Ion Exchange Membranes for Reverse Electrodialysis (RED) Applications - Recent Developments

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1. Introduction

It has a vital importance to use renewable energy today for reducing the fossil energy consumption rate thus air pollution and carbon dioxide emission. In recent years, the development of technologies that generate renewable energy from solar, wind and geothermal sources has attracted considerable attention. In addition to such sources, salinity gradient, a novel form of sustainable energy obtained by combining two different types of water with variable salinities, is considered to have a great potential [1]. The calculated amount of salinity gradient energy is estimated to be in the range of 1.4-2.6 TW [2]. This amount is more than the total global energy needed.

Pressure-retarded osmosis (PRO) and RED are two membrane-based techniques that are capable to convert blue energy into electricity [3]. Due to the increased power density and higher energy recovery, PRO appears to be more suitable for power generation from highly concentrated brines. PRO is based on water transport through semi-permeable membranes, where the driving force to generate energy for PRO is the pressure difference. On the other hand, RED appears to be more favorable for power generation by mixing seawater and river water. RED harvests the change in Gibbs free energy when waters with different salinities are mixed. Another reason of...
choice between RED and PRO in certain situations is that RED is less prone to fouling than PRO because in RED process, only ions move through the hydrophilic membranes in RED while water permeation is the case in PRO when osmotic pressure gradient is utilized [4-7].

The RED system has the similar design of the conventional electrodialysis (ED) system. The only difference is that while the feed solutions with the similar compositions are pumped to each compartment in the ED system, two feed solutions having different salinities are fed to the RED system. The driving force in the ED process is electrical potential, while the salt concentration difference in the RED process to generate electrical power [8].

The essential parts of a laboratory scale RED membrane stack and its view are depicted in Figure 1. The membrane stack consists of a successive arrangement of certain numbers of ion exchange membranes (IEMs), known as cation exchange membranes (CEMs) and anion exchange membranes (AEMs) placed between electrodes, forming cell pairs. The salinity gradient on both sides of a membrane allows ions to pass through in opposite directions as shown in Figure 2. The ionic mobility creates a potential difference in the cell pair. As the number of cell pairs increases, it is possible to create a significant amount of potential difference. This potential difference activates the redox reactions in the electrodes. The redox pairs used in the electrode compartment have an important role in the RED system as they convert the ionic current into the electrical current. The electrode solution is constantly circulated between anode and cathode. By providing an external circuit between anode and cathode, an electrical current is created by the electron transport. This current then generates the electrical power [9,10].

A membrane connects or divides two contiguous stages and let substances between phases be transferred [11]. These boundaries are referred to as ion exchange membranes (IEMs) when they include functional groups. IEMs are classified into two types as CEMs and AEMs.

While cations are allowed to move towards the CEMs, anions cannot pass through the CEMs due to their negative charges. In AEMs, because the fixed charges in the polymer matrix are positive, anions are transported through the AEMs while cations cannot pass through this membrane. This principle was first explained by the Donnan exclusion [1].

In RED stacks, there are some system related limitations. Spacer materials and geometry are important factor for the stacks. Spacers are frequently required to assist IEMs, create flow channels, and facilitate mixing. Increased mixing has been shown to reduce concentration polarization. The thickness of the spacer undeniably influences the electrical resistance of the low salinity compartment, so it has a significant effect on the power output [19]. Dlugolecki et al. [21] studied spacer shadow effect by using commercial Neosepta AMX, Neosepta CMX membranes and spacers with the thicknesses of 0.2 mm and 0.5 mm at different flow rates ranged between 0.06 and 1.1 cm/s. They demonstrated that concentration polarization occurs at low linear flow rates and it may be greatly reduced by raising the solution flow rate and decreasing the spacer thickness. They observed that stack resistance increased when 0.2 mm spacer was used.

