Chapter 8

Advanced Functional Membranes for Energy Applications

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Abstract

Global warming has become a serious threat to the environment as well as human life. The application of renewable and green energy sources has been emphasized in recent years to overcome the energy demand and save the environment. As a competent alternative to renewable energy sources, membrane-based energy generation has attracted the attention of researchers. In the past few decades, the application of advanced functional membranes in green energy production has gained importance. The application of polyelectrolyte membranes in fuel cells has become an emerging technology due to high proton conductivity, excellent thermal, chemical stability, and mechanical strength. Pressure retarded osmosis is also one of the membrane-based energy generation techniques which have been upgraded with significant developments. The various polymeric membranes, both inorganic and organic, have been employed in the energy production processes. In the past few years, the application of biopolymeric membranes made up of chitosan blends has shown excellent progress. The storage of energy also plays an equivalent role in energy production. The application of membranes has a vital role in energy storage batteries. This chapter deals with all the advanced functional membranes for energy production and storage.

Keywords

Osmosis Membrane, Hybrid Membrane, Fuel Cell, Batteries

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1. Introduction

With swift growth in population, industrialization, and change of living style, the global energy crisis has become a serious concern. Worldwide, global warming has become a serious threat that needs more attention. To overcome this issue, now a day there has been a concern to adopt renewable energy resources. Also, there is a concern to reduce the consumption of the prime energy source fossil fuels. It involves the combustion of fuel to get energy and the emission of CO₂ from burning fossil fuels causing environmental pollution. In recent years, there is a thirst for green energy sources like fuel cells, biofuels, geothermal and solar energy, etc. [1]. Even these clean energy sources suffer from certain limitations. In the H₂ fuel cell, it produces by-product gases in the energy generation process, and there is a problem of catalyst poisoning due to the presence of contaminants [2]. Generally, biofuels are produced from the fermentation of biomass, followed by azeotropic products that involve a higher cost of production. It is essential to develop the technologies to produce, store, and efficiently consume the energy in green energy production by overcoming these issues.

Renewable energy resources such as wind energy, solar power, hydropower, etc., have been employed to minimize the consumption of fossil fuels for energy generation. The highly advanced membrane processes for energy generation have received significant attention in the past few decades [3]. Pressure retarded osmosis is one among those advanced membrane technologies but not yet commercialized. Statkraft Company, located in Norway, is the first unit to demonstrate it at the pilot plant level.

The global community is concerned about energy shortages and environmental pollution. The fuel cell mechanization may address these issues since it is capable of generating energy efficiently without emitting pollutants (if hydrogen is used as fuel, the final product is water) [4]. In modern electrochemistry, fuel cells (FCs) are electrochemical devices that convert chemical energy to electricity provided that it is supplied with enough fuel and oxidant [5]. Historically, fuel cells were developed in the 19th century by William Grove. He created a "gaseous voltaic battery" using platinum as an electrode material with oxygen and hydrogen as reactants [5]. The solid oxide fuel cell was developed in 1937 by Baur and Preis using a ZrO₂ and Y₂O₃ blend as electrolytes [5]. The FC was operated at a high temperature (1050 °C). In a fuel cell system, phenol-sulfonic acid and formaldehyde were polymerized to make phenolic polymer membranes. They were also temperamental in mechanical strength and lifespan, and showed a relatively low power density [6]. DuPont's Nafion membrane, developed in the 1970s, doubled the maximum conductivity and operating lifespan to 105 hours.

The Nafion membrane developed by DuPont in the 1970s doubled the maximum protons conductivity and doubled the operational lifetime to 10^5 – 10^6 hours [7]. Fuel cell systems were rapidly equipped with Nafion membranes, and fuel cells established themselves as a competitive energy source. At present, power plants, compact transformers, and vehicles, notably the Chevrolet Equinox and Ford CEVs, are all being tested with fuel cells [8].

The different fields of fuel cell applications are as follows:

- Enhanced power stability (telecoms, high-tech manufacturing, data analysis, and customer support)
- Reduction of emission (metropolitan areas, industrial establishment, aerodromes, means of transport)
- Access to the power supply is limited in some areas (mobile applications and remote locations)
- Monitoring and management of biowaste gases (effluent treatment)

The Polymer electrolyte membrane fuel cell (PEMFC) represents the most frequent fuel cell used in stationary power applications. Still, molten-carbonate fuel cells, solid oxide fuel cells, phosphoric acid fuel cells, and alkaline fuel cells are also used [9]. Stationary applications could, in principle, rely on both low- and high-temperature fuel cells. The main issue with low-temperature fuel cells is their fast startup time. Still, high-temperature fuel cells (molten-carbonate and solid oxide fuel cells) generate heat without any external reformation, resulting in higher efficiency than low-temperature fuel cells.

Fuel cells may be utilized in various ways: They may replace the grid or provide supplemental power, serve as both primary and secondary power, or provide standby power [10-11]. Mobile power production has been driven primarily by the need for higher quality, higher density, and higher time performance resulting from increased product development (CD players, mini-disk players, notebook computer systems, and cellphones). As technology advances, there is always a race for smaller, cheaper, lighter products with greater functionality [12]. Telecommunications, computers, social networks, and the Internet require ample power sources, which implies a need for fuel cells as portable power systems [13]. In general, fuel cell systems are perfect for mobile power applications since they have a high capacity, reliability, ease of operation, and are relatively inexpensive [14].

Fuel cells can reduce harmful emissions in the transportation industry while maintaining vehicle efficiency without compromising the vehicle's propulsion system. According to recent research, fuel cells have demonstrated efficiencies almost twice that of internal combustion engines. Because fuel cells do not require moving parts, they become a suitable

alternative to current combustion engines due to their easy functionality, fuel versatility, ease of installation, and minimal maintenance.

Energy derived from renewable sources is intermittent by nature, and the electricity generated from them is not dispatchable, causing supply and demand to be unpredictable. Due to unbalanced supply and demand, it is, therefore, necessary to store energy. As an added benefit, energy storage can also help utility planners bridge the gap between the drop in electricity generated by photovoltaic panels or a reduced wind speed caused by cloud cover and the ramp-up rate of gas-fired peaker plants, which usually take 15 minutes to ramp up. The chapter describes the different type of membranes used in energy applications.

2. Pressure retarded osmosis membranes

The increased demand for energy resources, has attracted the attention of researchers towards alternate renewable energy resources [15]. Water is the prime source for hydrothermal energy generation. In recent years, it has also become the energy resource for power generation from wastewater by membrane processes. The concentration gradient between seawater and fresh water has been utilized to capture energy by membrane based processes. Pressure retarded osmosis and reverse electrodialysis are the emerging membrane based technologies for producing energy from saline water [16]. Both are promising and also efficient membrane technologies to generate energy by utilizing the salinity gradient [17-19]. However, there are certain limitations of these technologies such as fouling and also cost of the membrane. The processes are still in pilot scale stage and will be commercialized in near future.

The pressure retarded osmosis involves the separation of saline water and fresh water by a semi permeable membrane. Osmosis is a phenomenon which involves the flow of water from higher chemical potential to lower chemical potential of water. The molar concentration difference of solute acts as the driving force for the transport of water across the membrane and solute molecules are retained by the membrane. Osmosis utilizes the osmotic pressure difference across the membrane for the flow of water from pure water to saline water. The pressure retarded osmosis process phenomenon lies intermediate between osmosis and reverse osmosis. In this process, the hydraulic pressure is applied to the saline water side, like reverse osmosis process, however, the net flow of water is from feed water to the saline water side like osmosis [20].

The source of renewable energy produced by mixing fresh water and saline water could be utilized by pressure retarded osmosis [21]. Due to the salinity gradient, water will flow from fresh water side to saline water. The membrane allows only water to permeate through

it. The flow of water increases the volume of water in the saline water side. This in turn increases the pressure which is sufficient to operate the turbine to generate power. The economic and efficient membrane are the key factor in this process. In the case of reverse electrodialysis, the saline and fresh water are allowed to flow through the chamber containing anion exchange and cation exchange membranes arranged alternately. The salinity gradient acts as the driving force for the generation of voltage by the movement of ions.

