Review Paper

Modification of Polymeric Membrane for Energy Generation through Salinity Gradient: A Short Review

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Graphical abstract

Highlights

• The overview of salinity gradient energy is provided
• The modifications of polymer membranes used for salinity gradient energy generation is reviewed
• Membrane modifications overcome the limitations of conventional polymeric membranes

Abstract

Salinity gradient energy (SGE) refers to the energy created from the difference in salt concentration between two streams. There are three types of SGE namely, pressure retarded osmosis (PRO), reverse electrodialysis (RED), and capacitive mixing (CapMix). All these technologies require membrane for the system to be operational. In this short review, the membranes modifications for each principle and its strategies in improving the performance of their membranes are presented. The technological progress of SGE is currently constrained by its ability in generating low power density. Thus, further modifications on every aspect of the systems is needed to overcome this bottleneck. This review focuses on the modifications of polymer-based membranes for salinity gradient energy generation. Finally, some challenges and future perspective of SGE development are discussed.
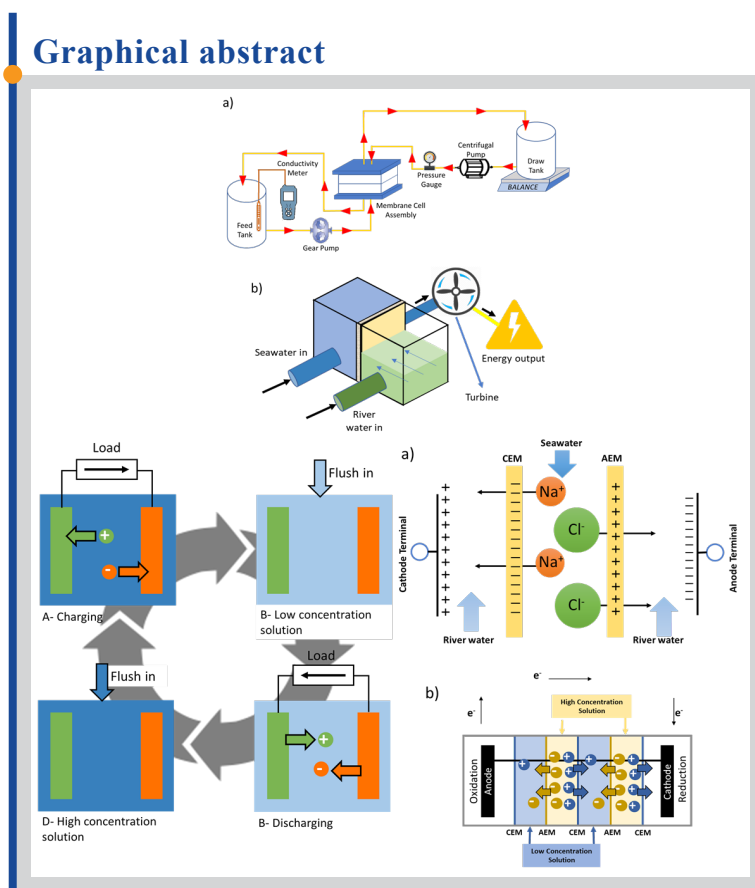
Contents

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1. Introduction to renewable energy

Energy is defined by power that derived from the exploitation of chemical or physical resources to supply heat and give light or to work machine. This crucial aspect of every life on earth are derived mostly from fossil fuel as such petroleum and coals [1]. With the rapid development in industrialization and the increasing world population, global energy consumption of coal, petroleum and natural gas has increased by 27% to 71% from 1980 to 2001 [1]. This current situation of increasing energy consumption will undoubtedly lead to the exhaustion of fossil fuel resources. It is predicted that by 2042, coals is the only remaining of fossil fuel available, and it can only sustain until 2112 [2]. Although the reserve of fossil fuel is in no danger in foreseeable future, but the combustion of these fuel will lead to the increasing greenhouse gasses in atmosphere. In year 2009, it is reported that 5 billion metric tons of carbon equivalent was released from the consumption and burning of fossil fuel globally. This amount will continue to increase to 6.6 billion metric tons and release more greenhouse gas which directly contributes to global climate changes [1].

Renewable energy is a key component in reducing the global climate changes and increasing resilience toward the dependency on fossil energy. According to International Renewable Energy Agency (IRENA), renewable energy can be divided into six major groups which are bioenergy, geothermal, hydropower, ocean, solar, and wind [3][4]. In the matter of fact, by using salinity gradient as one of the energy source, roughly about 2 terawatts available globally of which possibly 980 GW of energy can be harnessed if all river water discharge into the sea are systematically utilized and this equivalent to the supply of 80% of global electricity demand for 2018 [5][6]. Previous research stated that around 0.8 kilowatts per cubic metre power can be generated from salinity gradient which is equivalent to the energy generated from free water falling from 280 metres high [7,8]. By continuing research and development of salinity gradient as an alternative for energy generation, it is believed that reliability on fossil fuel will decline and delay the effect of climate change. An utmost advantage of salinity gradient energy as the process and their system is not depending on the periodic climate changes like solar-based and wind technologies which make them viable and feasible whenever the process is operated as long as the location of the plant is situated between river and the sea. This salinity gradient energy can be further divided into three different types of processes namely pressure retarded osmosis (PRO), reverse electrodialysis (RED), and capacitive mixing (CAPMIX) which will be further discussed in this paper. The modifications of polymeric membranes to further enhance the efficiency of these technologies will be presented. Currently CAPMIX is still in the research and development stage while both PRO and RED are close to commercialization, but all these three applications still facing same limitations associated to the cost and membrane fouling.

The major difference between these three applications is the process itself and how they generate energy from salinity gradient. PRO allows water transport from feed solution to draw solution to produce pressurized water which will be channelled to mechanical turbine to generate electricity. In contrast, RED allows ions transport, but not water through several sets of membrane consisting of cation exchange membrane (CEM) and anion exchange membrane (AEM) and the flow of ions is captured in this process to generate electricity. As for CAPMIX, the generation of electricity is based on the series of charging (using salt water) and discharging (using freshwater) of electrodes which may and may not involve membranes [9-11]. In fabricating CAPMIX, the three main devices are (1) capacitive double layer expansion (CDLE), (2) capacitive energy extraction based on the Donnan potential (CDP), (3) and mixing entropy battery (MEB) [11]. Table 1 below shows the summary of the three applications and its key components.

In this short review, we discuss the current trends in polymeric membrane modifications for energy generation through salinity gradient, i.e. through PRO, RED and CAPMIX. Firstly, the types of salinity gradient power are briefly presented. In the following section, the strategies used for

membrane modification are reviewed. The modifications and development of membrane is important to be discussed since membrane is the heart of the processes so it is essential to have membrane which can sustain for long operation with less maintenance. Some important criteria such as antifouling and high flux properties are discussed in detail. Finally, the review is wrapped up with challenges and future perspective in this field.

Table 1
Different process and concept of salinity gradient energy harvesting.

