted and concentrated salt water are contacted separately through anion exchange membranes (AEM) and cation exchange membranes (CEM). CEM is a crosslinked polymer layer with negatively charged groups (Yang et al. 2021), while AEMs conduct hydroxide ions but do not conduct electrons (Samsudin et al. 2021). The positive ions diffuse through CEM and give positive potential at the cathode, while the negative ions diffuse through AEM and give negative potential at the anode. The electrode rinse as redox solution is passed in external current (Post et al. 2009).

To support the implementation of RED technology, many studies have been reported in previous publications, including the effects of membrane characteristics (Shadravan et al. 2022, Sun et al. 2022, Yan et al. 2022), process parameters (e.g., feed concentration, flow rate, impurities) and stack design (Veerman et al. 2010, Vermaas et al. 2013, Hong et al. 2013, Veerman 2020) on the resulting RED power density. Veerman et al. (2010) evaluated the effect of electrode type. The result showed that the system with inert electrodes and a NaCl–HCl supporting electrolyte with the reversible Fe3+/Fe2+ redox couple or the [Fe(CN)6]3−/[Fe(CN)6]4− couple achieved the highest rank. Most recently, Veerman (2020) published a model-based investigation of co- and counter-current flow in various multistage configurations with varying electrical controls. Li et al. (2022) have studied the effect of flow rate and feed concentration on voltage output in which the concentrated salt water is constant and diluted salt water is varied. Their experiment resulted in an increase in voltage by increasing flow...
rate and feed concentration. Finally, Veerman et al. (2009b) compared six commercial membranes on thermodynamic efficiency and power density. The result showed that Fumasep (FKD/FAD) membrane and Selenium (AMV/CMV) membrane generated the highest power density, i.e. 1.17 W/m² and 1.18 W/m², respectively.

In sum, many studies have been reported in publications, but since different conditions can be found during real applications, many other aspects need further study. The impact of ion types on the resulting power density is a good example. It should be noted that the characteristics of seawater could be different from one place to another. Sea water contains not only monovalent ions such as Na⁺ and Cl⁻ ions but also contains multivalent ions, including Ca²⁺, Mg²⁺, SO₄²⁻, and many other ions (Naidu et al. 2015). This research aims to study the impact of ions, i.e. monovalent, divalent, and multivalent, on the resulting RED power density. In addition, other experiments to obtain comprehensive discussions, such as the effects of concentration difference and electrode rinse solution, are also investigated.

2. Materials and Methods

2.1 Materials

NaCl (technical grade, 99.25 %) was obtained from Unichem Candi Indonesia Company, and MgSO₄ (99.5 %) was obtained from Merck, Germany. The electrode rinse solutions included NaCl (pro analysis grade ≥ 99.5 %, obtained from Merck, Germany, called NaCl pa), NaCl (technical grade, Refined Salt, 99.25% called NaCl non-pa), Na₂SO₄ (99%), potassium iron(II) hexacyanoferrate (K₃Fe(CN)₆) (≥98.5%) and potassium iron(III) hexacyanoferrate (K₂Fe(CN)₆) (≥99%) were obtained from Sigma-Aldrich, Germany.

The RED stack consisted of AEM and CEM, electrodes, spacers, and gaskets. The commercial ion exchange membranes, SeleniumTM (AMV/CMV, obtained from AGC Engineering Co. Ltd., Japan), were used. In addition, titanium mesh electrode-coated Ru/Ir, Nylon woven, and Silicon were purchased from Magneto Special Anodes B.V. (Netherlands), Sefar AG (Switzerland), and Sikisei Company Ltd. (Indonesia), respectively.

2.2 RED experiment

The method and experimental equipment used have already been described in our previous publication (Susanto et al. 2017). Briefly, a RED self-made laboratory scale, composed of a RED stack, feed tank, pump, flow meters, and potentiostat, was used. First, the RED stack arranged of AEM and CEM, a spacer, and a gasket of 12×12 cm², respectively. Then endplates made of acrylic and electrodes with the size of 12×12 cm² were used to cover the gap. Fig. 1 shows the RED experiment setup.

