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Review

Ion-exchange membranes for blue energy generation: A short overview focused on nanocomposite

Jin Gi Hong[1,✉] and Tae-Won Park[2,✉]

[1]*Department of Civil Engineering and Construction Engineering Management, California State University, Long Beach, CA, 90840, United States*
[2]*Department of Earth Science Education, Chonnam National University, Gwangju, South Korea*

Corresponding author: ✉JinGi.Hong@csulb.edu; Tel.: +1-562-985-2440; Fax: +1-562-985-2380
✉park2760@jnu.ac.kr; Tel.: +82-62-530-2511; Fax: +82-62-530-2510

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Abstract

Blue energy can be harvested from salinity gradients between saline water and freshwater by reverse electrodialysis (RED). RED as a conversion technique to generate blue energy has received increasing attention in recent decades. As part of the RED system, ion exchange membranes (IEMs) are key elements to the success of future blue energy generation. However, its suboptimal performance often limits the applications and stagnates the development of the technology. The key properties of IEMs include ion exchange capacity, permselectivity, and electrical resistance. The enhancement of such physical and electrochemical properties is crucial for studying energy production with acceptable output efficiency on a commercial scale. Recently, many studies have tried blending nanotechnology into the membrane fabrication process. Hybridizing inorganic nanomaterials with an organic polymeric material showed the great potential of improving electrical conductivity and permselectivity, as well as other membrane characteristics for power performance. In this short review, recent developments on the IEM synthesis in association with potential nanomaterials are reviewed and raising issues regarding the application and commercialization of RED-based energy production are discussed.

Keywords
Salinity gradient energy; electrochemical properties; membrane fabrication, reverse electrodialysis

Introduction

Clean and renewable energy is increasingly important to sustain the global energy supply and lessen the escalating environmental deterioration issues. Salinity gradient is one of the emerging energy sources that has yet to be tapped. Its utilization is widely considered promising due to its abundance in various forms of different salinity levels. The technology of extracting electrical energy from water salinities is often named blue energy, or salinity gradient energy (SGE). The blue energy has received attention as zero-emitting technology that could potentially supplement or replace the current global energy resource. Such technology not only can produce electricity from salinity gradients, but it also can provide the additional benefits of energy storage and wastewater treatment. The chemical energy available in seawater-freshwater gradients is significant, mixing one cubic meter of freshwater (the volume of six oil barrels) into the ocean releases energy equivalent to the same volume of water falling from nearly 1,000 feet. Tapping these waters where rivers and secondary effluent pour into the ocean could yield nearly 2 TW of power production globally, roughly half of current global electricity production [1-4].

Reverse electrodialysis (RED) is one method that utilizes ion exchange membranes (IEMs) to harvest SGE. RED generates electricity when solutions of different salinities are separated by multiple membranes that allow only ions (*e.g.*, sodium and chloride) to pass through them. Ionic diffusion in water allows the transport of ions that are selectively determined by corresponding IEMs. A continuous ion flux using alternating series of cation exchange membranes (CEMs) and anion exchange membranes (AEMs) can be maintained inside the RED stack. The flow of ions through the membranes to even out the salinity gradients is then converted to electric current on the surface of two terminal electrodes *via* redox reactions. Therefore, electrons travel through the closed electrical circuit and generate power for an energy-consuming load (Figure 1).