Process / Concept		Approaches	Key Components	Ref.
PRO		Water transport from feed to draw solution	Pressurized water & mechanical turbine	[8,13]
RED		Ions transport capture	CEM & AEM	[5]
CAPMIX				
-	CDLE		Porous carbon electrodes	[13]
-	CDP	Charging and discharging of electrodes	Porous carbon electrodes & Ion-exchange membranes	[14]
-	MEB		Battery electrode	[15]

2. Types of salinity gradient power

As mentioned above, salinity gradient power can be further divided to PRO, RED, and CAPMIX and each of these methods is based on different principle to generate electricity from salinity gradient. But the same parameter is used to measure the efficiency of the system which is the power density. Power density is defined by 1-watt energy produce by 1 meter squared of membrane area.

2.1. PRO for power production

PRO is one of the ways to generate electrical power based on the difference in osmotic pressure from two different solutions. The fresh river water and seawater have a significant difference in salinity gradient to result in high osmotic pressure difference. The natural osmotic phenomenon take place when two different solutions with independent salinity concentration are put in two different containers that are separated by a semi-permeable membrane. Water transport from freshwater part to seawater will pressurize the seawater container, and this pressure drives the turbine to produce electricity. Over the last decade, PRO has become a main topic of discussion for energy harvesting from salinity gradient and considerable research has been done to improve its efficiency for energy generation. PRO has been outstandingly evolved since 1973 due to the fast development of membrane technology. By this energy conversion, the first pilot PRO prototype plant system was developed in Norway by Statkraft in late 2009 by using combination of river and sea water as feed and draw solution [16]. The PRO pilot-scale plant generated electricity up to 10kW based on 1W/m^2 power density and it has been operated by SINTEF Energy Research [18,19]. In this plant, two different chambers separated by PRO membrane were used to store freshwater and seawater side by side. The water transport from freshwater chamber to seawater chamber passes through PRO membrane from substrate

layer to the selective layer and this process also known as osmosis. The pressure generated in seawater chamber was used to push the turbine for electricity generation [18]. This energy can be quantified as by visualising that every river ends at its mouth by a waterfall at 225 m high, the height of seawater column can develop 22.4 atm of pressure and this can be used to drive the turbine for electrical energy generation [18]. Despite the attractive demonstration, the pilot plant has been shut down due to the economic concerns of PRO technology. In lab-scale, during PRO operation the power generated cannot be measured as there is no turbine in lab setup. The power density can be used to evaluate the performance of PRO membranes. Figure 1 below shows the difference in lab-scale PRO test system and the pilot plant of PRO. Bijmans et al. mentioned that, in order to make PRO energy generation become commercially attractive, the power density of 5 W/m² need to be achieved however the commercial membrane during that time managed to achieved 3 W/m² of power density [19].

Some advantages of PRO include its no downtime operation, not affected by the source of renewable energy such as solar radiation and wind, easy to scale-up, and small footprint. But the performance of PRO is very depending to a several factor which are the cleanliness of both feed and draw solutions, difference of salinity gradient of both solutions, volume of feed water supply, and the membrane itself [20]. The cleanliness of seawater and freshwater for PRO operation is vital to reduce the fouling problem on the PRO membranes so that the membrane performance will not be degraded. During the operation, the support layer of the membrane is facing river freshwater, it is more important to have clean river water to be used in PRO to minimize the occurrence of membrane fouling [21]. The volume of feed water supply in PRO plays a big role in determining the operation of PRO plant. If the rainfall catchment areas did not receive any rain for a long period of time, it will affect the river water flows hence the operation of PRO plant will be affected due to low feed water supply. As the membrane plays the most important role in determining the PRO performance, the membrane modification related to

PRO operation will be discussed further in the subsequent session.

2.2. Production of electricity using RED

Unlike PRO which allows water transport from freshwater to seawater region, RED allows ion transport across ion exchange membranes (IEM) to the electrodes to produce electricity. In RED, several stacks of IEM consist of anion exchange membrane (AEM) and cation exchange membrane (CEM) are placed alternately between two electrodes. As the common practice of RED energy generation is by using river and seawater, Kim et al. developed energy generation from the principle of RED by using wastewater stream. Other application from RED is such energy storage as for example acid-based batteries [22]. The alternate stacking of AEMs and CEMs create a narrow compartment enough for several sets of two different salinity solutions to flow next to each other. The higher salinity solution and lower salinity solution are fed between the stacks alternately. This creates ionic diffusion in water and allows the ions transport through the IEMs where the passage of anions through AEMs and the passage of cations through CEMs. The ions discrimination by AEMs and CEMs results in electrochemical potential difference that will further moves the anions toward the anode and the cations toward the cathode. On the surface of anodes and cathodes, these anions and cations respectively convert to electron current via oxidation-reduction reactions. This conversion results in the electron travel to cathode from anode via an external electrical circuit thus will create electrical current for consumption [23]. Figure 2-a shows the schematic set up of RED with a single pair of IEMs as an example. The anions flow through positively charge AEM towards anode terminal and cations will flow through negatively charge CEM towards cathode terminal. Figure 2-b shows how the AEMs and CEMs are placed alternately and the oxidation at anode results in electron flowing to cathode resulting in reduction reaction.
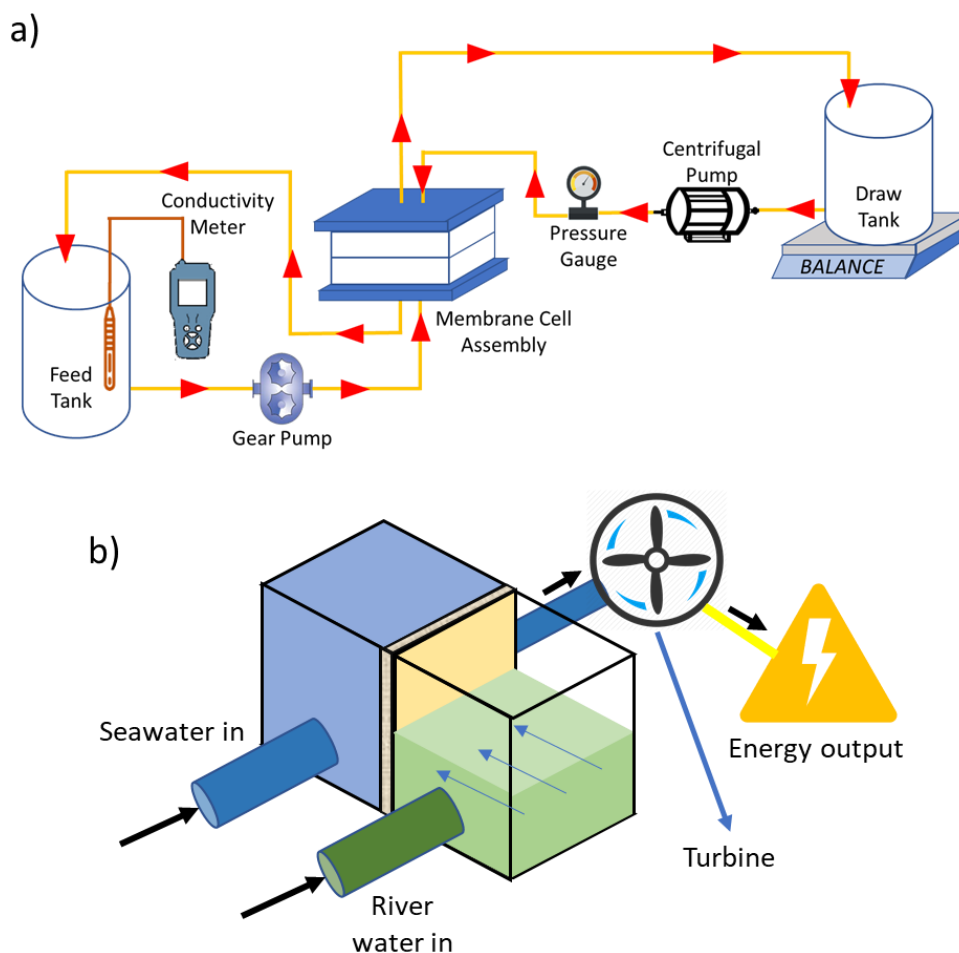

