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Chapter 2

Hydrogen Production by Membrane Water Splitting Technologies

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.76727

Abstract

Hydrogen production by membrane water splitting technologies is a sustainable method to synthesize hydrogen and provides an alternative to hydrogen production instead of conventional process of synthesizing hydrogen from steam methane reforming. A hybrid polymer electrolyte membrane electrolyzer operational at working temperature of above 80–200°C is advantageous for faster electrochemical kinetics, higher current exchange density, and more resistance to fuel impurities. Phosphoric acid (PA) doping onto polybenzimidazole (PBI) membrane shows significant improvement in proton conductivities, permeability, and thermal stability. PBI-based electrolyzer is relatively new to the hydrogen production technologies as compared to Nafion-based electrolyzer. However, the high cost of purchasing Nafion membrane and inability to execute electrolysis operational above 90°C has sparked new interest on PBI-based membrane, which is known for its good thermal stability.

Keywords: hydrogen production, water splitting, polymer electrolyte membrane, electrolysis, sustainable

1. Introduction

Sustainable energy from renewable resources has become a focal point for many researchers around the world in their search to minimize the carbon emission released to the atmosphere. Hydrogen energy is the cleanest available energy, which only releases heat and water as by-products. Moreover, hydrogen combustion contributes to zero carbon emission. The Kyoto Protocol tabled in 1997 that came into effect in 2005 aimed to reduce the greenhouse gases

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(GHG) by 5% (2005–2012) and 18% (2013–2020) against 1990 levels [1]. Unlike a conventional steam methane reforming process, the hybrid polymer electrolyte membrane (PEM) combines with copper (I) chloride and hydrochloric acid electrolytes that have a promising future of providing a sustainable hydrogen production.

Currently, there has been a crucial need for rapid changes from the hydrocarbon-based economy to the one with sustainable and renewable sources [2–4]. Many green technologies are available right now, such as the generation of hydrogen [5], solar electricity [6, 7], and other renewable energy technologies, but the capital expenditure to acquire this technology is very high as compared to conventional energy resources [8, 9]. For example, solar energy is limited by the efficiency of the panel and battery, while the electric vehicle is limited by the lack of charging facility and unsustainable production of electricity generation from coal- and petroleum-based fuel. It has been reported by Nicoletti et al. and Ball and Weeda [10, 11] the by-products from the combustion of hydrocarbon-based fuels are the major factors to the phenomena like global warming, the thinning of the ozone layer, acid rains, and air pollution and its harmful effect on respiratory problems. This is where hydrogen as the vital energy carrier and fuel sources offers sustainable and clean energy for the future [10, 12, 13].

Hydrogen does not exist individually, but it formed water molecules (H_2O) which contain single oxygen atom and dual hydrogen atom makes it an enormous amount of elements in the world. Hydrogen is able to generate sustainable, immaculate and cost-effective energy resources, which can uplift the economic activities of the world with environmentally friendly and secure energy. This is due to no carbon dioxide or carbon monoxide being produced in the process of combusting hydrogen with only water as by-products [14]. Hydrogen production can be synthesized from many types of resources like water, biomass, coal, methane, and others via chemical, thermal, and biological processes [15].

Hydrogen is also an important feedstock for chemical processes [16], and 97% of the world hydrogen supply comes from hydrocarbon-based fuels via reforming process [17] with the world's production of 50 million tons of hydrogen every year [15]. Among the various hydrogen production technologies that are available, electrolysis plays a vital role in producing sustainable hydrogen [18, 19]. Water electrolysis is also acknowledged as a crucial element in the forthcoming energy system [16]. Although this electrolysis technology was invented more than 100 years ago, the hydrogen production from water electrolysis is substantially more costly with the efficiency rate only 18–24% and mainly used when the high purity of hydrogen is needed or in a remote area where methane gas is not available. The cost of producing hydrogen from water electrolysis is more expensive because hydrogen does not exist as an independent gas but occurs naturally in the form of chemical compounds like the hydrocarbons and water [11, 20].

2. Types of membranes for hydrogen production

To date, there are few ways of synthesizing the ion exchange or polymer membranes including sulfonation, polymer blending, acid or base doping, addition of inorganic fillers, pores

filling, in-situ polymerization, and electrospinning [21, 22]. High-performance polymer electrolyte membranes (PEMs) must have the following characteristics [22]:

a. high proton conductivity

b. good electrical insulation

c. high mechanical and thermal stability

d. good oxidative and hydrolytic stability

e. cost-effectiveness

f. low tolerance to ion crossover/good barrier property

g. low swelling stress

h. capability for fabrication of membrane electrode assemblies (MEA)

One of the most important characteristics of the proton exchange membranes is water uptake that influences the electrochemical activity and hydromechanical stability of the membrane. Certainly, water is the fundamental element for proton transfer mechanism from the anode to the cathode in an electrochemical cell including an operation using non-sulfonated membranes in almost anhydrous condition and at a temperature range of 90–160°C [23]. However, the mechanical strength for a membrane with a higher water uptake reduces due to exorbitant swelling of the membrane. As a matter of fact, sulfonated membranes absorb more water molecules per acid group (λ) when compared with phosphonated membranes that make phosphonated membranes more favorable for PEM applications due to higher ionic exchange capacity (IEC) [24].