To achieve the goal of zero liquid discharge and green energy, utilizing the salinity gradient by pressure retarded osmosis, an emerging and efficient process could cater the energy demand. Over the past few years, the technology has been lacking in achieving adequate flowrate. The composite matrix of RO membrane has the bulk supporting layer that significantly affects the water flux due to the internal concentration polarization. Hence, in the recent years, research has been directed towards, developments in the fabrication of membrane with better water flux and also reduced internal concentration polarization. A specially fabricated cellulose acetate forward osmosis membrane and thin film composite polyamide membrane were employed in pressure retarded osmosis process to increase the water flux and decrease the internal concentration polarization [22-24]. However, to avoid fouling and drop in the water flux, the fresh water stream and saline water stream should be pretreated extensively. The schematic diagram of power generation by pressure retarded osmosis process is shown in figure 1.

This process consumes river water as the feed water and sea water as the draw solution. Several studies have been attempted to improve both the technical and economical feasibility of this process. The studies investigated by Bajraktari et al., (2017) and Manzoor et al., (2020) employed highly saline water as the draw solution to extract high energy [26, 27]. Fouling of the membrane is the main drawback of this process. In the composite matrix of the membrane, the porous supporting layer faces the feed side. The feed is most often the treated effluent which may contain organic and inorganic contaminants. These contaminants can permeate through the pores of the membrane and get stuck below the dense layer of the composite matrix. This leads to significant reduction in the water flux [28]. Several attempts have been tried to overcome the fouling by surface modification, synthesis of double-skinned membrane and also the pretreatment of the feed stream [29-32]. Cellulose triacetate composite membrane matrix with active layer facing the feed solution configuration has been investigated to minimize fouling and also to increase the mechanical stability of the membrane [33]. Li et al., (2018) fabricated the integral pressure retarded hollow fiber membrane with active layer facing feed solution configuration to reduce the fouling with increased energy harvesting [34]. The membrane was prepared by

phase inversion technique using polyamide-imide substrate, since it possesses excellent mechanical and chemical stability.

Figure 1 Schematic diagram of pressure retarded osmosis [25]

2.1 Hybrid pressure retarded osmosis processes

In the past few years, the closed loop pressure retarded osmosis process has been gaining attention, since it provides better performance and also it is a eco-friendly process [35]. In the closed loop process, due to the necessary for the additional separation technique to recover the draw solution and also to improve the energy generation, hybrid pressure retarded osmosis has been adopted. Several hybrid systems have been investigated by researchers in the recent years to utilize the benefits of the both the processes of hybrid systems. The hybrid systems such as pressure retarded osmosis-membrane distillation [36, 37], pressure retarded osmosis – thermosiphon [38, 39], pressure retarded osmosis – solar pond [40,41], etc., have been investigated in the recent years.

2.1.1 Pressure retarded osmosis-membrane distillation

The hybrid process forward osmosis-membrane distillation has proven to be a promising technology for desalination, reuse of effluent from industries, reclamation of wastewater [42-44]. Based on this concept, pressure retarded osmosis -membrane distillation system

has been attempted to produce energy as well as clean water. The retentate from the reverse osmosis process, which the concentrated brine is fed to the membrane distillation module. From the membrane distillation module, the clean water and concentrated and high temperature draw solution are obtained. The concentrated and high temperature draw solution is passed through the pressure retarded osmosis unit. The low salt concentration wastewater is used as a feed solution in this unit. The salinity gradient act as the driving force for the transport of water to the permeate side followed with the operation of hydroturbine leading to the power generation [45].

2.1.2 Pressure retarded osmosis – thermosiphon

This process involves the natural circulation currents generated due to the difference in the density to produce energy due to thermal gradient. The procedure has been adopted from Arias et al., (2018). The aqueous salt solution is passed through the solar collected where part of water evaporates. The evaporated stream with very less salinity has been taken as the feed stream to the pressure retarded osmosis system. The concentrated solution from the solar collector has been taken as the draw solution. Water transport takes place from feed side to draw solution side, followed with the operation of hydroturbine to generate power. The hot stream that comes out is fed to the heat exchanger to cool down the solution. Then the solution is sent to the solar collector and the cycle of operation has been continued [46]. The future feasibility of the process depends on the optimized temperature to yield maximum output of power in the long term process.

2.1.3 Pressure retarded osmosis – solar pond

This hybrid system has been developed to generate power as well as to reduce the adverse environmental effect of brine solution. The solar pond is the manmade solar collector that can absorb the heat and retain the heat in the bottom layer of the pond due to the salinity gradient. Mohamed and Bicer, 2019, proposed the hybrid system pressure retarded osmosis-solar pond. The solar pond as a solar collector receives the solar heat and retains the heat in the bottom layer of the pond with higher saline concentration. This high temperature stream has been sent to the multiple effect desalination units to heat seawater. The concentrated brine from the desalination units has been fed to the pressure retarded osmosis system as a draw solution and the treated effluent with low salt concentration has been fed to the feed stream. The water transport occurs from feed side to draw solution side. This dilutes the draw solution and increases the volume of it, which is sufficient to drive the hydroturbine to generate power. This hybrid system could enjoy the benefit of improved solar efficiency and minimizes the greenhouse gas emission [47].

3. Fuel cell applications

Fuel cells are one of the most powerful tools that must be developed to meet the growing demand for renewable energies. In contrast to combustion-based heat engines, chemical energy in fuel cells is directly transformed into electrical energy without any intermediate steps [48]. In contrast to other energy sources derived electrochemical reactions such as batteries, which temporarily store their reactants in the cells, these sources are continuously supplied with reactants from outside the cells. Fuel cells also do not consume electrodes, and do not participate in reactions like batteries. Fuel cell technology is considered to be a promising technological advancement for the development of renewable energy sources [49].

Fuel cells have developed to the point where they are becoming more advanced. They appear to offer promising markets where electricity can be generated efficiently and environmentally friendly. In addition, there are a number of plants that employ fuel cell technology that has been developed and is operational, ranging from megawatts to milliwatt capacity [50]. Essentially, fuel cells are composed of an electrolyte and a porous electrode, which has catalysts that accelerate electrochemical reactions. There is a negative charge on one electrode (the anode) and a positive charge on the other (the cathode). An electric current is produced by electrochemical reactions at the electrodes.

For the lower to medium scale power generation applications, the best source is the fuel cells with methanol as a fuel. Due to their lower weight and volume as compared to other energy sources such as indirect fuel cells, they can be employed for various transportation applications [51]. In the recent years, direct methanol fuel cells have attracted the attention of many researchers for the generation of green energy. This technology involves the conversion between chemical and electrical energy by utilizing fuel based on methanol. In this process we employ mediator such as polyelectrolyte membrane for the transport of proton and also this prevents the combustion of fuel by acting as a barrier between the reactants. The synthesis of polyelectrolyte membrane with excellent proton conductivity, chemical, mechanical, thermal and electrical stability, and also less permeability of methanol is the crucial part in the fabrication of fuel cells that run on methanol [52, 53].

3.1 Proton exchange membrane

The key component, in fuel cells, is the proton exchange membranes (PEMs). PEMs must meet a number of characteristics, including highly proton-conductive, exceptional strength and durability, chemical and electrochemical stability, minimal fuel crossover, and the ability to fabricate membrane-based electrode assemblies. PEMFCs have become a popular choice of fuel cell systems for portable energy storage because of their portability, long-term durability, fast response time, extensive power output, and low emissions [54],

together with their silent operation [55]. An anode and a cathode are connected by a PEMFC proton exchange membrane (PEM). Many of the functional groups in PEM work as proton-conductive groups, allowing the protons to move from one group to another.