Fig. 1. a) Lab-scale setup for PRO operation. Weighting balance is used to measure the change of mass in feed tank to calculate power density, b) PRO pilot-plant setup, turbine is used to generate, and measure electricity generated. Adapted from [16].

The RED principle was first introduced by Pattle and the system achieved 0.05 W/m^2 of power density from 47 pairs of IEM in a single module [24]. Many researches have been conducted in term of module design and membrane fabrication to optimize the power density from RED. Veerman et al. has conducted a study on designing RED cell operation by stacking 25 pairs of cells on the mixing of the river and sea water. The maximum power density achieved from this design was 0.93 W/m^2 [25]. Pawlowski et al. has designed the chevron profile membrane in RED module and it shows significant improve in power density from 0.4 W/m^2 to 0.5 W/m^2 [26]. Further study on designing membrane electrode assembly has been done at Ajou University, South Korea. The maximum achievable power density from this design was 4.1 W/m^2 [27]. Figure 3 shows the schematic diagram of membrane electrode assembly. All the IEMs are sandwiched with the anode and cathode to reduce the electrical resistance hence increasing its power density.

2.3. CAPMIX energy extraction

CAPMIX is generally used to describe a few electrode-based technologies which currently being developed to generate electrical energy through salinity gradient. The CAPMIX technology was inspired by batteries mechanism and superconductor. Unlike battery which requires external electrical energy to charge, CAPMIX uses renewable energy in the form of salinity gradient to charge. CAPMIX process is a continuous cycle of charging and discharging pair of electrodes in generating electrical energy. The electrodes in this system are alternately exposed to two different solutions, such as seawater and freshwater, which have an enormous difference in their salinity. The pair solutions can also be created by using thermolytic salts and waste heat from industrial process in which

conventional technologies like distillation. This new CAPMIX technology has been introduced by various researchers and still in the development process to achieve the highest power density as possible to make this technology feasible [14,15,20,29-31,32]. As mentioned in the introduction, there are three different approaches in creating CAPMIX which are capacitive double layer expansion (CDLE), capacitive energy extraction based on the Donnan potential (CDP), and mixing entropy battery (MEB). All the approaches mentioned are differentiated based on how the charging are and discharging of electrodes happen. In PRO and RED, the power density is measured by 1-watt energy generated by 1 meter squared of effective membrane area. But in CAPMIX, power density is measured by 1-watt energy generated by 1 meter squared of effective area of electrodes.

2.3.1. Capacitive double layer expansion (CDLE)

The key component of CDLE is the porous electrodes to allow the ion transport in charging and discharging process. When the CAPMIX is flushed with seawater, the external charges are used to drive external charges from seawater to the electrodes. After the circuit is opened, seawater is drained, and freshwater will be flushed to the system. After the circuit is close back, more energy is generated than invested from the discharging of the electrodes. The net energy output is the product of CDLP CAPMIX. Figure 4 shows the cycle of CDLP of CAPMIX. At A, high salinity solution is flushed into the system and external electrical charge used to attract the opposite ion to layer of expansion on the electrodes. At B, seawater is drained, and low concentration solution is flushed into the system and at C, when circuit is closed, discharging of electrodes occur and produces more electricity. At D, the system will be flushed again with seawater after the drainage of low concentration of solution and the cycle continue [30].
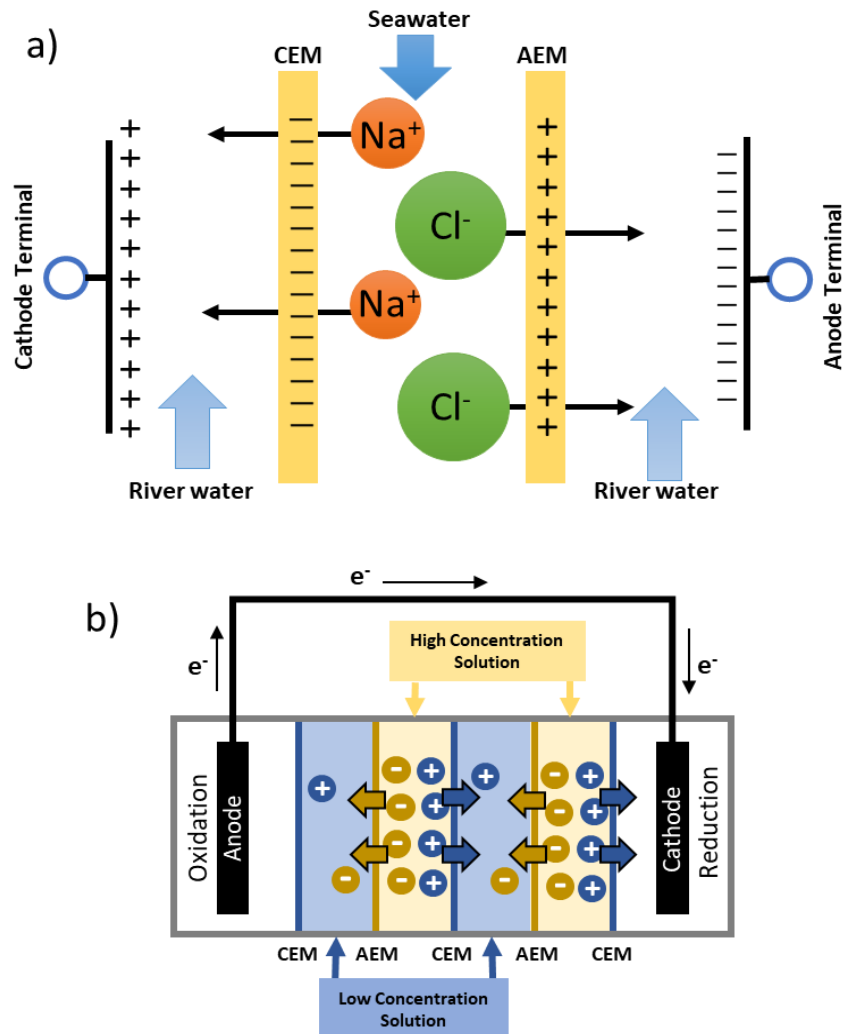

Fig. 2. a) Schematic of a single pair of IEM in RED, b) Schematic of a RED stack and electrodes. Adapted from [23].