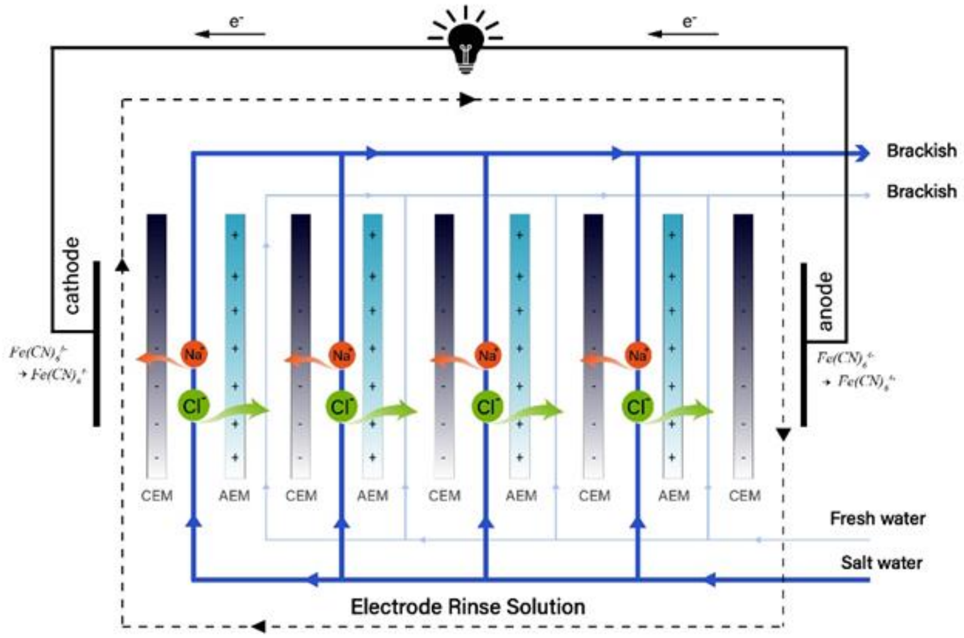

Figure 1. *Schematic of RED stack. The arrows indicate fluid and ion transport through the IEMs; CEM= cation exchange membrane, AEM= anion exchange membrane*

Compared to other conventional energy technologies, the RED power generation using salinity gradient has a great potential to play due to its technical and economic superiority. Since natural salinity gradients are renewable and located near land, RED also avoids the problems of intermittent electricity generation and high offshore installation costs facing many other ocean energy technologies. Like many other membrane-based systems, the role of membranes is of considerable importance in the development of the RED operation. Nowadays, the IEMs are widely used in various applications ranging from water treatment to industrial separation, to power generation, particularly in electrodialysis (ED), electrodialysis reversal (EDR), and fuel cell processes. However, each application addresses different physical and electrochemical requirements as their goals and compositions vary. Considering the nature of the electrochemical system, the performance of IEMs used in RED is significantly affected by electrical resistance, permselectivity, and biofouling tendency [5-8]. Optimizing any of these properties in existing membrane materials or through the development of improved membranes would improve RED system performance. Despite the importance of IEM characteristics and performance, most previous studies on RED have focused on system design and optimization. The lack of suitable IEMs for RED, which entails low ionic resistance and high permselectivity has become a major challenge toward the commercialization of the technology [9,10].

Recently, some efforts have been made to develop RED-customized IEMs on a lab scale for enhancing the physical and electrochemical properties. Reinforcing the physical structure of existing membrane material is one good way to decrease the electrical resistance in high salinity electrolyte conditions. The performance of IEMs deteriorates when they are in contact with high-salinity electrolytes in part due to shrinkage caused by osmotic effects. To address this problem, many studies are focused on reinforcing structural formation with nanomaterials while maintaining conductive characteristic. Nanocomposite structural combination has received increasing attention due to their synergistic impact, which mainly stems from the properties of both inorganic and organic components. Nanocomposite structure of the IEMs specifically designed for RED application was first proposed by Hong and Chen in 2014 [11]. The concept of composite structures created by introducing inorganic nanomaterials into an organic polymer matrix was demonstrated to be highly competent for RED application, as it allows carrying extra ion-exchangeable functional groups by revamping the membrane structure. Inorganic nanoparticles have unique electronic, magnetic, and optical properties that can be incorporated into the polymer matrix. These small particles are considered fillers and are widely used in various forms and applications. Its high specific surface increases the interface between the inorganic particles and polymer molecules and makes the particle more easily coated on surfaces. Moreover, its ability to conduct proton at lower activation energy allows the nanocomposite membranes more attractive to lessen the electrical resistance as well [12]. Also, when the small particles are furnished with the ionic charged group, the polymeric matrix increases the affinity to adsorb the inorganic materials, and thus, the composite maintains the homogeneity characteristics to a certain extent. Sustaining homogeneity of the IEMs is crucial for the transport of counter ions, which may affect the area resistance and charge density of the membrane. It is often critical to have polymeric materials and filler particles functionalized via sulfonation or quaternization, thus the membranes avoid the tendency of having distinct regions of charged and uncharged in the composite structure. Moreover, if there are ionic charged groups on the surface of small nanoparticles, membrane hydrophilicity and surface charge density also increase, which is preferable in the RED application. These unique features of inorganic nanoparticles are favorable as it combines with organic polymers, deriving synergies for their physical and electrochemical characteristics. Such synergy enables enhanced power performance in blue energy RED cells. This short review focuses on the overview of IEM preparation, emerging nanomaterials, and nanocomposite structures for potential applications in RED. Considering the importance of membranes in RED-SGE, the incorporation of nanotechnology in membrane preparation offers broader opportunity to promote blue energy from the laboratory bench to practical application at a greater scale.