Figure 2 Schematic representation of Proton exchange membrane fuel cell

3.2 Nafion membrane

Nafion membranes were developed by Dupont in the 1970s. In this membrane, the sulfonic acid groups associated with the polymers act as proton-conductive groups. Nafion membranes have a strong influence on proton conductivity depending on their water content and temperature. Nafion membranes offer many of the desirable features that make them suitable for FC systems. This membrane has excellent chemical and mechanical stability, high proton conductivity under normal conditions, and low permeability to fuel and oxidant [57]. Nafion™ membranes are at the heart of a new generation of fuel cells offering a clean energy source to power anything that moves. Using Nafion™ membrane in fuel cells for power generation benefits vehicles ranging from automobiles, buses, forklifts, boats, planes, and spacecraft due to:

High efficiency: Without combustion, fuel cells convert chemical energy to electrical energy.

Low emissions: Emissions from fuel cells are negligible, consisting mostly of water.

Quiet operations: Due to its lack of moving parts, a fuel cell produces only the noise produced by its auxiliary equipment.

Minimal intervention: The operation and maintenance of a fuel cell is simple because there are no moving parts, reducing operational costs and maintenance.

The nafion, however, only works at a relatively low temperature (80-100 °C). When the temperature is above 80 °C, the Nafion dehydrates (and their proton conductivity drops) and at 120 °C, the proton conductivity starts to drop significantly [58]. Consequently, Nafion has very poor proton conductivity when relative humidity (RH) is low [59]. Furthermore, Nafion has a relatively high permeability to methanol [60], which significantly reduces the performance of methanol fuel cells.

The Nafion membrane has many drawbacks, but new polymer electrolytes, or PEMs, have been developed that could replace it, especially when operating at high temperatures. In general, recent PEMs can be categorized into three broad groups: (1) polymer membrane, (2) ceramic, and (3) organic-inorganic composite membrane.

3.3 Polymeric membranes

There are several types of membranes that are used in fuel cells, but polymer PEM is the most commonly used. Polymers typically contain proton-conductive groups such as sulfonic acid in their side or main chains. To make the polymers chemically and thermally stable, they are typically fluorinated. The most commonly used PEM in fuel cells is Nafion. There has been extensive research on the possibility of modifying the properties of the Nafion membrane to make it more suitable for conduction of protons at high temperatures and low humidity. Table 1 represents the different modifications of the Nafion membrane with their characteristics.

3.4 Polystyrene-based membranes

A polymer membrane made of polystyrene-sulfonic acid (PSSA) was the first polymer membrane available for commercial use. There is a growing interest in membrane materials fabricated from polystyrene which can function at medium and high temperatures, as well as low water content [64]. Styrene-based polymers are relatively cheap, which makes PSSA-based membranes an attractive option for FC. Membranes based on PSSA have permeability to methanol lower as compared to Nafion [65]. In real-world applications of FC, PSSA membranes are unstable. In addition to the loss of IEC and conductivity, the performance of the membrane is negatively affected by the loss of SSA fragments (up to approximately 0.1% per hour) [66].

3.5 Polyimide-based membranes with sulfonated groups

Polyimides are thermostable polymers that have excellent thermal and mechanical characteristics and are resistant to harsh chemicals and extreme temperatures [67]. Sulfonic

groups can be added to these polymers to improve their insulating properties. As a result of this modification, the molecule becomes hydrophilic and proton-conductive. The development of polyimide-based membranes was driven by the expectation that material prices would be significantly lower than Nafion [68]. In humid environments, sulfonated polyamide membranes inflated and needed hydration to allow for proton conductivity (which is comparable to the properties of Nafion). However unlike Nafion, its water absorption, water sorption and drag resistance of the water were not affected significantly within a wide range of temperatures. Due to these features, it is suitable for operations at moderate temperatures [69].

Table 1 Types of Nafion modified membranes

Type of membrane	Operating conditions	Reference
Cs ⁺ cations doped Tricoli Nafion	➤ Reduces the surface area of hydrated micellar regions, and reduces methanol permeability considerably	[61]
A fluorinated polymer (ethylene and propylene (EP) or Teflon and fluoroalkyl resin mixed with Nafion (PFA)	➤ Lower the diffusion rate of methanol	[62]
The side chains of Nafion are changed, resulting in Hyflon, a novel perfluorinated membrane.	➤ To increase thermal stability ➤ The membrane exhibits a greater glass transition temperature than Nafion, which allows it to function at higher temperatures without degradation. ➤ The proportion of -CF ₂ - groups in Hyflon's backbone affects the hydrogen bonds between water and sulfonic acid groups, presenting more water molecules needed for proton transport to occur.	[63]

3.6 Polyphosphazene membranes

Polyphosphoric structures are made up of nitrogen and phosphorus elements that have attached organic, inorganic, or organometallic side groups. Through their modifications across different phosphonate groups, phosphazene offers a variety of beneficial properties. The glass transition temperature of these polymers is low [70]. Each subunit contains phosphorus and nitrogen in their maximum oxidized form, making the subunits

non-flammable. Phosphates have the advantage of being exceptionally resistant to the deprotonation reaction, making them a perfect candidate for PEM fuel cell formulations [71]. The combination of these features and their low cost make phosphates a good platform for PEM fuel cells [72].

3.7 Ceramic PEM

Researchers have been focusing more and more on investigating the performance of ceramic materials for use in fuel cell technology in recent decades [73,74]. PEM made of ceramic can be classified into two types as non-metallic metal oxide. Non-metal ceramic PEMs, like crystalline silica, have good chemical and mechanical durability, a low cost of construction, and great temperature tolerance. Non-metal ceramic PEM, on the other hand, has a substantially lower protonic conductivity than Nafion. [75].

For metal oxide ceramic PEM oxygen ions are the major transfer ions in metal oxide ceramic membranes, which are primarily used in solid oxide fuel cells. At various humidities, many metal oxides and metal oxyhydroxides, such as TiO_2 , Al_2O_3 , BaZrO_3 , and FeOOH , have demonstrated the ability to conduct protons [76]. Both TiO_2 and Al_2O_3 have low protonic conductivities, similar to silica glass [77]. The protonic conductivity of FeOOH is substantially higher than that of TiO_2 and Al_2O_3 , and much higher than that of Nafion [78]. The ferroxane ceramic membranes, on the other hand, have low elasticity and compression resistance. Because the precursor of those membranes, lepidocrocite, has poor mechanical qualities, they are brittle and easily break into little pieces.

3.8 Inorganic–organic composite PEM

Membranes that contain an organic polymer and an inorganic solid are called inorganic–organic membranes. Fuel cells perform better under high temperature, low relative humidity conditions when an inorganic phase is present because it enhances the interaction between components, limits dimensional change, and enhances performance. As a result, multiple concepts of organic and inorganic fuel cell membranes were developed and implemented into fuel cell stacks. A novel approach uses bimodal/spinodal transformations, nanoporous technologies, or nanoporous synthesis to organize the organic and inorganic components.

There are two basic categories of inorganic–organic composite membranes:

- Membranes made up of proton-conducting polymers and inorganic particles that are less proton-conducting.
- Membranes made up of proton-conducting particles and organic polymers that are less proton-conducting

Nafion is generally combined with solid inorganic acids, silicon dioxides or metal oxides to create composite membranes because it improves the conductivity of protons and maintains chemical and mechanical stability at high temperatures and relatively low humidity [79].

4. Batteries

The growing usage of variable renewable energy sources necessitates battery storage devices to fulfill high demand during energy consumption peaks. The energy storage will be essential for the future network and a carbon-free world, enabling intermittent renewable energy sources to supply energy to household consumers and businesses and hybrid vehicles. Battery storage is proving to be a promising option for electricity storage, offering flexibility to the system due to its unique ability to support, hold and emit electricity, as well as the benefits of partnering with renewable energy sources. The spatial versatility sets it apart from traditional energy storage technologies, such as pumping storage, allowing the batteries to be installed closer to their customers.