2.3.2. Capacitive energy extraction based on the Donnan potential (CDP)

As the CDLE requires external energy to charge the electrodes during the flushing with high concentration solution, CDP uses IEM to charge the electrodes during first cycle of flushing with high concentration solution. The AEM and CEM are placed on top of the anode and cathode respectively, and this will create a potential charge to attract the anions and cations to its respective membranes and electrodes. The membranes and electrodes are charged at high concentration solution while it discharged at lower concentration solution. Both CDLE and CDP requires and very dependent to substance or material that will build up the charge in the electrode for CDLE and on the membranes for CDP [9]. Along with the process of both approaches in CAPMIX in generating energy, no chemical reaction involved during the process. To maximize the energy output through CDP approach, force CDP technique is used. While the electrodes are covered with AEM and CEM, external charge is applied to the electrode to drive more ions to attract to the membranes. During the discharge process with low concentration solution, more voltage is produced. Figure 5a shows the force CDP take place in 2nd cycle. Figure 5b shows the voltage profile graph, voltage versus charge. With force CDP take place in process, higher net voltage can be achieved with smaller external charges needed [10].
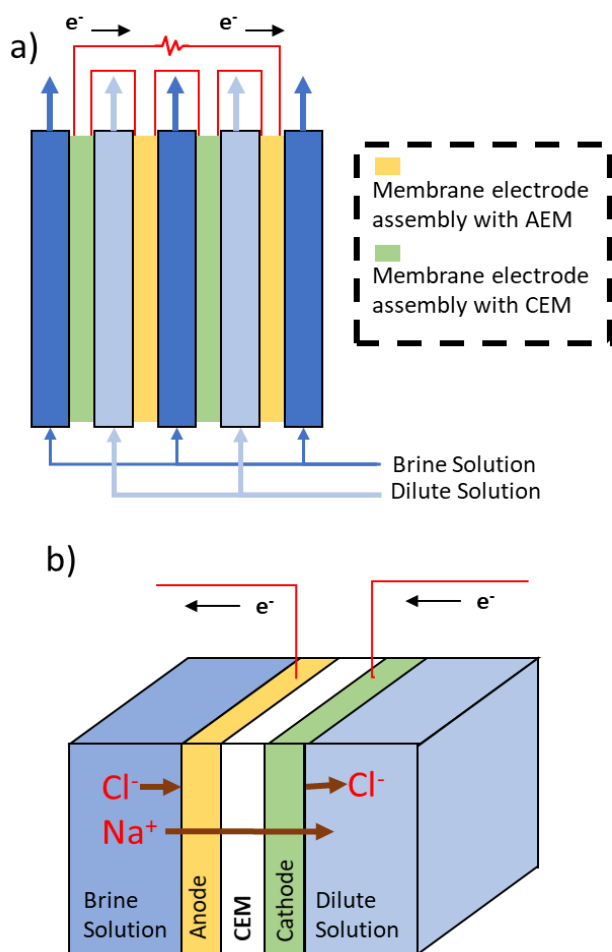

Fig. 3. a) Schematic diagram on RED stacking with no electrodes at both sides. b) Schematic of porous electrode assembly cation exchange membrane. Adapted from [27].

2.3.3. Mixing entropy battery (MEB)

In this MEB approach of CAPMIX technology, it still uses the same 4 step cycle in generating electricity. But the difference here is the system is in charging state when low concentration of solution is used and will be in discharging state when high concentration of solution is used. Thus making the voltage is higher when discharge in high concentration of solution, and the

voltage use to charge in low concentration of water is lower [31]. This MEB approach earlier has been proposed by Mantia et al. by introducing $Na_{2-x}Mn_5O_{10}$ nano electrode to capture sodium ions and Ag electrode to capture chlorine ions [15]. It is reported that by using 0.03M and 1.5M solutions for charging and discharging process, highest power density achieved during 100 stable cycle is 13.8 $\mu W/m^2$ [15]. Marino et al. also reported that by using sodium-ion batteries made of $Na_{0.44}MnO_2$ paired with Ag electrode give maximum power density of 15 mW/m^2 while having 20 and 500 mM of NaCl as pair solution [32].

3. Membranes modification for PRO

In the early development of PRO system, RO membrane has been commonly used due to its durability in sustaining high pressure during the operation. However, the usage of RO membrane in PRO process possesses several limitations such as low water flux and fouling. It is essential to have PRO membrane to deliver high water flux for higher power density, and good anti-fouling performance to extend the PRO membrane lifetime from being replaced from time to time due to performance declination. Thus, in past decades, researchers have studied, developed, and fabricate PRO membrane that can give high water flux, can sustain high operating pressure, and have good anti-fouling properties. Liu et al. had introduced the silver nanoparticles (AgNP) in the membrane substrate by using one-step phase inversion technique [21]. AgNP is one of the nanoparticles biocides that attract many researchers for its effectiveness against various aquatic microorganism including algae, fungi, bacteria, etc [35-37]. Before the development of PRO membrane with AgNP incorporation, it have been incorporated into nanocomposite microfiltration membranes, ultra-filtration membranes, nanofiltration membranes, and reverse osmosis membranes [38-41]. In this representative example, the polyacrylonitrile (PAN) polymer with molecular weight of 150 000, lithium chloride, and *N,N*- dimethylformamide (DMF) solvent were used. The loading of AgNP incorporated in the substrate was varied from 0.00 wt% to 0.1 wt%. Layer-by-layer assembly was performed after treating membrane with 1.5M NaOH solutions by using positively charged of 1g/L poly(allylamine hydrochloride) and negatively charged of 1g/L poly(sodium 4-styrene-sulfonate). The crosslinking process was accomplished by immersing membrane in 0.1 wt% of glutaraldehyde. Other procedures of layer-by-layer assembly and crosslinking have been reported by other researchers [42-45]. In determining the membrane hydrophilicity, contact angle test has been conducted. PAN substrate with 0.0 wt% of AgNP loadings, have 60.6 ± 2.3° of contact angle and decreased to ~43° when AgNP loadings increased to 0.02 wt% [21]. In term of water flux performance, the membranes were tested in RO mode where the membrane with 0.02 wt% of AgNP loadings gives the highest flux with 24% enhanced permeability.
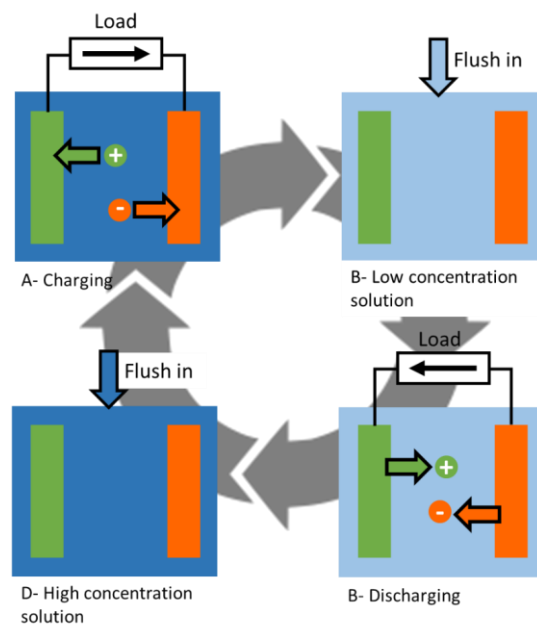