In ED and RED applications, each process should have its own optimized cell design. For example, the spacers used in ED units are thicker than the spacers used in RED units to minimize the electrical resistance and increase the power output [8]. Currently, commercial ion exchange membranes have been developed mainly for ED applications. However, ion exchange membranes in the RED system should have some specific properties such as high selective-permeability, low electrical resistance, high mechanical strength, acceptable chemical stability and low cost [11,12]. The existing ion exchange membranes contain a reinforcing filler material to provide mechanical strength and therefore, they are generally thick in ED applications. Thus, the existing ion exchange membranes need to be redesigned for RED applications.

The PEMs contain porous substrate and ion exchange polymer filled in the pores that can exhibit high ionic conductivity and high mechanical strength. Importantly, the strong porous substrate effectively inhibits IEMs from swelling excessively. Additionally, they might be manufactured in a more cost-effective manner, such as a continuous roll-to-roll process [62]. Production of PEMs with a relatively thin (~100 µm) film thickness can be a good alternative for RED systems. These membranes are formed by filling a fine-porous support material within polymer electrolyte structures [13-15]. Thus, the membrane synthesis of a desired thickness is possible by controlling the thickness of the porous support material.

Polymerization-chloromethylation-amination steps are required to prepare the AEMs [16,17]. Chloromethylation reaction is a process that should be avoided during membrane synthesis due to the release of some toxic chemicals. Using polymers that have inherent chloromethyl groups is a good solution to overcome this problem [17]. The best example of such polymers is polyepichlorohydrin polymer, a thermoplastic material that is cheap and easily synthesized [17]. These materials can increase the mechanical strength of the supporting inert polymers when they are added to the membrane structure because they have high elastic properties. It is possible to make a homogeneous mixture using polymers such as polyacrylonitrile dissolved in the same solvent.

Another way to enhance the mechanical strength is to crosslink the polymer chains and provide a reticulated network structure. The use of amine crosslinkers (eg DABCO-1,4-diazobicyclo [2.2.2] octane) provides a significant advantage in the preparation of AEMs in one step to provide both cross-linking and ion exchange characters to the IEMs [1]. It is possible to obtain clear solution when blending inert polymers, such as polyacrylonitrile, to the casting solution resulting in a homogenous mixture for membrane preparation by solvent evaporation.

Images:

- Figure 1. a) Essential parts of laboratory scale RED stack, b) side view of the stack and IEMs.
- Figure 2. Schematic of an RED system.

2. Properties of IEMs

Permeselectivity and electrical resistance of IEMs are two crucial parameters for their performances in the RED system. Changes in these two parameters affect water content, ion exchange capacity, and fixed charge density of IEMs. For the structural stability and ion transport characteristics, water content is of fundamental relevance. There is a relation between the ionic resistance and permeselectivity of AEMs, because polymers having higher degree of swelling have lower ionic resistance and lower...
permeability \([7,18]\). Degree of swelling (DS) can be found using Equation 1 \([7]\):

\[
DS = \frac{m_{\text{swet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100
\]  

(1)

In this equation, \(m_{\text{swet}}\) and \(m_{\text{dry}}\) are the wet and dry weights of the membrane, respectively.

Ion exchange capacity (IEC) represents the amount of the charged groups in the IEMs. It is expressed as the molar equivalents (meq) of charged groups contained in g amount of dry membrane \([7,19]\) and can be calculated by using Equation 2 \([7]\):

\[
IEC = \frac{V_{\text{AgNO}_3}}{w_{\text{dry}}} \times C_{\text{AgNO}_3}
\]  

(2)

in this equation, \(V_{\text{AgNO}_3}\) indicates the volume (mL) of AgNO\(_3\) solution consumed in a titration at the equivalence point, \(w_{\text{dry}}\), dry membrane weight (g), and \(C_{\text{AgNO}_3}\) indicates the concentration (mg/L), of AgNO\(_3\) solution used.

The ion transport of the membranes depends on the swelling degree and the type and amount of charged functional groups attached to polymer backbone. This parameter, defined as the fixed charge density, is preferred to be as high as possible. Fixed charge density \((C_{\text{fg}})\), is expressed as the IEC per unit swelling (mmol constant charge groups per g-membrane), and it is calculated by dividing the IEC by the degree of swelling, which is shown in Equation 3 \([7]\):

\[
c_{\text{fg}} = \frac{IEC}{SD}
\]  

(3)

Permeselectivity and electrical resistance are two crucial features that increase the efficiency of the RED system \([19,20]\). The co-ions should be entirely omitted from the membrane process to achieve a completely permeselective membrane and permeselectivity of ions is related to the Donnan exclusion \([11]\).