The most fundamental barrier to widespread of marketing strategy is the cost of batteries. Even if stationary applications do not require a long-standing potential, the possibility of periodic discharge requires high output voltages, greater power density, and long service life. Electrochemical energy storage systems can release energy quickly if required. System based on redox flow batteries (RFB) offers the added benefit of versatility, making them one of the most attractive electrical energy storage technologies. In RFBs, different redox pairs such as Sn/Cl, Cr/Ti, V/Sn, Fe/Cr, and V/Fe, were examined [80]. The vanadium redox batteries (Fig. 1) were popular because the other methods get away from the crossing of contaminants as the electrolyte contains various components and, as a result, experiences self-discharge and loss of capacity.

Another method is to find a new membrane technology that is usually followed by structural changes. The optimal membrane includes the following features:

- Substantial ion-exchange specificity
- Higher ionic conductance
- A low rate of water absorption
- The lower proportion of dilatation
- The conductivity of high order
- Chemically and thermally stable
- Cost-effective

Figure 3 Schematic representation of a VRB system [81]

4.1 Types of exchange membranes

The different membrane types used in redox flow battery (RFB) systems are as follows (Fig. 4.):

- Cationic exchange membranes (CEM)
- Anionic exchange membranes (AEM)
- Amphoteric ion-exchange membranes (AIEM)
- Zeolite membranes

Fig. 4. Classes of Exchange Membranes

4.1.1 Cationic exchange membranes

In the initial phase, sulfonated polyethylene and polystyrene components were used to make the membranes for vanadium redox batteries. Selemion and Nafion membranes exhibit properties that are suitable for VRB applications [81]. The following materials have been widely applied to overcome the limitations of conventional membranes:

- Polyethylene based membranes
- Fluorocarbon based membranes
- Nafion with polymeric composite membranes
- Nafion with inorganic integrated membranes

4.1.1.1 Polyethylene membranes

Polyethylene's affordability and easy production with desirable characteristics made it the subject of extensive studies in the 1990s. Sulfonic acid groups are often introduced into these materials as cation exchange sites, resulting in proton conductivity. Sulfonic groups can be introduced using various reactants, for example, sulfuric acid and sulfuryl chloride [82]. It is possible to modify the pores of the membrane by using different polymers, providing lower-cost supports, and the use of polymers like Nafion to fill the pores. As a result, the materials costs will be reduced. Examples of affordable and readily available membrane supports are shown in Table 2.

Table 2 Polyethylene Membranes [83]

Membrane	Properties
Daramic	Polyethylene with a high molecular weight has high strength. Furthermore, the material is oxidation-resistant.
Daramic incorporated with divinylbenzene mixture of Amberlite and methanol	Enhance the selectivity of the membrane.
Daramic pores infused with Polysodium 4-styrene-sulfate (PSSS)	Increase the cation capability with divinylbenzene cross link.

4.1.1.2 Fluorocarbon membranes

Polymers with fluorinated carbon backbones are used largely in membranes for VRB and fuel cells. These materials can be used as base material to enhance the stability of the VRB battery under oxidative conditions. Dupont Nafion and Nafion 117 are fluorocarbon polymers with a hydrophobic backbone similar to Teflon and hydrophilic side chains adorned with sulfonic acid groups [84]. Polymer names are coded with numbers that indicate the membrane's thickness and equivalent weight.

4.1.1.3 Polymeric composite membranes

Costs can be reduced by substituting cheaper materials for the Nafion. Nafion membranes can be laminated with poly(ether ketone) SPEEK membranes to reduce their cost. SPEEK has excellent conductivity, but it is chemically unstable when exposed to oxidative VO_2^+ environments. In VRB applications, coating the SPEEK material in the Nafion layer prevents substantial performance losses without affecting its stability [85]. A commercial hybrid membrane based on Nafion is now available, such as VANADion [86]. Multiple charges and discharges in a VANADion hybrid membrane have shown similar durability to Nafion 115 [87].

4.1.1.4 Inorganic hybrid membranes

The surface of Nafion has polar molecule clusters in the membrane that enhance V-crossover. Inorganic nanoparticles block these polar nanoclusters when filled with inorganic nanoparticles. The following are the examples of the Nafion based inorganic hybrid membranes:

- A silica sol-gel was used to fill the pores in the Nafion 117 membrane. Despite the composite Nafion/ SiO_2 membrane's high protons conductivity, the IEC properties were preserved. The V crossover, on the other hand, was drastically reduced [88].
- The Nafion/ORMOSIL membrane is made up of tetraethyl orthosilicate (TEOS) and diethoxydimethylsilane (DEDMS). Hybrid membranes achieve superior to Nafion membranes in terms of efficiency and Nafion-silica membranes as well as a reduced rate of self-discharge [89].

4.1.1.5 Polymerization of the Nafion surface

A polymer layer can be applied to Nafion or polyelectrolytes can be deposited to reduce the permeability of the membrane, however, these systems may cause membrane inflammation. The effects of inflammation on membrane longevity are detrimental. An interface polymerization of polyelectrolyte polyimide can reduce swelling when placed on

the surface of Nafion. On the surface of Nafion, a surface cationic charge is formed by forming a layer that is strongly bonded with Nafion. Consequently, the membrane decreased crossover rate of vanadium ions, but a higher resistance per unit area. The membrane's lower permeability causes a reduction in water transfer and self-discharge [80]. Graphene materials have attracted attention in recent decades due to their excellent conductivity, mechanical properties, and barrier characteristics [85]. Graphene oxide (GO) is blended with nylon to form a well organized membrane that maintains an efficient barrier, preventing the electrons in the direction of the V from cross-over [85].

4.1.1.6 Poly aryl ether membranes

SPEEK, SPES, and SPESK are sulfonated aryl backbone polymers that could be used as an alternative to Nafion. The quaternary ammonium groups, imidazole, and sulfonic acid can easily be incorporated into these materials to achieve excellent thermomechanical stability and proton permeability [90]. The SPES, SPESK and SPEEK are attractive alternatives for vanadium redox battery usage due to their low cost, excellent electrochemical stability, and potent mechanical behavior. Depending on the amount of sulfonation, these materials exhibit varying proton conductivities; however, they are generally lower than Nafion [91].

Cell discharge and membrane degradation cause lower membrane lifetime due to interactions with cationic exchange membranes and V electrolytes. It is envisaged that commercial membranes would be treated with organic nanoparticles, such as graphene oxide, to produce the most promising outcomes. Current VRB membrane technology uses Nafion 117, which is costly and has a high V permeability. Also, hybrid membranes made from Nafion and SPEEK were researched in the hopes of reducing membrane costs. One other promising method uses relatively inexpensive polypropylene or polyethylene membranes.

4.1.2 Anion membrane

The ionic exchange membrane (AEM) is an alternative membrane class. A positive charge on their functioning groups repels the positively charged species of V from the membrane. It is also known as the Donnan effect [92]. In spite of the AEM's reduced V permeability being of high interest, they are not suitable for VRB use. These AEMs exhibit reduced proton conductivity along with poor chemical stability, making them unsuitable for commercial applications. Polymer backbones and functional groups are the primary factors affecting membrane stability. AEM materials for VRB have recently been investigated for their stability and conductivity. Due to the chemical stability of polybenzimidazole (PBI),

it is suitable for use in VRB, which is strongly acidic and oxidative and is therefore more attractive [93].

PBI also reduces water permeability by providing narrow pore sizes [94]. This type of membrane is also known as an acid-doped membrane. Nonfluorinated hydrocarbons undergo highly reactive reactions when exposed to VRB conditions due to their high charge. In addition, quaternary ammonium and imidazole functionalized poly(p-phenylene) based membrane was prepared as an AEM. Results showed that quaternary ammonium groups were best suited to prepare the membrane. In recent years, researchers have focused on improving the stability of these groups by changing the polymer's chemical structure [95].