Preparation of nanocomposite IEMs

Cation exchange composite membranes

As a key component of the RED power system, the dependency on good IEMs has assumed considerable importance. IEMs should contain respective charged groups attached to their backbone; thus, the membrane selectively allows the migration of a specific groups of ionic species. Nanocomposite CEMs generally consist of the polymeric matrix and inorganic nanoparticles (i.e., nanofiller), and are often tailored to enhance the membrane performance. Different combinations of composite materials with various ranges of functionalization may be tested via different methods. The negatively charged functional groups execute the selectivity of CEMs. In many cases, the main functional groups for CEMs are based on sulfonic acid. These ion exchange groups are introduced into polymeric membranes by reaction with sulfonating reagents such as chlorosulfonic acid, sulfuric acid, dioxane-SO_3 complex, etc. Specifically, sulfonic groups are introduced into the aromatic rings to provide negatively charged ion groups in the form of $–RSO_3^-$. Fundamental understanding of preparing of preparing organic-inorganic hybrid nanocomposite membrane systems pursue the same idea with various forming materials in diversified ways.

Anion exchange composite membranes

The AEMs function is based on cationic moieties combined with a polymer matrix. These positively charged ligands are introduced to dissolved polymer, forming a casting solution that later attracts anions. A preformed polymer can also be modified chemically to bring required cationic moieties. For ion-exchangeable ligands, most commercially available AEMs have quaternary ammonium groups. Thus, the common and physically stable way to modify polymeric films for the preparation of AEM usually involves two processes: chloromethylation and quaternary amination. Chloromethylation reaction is an electrophilic substitution process of aromatic polymer for allowing ionic characteristics. It is rendered by copolymerization of chloromethylstyrene with other vinyl or divinyl monomers (e.g. sodium p-styrene sulfonate). The aim of this process is to get the polymeric backbone ready for the quaternary ammonium function group to be inserted during the following quaternization reaction. An ordinary method for chloromethylation procedure involves the large excess of chloromethyl methyl ether (CMME) or bis-chloromethyl ether (BCME) reagent, which provide good conversion and yields [13]. However, these toxic agents are known as carcinogens and often result in poor control of chloromethylation positioning and quantity. As an alternative, N-bromosuccinimide (NBS) or para-formaldehyde were proposed in some reported studies as much safer and more controllable options [13-17].

General approach to the synthesis of nanocomposite IEMs

One simple method to combine inorganic precursor (monomer and oligomer) and polymer matrix is blending (Figure 2). Blending can be performed if no strong chemical interaction exists between the inorganic and organic building blocks. The inorganic moiety is embedded into the organic polymer under mixing in common solvents or melts at specific temperatures. The physical interaction of the organic polymer with entrapped discrete inorganic nanoparticles often provides easy hybridization of multiple components and good flexibility that many types of polymers and inorganic nanoparticles can be employed to form nanocomposite CEMs. For a conductive nanocomposite IEM, an appreciable strength of ion selectivity is always desired, and such characteristics can be enhanced when embedded nanoparticles are evenly distributed in the polymer matrix. However, nanoparticles tend to aggregate easily, often causing performance deterioration. Therefore, proper mixing and optimized dosage of nanoparticles are needed. Inorganic nanoparticles and organic polymer can be blended either by melting or in a liquid state. Melt blending is common but often found more vulnerable to unwanted agglomeration, leading to the uneven distribution of nanoparticles in the polymer matrix and alteration of membrane properties and morphology. Liquid-state blending, on the other hand, lessens the constraints of such challenges to a certain extent and thus receives more attention as a better preparation technique in nanocomposite synthesis [18].