Fig. 4. Schematic of the cycle of CDLP approach in CAPMIX. Adapted from [30].
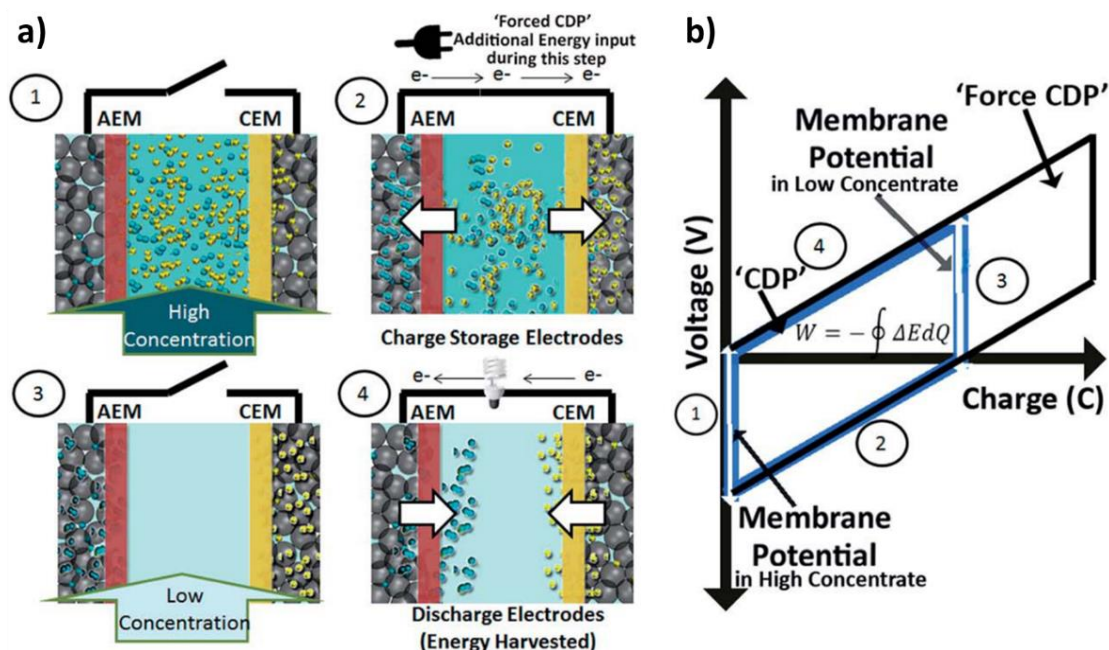
Fig. 5. a) Additional charge is needed in force CDP, very much the same as CDLE but with membranes, b) voltage profiles during the cycle [10].

On the other hand, TiO$_2$ nanoparticle (TNPs) has been introduced in modifying PRO membrane. It has been reported that by introducing TiO$_2$ into the membrane, the surface hydrophilicity can be increased and consequently the permeate flux in FO and RO processes can be improved [46,47]. Kim et al. have developed novel TiO$_2$ coated membrane for PRO [41]. In this study, support layer of commercial membrane was used and the TNPs has been introduced to the membrane via sol-gel derived spray coating method. The loading of TNPs was varied in this study which TNP1.0 (1.0 mL of TiO$_2$ solution) and further discussion on TiO$_2$ solution preparation can be found elsewhere [41]. All the tests in this study were conducted in cross flow PRO mode where the active layer of the PRO membrane facing draw solution. In determining the hydrophilicity of the membrane, contact angle and zeta potential test has been conducted. The TNP1.0 showed the lowest water contact angle value of 16.4° while TNP0.1 and TNP0.5 showed the water contact angle of 27.4° and 16.6° respectively. These values showed significant improvement in hydrophilicity compared to commercial TFC. Zeta potential test showed the decreasing value of negative charge of the membrane as the loading of TNP increased. The surface charge of TNP1.0 and TFC was -41.9 mV and -9.3 mV, respectively. The membrane performance test was conducted in lab-scale crossflow osmotically driven membrane system. TNP1.0 achieved 26.4 LMH water flux which equivalent to enhancement of 25% of water flux and 50% decrease in reverse salt flux. While in the presence of humic acid foulants, normalized flux (J/J$_o$) of TNP1.0 decreased to 0.76 while J/J$_o$ of commercial TFC dropped to 0.44, which showed that TNP membrane exhibited 32% less flux reduction compared to the commercial TFC [41]. However, this study also does not conduct any membrane performance test under PRO system. Thus, the value of power density cannot be obtained.

While most PRO membranes have a finger like porous structure, M. Tian et al. fabricated a high performance of novel thin-film nanocomposite PRO membrane with tiered nanofiber support [42]. Polyetherimide (PEI) polymer and NMP/DMF solvent were used in making this support. The PEI nanofibrous support reinforced by functionalized multi-walled carbon nanotubes (f-CNTs) with carboxyl group of HNO$_3$ under reflux at 150°C for 6h. In this study, dual layer of membrane support has been prepared where the thicker part assigned as bottom, and the thin part assigned as top. Polyamide selective layer was also fabricated on top of the support by using TMC and MPD. Substrates where fabricated by varying the dope condition into three; T1) both top and bottom layer of this membrane support does not incorporated with f-CNTs; T2) only bottom layer of the membrane support was incorporated with f-CNTs; T3) both top and bottom layer of the membrane support were incorporated with f-CNTs. Figure 6 showed the cross-sectional structure of the support layer with tiered structure. The hydrophilicity was improved when PA layer was formed on top of the membrane. Post-treatment by a bench-top heat-press was performed to strengthen the bonding of the nanofiber layers. By adding f-CNTs in the PEI substrate, the mechanical strength of the membrane increases with exceptional value of tensile modulus and yield strength compare to neat PEI substrate. As for the results, the highest power density recorded on PRO membrane performance test was T3. Membrane T3 can reach up to 17.3 W/m^2 power density at 16.9 bar operating pressure by using 1.0M of NaCl as draw solution while DI water as its feed pair. It is also recorded that the burst pressure of T3 membrane was the highest among three membranes.