4.1.3 Amphoteric ion-selective membrane (AISM)

Membranes containing cationic and anionic selective membranes that have the combined features of AEMs and CEMs are known as amphoteric ion selective membranes (AISMs). CEMs exhibit better resistance to chemical degradation and higher conductivity, while AEMs exhibit lower V cross-over rates [96]. Sulphate and vanadium species can be made less permeable by adding both AEM and CEM properties at the same time [97].

4.1.4 Zeolite membranes

Molecular separation is possible in zeolite due to their uniform porosity, which allows them to be used for separating molecules by selecting the shape and size of molecules that penetrate. Zeolites contain many Bronsted Acidic Sites, which contribute to an increased concentration of protons [98]. Within the configuration, these sites are created by the formation of Silicon-Oxygen-Aluminum linkages. VRBs made from zeolite have recently attracted attention for their use as membranes [99]. Proton at a high concentration and a lower thickness led to a high conductivity of the material [100]. The material's higher conductivity is due to the increased proton concentration as well as the reduced width. The polymer also possesses an excellent affinity for membranes because of its small pore sizes

Conclusions

Globally, the change in the climatic condition, especially the CO₂ emission has becoming the impending and serious crisis. The utilization of renewable energy resources could reduce the environmental impact. The viable alternative to renewable energy is the membrane based power generation processes. In the recent years, the membrane based energy production has proven to be a promising technology interms of ease of operation, thermal, chemical and mechanical stability, and also easy scale up of operation. The bio-polymeric membranes have shown significant results in the application of fuel cells

compared to the commercially available membranes. Various developments have been implemented in the fabrication of advanced functional membranes to enhance their performance, permeability, technical and economical feasibility. However, there are still lack of experimental results to enhance the scale up of processes. Also, the successful application of the process depends upon the adoptability of efficient and inexpensive membranes. In the past few decades, tremendous improvements have been carried out to increase the feasible applications of membrane based energy generation processes. In the future, it could be implemented successfully in large scale.

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References

- [1] L. Dai, K. Huang, Y. Xia, Z. Xu, Two-dimensional material separation membranes for renewable energy purification, storage, and conversion, *Green Energy Environ.* 6 (2021) 193–211. <https://doi.org/10.1016/j.gee.2020.09.015>
- [2] H. Wang, J. Xu, L. Sheng, X. Liu, Y. Lu, W. Li, A review on bio-hydrogen production technology, *Int. J. Energy Res.* 42 (2018) 3442–3453. <https://doi.org/10.1002/er.4044>
- [3] S.J. Einarsson, B. Wu, Thermal associated pressure-retarded osmosis processes for energy production: A review, *Sci. Total Environ.* 757 (2021) 143731. <https://doi.org/10.1016/j.scitotenv.2020.143731>
- [4] J. Zaidi, T. Matsuura (Eds.), *Polymer membranes for fuel cells*, Springer Sci. Rev. 2008.
- [5] G. Hoogers, *Fuel Cell Technology Handbook*, CRC Press, Boca Raton (FL), 2003. <https://doi.org/10.1201/9781420041552>
- [6] C. Berger, *Handbook of Fuel Cell Technology*, Prentice-Hall, Englewood Cliffs (NJ), 1968.
- [7] B. Smitha, S. Sridhar, A.A. Khan, Solid polymer electrolyte membranes for fuel cell applications – a review, *J. Membr. Sci.* 259 (2005) 10-26. <https://doi.org/10.1016/j.memsci.2005.01.035>
- [8] N.M. Sammes, *Fuel Cell Technology: Reaching Towards Commercialization*,

Springer, London, 2006. <https://doi.org/10.1007/1-84628-207-1>

- [9] G.F. McLean, T. Niet, S. P. Richard, N. Djilali, An assessment of alkaline fuel cell technology, *Int. J. Hydrog. Energy* 27 (2002) 507-526. [https://doi.org/10.1016/S0360-3199\(01\)00181-1](https://doi.org/10.1016/S0360-3199(01)00181-1)
- [10] M.W. Ellis, M.R.V. Spakovsky, D.J. Nelson, Fuel cell systems: efficient, flexible energy conversion for the 21st century, *Proc. IEEE*. 89(12) (2001) 1808-1818. <https://doi.org/10.1109/5.975914>
- [11] F. Barbir, PEM fuel cells, In *Fuel Cell Technology*, Springer, London, 2006, pp. 27-51. https://doi.org/10.1007/1-84628-207-1_2
- [12] S. Giddey, S.P.S. Badwal, A. Kulkarni, C. Munnings, A comprehensive review of direct carbon fuel cell technology, *Prog. Energy Combust. Sci.* 38(3) (2012) 360-399. <https://doi.org/10.1016/j.pecs.2012.01.003>
- [13] P. Hoffmann, *Tomorrow's energy: hydrogen, fuel cells, and the prospects for a cleaner planet*, MIT press, 2012. <https://doi.org/10.7551/mitpress/8625.001.0001>
- [14] Y. Song, C. Zhang, C.Y. Ling, M. Han, R.Y. Yong, D. Sun, J. Chen, Review on current research of materials, fabrication and application for bipolar plate in proton exchange membrane fuel cell, *Int. J. Hydrog. Energy* 45(54) (2020) 29832-29847. <https://doi.org/10.1016/j.ijhydene.2019.07.231>
- [15] B.E. Logan, M. Elimelech, Membrane-based processes for sustainable power generation using water, *Nature*. 488 (2012) 313-319. <https://doi.org/10.1038/nature11477>
- [16] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—Development to date and future potential, *J. Membr. Sci.* 370 (2011) 1-22. <https://doi.org/10.1016/j.memsci.2010.12.036>
- [17] S. Chou, R. Wang, L. Shi, Q. She, C. Tang, A. Fane, Thin-film composite hollow fiber membranes for Pressure Retarded Osmosis (PRO) process with high power density, *J. Membr. Sci.* 389 (2012) 25–33. <https://doi.org/10.1016/j.memsci.2011.10.002>
- [18] J.W. Post, H.V.M. Hamelers, C.J.N. Buisman, Energy Recovery from Controlled Mixing Salt and Fresh Water with a Reverse Electrodialysis System, *Environ. Sci. Technol.* 42 (2008) 5785-5790. <https://doi.org/10.1021/es8004317>

- [19] A. Achilli, T.Y. Cath, A.E. Childress, Power generation with pressure retarded osmosis: An experimental and theoretical investigation, *J. Memb. Sci.* 343 (2009) 42–52. <https://doi.org/10.1016/j.memsci.2009.07.006>
- [20] A. Achilli, A.E. Childress, Pressure retarded osmosis: From the vision of Sidney Loeb to the first prototype installation - Review, *Desalination* 261 (2010) 205–211. <https://doi.org/10.1016/j.desal.2010.06.017>
- [21] K. Nijmeijer, S. Metz, Chapter 5 Salinity Gradient Energy, in: I.C. Escobar, A.I.B.T.-S.S. and E. Schafer (Eds.), *Sustain. Water Futur. Water Recycl. versus Desalin.*, Elsevier, 2010, pp. 95–139. [https://doi.org/10.1016/S1871-2711\(09\)00205-0](https://doi.org/10.1016/S1871-2711(09)00205-0)
- [22] S. Loeb, Large-scale power production by pressure-retarded osmosis, using river water and sea water passing through spiral modules, *Desalination* 143 (2002) 115–122. [https://doi.org/10.1016/S0011-9164\(02\)00233-3](https://doi.org/10.1016/S0011-9164(02)00233-3)
- [23] N. Bajraktari, C. Helix-Nielsen, H.T. Madsen, Pressure retarded osmosis from hypersaline sources — A review, *Desalination* 413 (2017) 65–85. <https://doi.org/10.1016/j.desal.2017.02.017>
- [24] H. Manzoor, M.A. Selam, S. Adham, H.K. Shon, M. Castier, A. Abdel-Wahab, Energy recovery modeling of pressure-retarded osmosis systems with membrane modules compatible with high salinity draw streams, *Desalination* 493 (2020) 114624. <https://doi.org/10.1016/j.desal.2020.114624>
- [25] Q. She, Y.K.W. Wong, S. Zhao, C.Y. Tang, Organic fouling in pressure retarded osmosis: Experiments, mechanisms and implications, *J. Membr. Sci.* 428 (2013) 181–189. <https://doi.org/10.1016/j.memsci.2012.10.045>
- [26] X. Li, T. Cai, T.-S. Chung, Anti-Fouling Behavior of Hyperbranched Polyglycerol-Grafted Poly(ether sulfone) Hollow Fiber Membranes for Osmotic Power Generation, *Environ. Sci. Technol.* 48 (2014) 9898–9907. <https://doi.org/10.1021/es5017262>
- [27] L. Zhang, Q. She, R. Wang, S. Wongchitphimon, Y. Chen, A.G. Fane, Unique roles of aminosilane in developing anti-fouling thin film composite (TFC) membranes for pressure retarded osmosis (PRO), *Desalination* 389 (2016) 119–128. <https://doi.org/10.1016/j.desal.2015.12.024>
- [28] G. Han, Z.L. Cheng, T.-S. Chung, Thin-film composite (TFC) hollow fiber membrane with double-polyamide active layers for internal concentration polarization and fouling mitigation in osmotic processes, *J. Membr. Sci.* 523 (2017) 497–504. <https://doi.org/10.1016/j.memsci.2016.10.022>