Permeselectivity means that IEMs may preferentially carry counter-ions (e.g. CEM cations) and rule out co-ions (e.g. CEM anions). Theoretically, perfect ion exchange membranes have permeselectivity of 1; but in practice, permeselectivity value is less than 1 because transport of co-ions are unavoidable \([19]\). The permeselectivity is commonly determined by dividing the calculated electrical potential difference by the theoretical value that should apply if the membrane is ideal, which is shown in Equation 4 \([19]\):

\[
\text{Permeselectivity} = \frac{E_{\text{meas}}}{E_{\text{Nernst}}} \times 100
\]  

(4)

Membrane resistance can be explained as the impediment of the passage of ionic current through the polymer matrix. If membrane resistance is higher in the RED stack, voltage decreases and power output will be reduced \([21]\). Resistance measurement can be done by direct current (DC) or alternative current (AC) methods. For the DC method, chronopotentiometry is used while electrochemical impedance spectroscopy method is used in the AC method \([18,19]\). IEMs with high IEC and high SD typically have a poor area resistance and limited permeselectivity \([19]\).

Potentiostat device is used for the measurement of power density and open circuit voltage (OCV) values with the method of multiple step chronopotentiometry. OCV can be defined as the potential difference caused by the salinity gradient defined by the Nernst equation which is calculated from Equation 5:

\[
E_{\text{OCV}} = N \frac{2aRT}{zF} \ln\left(\frac{a_+}{a_-}\right)
\]  

(5)

in this equation, \(a\) is the average permeselectivity of a membrane pair (dimensionless), \(N\) is the number of membrane cells (dimensionless), \(R\) is the gas constant \((8.314 \text{ J/mol K})\), \(T\) is the absolute temperature \((K)\), \(z\) is the electrochemical valence, \(F\) is the Faraday constant \((96,485 \text{ C/mol})\), \(a_+\) is the activity of the concentrated salt solution \((\text{mol L}^{-1})\) and \(a_-\) is the activity of the diluted salt solution \((\text{mol L}^{-1})\).

Stack resistance is related with the AEM \((R_{\text{AEM}})\) and CEM \((R_{\text{CEM}})\) resistances and the electrode resistance and the thickness of the membranes and also inversely proportional with the conductivity of the diluted and concentrated salt water compartments (Equation 6):

\[
R_{\text{stack}} = \frac{N}{A} \left( \frac{R_{\text{AEM}} + R_{\text{CEM}} + \frac{d_{\text{mem}}}{k_{\text{A}}}}{R_{\text{ele}} + \frac{d_{\text{mem}}}{k_{\text{C}}}} \right) + R_{\text{el}}
\]  

(6)

Maximum power density is calculated from Equation 7:

\[
P_{\text{max}} = \frac{\left( E_{\text{OCV}} \right)^2}{4R_{\text{stack}}}
\]  

(7)

Accordingly, gross power density is defined as maximum power density per unit area and calculated from Equation 8:

\[
P_{\text{gen}} = \frac{P_{\text{max}}}{2AN}
\]  

(8)

\(A\) is the effective single membrane area \((\text{m}^2)\) and \(N\) is the number of the membrane cells (dimensionless).