In recent years, researchers have shown interest in developing polymeric membrane with the incorporation of zwitterionic polymer. The key components that make zwitterionic polymer as a new material to be incorporated in separation membranes are the ability to improve hydrophilicity of the membrane itself and having excellent antifouling properties. It also has been reported that by using zwitterionic poly(arylene ether sulfone) incorporated with poly(vinylidene fluoride) (PVDF) give excellent antifouling properties and good thermostability [43]. Zwitterion or which can be known as dipolar ion is a molecule that have two or more functional groups, in which one has a positive electrical charge and the another one has the negative electrical charges such that the net electrical charge of the entire molecule is zero [44]. The incorporation of zwitterion and the membrane can be done via phase inversion, interfacial polymerization or spray grafting method. Zhu et al. blended zwitterion with PVDF to create a membrane via phase inversion method for oil in water emulsion separation [45]. It was reported that the zwitterion cross-linked membrane has nearly 91% of permeate recovery. On the other hand, nanofiltration membrane zwitterion polyamide was form via interfacial polymerization of 3, 3′-diamino-N-methyldipropylamine (DNMA) zwitterion and trimesoyl chloride (TMC) [44].

In PRO application, Cai et al. have introduced grafting method of zwitterion polymer on PES hollow fiber membrane [46]. Based on the normalized water flux chart, after backwashing the membrane for 30 minutes, the performance of the PRO membrane after backwash was recovered to almost the same as its initial state. This indicated that the antifouling behaviour of the modified membrane is excellent. Zhao et al. have developed a zwitterions coated hollow fiber membranes in which not only enhanced its antifouling properties but also gives high power density for energy generation [47]. In this study, the TFC-PES hollow fibre substrate was used as control and modification have been made coating the TFC-PES hollow fibre substrate with polydopamine (PDA) and further grafted with 2-methacryloyloxyethyl phosphoryl choline (MPC). The TFC-PES-PDA-MPC membrane shows significant improvement in power density than control TFC-PES from 6.0 W/m^2 to 7.7 6.0 W/m^2 [47]. A study on controlling the water permeability and selectivity via active layer modification has been conducted [48]. Yip et al. has carefully tailored the active layer of TFC-PSF membrane by exposing the PA active layer to chlorine for structure and morphology alteration. It is

reported that if membrane with high selectivity used in PRO, it will result in lower water permeability thus give lower power density. When the selectivity of the membrane was lowered by exposing PA layer with higher concentration of chlorine and with longer time exposure, it resulted in higher power density due to higher water flux achieved during PRO process. Balanced selectivity and permeability resulted in the highest power density output of 10.2 W/m^2 [48]. Other study reported by Wan et al. demonstrated that the highest ever power density of 38 W/m^2 could be achieved by adding CaCl$_2$ inorganic salt additives in the substrate. The purpose of this study was to increase its mechanical strength and to reduce mean pore size and narrow pore size distribution of PES hollow fibre substrate [49]. In short many strategies and modifications on the polymeric membrane have been made throughout the development of PRO for energy generation and has been summarize in Table 2 along with their performance.

4. Membranes modification for RED

Throughout the RED development, membrane plays a big role in determining the efficiency of RED system. As discussed earlier, IEM consist of two other membrane which are AEM and CEM. The modifications of both AEM and CEM will play significant role in producing energy. As the higher ion transport results in higher power output, the IEMs' role in transporting ions need to be enhanced. Both AEM and CEM are discussed separately due to different charged introduced to membranes. In these modifications,

researchers used different materials to enhance the positive and negative charges to AEM and CEM respectively. Different techniques in introducing those charges on IEM were also discussed.

4.1. AEM modification

According to Guler et al., between AEM and CEM, the development of AEM is much more complex than CEM. In their study, they proposed to use halogenated polyether such as polyepichlorohydrin (PECH) to be blended with polyacrylonitrile (PAN) for their AEM. The permselectivities of the AEM and the resistances area of the series of membranes ranging from 87% to 90% and 0.82 to 2.05 Ωcm^2 respectively. There is one step in this AEMs preparation that involved the chloromethylation reaction, which is hard to manage and they are high in toxic and carcinogenic due to the usage of chloromethyl methyl ether [50]. Chloromethylation reaction can be avoided by adopting PECH as polymer matrix which has the insintric chloromethyl groups. The AEM needs to be positively charged by introducing tertiary diamine 1,4-diazabicyclo-[2.2.2]octane (DABCO). In this study, PECH, PAN and DABCO were dissolved in dimethyl sulfoxide (DMSO) separately with various loading ratio. After all three solutions were fully dissolved, they were mixed and combined in a round-bottomed three-neck flask at 80°C for 30 minutes. A clear dense structure without pores was obtained after the treatment. The application of this membrane in RED system resulted in 1.27 W/m^2 of high power density, higher than commercial AEM membrane used in this study [50].
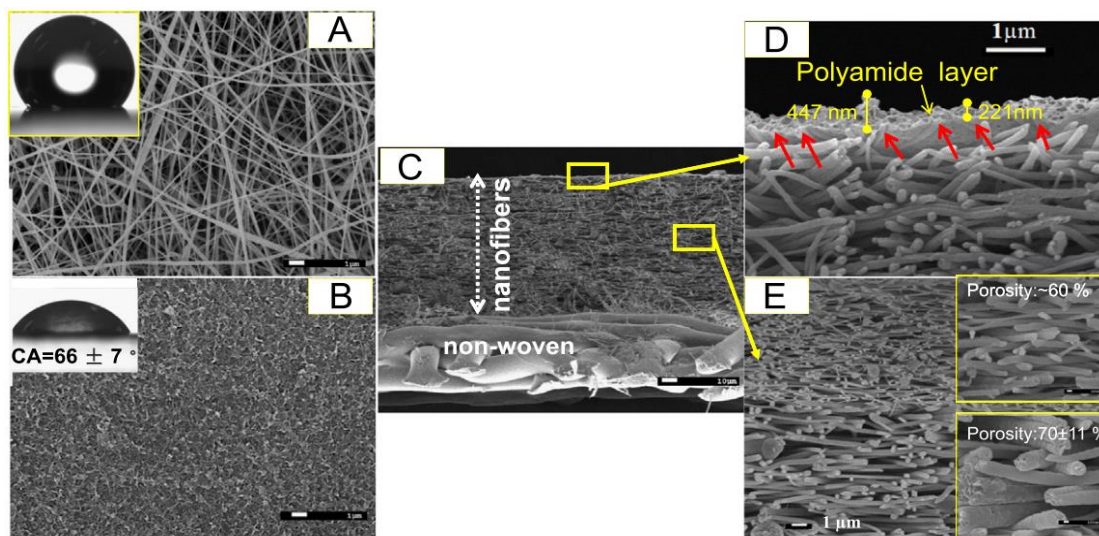

Fig. 6. A) surface morphology of membrane before IP and contact angle at 130°, B) surface morphology after he IP and the contact angle recorded at 66 ± 7°, C) FESEM image of membrane cross section, D) enlarged image of layer underneath PA layer, E) enlarged image of membrane at centre cross section [42].

Table 2
Comparison of polymeric PRO membrane modifications and its performance.