- [29] E. Abbasi-Garravand, C.N. Mulligan, C.B. Laflamme, G. Clairet, Role of two different pretreatment methods in osmotic power (salinity gradient energy) generation, *Renew. Energy*. 96 (2016) 98–119.
<https://doi.org/10.1016/j.renene.2016.04.031>
- [30] Q. She, X. Jin, C.Y. Tang, Osmotic power production from salinity gradient resource by pressure retarded osmosis: Effects of operating conditions and reverse solute diffusion, *J. Membr. Sci.* 401–402 (2012) 262–273.
<https://doi.org/10.1016/j.memsci.2012.02.014>
- [31] Y. Li, S. Zhao, L. Setiawan, L. Zhang, R. Wang, Integral hollow fiber membrane with chemical cross-linking for pressure retarded osmosis operated in the orientation of active layer facing feed solution, *J. Membr. Sci.* 550 (2018) 163–172.
<https://doi.org/10.1016/j.memsci.2017.12.074>
- [32] I. MS, S. Sultana, S. Adhikary, R. MS, Highly effective organic draw solutions for renewable power generation by closed-loop pressure retarded osmosis, *Energy Convers. Manag.* 171 (2018) 1226–1236.
<https://doi.org/10.1016/j.enconman.2018.06.031>
- [33] Z. Yuan, Y. Yu, L. Wei, X. Sui, Q. She, Y. Chen, Pressure-retarded membrane distillation for simultaneous hypersaline brine desalination and low-grade heat harvesting, *J. Membr. Sci.* 597 (2020) 117765.
<https://doi.org/10.1016/j.memsci.2019.117765>
- [34] S.K. Hubadillah, Z.S. Tai, M.H.D. Othman, Z. Harun, M.R. Jamalludin, M.A. Rahman, J. Jaafar, A.F. Ismail, Hydrophobic ceramic membrane for membrane distillation: A mini review on preparation, characterization, and applications, *Sep. Purif. Technol.* 217 (2019) 71–84. <https://doi.org/10.1016/j.seppur.2019.02.014>
- [35] F.J. Arias, S. de las Heras, The brinesiphon: A homolog of the thermosiphon driven by induced salinity and downward heat transfer, *Sol. Energy*. 153 (2017) 454–458.
<https://doi.org/10.1016/j.solener.2017.05.091>
- [36] F.J. Arias, A first estimate for a pressure retarded osmosis-driven thermosyphon, *Sol. Energy*. 159 (2018) 962–965. <https://doi.org/10.1016/j.solener.2017.10.064>
- [37] A.M.O. Mohamed, Y. Bicer, Integration of pressure retarded osmosis in the solar ponds for desalination and photo-assisted chloralkali processes: Energy and exergy analysis, *Energy Convers. Manag.* 195 (2019) 630–640.
<https://doi.org/10.1016/j.enconman.2019.05.032>

- [38] N. Sezer, M. Koç, Development and performance assessment of a new integrated solar, wind, and osmotic power system for multigeneration, based on thermodynamic principles, *Energy Convers. Manag.* 188 (2019) 94–111.
<https://doi.org/10.1016/j.enconman.2019.03.051>
- [39] P. Wang, Y. Cui, Q. Ge, T. Fern Tew, T.S. Chung, Evaluation of hydroacid complex in the forward osmosis–membrane distillation (FO–MD) system for desalination, *J. Membr. Sci.* 494 (2015) 1–7.
<https://doi.org/10.1016/j.memsci.2015.07.022>
- [40] N. Cong Nguyen, H. Cong Duong, S.-S. Chen, H. Thi Nguyen, H. Hao Ngo, W. Guo, H. Quang Le, C. Cong Duong, L. Thuy Trang, A. Hoang Le, X. Thanh Bui, P. Dan Nguyen, Water and nutrient recovery by a novel moving sponge – Anaerobic osmotic membrane bioreactor – Membrane distillation (AnOMBR-MD) closed-loop system, *Bioresour. Technol.* 312 (2020) 123573.
<https://doi.org/10.1016/j.biortech.2020.123573>
- [41] F. Gao, L. Wang, J. Wang, H. Zhang, S. Lin, Nutrient recovery from treated wastewater by a hybrid electrochemical sequence integrating bipolar membrane electrodialysis and membrane capacitive deionization, *Environ. Sci. Water Res. Technol.* 6 (2020) 383–391. <https://doi.org/10.1039/C9EW00981G>
- [42] S.H. Chae, J. Seo, J. Kim, Y.M. Kim, J.H. Kim, A simulation study with a new performance index for pressure-retarded osmosis processes hybridized with seawater reverse osmosis and membrane distillation, *Desalination* 444 (2018) 118–128.
<https://doi.org/10.1016/j.desal.2018.07.019>
- [43] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, Advances in Direct Methanol Fuel Cells, *J. Power sources* 47 (1994) 377–385.
[https://doi.org/10.1016/0378-7753\(94\)87016-0](https://doi.org/10.1016/0378-7753(94)87016-0)
- [44] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative polymer systems for proton exchange membranes (PEMs), *Chem. Rev.* 104 (2004) 4587–4611. <https://doi.org/10.1021/cr020711a>
- [45] H. Matsuyama, Y. Kitamura, Y. Naramura, Diffusive Permeability of Ionic Solutes in Charged Chitosan Membrane, *J. Appl. Polym. Sci.* 72 (1999) 397–404.
[https://doi.org/10.1002/\(SICI\)1097-4628\(19990418\)72:3<397::AID-APP9>3.0.CO;2-C](https://doi.org/10.1002/(SICI)1097-4628(19990418)72:3<397::AID-APP9>3.0.CO;2-C)