Although commercial ion exchange membranes have been used in most of the published research on RED, in recent years, there have been rising publications on tailor-made ion exchange membranes. Gül et al. \([17]\) first reported environmentally friendly tailor-made ion exchange membranes for RED applications using polyethylenimine (PECH) and 1,4-diazabicyclo[2.2.2]octane (DABCO). The thickness of AEMs was around 33 \(\mu\)m with low area resistance \((0.82 \Omega \text{cm}^2)\) and high power density of 1.27 \(\text{W/m}^2\). The CEMs were manufactured from sulfonated polyethylenimine (SPEEK) \([9]\). Lopez et al. \([22]\) prepared both AEMs and CEMs using poly(ethylenimine) and polyvinyl chloride and modified with chemical agents for laboratory-scale RED stack. The properties of their AEMs and the reference AEMs were similar \([17]\). CDMx and consequently permeselectivity were observed to be slightly higher. After modification with polyethylenimine, the membrane properties were observed as similar to the Fujifilm Type 10 commercial membrane \([23]\). In that work, by comparing both synthesized and commercial CEMs, IEC of the membranes was found to be similar, but SD was slightly higher. For the modified CEMs, the IEC, CDfix and perme selectivity values were found to be lower than the commercial Fujifilm Type 10 CEM because commercial membranes were profiled and this profile keep the intermembrane gap in the section of feed \([23,26] - 26\).

In order to improve ion selectivity in IEMs, surface modification technique is used. They are divided into four groups which are highly crosslinked layer, layer by layer (LBL) film, oppositely charged layer, dense and neutral layer. Novel bulk morphology, blending of polymers, organic and inorganic hybrid IEMs and different ion exchange groups can be used to control the ion selectivity \([27]\). Liu et al. \([28]\) prepared surface modified AEMs to have monovalent anion selectivity by infiltration and photo crosslinking technique. Optimum membrane exhibited the highest perme selectivity of 11.21 for achieving monovalent anion selectivity that remains constant and this value is higher than the commercial SelemonVR ASV membrane and the other monovalent anion selective membranes published in the literature. Liu et al. \([29]\) used layer by layer deposition method to acquire monovalent selectivity. In this study, poly electrolyte multilayers added to the commercial AEMs and the perme selectivity value of the optimum membrane was increased from 0.39 to 4.36.

3. Types of IEMs in RED system

The IEMs are the essential parts for the RED system because the membrane properties and production of salinity gradient energy are directly proportional to each other. CEMs and AEMs are used in the RED system. AEMs have positively charged fixed groups, in contrast, CEMs have negatively charged groups \([30]\). Cation and anion exchange groups are shown in Table 1.

In accordance with their manufacturing processes and spatial layout, IEMs can be categorized as homogeneous and heterogeneous \([31]\). Membrane heterogeneity is an important factor for characterization of the ion exchange membranes especially for determining the water uptake (WU). It represents the fraction of empty space in a membrane matrix that is filled with a solution or electrolyte. Heterogeneous IEMs have a greater inter gel phase than homogeneous IEMs as seen in Figure 3. As a result, the perme selectivity of membrane and counter-ion transport number will be reduced. IEC is a parameter that the number of functional sites in a membrane matrix. The concentration of functional sites in the membrane is critical for achieving a higher selectivity. The ratio of IEC to WU will define the effect of Donnan exclusion.

3.1. Nanocomposite IEMs
Nanocomposite IEMs are modified version of conventional polymeric membranes and they are prepared through incorporation of organic and inorganic nanoparticles (NPs) into the polymeric membranes. Nanocomposite membranes are divided into two groups as thin film and mixed matrix (Figure 4). Blending of nanoparticles with polymer solution, in-situ polymerization, melt-mixing, in-situ sol-gel and dipping are the methods available for the incorporation of nanomaterials into ion exchange membranes [33,34]. Among them, the most common technique used in the production of polymeric nanocomposite IEMs is solution blending. In this method, the polymer is first dissolved in a solvent, and then nanoparticles are added into the polymeric solution. Homogeneous distribution of nanoparticles within the polymer is achieved by sonication or mixing. The solvent is then evaporated and the nanoparticles are incorporated in the polymer [33]. It is a simple method and has the advantage of being easily reproducible, so it is suitable for large scale production.