PRO membrane modification	Draw / Feed Pair	Water Flux, LMH	Power Density, W/m^2	Ref.
PAN-AgNP	0.5 M MgCl$_2$ / Milli-Q water	45	n/a	[21]
TNP-coated TFC membrane	4 M NaCl / 10 mM NaCl and 1 mM CaCl2	26.4	n/a	[41]
Dual layer PEI tiered fibrous support with functionalized CNT	1.0 M NaCl / DI water	38	17.3	[42]
Zwitterionic polymers grafted poly(ether sulfone) hollow fiber membranes	Synthetic brine 1M NaCl / concentrated wastewater	n/a	n/a	[46]
Zwitterion coating at bottom of PES substrate	Synthetic seawater brine / wastewater from municipal recycle plants	n/a	7.2	[47]
Active layer etching with 1000 ppm NaOCl	Synthetic seawater / brackish water	40	7.9	[48]
Active layer etching with 1000 ppm NaOCl	Synthetic seawater / river water	53	10.2	[48]
PES TFC membranes with CaCl$_2$	1.2 M NaCl solution / DI water	50	34.7	[49]
PES TFC membranes with LiCl	1.2 M NaCl solution / DI water	46	32.4	[49]
PES TFC membranes with MgCl	1.2 M NaCl solution / DI water	38	27.4	[49]

Guler et al. performed surface coating of the standard commercial AEM [51] which known to have low monovalent-ion selectivity. By forming coating layer by using UV irradiation with copolymerization of 2-acryloylamido-2-methylpropanesulfonic acid (AMPS) as the active polymer and N,N-methylenebis(acrylamide) (MBA) as the crosslinker, can increase the monovalent-ion selectivity [51]. In this study, four commercial membranes were used in which two membranes Neosepta AMX (Tokuyama) and Neosepta ACS (Tokuyama) have a polymer matrix formed by copolymerization of either styrene or divinylbenzene. All the four membranes were reinforced with either polypropylene or polyvinylchloride. One of the clear improvements shown by coating membrane with AMPS is the permselectivity and power density on RED system increase. In term of antifouling potential evaluation, modified Fuji A membrane promoted lower tendency on fouling from the membrane potential over time test. The modified membrane transition time was found to be at 90 minutes whereas the original unmodified membrane transition time is at 50 minutes. Between the Fuji A modified membrane stacking, 0.45 M NaCl and river water of 12mM NaCl + 2 mM Na_2SO_4 were used and the highest power density achieved was 1.01 W/m^2 [51].

4.2. CEM modification

Aside from AEM, CEM modification also brings some changes in RED performance. A study has been made by Ariono et al. on the preparation of heterogenous PSf/PEG CEM for RED [52]. Strong acid cation-exchange resin was used in membrane as functional groups. The membranes were prepared by phase inversion and solution casting method. Cation-exchange resin particles was finely dispersed in *N,N*-dimethylacetamide (DMAc) solution of PSf and PEG400 was used as membrane modifier. In this study, the effect of cation exchange resin and PEG400 concentration on water uptake and ion exchange capacity (IEC) were analysed. Aligned with the hydrophilicity nature of PEG, the higher the concentration of PEG400, the higher the water uptake of the membrane. By increasing the concentration of PEG400 in the dope solution, the concentration of PSf become lower thus weakened the membrane structure. In term of IEC, the membrane with higher PEG concentration exhibited a negative effect on IEC. Figure 7A shows that as the PEG400 concentration was increased to more than 15%, the IEC of the membrane dropped. The author mentioned that the IEC drops may be due to the wash-out of the cation-exchange resin particles during the membrane immersion in the RED system. Lower bonding between polymer matrix or binder and the resin could be the reason of the resin particles wash-out. Membrane conductivity was also mesured in this experiment. As the water uptake increased with the increasing loading of PEG, the electrical conductivity also increased. The maximum IEC achieved from 15% of PEG400 and 50%-wt of resin resulted in the maximum conductivity of the membrane. Figures 7-b and 7-c show the membrane conductivity with various PEG400 loading and with different IEC respectively.

Wilson et al. performed a research on radiation-grafted CEM (RG-CEMs) for ex situ feasibility study on RED application [53]. The primary IEM factors that have significant effect on RED application are area selective resistance and permselectivity. Good IEM for RED application should achieve high power density as well as characterized by low resistivity and high in permselectivity. In this study, researchers used styrene and 4-vinylbenzene sodium sulfonate (VBS) as a monomer for the introduction of sulfonate functional groups into the membrane. The uses of styrene as grafting material require to undergo two-step processes, whereby grafting and sulfonation. While the use of VBS as a grafting material only requires grafting process. The crosslinking and co-monomers used in this study was divinylbenzene (DVB) and bis(vinylphenyl)ethane (BVPE). Three variants of CEM were prepared; 1) PVDF based RG-CEM using styrene as grafting monomers (PS-0); 2) PVDF based RG-CEM using VBS as grafting monomers and (PV-0); 3) ETFE based RG-CEM using styrene as grafting monomers (ES-0). As the ES-0 showed the highest water uptake and permselectivity, further investigations were conducted by introducing both DVB and BVPE crosslinker on membranes. ETFE based RG-CEM with styrene monomer using DVB as crosslinker were designated as ES-D0, ES-D5, and ES-D10 (with 0% mol, 5% mol, and 10% mol of DVB accordingly) where ETFE based RG-CEM with styrene monomer using BVPE as crosslinker were designated as ES-B0, ES-B5, and ES-B10 (with 0% mol, 5% mol, and 10% mol of BVPE accordingly). In term of permselectivity, ES-B10 exhibited the highest value of 92% which approaching value of the commercial CEMs [54]. As for the resistivity of the membrane, all the cross-linked RG-CEMs exhibited value of ranging between 1 and 3 Ω cm^2 which correctly suggested that RG-CEMs have low ASR and high permselectivity [53].
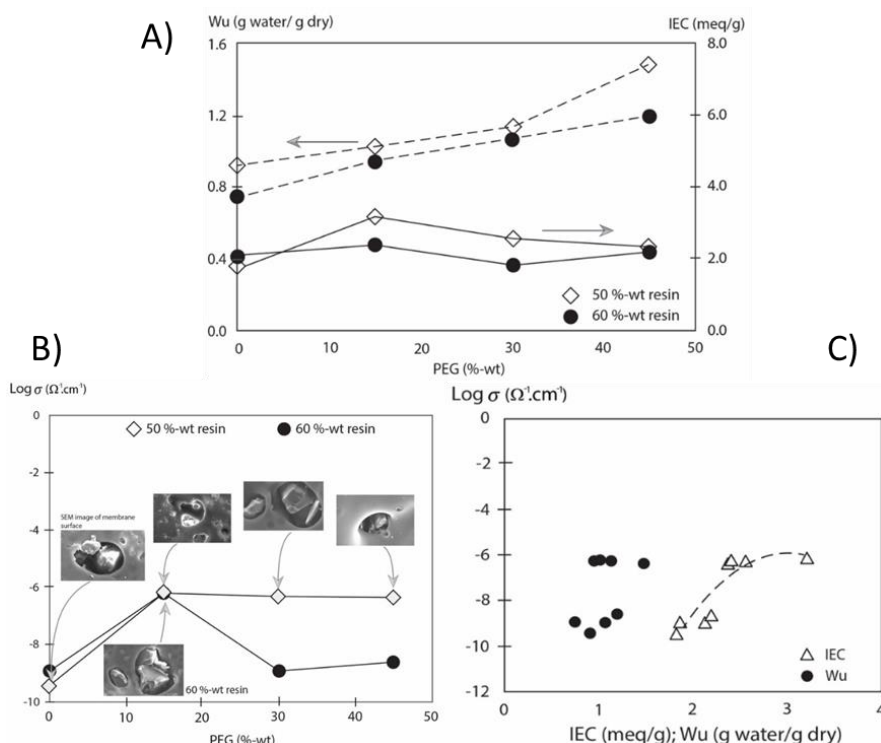

Fig. 7. A) Water uptake and IEC for various loading of PEG in the membrane, B) Membrane conductivity for various PEG loading, and C) membrane conductivity for various water uptake and IEC [52].