- [46] R. Xu, Y. Wu, X. Wang, J. Zhang, X. Yang, B. Zhu, Enhanced ionic conductivity of yttria-stabilized ZrO₂ with natural CuFe-oxide mineral heterogeneous composite for low temperature solid oxide fuel cells, *Int. J. Hydrogen Energy* 42 (2017) 17495–17503. <https://doi.org/10.1016/j.ijhydene.2017.05.218>
- [47] L. Li, Q. Shi, L. Huang, C. Yan, Y. Wu, Green synthesis of faujasite-La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} mineral nanocomposite membrane for low temperature advanced fuel cells, *Int. J. Hydrogen Energy* 46 (2021) 9826–9834. <https://doi.org/10.1016/j.ijhydene.2020.05.275>
- [48] U. Lucia, Overview on fuel cells, *Renew. Sustain. Energy Rev.* 30 (2014) 164-169. <https://doi.org/10.1016/j.rser.2013.09.025>
- [49] O.Z. Sharaf, M.F. Orhan, An overview of fuel cell technology: Fundamentals and applications, *Renew. Sustain. Energy Rev.* 32 (2014) 810-853. <https://doi.org/10.1016/j.rser.2014.01.012>
- [50] G. Cacciola, V. Antonucci, S. Freni, Technology up date and new strategies on fuel cells, *J. Power Sources* 100(1-2) (2001) 67-79. [https://doi.org/10.1016/S0378-7753\(01\)00884-9](https://doi.org/10.1016/S0378-7753(01)00884-9)
- [51] V.S. Bagotsky, *Fuel cells: problems and solutions*, 56, John Wiley & Sons, 2012. <https://doi.org/10.1002/9781118191323>
- [52] J. A. Flores, Comparative study of different fuel cell technologies, *Bol. Soc. Esp. Ceram. Vidr.* 52(3) (2013) 105-117. <https://doi.org/10.3989/cyv.142013>
- [53] L. An, T.S. Zhao, Transport phenomena in alkaline direct ethanol fuel cells for sustainable energy production, *J. Power Sources* 341 (2017) 199-211. <https://doi.org/10.1016/j.jpowsour.2016.11.117>
- [54] E.H. Majlan, D. Rohendi, W.R.W. Daud, T. Husaini, M.A. Haque, Electrode for proton exchange membrane fuel cells: A review, *Renew. Sustain. Energy Rev.* 89 (2018) 117-134. <https://doi.org/10.1016/j.rser.2018.03.007>
- [55] S. Shahgaldi, A. Ozden, X. Li, F. Hamdullahpur, A novel membrane electrode assembly design for proton exchange membrane fuel cells: Characterization and performance evaluation, *Electrochim. Acta.* 299 (2019) 809-819. <https://doi.org/10.1016/j.electacta.2019.01.064>

- [56] A. Abaspour, N.T. Parsa, M. Sadeghi, A new feedback Linearization-NSGA-II based control design for PEM fuel cell, *Int. J. Comput. Appl.* 97(10) (2014) 25-32. <https://doi.org/10.5120/17044-7354>
- [57] L. Zhang, S.R. Chae, Z. Hendren, J.S. Park, M.R. Wiesner, Recent advances in proton exchange membranes for fuel cell applications, *Chem. Eng. J.* 204 (2012) 87-97. <https://doi.org/10.1016/j.cej.2012.07.103>
- [58] S. Bose, T. Kuila, T.X.H. Nguyen, N.H. Kim, K.T. Lau, J.H. Lee, Polymer membranes for high temperature proton exchange membrane fuel cell: recent advances and challenges, *Prog. Polym. Sci.* 36(6) (2011) 813-843. <https://doi.org/10.1016/j.progpolymsci.2011.01.003>
- [59] B. Zhang, Y. Cao, S. Jiang, Z. Li, G. He, H. Wu, Enhanced proton conductivity of Nafionnanohybrid membrane incorporated with phosphonic acid functionalized graphene oxide at elevated temperature and low humidity. *J. Membr. Sci.* 518 (2016) 243-253. <https://doi.org/10.1016/j.memsci.2016.07.032>
- [60] S. Ren, G. Sun, C. Li, Z. Liang, Z. Wu, W. Jin, X. Qin, X. Yang, Organic silica/Nafion® composite membrane for direct methanol fuel cells, *J. Membr. Sci.* 282(1-2) (2006) 450-455. <https://doi.org/10.1016/j.memsci.2006.05.050>
- [61] V. Tricoli, Proton and methanol transport in poly(perfluorosulfonate) membranes containing Cs⁺ and H⁺ cations, *J. Electrochem. Soc.* 145 (1998) 3798-3801. <https://doi.org/10.1149/1.1838876>
- [62] L. Merlo, A. Ghielmi, L. Cirillo, M. Gebert, V. Arcella, Membrane electrode assemblies based on HYFLON® ion for an evolving fuel cell technology, *Sep. Sci. Technol.* 42(13) (2007) 2891-2908. <https://doi.org/10.1080/01496390701558334>
- [63] S.J. Paddison, J.A. Elliott, Molecular modeling of the short-side-chain perfluorosulfonic acid membrane, *J. Phys. Chem. A.* 109(33) (2005) 7583-7593. <https://doi.org/10.1021/jp0524734>
- [64] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative polymer systems for proton exchange membranes (PEMs), *Chem. Rev.* 104(10) (2004) 4587-4612. <https://doi.org/10.1021/cr020711a>
- [65] G.S. Prakash, M.C. Smart, Q.J. Wang, A. Atti, V. Pleyne, B. Yang, ... S. Surampudi, High efficiency direct methanol fuel cell based on poly (styrenesulfonic) acid (PSSA)–poly (vinylidene fluoride)(PVDF) composite membranes, *J. Fluor. Chem.* 125(8) (2004) 1217-1230. <https://doi.org/10.1016/j.jfluchem.2004.05.019>

- [66] A. Shukla, P. Dhanasekaran, S. Sasikala, N. Nagaraju, S.D. Bhat, V.K. Pillai, Covalent grafting of polystyrene sulfonic acid on graphene oxide nanoplatelets to form a composite membrane electrolyte with sulfonated poly (ether ether ketone) for direct methanol fuel cells, *J. Membr. Sci.* 595 (2020) 117484. <https://doi.org/10.1016/j.memsci.2019.117484>
- [67] K.I. Okamoto, Sulfonated polyimides for polymer electrolyte membrane fuel cell, *J Photopolym Sci Technol.* 16(2) (2003) 247-254. <https://doi.org/10.2494/photopolymer.16.247>
- [68] F. Zhang, N. Li, S. Zhang, S. Li, Ionomers based on multi sulfonated perylenedianhydride: Synthesis and properties of water resistant sulfonated polyimides, *J. Power Sources* 195(8) (2010) 2159-2165. <https://doi.org/10.1016/j.jpowsour.2009.10.026>
- [69] Y. He, C. Tong, L. Geng, L. Liu, C. Lu, Enhanced performance of the sulfonated polyimide proton exchange membranes by graphene oxide: Size effect of graphene oxide, *J. Membr. Sci.* 458 (2014) 36-46. <https://doi.org/10.1016/j.memsci.2014.01.017>
- [70] H.R. Allcock, Polyphosphazene elastomers, gels, and other soft materials, *Soft Matter.* 8(29) (2012) 7521-7532. <https://doi.org/10.1039/c2sm26011e>
- [71] H.R. Allcock, Generation of structural diversity in polyphosphazenes, *Appl. Organomet. Chem.* 27(11) (2013) 620-629. <https://doi.org/10.1002/aoc.2981>
- [72] H. Tang, P.N. Pintauro, Polyphosphazene membranes. IV. Polymer morphology and proton conductivity in sulfonated poly [bis (3-methylphenoxy) phosphazene] films, *J. Appl. Polym. Sci.* 79(1) (2001) 49-59. [https://doi.org/10.1002/1097-4628\(20010103\)79:1<49::AID-APP60>3.0.CO;2-J](https://doi.org/10.1002/1097-4628(20010103)79:1<49::AID-APP60>3.0.CO;2-J)
- [73] F.M. Vichi, M.I. T. Tejedor, M.A. Anderson, Effect of pore-wall chemistry on proton conductivity in mesoporous titanium dioxide, *Chem. Mater.* 12(6) (2000) 1762-1770. <https://doi.org/10.1021/cm9907460>
- [74] S.M. Haile, Fuel cell materials and components, *Acta Mater.* 51(19) (2003) 5981-6000. <https://doi.org/10.1016/j.actamat.2003.08.004>
- [75] E.M. Tsui, M.R. Wiesner, Fast proton-conducting ceramic membranes derived from ferroxane nanoparticle-precursors as fuel cell electrolytes, *J. Membr. Sci.* 318(1-2) (2008) 79-83. <https://doi.org/10.1016/j.memsci.2008.02.025>