In-situ polymerization method uses monomers instead of polymers, similar to the solution blending method. The melt-mixing process is solvent-free. The in-situ sol-gel technique involves mixing a polymer with a nanoparticle precursor such as tetraethoxysilane for silica (TEOS) and titanium dioxide. Sol-gel is more costly and time-consuming than the solution blending technique, since it includes hydrolysis and polycondensation stages [33]

The described papers present the effect of titania nanoparticles on various filtration mostly. Vatangour et al. [35] produced a TiO2-trapped mixed matrix membrane by blending the nanoparticles with casting solution by phase inversion and the fouling resistance of the membranes were examined. They found that the flux recovery was increased by mixing 4 wt % of TiO2 nanoparticles and at low quantities of TiO2, the relatively small size nanoparticles led to increased reduction of biofouling. In another study, polyethersulfone (PES) / poly (vinyl alcohol) (PVA) / TiO2 composite nanofiltration (NF) membranes were prepared by dipping the membrane into aqueous solutions of TiO2 nanoparticles, and glutaraldehyde (GA) was used as a crosslinker to increase stability and the thermal, chemical and mechanical properties of membranes [36]. Madaeni and Ghaemi [37] investigated the characterization of anti-fouling self-cleaning RO membranes coated with TiO2 particles by the method of dipping in nanoparticle solution. Damodar et al. [38] studied the fouling resistance, antibacterial and photocatalytic properties of polyvinylidene fluoride (PVDF) membranes prepared by adding different amounts of TiO2 particles (0-4% by weight) to the casting solution.

Nanomaterials used in ion exchange membranes are silica, copper, silver, titanium dioxide, iron (II, III) oxide, zinc oxide, zeolite, graphene and carbon nanotube [33]. Silver nanoparticles have antimicrobial properties due to their small size, large surface area and ability to attach to matrices. Various nanoparticles such as zinc, titanium, copper, alginate, gold have been used to provide antimicrobial properties, but silver is the most effective nanoparticle against viruses, bacteria and other eukaryotes [39]. In addition to its antimicrobial properties, an improvement was observed in selective permeability, permeability, ionic conductivity, thermal stability and membrane potential values compared to the unmodified membrane when anion-exchange membranes were coated with silver nanoparticles [33]. Silver nanoparticles are produced either by synthesizing first and then adding it to the casting solution as an organic suspension, or by in situ reductions of ionic silver by the polymer-solvent.

For less porous membranes, the effects of filler addition are more pronounced. This provides an improvement in separation properties with only a small reduction in rejection and a significant reduction in hydraulic resistance [39]. For casting mixtures giving membranes of relatively low porosity, there is macro-void expansion and an increase in surface pore size and density. To control the agglomeration and distribution of nanoparticles, limiting agents and ionic strength control are often used. Many synthetic and natural polymers such as polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), polyacrylates, polyacrylamide, dextrin and casein are used as silver nanoparticle stabilizers [40].

Li et al. [41] prepared PVDF membranes modified with polyacrylic acid (PAA) grafted silver nanoparticles in three steps. Firstly, the membrane was prepared by phase inversion method, in the second stage, polyacrylic acid grafting was carried out by wetting the membrane surface with azo-bis-isobutylxinitril (AIBN) and immersion in acrylic acid solution and the fouling resistance of the membranes was studied. Lee et al. [42] investigated the fouling resistance of thin film polyamide composite membranes on which silver nanoparticles were fixed by polymer blending technique. In another study, silver nanoparticles were added to thin film composite membranes by blending with a polymer casting solution to prevent biological contamination and contamination resistance was investigated [43]. Uz et al. [44] worked on the development of antibacterial polyacrylonitrile membranes trapped with AgCl-TiO2 xerogels. The membrane is produced by the phase inversion, the nanoparticles are added to the membrane by blending with the polymer casting solution and the fouling resistance was examined.

The first study on nanocomposite ion exchange membranes for RED applications was reported on CEMs [45]. In that study, functionalized iron (III) oxide (Fe3O4-SO3-) was taken as inorganic filler. Custom-made nanocomposite membrane was equated with commercial membrane in terms of power generation performance. Tong et al. [46] studied nanocomposite CEMs made of oxidized multi-walled carbon nanotube (o-MWCNT) and they reported that the membrane properties were improved greatly [46].