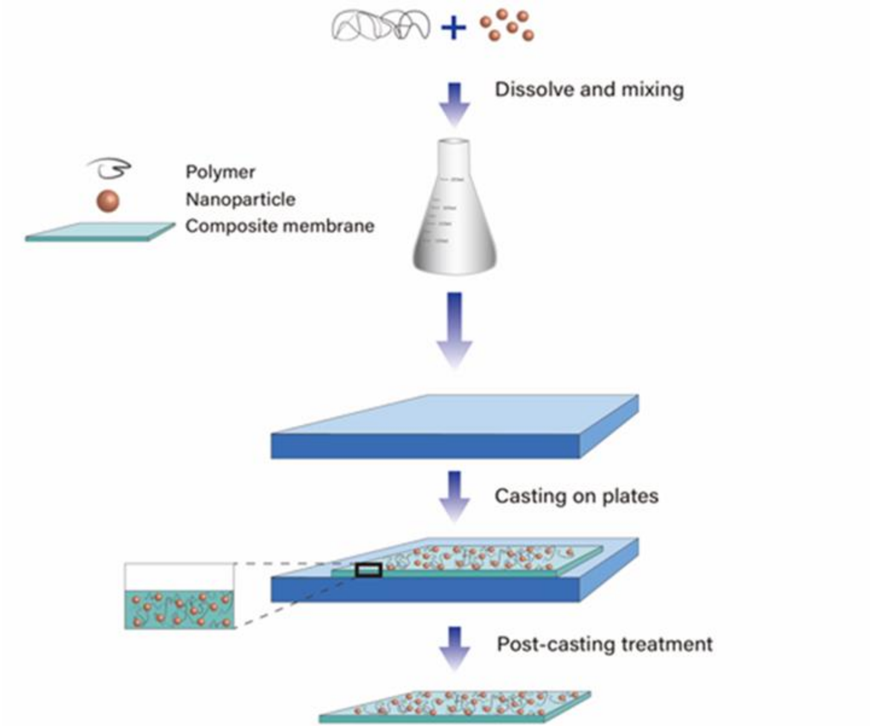

Figure 2. *Simplified experimental procedure of nanocomposite IEM preparation via blending method.*

Doping (or pore-filling) is another technique, making inorganic nanoparticles or precursors infiltrate the polymeric membrane. The pore and void spaces of the polymeric membranes are swelled in solvent to increase the space for nanoparticles to be well positioned and dispersed. The nanocomposite is then cured with heat or chemical grafting to promote the proper bonding of particles with the polymer matrix. However, this method often results in a concentration gradient of the particles throughout the pore depth of the membrane: a greater amount of particle deposit near the surface and less in the deeper region. This is due to the nature of diffusion that alters the access for fillers in the narrow pore space of polymer membrane. Such inhomogeneity of particle distribution may also cause unwanted leaching of particles from the matrix. The use of metal alkoxides in the preparation of composite helps to avoid the problem as they often increase the diffusivity within the composite.

The method of sol-gel reaction has long been used for the preparation of organic-inorganic hybrid materials. The fundamental concept of the sol-gel process was established considerably earlier but has gained wider attention and has been studied more extensively since the late 1970s. The alkoxides of mainly silicon, titanium, aluminum, zirconium and boron and a variety of polymeric media are condensed to form a gel. The sol-gel approach provides enhanced bonding and properties created from organic and inorganic components. The improved dispersion of inorganic nanoparticles in the polymeric matrix allows better network between inorganic nanoparticles and organic polymer than blending method does. The use of a catalyst also determines the structure and morphology of the hybrid composites, which is often recommended for silicon-based metal alkoxides [19,20].

Another method that is often adopted for the enhancement of monovalent-ion selectivity with antifouling potential is called the layer-by-layer (LBL) self-assembly technique [21-25]. The technique of layered polymeric multicomposites was first introduced in 1997 by Decher to prepare hybrid systems [24]. The LBL self-assembly can be established by creating an electrostatic association between oppositely charged layers of polyelectrolytes on the membrane surface. These multilayers constitute greater repulsion between multivalent anions and negative surface charge, which enhances selectivity for monovalent ions through the membrane. This preparation approach is particularly helpful for RED membrane development because the negative impact of multivalent ions on SGE-RED power generation is not negligible as it results in a significant decrease in power output.

RED power performance test

The power performance of the IEMs can be demonstrated in a RED electrochemical cell as depicted in Figure 1. A typical RED stack uses multiple membrane couples, consisting of an AEM and a CEM stacked alternately between cathode and anode (Figure 3). An additional CEM is used as a shielding membrane at the end of the stack next to the electrode to close the end compartment. The stack with membranes may contain spacers to form compartments for the feeding solutions to pass through. In a laboratory setting, high concentration (HC) stream often mimics artificial seawater using 0.5 M NaCl solution and low concentration (LC) stream with 0.017 M NaCl for artificial river water [3,11,26]. However, the feeding streams for RED application can potentially be ranged from brine, seawater, river water, and wastewater to reclaimed water [1,27,28].

The feed streams (HC and LC) can be fed into the RED stack using peristaltic pumps at desired flow rates. During operation, an electrode rinsing solution is also pumped to the electrode compartments and circulate the system for facilitating the electron transfer in the stack. Performance evaluation of the RED stack can be measured with an external potentiostat. Typically, the gross power density is the term used as an outcome and is estimated from the product of the maximum measured values of voltage and electrical current and divided by the total membrane area applied in the system. Lastly, the power output values are further corrected by subtracting the power values obtained in a blank test with only one CEM in the stack.