Three flow configurations were conducted, i.e., (i) the internal circuit is drained salt water in the RED stack without using electrode rinse solution, (ii) the external circuit is drained electrode rinse solution outside of stack RED, (iii) the combination of the internal and external circuit simultaneously. The Natural Organic Matter (NOM) models varied from 0 to 50 mg/L and were added to diluted and concentrated water. In addition, the cell number of the RED unit varied from 4 to 14.

2.3 Power density analysis

A potentiostat measured the resulting voltage and current (EZstat Nuvant Systems Inc.). RED's electrical energy was assessed regarding power density. The energy produced per entire membrane active area is known as the power density. The power density was determined by Eq 1,

\[
P = \frac{V \cdot I}{A}
\]

in which P represents the power density (W.m⁻²), V represents the stack voltage in volt (V), I represents the current in ampere (A), and A represents the total membrane area (m²).

2.4 Gibbs free energy theory

The equation 2 generally gives the membrane potential,

\[
\Delta V = \frac{RT}{zF} \ln \left( \frac{\alpha_c}{\alpha_d} \right)
\]

where \(\Delta V\) represents the membrane potential (volt), R represents the universal gas constant (8.314 J.mol⁻¹.K⁻¹), T for the absolute temperature (K), z for an ion's valence, F for the Faraday constant (96,485 C.mol⁻¹), \(\alpha_c\) is concentrated salt water activity (mol.L⁻¹), and \(\alpha_d\) is the diluted salt water activity (mol.L⁻¹).

The quantity of energy produced by mixing two salt waters can theoretically be determined from Gibbs free energy by Eq 3,

\[
\Delta G_{\text{mix}} = \Delta G_{\text{ib}} - (\Delta G_{\text{c}} + \Delta G_{\text{d}})
\]

\(\Delta G_{\text{mix}}\) can be calculated by Eq. 4,

\[
\Delta G_{\text{mix}} = -nT\Delta S
\]
then $\Delta G_{\text{mix}}$ can be substituted by Eq. 5,
\[
\Delta G_{\text{mix}} = -(n_c + n_d)T\Delta S_{\text{mixb}} - (n_c T\Delta S_{\text{mixc}} - n_d T\Delta S_{\text{mixd}}) \tag{5}
\]
where $\Delta S_{\text{mix}}$ can be calculated by Eq. 6,
\[
\Delta S_{\text{mix}} = -R \sum x_i \ln x_i \tag{6}
\]
where subscript c, d, and b denote concentrated, diluted, and brackish salt water; $n$ represents the number of moles, $[\Delta S]_{\text{mix}}$ represents the mixing entropy molar $$(\text{J.mol}^{-1}.\text{K}^{-1})$$, and $x$ represents component’s mole fraction ($i = \text{Na, Cl, H}_2\text{O}$).

The correlation of cell potential and the resulting Gibbs energy of the electrochemical cell can be seen in Eq. 6. The correlation of concentration and cell potential can be described using the Nerst equation Eqs. (7) to (10).
\[
\Delta G^0 = -nFE^0 \tag{7}
\]
\[
\Delta G = \Delta G^0 + RT \ln Q \tag{8}
\]
\[
-nFE = -nFE^0 + RT \ln Q \tag{9}
\]
\[
E = E^0 - \frac{2.303RT}{nF} \log Q \tag{10}
\]
where $\Delta G$ is the Gibbs free energy, $\Delta G^0$ is the Gibbs free energy at standard condition, $E$ is the cell potential, $E^0$ is cell potential at the standard condition, and $Q$ is the concentration ratio of ion product and reactants.

3. Results and discussion

3.1 The effect of cell number on power generation

Cell number was changed to study power density. The experiments were performed using artificial seawater (30 g/L NaCl) and artificial river water (1 g/L NaCl) as concentrated and diluted salt water. Both solutions were passed into the RED stack’s internal circuit with a flow rate of 0.04 L/min, whereas electrode rinse solution, K$_4$Fe(CN)$_6$ 0.05 M and K$_3$Fe(CN)$_6$ 0.05 M in bulk NaCl 0.5 M, was passed into the external circuit of the RED stack. The results are presented in Fig. 2.