2.1. Polymer electrolyte membrane

Polymer electrolyte membrane usage in fuel cell technologies (PEM-FC) is widely accepted, and more advanced version of this PEM can significantly transform the energy security for probably 20–30 years from now. It has turned into an attractive research due to its advantages of generating minimum pollution, great power density, and excellent conversion. This is a promising path to be fossil fuel free and to contribute to other sustainable energy sources [25, 26].

Currently, perfluorosulfonic acid polymer membranes like Nafion is accepted as the most widely used applications for both PEM-FC and direct methanol fuel cell (DMFC) because of their superiority and exceptional performance in thermal stability, eminent ionic exchange capacity, and proton conductivity [26, 27]. However, the Nafion is costly, and it experiences huge methanol crossover for DMFC with the addition of depletion of proton conductivity when subjected to working temperature beyond 100°C [27]. Apart from isolating reactants from mixing together, PEM can allow proton to pass through while being nonelectrically conductive. Furthermore, PEMs have other functions of providing high ionic conductivity, good mechanical properties, and minimum to no ion crossover [28]. However, moderate operation

temperature from 80 to 180°C for PEM fuel cells is ideal for heat co-generation. In addition, with current low-temperature operation, a huge capital expenditure is required for acquiring the commercial perfluorosulfonic acid (PFSA) membrane.

Major obstacles for the development of Direct Methanol Fuel Cell (DMFC), PEM-FC, Redox Flow Batteries (RFB) technologies, which have a high crossover of ion via the membrane can be improved and rectified with the use of low feed/water/electrolyte crossover [28]. Multiple approaches and new types of materials have been formulated to mitigate the problem but with serious concerns in the chemical stability and proton conductivity. The membrane ionic conductivity can be enhanced by means of doping with acids such as heteropoly acids (HPA) [28].

In fuel cell development, the PEM needs to have the following characteristics including excellent proton conductivity, favorable mechanical properties, exceptional resistance to chemicals, and durable enough for endurance testing [4]. Nafion-based PEM is used for low temperatures operation <80°C, while for higher temperature of 120–200°C hydrocarbon polymers like polybenzimidazole (PBI), sulfonated poly(arylene ether ether ketone) and poly (bis(phenoxy) phosphazene) are being used as described in the literature. **Table 1** shows some of the proton exchange membranes that are manufactured by established organizations.

Currently, Nafion is used as a common membrane for solid polymer electrolyte although it has disadvantages for being expensive and a fluorinated-based polymer. Thus, recent studies are more focused on the improvement of cheaper and non-fluorinated polymers like polybenzimidazole (PBI), polyethersulfone (PES), sulfonated polysulfone (SPSF), polyaryleneethers, polyphosphazene, sulfonated polyetheretherketone (SPEEK), and polyimides. The advantages of these polymers are that they are cheaper and have good thermal, mechanical, and chemical properties. Out of these polymers, membranes from SPEEK polymer have demonstrated a very good performance for water electrolysis. The proton conductivity can be increased by adjusting the higher degree of sulfonation (DS) for SPEEK polymer due to its excellent mechanical properties. This will allow the optimization of DS onto the polymer

Organization	Type of membranes
US Polyfuel Inc.	Acid-based polyether ether ketone
Toshiba	Acid-based polyether ether sulfone
Sony	OH-modified fullerene based membranes
JSR Corporation, Japan	Polystyrene sulfonic acid-based compounds
Stuttgart University, Germany	Acid-based ionomer blends
Los Alamos National Laboratory (LANL)	Sulfonation sulfone polymer; PVDF-g-SPS
Ballard	Sulfonated F-styrene
DuPont	Modified Nafion
Asahi Glass	PFS/PTFE fibrils

Table 1. Proton exchange membrane of established manufacturers [4].

membrane by manipulating the temperature and immersion time of the sulfonation reaction. The DS of the polymers can also be manipulated by varying the sulfonating agent concentration and the sulfonated monomers content. Furthermore, the sulfonic group ($-SO_3H$) enhances the selectivity, solubility, and water uptake, which contributes to superior chemical properties [29, 30]. Aromatic polymers that are exposed to high sulfonation (higher DS) will have a better proton conductivity. However, higher DS can lead the polymer to become more soluble and swell in water, thus decrease the mechanical strength of the membrane significantly. Therefore, the method used to improve the electrochemical and mechanical properties of the membrane is by forming a composite membrane using the addition of organic and inorganic compounds [29].

Generally, PEM fuel cell working temperature is limited by the Nafion membrane electrochemical properties, which can only operate at a temperature less than 100°C. Although, the ideal working temperature of the PEM-FC based on Pt catalyst should be higher than 100°C as it can significantly mitigate the effect of CO poisoning [27]. Principally, fuel cell consumes oxygen and hydrogen gas to produce electricity, water, and heat as compared to an electrolyzer that produces hydrogen and oxygen as the products.

There are four types of polymer electrolytes for hydrogen economy, which includes fluorinated and partially fluorinated membranes, hydrocarbon membranes, aromatic membranes, and hybrid membranes.