- [76] S. Shamim, K. Sudhakar, B. Choudhary, J. Anwar, A review on recent advances in proton exchange membrane fuel cells: materials, technology and applications, *Adv. Appl. Sci. Res.* 6(9) (2015) 89-100.
- [77] S.P. Jiang, Functionalized mesoporous structured inorganic materials as high temperature proton exchange membranes for fuel cells, *J. Mater. Chem. A.* 2(21) (2014) 7637-7655. <https://doi.org/10.1039/C4TA00121D>
- [78] J. Lu, J. Zhang, Mesoporous Structured Materials as New Proton Exchange Membranes for Fuel Cells, In *Mesoporous Materials for Advanced Energy Storage and Conversion Technologies*, CRC Press, 2017, pp. 97-151. <https://doi.org/10.1201/9781315368580-3>
- [79] X. Sun, S.C. Simonsen, T. Norby, A. Chatzitakis, Composite membranes for high temperature PEM fuel cells and electrolyzers: a critical review, *Membranes.* 9(7), (2019) 83. <https://doi.org/10.3390/membranes9070083>
- [80] C.H.L. Tempelman, J.F. Jacobs, R.M. Balzer, V. Degirmenci, Membranes for all vanadium redox flow batteries, *J. Energy Storage.* 32 (2020) 101754. <https://doi.org/10.1016/j.est.2020.101754>
- [81] Z. Mai, H. Zhang, X. Li, C. Bi, H. Dai, Sulfonated poly (tetramethyldiphenyl ether ether ketone) membranes for vanadium redox flow battery application, *J. Power Sources.* 196(1) (2011) 482-487. <https://doi.org/10.1016/j.jpowsour.2010.07.028>
- [82] D. Ariono, I.G. Wenten, Surface modification of ion-exchange membranes: Methods, characteristics, and performance, *J. Appl. Polym. Sci.* 134(48) (2017) 45540. <https://doi.org/10.1002/app.45540>
- [83] J. Zuo, S. Bonyadi, T.S. Chung, Exploring the potential of commercial polyethylene membranes for desalination by membrane distillation, *J. Membr. Sci.* 497, (2016) 239-247. <https://doi.org/10.1016/j.memsci.2015.09.038>
- [84] J. Liao, Y. Chu, Q. Zhang, K. Wu, J. Tang, M. Lu, J. Wang, Fluoro-methyl sulfonated poly (arylene ether ketone-co-benzimidazole) amphoteric ion-exchange membranes for vanadium redox flow battery, *Electrochim. Acta.* 258 (2017) 360-370. <https://doi.org/10.1016/j.electacta.2017.11.063>
- [85] A. Eftekhari, Y.M. Shulga, S.A. Baskakov, G.L. Gutsev, Graphene oxide membranes for electrochemical energy storage and conversion, *Int. J. Hydrog. Energy.* 43(4) (2018) 2307-2326. <https://doi.org/10.1016/j.ijhydene.2017.12.012>

- [86] M. Ulaganathan, V. Aravindan, Q. Yan, S. Madhavi, M. S. Kazacos, T.M. Lim, Recent advancements in all-vanadium redox flow batteries, *Adv. Mater. Interfaces* 3(1) (2016) 1500309. <https://doi.org/10.1002/admi.201500309>
- [87] P. Yang, J. Long, S. Xuan, Y. Wang, Y. Zhang, J. Li, H. Zhang, Branched sulfonated polyimide membrane with ionic cross-linking for vanadium redox flow battery application, *J. Power Sources* 438 (2019) 226993. <https://doi.org/10.1016/j.jpowsour.2019.226993>
- [88] J. Xi, Z. Wu, X. Qiu, L. Chen, Nafion/SiO₂ hybrid membrane for vanadium redox flow battery, *J. Power Sources* 166(2) (2007) 531-536. <https://doi.org/10.1016/j.jpowsour.2007.01.069>
- [89] M.A. Aziz, S. Shanmugam, Zirconium oxide nanotube–Nafion composite as high performance membrane for all vanadium redox flow battery, *J. Power Sources* 337 (2017) 36-44. <https://doi.org/10.1016/j.jpowsour.2016.10.113>
- [90] J. Ran, L. Wu, Y. He, Z. Yang, Y. Wang, C. Jiang ... T. Xu, Ion exchange membranes: New developments and applications, *J. Membr. Sci.* 522 (2017) 267-291. <https://doi.org/10.1016/j.memsci.2016.09.033>
- [91] H. Prifti, A. Parasuraman, S. Winardi, T.M. Lim, M. Skyllas-Kazacos, Membranes for redox flow battery applications, *Membranes* 2(2) (2012) 275-306. <https://doi.org/10.3390/membranes2020275>
- [92] B. Shanahan, T. Böhm, B. Britton, S. Holdcroft, R. Zengerle, S. Vierrath, ... M. Breitwieser, 30 µm thin hexamethyl-p-terphenyl poly (benzimidazolium) anion exchange membrane for vanadium redox flow batteries, *Electrochem. Commun.* 102 (2019) 37-40. <https://doi.org/10.1016/j.elecom.2019.03.016>
- [93] L. Wang, A.T. Pingitore, W. Xie, Z. Yang, M.L. Perry, B.C. Benicewicz, Sulfonated PBI gel membranes for redox flow batteries, *J. Electrochem. Soc.* 166(8), (2019) A1449. <https://doi.org/10.1149/2.0471908jes>
- [94] J.K. Jang, T.H. Kim, S.J. Yoon, J.Y. Lee, J.C. Lee, Y.T. Hong, Highly proton conductive, dense polybenzimidazole membranes with low permeability to vanadium and enhanced H₂SO₄ absorption capability for use in vanadium redox flow batteries, *J. Mater. Chem. A* 4(37) (2016) 14342-14355. <https://doi.org/10.1039/C6TA05080H>
- [95] D. Chen, X. Chen, L. Ding, X. Li, Advanced acid-base blend ion exchange membranes with high performance for vanadium flow battery application, *J. Membr.*

Sci. 553 (2018) 25-31. <https://doi.org/10.1016/j.memsci.2018.02.039>

- [96] M. Bhushan, S. Kumar, A.K. Singh, V. K. Shahi, High-performance membrane for vanadium redox flow batteries: Cross-linked poly (ether ether ketone) grafted with sulfonic acid groups via the spacer, *J. Membr. Sci.* 583 (2019) 1-8. <https://doi.org/10.1016/j.memsci.2019.04.028>
- [97] P.K. Leung, Q. Xu, T.S. Zhao, L. Zeng, C. Zhang, Preparation of silica nanocomposite anion-exchange membranes with low vanadium-ion crossover for vanadium redox flow batteries, *Electrochim. Acta.* 105 (2013) 584-592. <https://doi.org/10.1016/j.electacta.2013.04.155>
- [98] S.H. Cha, Recent development of nanocomposite membranes for vanadium redox flow batteries, *J. Nanomater.* (2015) 207525. <https://doi.org/10.1155/2015/207525>
- [99] J. Kim, J.D. Jeon, S.Y. Kwak, Sulfonated poly (ether ether ketone) composite membranes containing microporous layered silicate AMH-3 for improved membrane performance in vanadium redox flow batteries, *Electrochim. Acta.* 243 (2017) 220-227. <https://doi.org/10.1016/j.electacta.2017.05.079>
- [100] X. Teng, Y. Guo, D. Liu, G. Li, C. Yu, J. Dai, A polydopamine-coated polyamide thin film composite membrane with enhanced selectivity and stability for vanadium redox flow battery, *J. Membr. Sci.* 601 (2020) 117906. <https://doi.org/10.1016/j.memsci.2020.117906>