The resulting voltage increased almost linearly with increasing the cell number. The RED generates the largest voltage with the number of cell 14, which corresponds to ~2 volts. This result explains that the large stack reduces loss due to leaking currents. In larger cells, flow pathways are far; thus, residence time in the RED stack is long. Consequently, many ions diffuse through the membrane, increasing the power density. This explanation is similar to a previous finding by Veerman et al. (2009a).

3.2 The effect of feed concentration on power density

This study passed concentrated and diluted salt water into the RED stack's internal circuit at a rate of 0.04 L/min without electrode rinse solution. The concentration of the concentrated feed solution was varied. The results are presented in Fig. 3.

The power density increases with increasing concentration of concentrated feed solution. The largest power density is generated at a concentration difference of 40 g/L. This phenomenon can be attributed to the higher salt concentration enhancing ion transport from concentrated to diluted salt water. This diffusion increases the ionic current, which will be converted into electric current to the electrode. This explanation corresponds to a previous work by Post et al. (2009). According to the Nerst equation (Eq. 1), the salt concentration ratio is directly comparable to the generated voltage and different power density (cf. Eq. 10) (Vermaas et al. 2012). These results are similar to Turek and Bandura (2007), which varied the concentration of the diluted solution and fixed the concentration of the concentrated feed solution.

3.3 The effect of flow rate on power density

In this study, concentrated salt water (20 g/L) and diluted salt water (~0 g/L) was passed into the RED stack's internal circuit with various flow rates of 0.04 to 0.10 L/min without electrode rinse solution. The results are depicted in Fig. 4. The resulting power density increases with increasing flow rate. The largest power density was obtained at the flow rate of 0.10 L/min.
These results are similar to the study by Turek et al. (2008). Furthermore, there were no significant differences in power density when the flow rate was increased by more than 0.1 L/min. Power density as a function of flow rate can be explained from three different aspects. The first one is the velocity of ion transfer towards the electrode rises as the feed flow rate rises, causing a higher power density.

The second one is the increase in feed flow rate decreases the polarization of ion concentration on the membrane surface, leading to higher power density. The third one is the pressure drop rises as the feed flow rate rises, causing a lower power density. The results in Fig. 4 suggest that at low flow rates (here is lower than 0.1 L/min), the first and second aspects are dominant, whereas as the flow rate increase, the pressure drop aspect is getting more significant.

3.4 The effect of electrode rinse solution on power density

In this study, both concentrated salt water (i.e. 30 g/L NaCl) and diluted salt water (1 g/L NaCl) were passed into the internal circuit at the flow rate of 0.04 L/min with and without electrode rinse solution (NaCl 0.05 M) through the external circuit. The results are shown in Fig. 5.

It is seen that the power density obtained by using an external circuit was greater than the power density obtained by using an internal circuit. It can be explained that ionic currents from the internal circuit are transformed into electron currents at the electrode using a redox reaction by electrode rinse solution at the external circuit. Electrode rinse solution works to maintain the neutrality of electrons (Vermaan et al. 2010). Therefore, combining both external and internal circuits resulted in higher power density than external or internal circuits.

Fig. 6 shows the effect of various electrode rinse solutions on power density. Using NaCl (1 M) as a rinse solution demonstrated the highest power density. NaCl pro analysis grade (pa) with the same concentration tended to generate a slightly larger power density than NaCl technical grade (non-pa). The presence of other ions in NaCl technical grade lowered the resulting power density. This result was confirmed by an experiment using Na2SO4 with the same concentration, resulting in a lower power density than NaCl. Using NaCl (pa) as an electrode rinse solution generated a larger power density than Na2SO4. Furthermore, the highest power density was generated using K3Fe(CN)6 0.05 M and K4Fe(CN)6 0.05 M in bulk NaCl 0.5 M as an electrode rinse solution. These findings are consistent with priorly reported results (see Table 1).

The resulting power density from this study was lower than power density reported in previous publications. The possible reasons for this observation are the differences in the stack design and the number of cells used. The correlation between cell potential and Gibbs energy by the electrochemical cell is depicted in Eq. 6. While the correlation of concentration and cell potential can be described using the Nerst equation (Eq. 7 to Eq. 9).