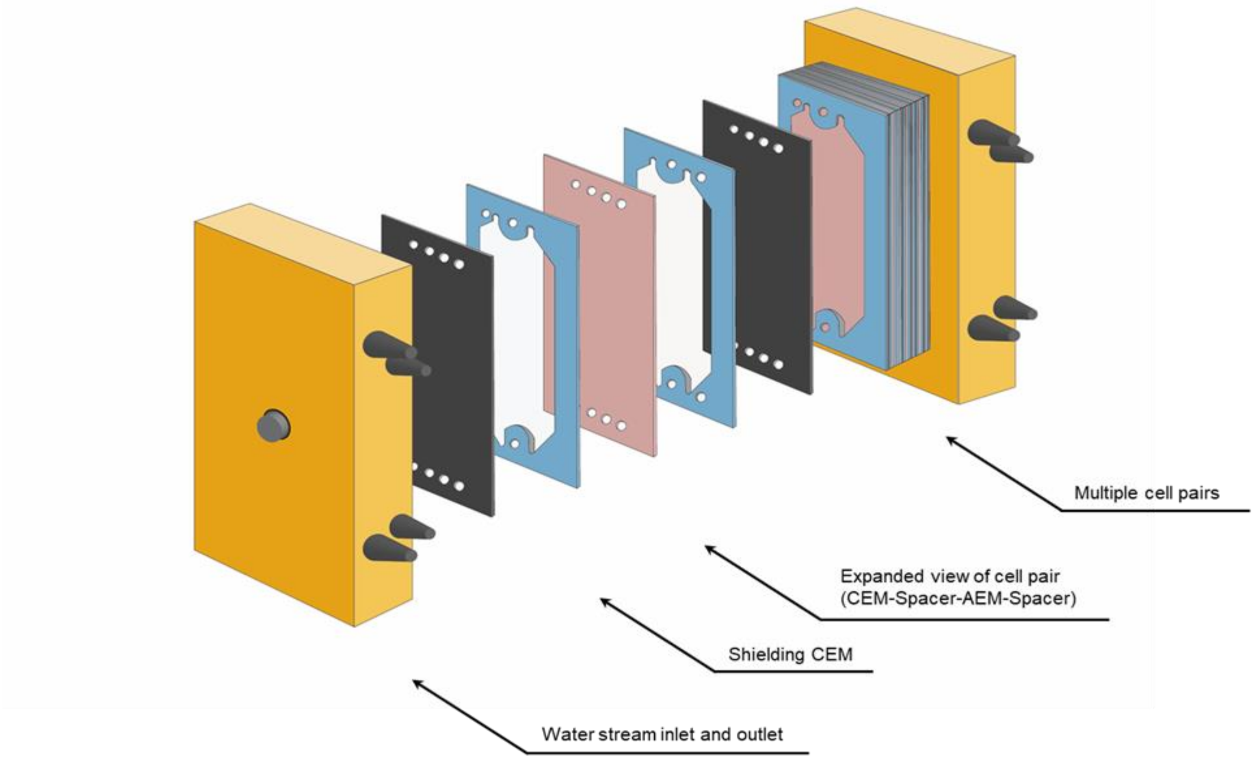

Figure 3. *Exploded view of the membrane configuration in a RED stack*

Potential IEM materials for SGE-RED performance

Structural composition for RED IEMs

The preparation and fabrication of IEMs are well developed and studied for various fields of applications. There have been studies on utilizing diverse monomers and inorganic materials in various preparation methods. The most critical aims are focused on developing high-quality membranes using materials that are commonly available, cost-competitive, easy to handle, and environmentally friendly via simple fabrication methods. However, it has often been challenging to compromise adequate materials and methods with a fine performance, especially under unique circumstances such as RED. The membrane performance has a direct correlation with associated properties of IEM and thus relative to its structural representation of charged functional groups.

The physicochemical characteristics of the membrane and material durability are of common importance in many ion exchange applications. Many physicochemical properties dominate the ion mobility within the membrane matrix. Swelling degree, permselectivity, ion exchange capacity (IEC), and ionic conductivity (or resistance) are the crucial IEM characteristics, which are often determined empirically (Figure 4). In RED, some of these physical and electrochemical characteristics regulate the performance more vigorously than the others and is largely affected by their active domain of charged polymer matrix. The CEMs contain anionic charged groups such as sulfonic acid, phosphoryl, phosphonic acid, carboxylic acid, monosulfate ester groups, mono-, and diphosphate ester groups, hydroxylic groups of phenol groups, perfluoro tertiary alcohol groups, sulfonamide groups and other groups that provide a negative fixed charge in aqueous or organic solvent solutions to selectively allow the passage for cations in the membrane structure. The AEMs, on the other hand, are amino groups, quaternary ammonium groups, tertiary sulfonium groups, and quaternary phosphonium groups that provide positive fixed charge groups to allow selective permeation of anions through the membrane.