Table 1

<table>
<thead>
<tr>
<th>Cation exchange groups</th>
<th>Anion exchange groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CF3SO3-H</td>
<td>N(CH3)3OH</td>
</tr>
<tr>
<td>-SO3-H</td>
<td>-N(CH3)2OH(CH3)2OH</td>
</tr>
<tr>
<td>-CF3COOH</td>
<td>-S(CH3)2OH</td>
</tr>
<tr>
<td>-COOH</td>
<td>-P(CH3)3 OH</td>
</tr>
<tr>
<td>-POH2</td>
<td>-NH2</td>
</tr>
<tr>
<td>-Phenolic OH</td>
<td>-NH</td>
</tr>
<tr>
<td>-C(FCF3)2OH</td>
<td>-Amine (NH3)</td>
</tr>
</tbody>
</table>

Fig. 2. Structures of the a) homogeneous and b) heterogenous IEMs. (Adapted from [32]).

Fig. 3. Structures of the a) homogeneous and b) heterogeneous IEMs. (Adapted from [32]).

Fig. 4. Representative structures of a) conventional nanocomposite membranes, b) surface coated membranes.
3.2. Pore filling membranes

Pore filling membranes (PFMs) can be prepared by filling ionomers into a porous polymer substrate. The PFMs synthesized with the addition of ionomer or polyurethane electrolyte can become extremely important in industrial applications of electrochemical energy conversion and storage technologies such as RED [45,51], fuel cells [52-55], and capacitive deionization [56,57].

Haq et al. [56] synthesized PFMs in a porous polyethylene supporting membrane for membrane capacitive deionization and found higher ion exchange capacity (3 meq/g), lower thickness (29 μm) and lower electrical resistance (0.30 Ω·cm²) than commercial Neosepta AEM membrane. Kim et al. [57] effectively developed pore-filled CEMs with enhanced selectivity for multivalent cations and superior electrochemical characteristics for membrane capacitive deionization.

First pore filling IEMs have been proposed by Yamaguchi et al. [58] for a methanol direct fuel cell. The general requirements such as high ionic conductivity and selectivity are essential for fuel cell and RED processes [59]. For this reason, PFMs have also been tested in a RED system. A low level of electrical resistance and a high degree of permselectivity are necessary features for IEMs in RED applications [60] and they are fundamental properties that prevail the efficiency of electrical energy conversion [61]. Good mechanical strength and high ionic conductivity are other important properties for the RED system. As shown in Figure 5, these features are achieved using pore filling IEMs composed of a porous substrate and an electrolyte polymer [61,62].

Over the past decade, some studies have examined the preparation of pore filling IEMs for RED applications and studies on this subject are in progress. The pore filling membrane studies on fuel cells applications in the field of electrochemical energy are more common in the literature. Some studies about PFMs in fuel cells are summarized in Table 2.

As shown in Table 2, for PFMs in the fuel cell applications, some porous substrates involved are PAN, CLPE, PP, PES, PI and PE. The pores are usually generated through the introduction of polymer electrolytes in the porous substrates. The easiest way to accomplish this is to pour the ionomers on the membrane surface. When the volatile solvents are totally vaporized, electrolytes flow into channels and an ion exchange membrane can be formed [69]. For the production of PFMs in fuel cells, different techniques were used. Li et al. [68] used plasma to produce composite membranes and excellent performance values were achieved. Jung et al. [52] prepared solid alkaline fuel cell membranes with the solution casting technique and showed that there was deep confinement of methanol and ammonia permeation during this period. Agarwal et al. [68] used an in-situ photopolymerization technique for preparing pore filling Donnan dialysis membrane to separate Au (III) from electronic waste solutions and 96.3% of the initial amount of Au (III) in the feed solution was removed from it. Wang et al. [64] prepared an environmentally friendly pore filling membrane using an in-situ redox graft polymerization technique and PMAA implanted successfully onto PES membrane. The PFMs are fabricated and characterized for direct methanol fuel cells (DMFC) with photopolymerization technique by Kuzumoto et al. [67] and the power efficiency tests showed that the power density was doubled in comparison with Nafion 112 commercial membrane. Hwang et al. [54] prepared anion exchange PFMs for solid alkaline fuel cells with radio chemical grafting technique and they found that membranes gave a good electrochemical performance with the maximum power and current density values of 127 mW cm⁻² and 174 mA cm⁻². The PFMs to be used in RED applications should have low DS, high IEC and low electrical resistance. Some details about the applications of PFMs in RED tests are explained in Table 3.