The Nerst equation shows that the higher concentration ratio decreases the cell potential (Eq. 9) and then increase the Gibbs energy (Eq. 6). This explains that electrode rinse solution of 1 M NaCl has highest power density than others. Furthermore, NaCl of technical grade and pro analysis grade influence the resulting power density. Because NaCl of pro analysis grade is more pure than technical grade, thus the power density of NaCl pa is larger than NaCl non-pa.
Redox reactions in various types of electrode rinse solutions

<table>
<thead>
<tr>
<th>Electrode rinse solution</th>
<th>Reaction at Cathode</th>
<th>Reaction at Anode</th>
<th>$E^0$ cell</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$</td>
<td>$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$</td>
<td>0.53 V</td>
<td>Veerman, et al. (2010)</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$</td>
<td>$\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$</td>
<td>0.4 V</td>
<td>Turek and Badura (2007); Turek, et al. (2008)</td>
</tr>
<tr>
<td>K$_2$Fe(CN)$_6$ and K$_2$Fe(CN)$_6$ in bulk NaCl</td>
<td>$\text{Fe(CN)}_6^{3^-} + \text{e}^- \rightarrow \text{Fe(CN)}_6^{2^-}$</td>
<td>$\text{Fe(CN)}_6^{2^-} \rightarrow \text{Fe(CN)}_6^{3^-} + \text{e}^-$</td>
<td>0.72 V</td>
<td>Veerman, et al. (2009a)</td>
</tr>
<tr>
<td>Low grade NaCl</td>
<td>$2\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$</td>
<td>$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$</td>
<td>0.048 V</td>
<td>this study</td>
</tr>
<tr>
<td>K$_2$Fe(CN)$_6$ and K$_2$Fe(CN)$_6$ in bulk NaCl</td>
<td>$\text{Fe(CN)}_6^{2^-} + \text{e}^- \rightarrow \text{Fe(CN)}_6^{3^-}$</td>
<td>$\text{Fe(CN)}_6^{3^-} \rightarrow \text{Fe(CN)}_6^{2^-} + \text{e}^-$</td>
<td>0.048 V</td>
<td>this study</td>
</tr>
</tbody>
</table>

$*: $ low quality consumption salt with NaCl content of 90-94.7%

Fig. 7 The RED membrane's power density varies with the type of ions

It is observed that the divalent ion (MgSO$_4$)’s power density was greater than that of the monovalent ion (NaCl). Furthermore, the power density resulting from the mixture solution of NaCl and MgSO$_4$ was in between NaCl and MgSO$_4$ as a single concentrated solution. The composition of multivalent ions in feed water with a ratio of 16:1 of NaCl and MgSO$_4$, respectively.

It can be explained that multivalent ions may irreversibly shield the membrane charge, lowering membrane permselectivity and increasing membrane resistance (Vermaas et al. 2014). Furthermore, the results are similar to Post et al. (2009), which found that MgSO$_4$ in the feed water lowers the stack voltage while increasing the stack resistance compared to NaCl-only solutions. These statements support the power density theory by Vermaas et al. (2012) that membrane resistance influences power density.

4. Conclusions

RED is an electrical energy generation technology that uses ion exchange through the membrane of meetings with different salinity solutions. SGE’s fundamental concept uses Gibbs energy produced by mixing two solutions with the difference in salinity or salt concentration. The performance of reverse electrodialysis is affected by process parameters such as flow rate, concentration difference, electrode rinse solution, and ions type. The increasing power density shows this effect as the resulting power generation indicator. Increased flow rate, concentration difference, and presence of electrode rinse solution all contribute to an increase in power density. The ions type, i.e. monovalent, divalent, and multivalent, influence RED power density. The results show that the highest voltage generation is 2.004 volts by 14 cells number of the RED membrane utilizing a RED self-made laboratory scale. Membrane characteristics and stack design are important factors that impact the power generation of RED. Commercial membrane type and contaminant type in feed water impact the power generation of RED. The resistance and selectivity membrane are of major importance for RED power generation. Therefore, choosing ion exchange membrane should have these characteristics. Furthermore, the pre-treatment process of feed water before the RED process must be conducted to obtain the desired feed water.

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