The membrane composition can further be customized by altering its microstructure, which classifies it into heterogeneous and homogeneous. The charged domain in the matrix of homogeneous IEMs is uniformly distributed, but in a heterogenous structure, finely powdered ion exchange resins are blended with an uncharged thermoplastic polymer, which separates domains of charged regions in the matrix. Homogeneous IEMs are usually prepared by either copolymerization of monomers or made from polymeric films or solutions, which then be functionalized by proper methods (*e.g.*, chloromethylation-amination, sulfonation, grafting functional monomers) for active ion mobility. Heterogeneous IEMs are typically synthesized by blending two or more materials (*e.g*. ion exchange resin, nanoparticles, nanofiber) with uncharged (or charged) polymer. Different fabrication strategies using various materials are proposed in the literature to optimize the properties specifically for RED application.

Microstructural tailoring is the common and crucial approach for enhanced membrane performance and depends on material composition and functionalization. The homogeneity and heterogeneity of the membranes thus carry different abilities and strengths, which directly affect their performance. For example, the electrochemical properties may become slightly inferior for heterogeneous membranes, although with greater mechanical strength. However, there also have been increasing efforts in combining appropriate materials to induce synergistic effects of each component, resulting in enhanced ion exchange processes. Various materials and preparation methods for the synthesis of RED IEM have been studied over the past decades. The quality and performance of salinity gradient energy generation via the RED membrane system have improved to a greater extent in recent years. Such progress is attributed to the membrane optimization primarily focused on obtaining preferred electrochemical characteristics for RED, leading to a more desirable power density level.

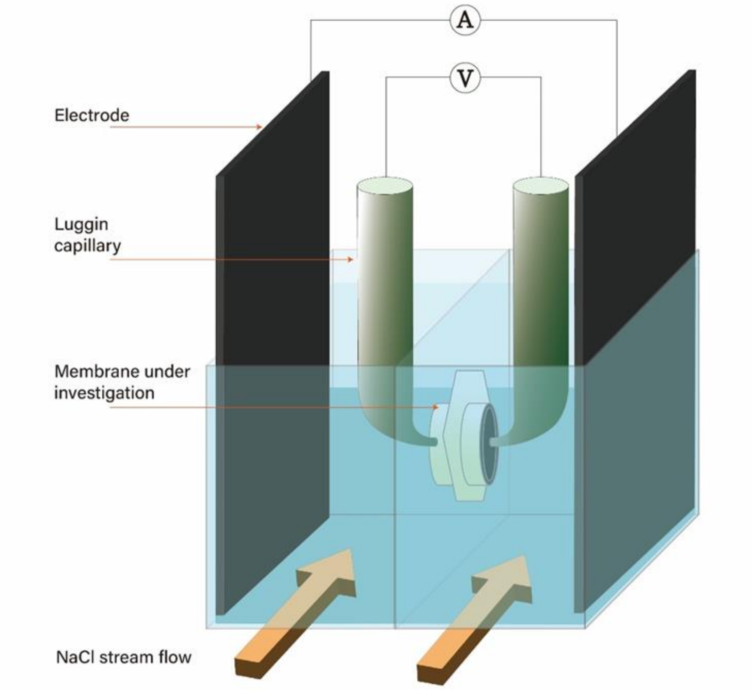

Figure 4. Common setup (four-electrode system) for membrane resistance measurement

Recent advances in nanocomposite for RED applications

There have been many studies focusing on composite membrane materials for water treatment, fuel cell, and electrodialysis applications (Table 1), but in recent years, it has gained more attention, particularly in the field of RED application. Inorganic nanoparticles offer enhanced charged species region for polymer matrix, thus facilitating more suitable counterion navigating paths. Introducing filler materials to the polymeric membrane may also derive advantageous features of various nanoparticles, which coordinate to highlight certain membrane characteristics. However, as the portion of nanoparticle filling increases, the heterogeneity structure becomes more prominent, and particles often tend to agglomerate. This leads to uneven particle distribution in the polymer matrix and thus disturbs the ionic path and weakens selectivity during the exchange process.