Lee et al. [70] prepared the anion conducting PFMs based on quaternized poly(styrene-co-ethylene glycol dimethacrylate) with different monomer: crosslinker weight ratios (1:1; 2:1; 3:1; 4:1; 9:1; 12:1; 16:1). Weight ratio of 4:1 membrane showed the highest maximum power density at 1.5 A m⁻² and highest mechanical strength (125.8 MPa) due to the highest transport number and lowest water content which are close to the commercial AEM properties. In that study, much lower area resistance, higher IEC and DS were obtained in comparison to the commercial Neosepta AEM membrane. Choi et al. [74] studied on preparation of anion exchange PFMs.

Kim et al. [57] fabricated thin film composite pore filling IEMs and evaluated them in the RED system with Nernst Plank analysis and model results were verified by testing 100 cell pairs of the single RED stack on a variety of parameters including voltage, current, and power. The modified Nernst Plank equation was proven to be valid for both commercial membranes and the heterogeneous thin composite PFMs.

Yang et al. [73] prepared pore filling CEMs (PFCEMs) with roll to roll fabrication using porous polyethylene supporter with green fabrication method and applied it in reverse electrodialysis. The IEC, permselectivity, and area resistance of these membranes were 1.80 mequiv g⁻¹, 95.7%, and 0.42 Ω cm², respectively, which are close to those of commercial membranes and they also exhibited higher power density of 1.95 W m⁻² in comparison to commercial membranes (1.46 Wm⁻²). Choi et al. [74] studied on fabrication of thin film PFMs with non-conductive materials and found the highest gross and net power density as 1.39 W m⁻² and 0.90 W m⁻², respectively, with 10 cell pairs.

**Table 2**

<table>
<thead>
<tr>
<th>Porous substrate</th>
<th>Polymer electrolyte</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ether sulfone) (PES)</td>
<td>Poly(methylacrylic acid) (PMAA)</td>
<td>Redox-graft polymerization</td>
<td>[64]</td>
</tr>
<tr>
<td>Crosslinked polyethylene (CLPE)</td>
<td>Amminated Asahi polysulfone (AM-APS) solution</td>
<td>Solution casting</td>
<td>[65]</td>
</tr>
<tr>
<td>Polycryonitrile (PAN)</td>
<td>Poly(ethylene glycol) methacrylate (PEO526OHMA)</td>
<td>Atmospheric dielectric barrier discharge (DBD) plasma grafting</td>
<td>[66]</td>
</tr>
<tr>
<td>Polyimide (PI)</td>
<td>Poly-2-acrylamide-2-methylpropanesulphonic acid (PAMPS) and poly styrene sulphonic acid (PSS)</td>
<td>Photopolymerization</td>
<td>[67]</td>
</tr>
<tr>
<td>Meso-porous polyethylene (PE)</td>
<td>Trimethylamine (TMA)</td>
<td>Radio-chemical grafting</td>
<td>[54]</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>Spacer-(3-acryloxypropyl) trimethoxysilane (APTS), Crosslinker-ethylene Glycoldimethacrylate (EGDMA)</td>
<td>In-situ photo polymerization</td>
<td>[68]</td>
</tr>
</tbody>
</table>
3.3. Antifouling IEMs

Although there are vast potential of energy generation from mixing seawater and river water using RED, one of the crucial restrictions of using RED process is fouling of IEMs causing some reduction in the net power density produced [3]. Membrane fouling is strongly affected by the source and type of feed solution due to different contaminants available. One of the difficulties associated with operating RED is fouling. Major types of pollutants are colloidal (clays, flocs), organic (oils, poly electrolytes, humic acids), scaling (mineral precipitates) and biological (bacteria, fungi) and multivalent ions (such as Mg2+). Scaling is more prone to occur with CEMs in RED system depending on the morphological and electrochemical properties. It has been demonstrated that novel membranes and specialized spacers are effective in limiting scaling [83]. Fouling is another issue that significantly reduces the power density (greater than 50%). Organic fouling depends on the amount of the total organic components in high salinity and low salinity compartments of the RED system. The chemical stability and structural deterioration of IEMs should be analyzed for determining the effect of organic fouling [83].