Tong et al. synthesized the new nanocomposite CEM by using oxidized multi-walled carbon nanotubes (O-MWCNT) physically mixed and blended with sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO) [55]. The AEM pair used in this study was an AEM (Fumasep FAS) and a CEM (Fumasep FKS) as control and the CEM was replaced by modified CEMs to further study the performance in RED system. In this study, nanocomposite CEM showed improvement in term of antifouling performance of energy generation in RED system. The O-MWCNT loadings of 0.5% gained the highest gross power density at value of 0.48 W/m^2. This power density value of 0.5% O-MWCNT was 14 % higher than the power density gained by Fumasep FKS. The PPO polymer chain was selected to be blended with O-MWCNT owing to its good chemical, good thermal stability, and good mechanical properties [56].

5. CapMix modifications on CDP approach

Between CDLE and CDP, only CDP approach requires membrane in its system. Ahualli et al. previously developed conductive electrodes made of an activated carbon core with a polyelectrolyte layer where the Fernandez et al. attributed this technique to the term soft electrodes (SE) [57][58]. A comparison was made by Fernandez et al. on polyelectrolyte electrode and membrane-coated electrode in producing energy. The IEM membranes used were commercial Fumasep FAS anion exchange and a Fumasep FKS cation exchange membranes. On the other hand, the SE modification has been tested by using poly (sodium 4- styrenesulfonate) (PSS) and poly(acrylic acid) (PAA) for anionic polyelectrolytes, while for the cationic polymer used were (poly(diallyldimethyl ammonium chloride)) (PDADMAC) and polyethyleneimine (PEI) [57]. Overall results showed that the open circuit voltage (OCV) results for CDP approach membrane-coated electrode method goes up tu 140mV, while for SE method the OCV goes up to 120mV. Even though the membrane-coated electrode achieved highest OCV results, the results of OCV for SE method is quite remarkable for the new method. But when considering the limitations possessed by membrane-coated method such as high membrane cost, fouling, and difficulties in assembly, the cheap SE method can be of interest. The SE method can be further developed by finding any other suitable polyelectrolyte to be incorporated with the electrodes in hoping that higher OCV can be achieved.

6. Challenges and future perspective

In a constant evolving technological advancement of membrane development for various applications, there are several challenges currently faced by researchers. Focusing onto membrane development for energy generation, there are some technological challenges that needs to be addressed as best as possible to ensure the continuation of membranes application in energy generation. As we can see the closure of first PRO plant operated by Statkraft in Norway was due to the fouling problem and maintenance cost for membrane treatment is very high. From the discussion on PRO, it is obvious that most of the promising strategies in increasing high power density is by incorporating the PRO membrane with zwitterion. But the method on how to incorporate the zwitterion in membrane have yet to fully discovered as most of the researchers applied coating of zwitterion on the membrane surface. Further development can be done in trying to incorporate zwitterion in membrane such as mixed matrix and thin film modification. The hybrid polymeric and ceramic membrane can be implemented in PRO operation as they have good chemical and physical stability [59]. In recent study conducted by Menne et al. [59] the regenerable polymer ceramic hybrid membrane has been developed for nanofiltration application. Among the interesting topics discussed in this study was the ability to regenerate its active layer on site, without having to dismounting the membrane modules. If this technique can be implemented in PRO application, lots of cost and non-productive operation time can be reduced. As we are currently still depending on the fossil fuel as the main source for energy generation and the estimated time for the depletion of fossil fuel source is still long, the political leader and industry players do not look into scaling up the application of PRO for commercial energy generation.

As the RED application yet to be commercialised, there is no exception that RED membranes also facing lots of challenges that need to be addressed. Güler and Nijmeijer have reviewed the challenges and future perspective on RED for power generation [5]. One of the important key point touched in the article is the creation for the new application for RED. Aside from the development of RED membranes to address its fouling problems, development of RED electrodes and the stacking formation in RED, the new application process from RED operation can be further explored. As one of the purposes of salinity gradient energy is to create new energy without leaving any carbon footprint as such green energy, the development of membrane in both PRO and RED must not give any negatives impact to environment. The modification of sustainable membranes through click chemistry or any other methods that will help reducing the usage of chemicals in membrane fabrication certainly will help in preserving our environment. As the current membrane fabrication used lots of chemicals resulting in leaving lots of chemical waste and membrane cleaning process that uses lots of chemical that can harm the environment, the needs for sustainable membrane development is vital and very much needed. Unlike PRO, RED has yet to have any large pilot commercial scale in producing energy. This is due lower power density achieved in lab scale. Further modification can be further explored to make this technology feasible to be developed in large scale.

For the development of CapMix, it is yet to have any open literature discuss on the modifications on membrane. As the CapMix system does not necessarily must have a membrane in its system, there are not much membrane modification has been done specifically for CapMix. Most of the membranes used in CapMix in CDP method are the same IEM used in RED applications as the purpose of the membrane for both system are the same, which is to transport ions [29].

7. Conclusions

In this short review, three approaches from SGE technology have been discussed namely, PRO, RED, and CapMix. These SGE technology is one of the best options to replace fossil fuel in foreseeable future towards global energy generation. To date, only PRO technology had been developed up to commercial stage. The pilot PRO plant was first developed by Statkraft Company in Norway. Even though the Statkraft Company discontinued their investment in PRO, this clearly shows potentials for PRO in generating energy through salinity gradient. In fact, this discontinuity creates more reason for researcher to discover more on PRO technology as such its membranes development. More research needs to be conducted in CapMix membranes development to increase its membrane potential. In CapMix technology, membrane's development is the only thing which can be developed to enhance the performance of CapMix. The electrodes modification, space between electrodes, and the treatment of seawater and river water used are the areas which can be studied further. To date, the highest power density from RED application does not make it feasible to be commercialised at bigger scale. The development of RED does not necessarily to be focused on membrane. There are still lots of area in RED can be touch and further improve for a better performance of RED such as the electrodes, stacking arrangement, spacer and lots more. In PRO, there are still gaps need to be fill even though PRO application now at a commercial state. As the first PRO plant closed due to membrane maintenance and high in cost, new cheaper materials need to be discovered in developing PRO membrane without sacrificing its anti-fouling properties and mechanical strength. With that, it is expected for PRO operation can be continued in reducing our dependency on fuel energy and promoting green energy to be more feasible.

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