Hosseini *et al*. reported the work on polyvinylchloride (PVC)-based heterogeneous CEMs, blended with graphene oxide nanoplates (GONs) and resin by solution casting technique [29]. Thus, the presence of -COOH (GONs) and $-SO_3H$ (resin) functional groups was allowed in the prepared membranes, providing additional conducting regions with higher charge density. The loading amount of GONs was controlled to observe the effect on ion transport characteristics of membranes. The results revealed that the IEC was enhanced to 1.4 meq/g as the concentration of GONs increased to 0.5 wt.% in the membrane solution. Low water content was also maintained while more GONs were loaded. However, further dosage (0.5-2.0 wt.%) plunged some of the transport properties (*e.g.* membrane potential, selectivity, transport number), possibly caused by disturbed flow channel and resin functional groups at a high dose of GONs concentration.

Hong *et al*. utilized the powder of Fe_3O_4 nanoparticles mixed with poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) polymer for the synthesis of CEM [30]. In this work, both nanoparticle and polymer were functionalized with anionic charged groups without blending the composite structure with resin particles. This membrane was compared with both commercial and other custom-made membranes and further tested for RED performance.

In this study, those PPO-based nanocomposite membranes with the lowest area resistance performed the highest power outputs among other membrane combinations investigated. Hong *et al.*

also concluded that there might be less dependency of permselectivity and other related properties on the SGE performance. Specifically, there appear to be greater links between area resistance and RED power production than permselectivity. This is owing to low consistency in the pattern portrayed by permselectivity and other related ones compared to membrane resistance.

Jashni *et al*. tested the efficacy of nanocomposite, Fe_3O_4/PVP, embedded in PVC-based heterogeneous CEM via casting solution technique [31]. The membranes fabricated in various blend ratios of Fe_3O_4/PVP combination also exhibited some notable degree of membrane characteristics. For example, the areal electrical resistance and permselectivity enhanced significantly with the one at 2.0 wt.% Fe_3O_4/PVP (*i.e*. resistance of 5.8 Ω cm^2 and permselectivity of >90 %). This result proved that the composite, Fe_3O_4/PVP, also has a good potential in ion exchange performance as a competent candidate over other composite combinations.

Zehra *et al*. also fabricated composite CEM by using various mass compositions of PVC and tin aluminium molybdophosphate (TAMP) [32]. Four combinations with different mass ratios of binder (PVC) and exchanger (TAMP) were tested and the ratio of 1:3 (polymer to inorganic filler) was found to be most reliable formation for obtaining fine ion transport properties (*e.g*. IEC, membrane potential) as well as enhanced thermal and structural stabilities. This work also confirms the good potentiality of IEM material selection for RED application.

Table 1. *Recent composite applications*

Inorganic material	Organic material	Thickness, µm	Swelling degree, %	IEC, meq/g	R / Ω cm^2	Permselectivity, %	Applications	Ref.
Fe_2O_3	PPO[1]	100	20-26	0.87-1.4	0.87-2.05	59.5-87.7	Salinity gradient RED	[11,30]
Fe_2O_3	Nafion	-	22.9-40.7	-	-	-	Fuel cell	[33]
GO[2]	SPEEK[3]	-	24 - 38	0.75-1.11	-	-	Fuel cell	[34]
Sulfonated GO	SPEEK	20-40	10 - 37	0.75-1.65	-	-	Fuel cell	[34]
Zwitterionic GO	PBI[4]	50	10.2-35.2	0.27-1.12	-	-	Fuel cell	[35]
GO	Nafion	-	20.9-29.9	0.92-1.02	-	-	High proton conductivity	[36]
GO	SPES[5]	180	12.12-15.19	1.27-1.40	-	87.0-96.0	Fuel cell and ED	[37]
GO	PVC[6]		8.5-13	1.15-1.40	5.5-7.0	87.0-89.0	Water deionization	[29]
ZrO_2	Nafion	120	-	-	0.13-0.15	-	Electrolyzer application	[38]
ZnO	PVC	70	10-50	-	15-18	85.0-92.0	Electrodialysis	[39]
SiO_2	Fumasep FAP	60	20-22	1.07-1.16	0.7-1.088	-	Flow batteries	[40]
SiO_2	PES	60	9.7-14.3	0.74-1.1	-	66.94-100	Electrodialysis	[41]
Fe_3O_4/PVP	PVC	-	11-14.7	-	14.7-5.8	77-90	Electrodialysis	[31]
TAMP[7]	PVC	900	10-12.5	0.57-0.83	-	-	Separation process	[32]
Al_2O_3	PVA[8]	200-400	-	-	0.2-0.4	-	Fuel cell	[42]
CeO_2	Nafion	25	17-22	-	-	-	Fuel cell	[43]
Fe_2NiO_4	PVC	80-100	17-23	1.5-1.6	9.1-12.8	79-84	CEM characterization	[44]
MWCNT[9]	PVA	100, 120	38.2-284.0	0.7-2.25	-	-	Fuel cell	[45]