Fouling reduces process efficiency and raises process cost. It is reported that the anti-organic fouling properties of the aliphatic anion exchange membranes are better than those of aromatic AEMs. Inorganic scaling takes place when salts in the water precipitate and accumulate on the membrane surface. The major scaling ions are calcium, magnesium, barium, sulphate and bicarbonate [75].

Flow channels and spacers clogging occur because of biofouling. This is a principal threat for this system due to the extra cost and increased energy losses for pumping [3]. Organic and biofouling are the main problems affecting AEMs in the ED system [48,76]. Scaling due to inorganic ions (Ca2+, Mg2+) is common in CEMs [7,72]. Periodic (back) washing techniques were used to prevent and control fouling in RED systems [74]. Solutions for membrane fouling are pre-treatment, operation optimization and chemical cleaning. On the other hand, these solutions may cause some difficulties. These are listed below [78]:

- Ineffective pre-treatment can lead to high rates of contamination.
- No comprehensive consideration on the mechanics of nucleation and scaling.
- Fouling may result in morphological deterioration to the membrane.

Constant loads on the membrane surface affect the type and rate of fouling [19]. It is stated that fouling of AEMs by organic matter (humic acids) is a possible cause that lowers RED performance. Aromatic AEMs have low permselectivity values while only resistance increase was observed with aliphatic AEMs having medium swelling degree. On the other hand, aliphatic AEMs with large swelling degree displayed permselectivity decrease. As a result, fouling of AEMs causes a certain decrease in OCV values and RED performances [79].

The pressure drop will increase with colloidal and biofouling and hence the net power density will decrease [7]. For the practical implementation of RED, one of the most significant challenges is pollution. Fouling enhances resistance and reduces permselectivity. Therefore it can reduce power density by 60%. It is stated that spacers are also important factor in membrane fouling and when compared to membranes they are more sensitive to biofouling [19].

Fouling is more prevalent in AEMs because of our interaction between their negatively and positively charged groups. To control fouling, highly selective AEMs can be developed without increasing the membrane electro-resistance. For this, different surface modification techniques can be applied. These modification techniques can be classified as graft polymerization, dip coating/immersion, electrodeposition, layer by layer deposition, plasma treatments, solution casting [80].

Humic acid adsorption, electrochemical impedance spectroscopy (EIS) and fluorescence spectroscopy methods are used for fouling resistance measurement in the RED system. To determine the humic acid sorption of different AEMs, they were left in the humic acid solutions and the absorbed humic acid ratios were measured with uv-vis spectrophotometer. The power density, membrane area resistance, and permselectivity values of the membrane were determined [79]. Pintonesi et al. [81] used EIS as a new approach to observe cleaning and fouling in the RED system. To improve fouling and cleaning monitoring, some experiments were performed with sodium dodecyl benzene sulphonate (SDBS), while at the same time EIS was measured at the RED stack level. The pollution property of the RED system caused by the dissolved organic substances in seawater and river water was determined by the fluorescence spectroscopy method. The color changes of AEMs and spacers in contact with river water were more greater than those in contact with seawater [82].

4. Conclusions

Salinity gradient energy (i.e. blue energy) can be directly transformed to electrical power using RED technology. The properties of the ion exchange membranes significantly affect the overall RED performances, particularly power density. Many works have concentrated on customizing the properties of IEMs in recent years to ensure low resistance and high permselectivity. Recently, nanocomposite IEMs and pore-filling IEMs attract the interests of membrane researchers greatly. In addition, preparing antifouling IEMs for RED applications is highly important because fouling increases the membrane resistance and decreases the permselectivity. Although recent advancements of the preparations of the ion exchange membranes and performances were proven at laboratory scale, further pilot-scale investigations are necessary to validate the performances of novel tailored-made IEMs in RED applications.

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