[1]poly(2,6-dimethyl-1,4-phenyleneoxide); [2]graphene oxide; [3]sulfonated polyetheretherketone; [4]polybenzimidazole; [5]sulfonated polyethersulfone; [6]polyvinyl chloride; [7]tin aluminium molybdophosphate; [8]polyvinyl alcohol; [9]multi-walled carbon nanotube

Many reported works on nanocomposite IEM investigated the optimum loading amount of nanomaterial to enhance the key membrane characteristics that determine the RED power performance. However, the optimum dosage may vary depending on the type of binding material, filler particle, and synthesis condition. Therefore, optimizing the membrane preparation and performance remains a great challenge for adopting nanocomposite membranes in RED power generation.

Several studies of composite IEM preparation have also been conducted mainly by surface modifications. For the first time, Gao *et al*. investigated the monovalent anion selectivity and antifouling potential using layer-by-layer deposition with negatively charged poly(styrenesulfonate) and positively charged PEI polyelectrolytes based on standard grade conventional AEM [21]. As a result, the modified membrane with 7.5 bilayers of poly(styrenesulfonate) and PEI (CJMA-2-7.5) showed comparable monovalent selectivity to commercial ACS membranes and exhibited around 30-38 % improved antifouling potential over unmodified and commercial membranes. In addition, the power performance of a RED system equipped with prepared membranes achieved up to 17% improvement in power density.

Tufa *et al*., on the other hand, chemically modified commercial CEM (Fuji CEMT1, The Netherlands) to investigate the key electrochemical properties (*e.g*., monovalent cation selectivity, resistance, IEC) using polypyrrole (PPy)/chitosan (CS) composites [46]. By controlling PPy concentrations (0.025-1 M) and polymerization time (0-8 h), the modified membrane with low PPy content (<0.05 M) exhibited better monovalent (*i.e*. Na^+) selectivity compared to the pristine membrane and is possibly due to slightly higher IEC characteristics of those modified ones. As a result, this work also demonstrated the great potential of composite IEM for RED application. The modified membranes achieved more than 42 % power density improvement over pristine commercial membranes in RED operation.

Conclusions

Although the advantages of SGE-RED harvesting over other conventional energy technologies are well recognized, there is still a great effort needed to facilitate large-scale electrical energy systems on the number of factors in the RED system. As part of such efforts, developing a new membrane and understanding the property optimization are the most crucial routes. In particular, the RED IEM studies should aim toward a performance enhancement, which entails proper fabrication methods using materials that are easy to handle and cost-competitive. Considering the large-scale (or pilot scale level) operation with newly developed IEMs, including nanocomposites, the economic aspects of membrane price and affordability and validation of power performance in a natural saline environment are still of great concern. The use of inorganic nanomaterial for the synthesis of the RED membrane is in an early stage of development and only a limited group of nanomaterials have been investigated for application in RED. Developing proper nanocomposite membranes usually deal with the amount of nanoparticle dosage for maximizing the property performance and the optimum loading varies depending on the type of materials used. Further studies are expected to demonstrate more variety of material combinations and to optimize the composition ratios in forming nanocomposite IEMs. Thus, exploring the new and innovative RED IEM preparation and demonstrating the researched IEMs at pilot and commercial settings under dynamic operating conditions should be entailed to overcome the existing challenges and expedite the nanocomposite application on a practical RED scale.

Some materials have already been characterized and tested in other related fields, such as electrodialysis and fuel cell. However, there are different property requirements depending on the applications, which implies the need for unique tailoring to specific conditions and solutions for the RED process. There are a few exemplary materials (*e.g*. GO, Fe_3O_4, TAMP) that showed great potential with significant improvement in ion transport efficiency. Also, some innovative fabrication methods have been introduced recently to advance the power performance in RED. If the cost of membrane material and fabrication methods are compromised to ensure better performance, large-scale SGE-RED implementation can be more practical. This review provides relevant insight into the recent development of RED IEMs for blue energy generation (*i.e.* SGE), focusing on nanocomposite. With further technological advancement and economic breakthrough in IEM development, the SGE-RED will become a more competitive option in the energy market.

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