The main polymer chain is used to categorize the type of polymer electrolytes. As a guideline, the primary chain indicates the surface morphology including physical and thermomechanical properties. Apart from that, the supporting chain contributes to the polymer functionality. Typical polymer chains consist of hydrocarbons, perfluorinated and aromatic, as their primary polymer chains. Majority of the polymers used in the research comprise sulfonic acid groups. It is located at supporting chains or as functional groups at the polymer backbone. The sulfonic group functions as a proton conductor in order to promote proton movement across the membrane [31].

2.1.1. Proton exchange membrane

In recent years, there has been an increasing amount of literature on proton exchange membrane particularly focusing on hydrogen production for fuel cells and electrolyzers. Di Noto et al. [32] reported that an excellent proton-conducting membrane for a fuel cell comprises the following attributes:

a. Exceptional stability on electrochemical and chemical properties

b. Great strength and stability on mechanical properties within process temperature limit

c. Membrane chemical properties are suitable for the membrane electrode assembly

d. Exceptionally very little reactant crossover

e. High water retention to maintain electrolyte species and avoid confined drying

f. Superior conductivity of proton to brace high current with the lowest resistance deprivation and minor electronic conductivity

g. Cheap in producing the membrane

Proton Exchange Membrane (PEM) is commonly used in the fuel cells setup. The most popular and widely used PEM is Nafion and Nafion-based membrane because of its excellent proton conductivity and good physicochemical properties. However, Nafion experiences very distinct fuel crossover, tedious process to synthesize, and weak proton conductivity at high temperature in low humidity condition. There are many types of research being conducted to find the alternative membranes for fuel cell systems. Polymers like poly (ether ether ketone), poly (arylene ether ketone), and poly (ether sulfone) have been studied and tested as solid electrolytes in fuel cell applications. All of the studies conducted for PEEK, PAEK, and PES support the fact that aromatic polymer electrolytes are suitable and perform very well in fuel cell systems. The criteria include excellent proton conductivity, good thermomechanical and chemical properties, and reasonable cost. This material is also cheaper and easier to form a membrane as compared to Nafion membranes.

Therefore, the PEEK is chosen as an alternative to Nafion primarily because it is cheaper and easier to synthesize with good electrochemical and stable physicochemical properties [27].

2.1.1.1. Nafion membrane

General Electric Co. (USA) is the first to develop proton exchange membrane (PEM) electrolyzer back in 1966 from a solid polymer electrolyte, which comprises of membrane, anode, and cathode. Nafion membrane produced by DuPont is the most well-known membrane that is made up of perfluorinated polymer with sulfonic acid functionalization as depicted in **Figure 1** [33].

Majority of the available PEM-FC are using proton exchange membranes that originate from perfluorosulfonic acid (PFSA) polymers such as Nafion 115, Nafion 117, and Nafion 212. Nafion has a very good chemical resistance, good mechanical properties, and are very durable [35]. Apart from that, Nafion shows good stability when subjected to radical degradation and

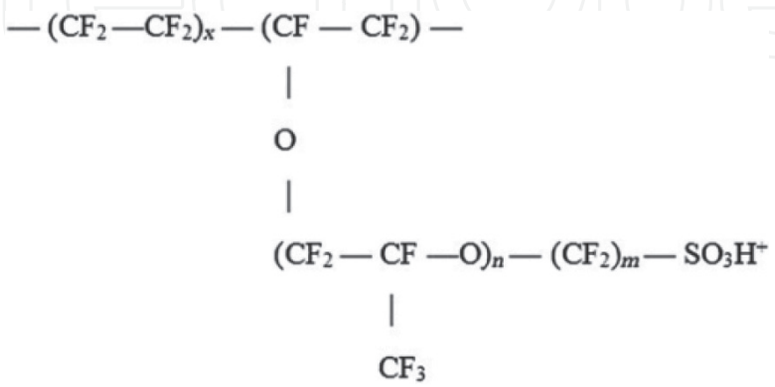


Figure 1. The structural formula of Nafion® membrane by DuPont de Nemours [34].

peroxide ions [36]. Despite all the advantages, Nafion also has few disadvantages such as they cannot function smoothly under dehydrated ambiance and cannot withstand higher operating temperature above 80°C (1 atm pressure) as it will deteriorate its good proton conductivity performance [35]. Moreover, Nafion is not suitable for temperature conditions below 0°C or beyond 100°C, and its proton conductivity is water dependent [36].

Nafion and perfluorinated membranes are considered as the benchmark for other new membrane synthesis [32]. There is also a study being carried out on the modification of Nafion-based membrane with polyaniline (PANI) by varying the membrane thickness. The physical properties such as ion exchange capacity (IEC), proton conductivity, and water uptake are investigated. Moreover, the Cu permeability or Cu crossover phenomena was studied using an ex situ Cu diffusion cell and the performance of the modified membrane was configured using a CuCl electrolytic system [37].

Perfluorosulfonic acid (PFSA) polymer electrolyte membrane conductivity and hydration properties can be enhanced by synthesizing composite membranes with organic fillers such as hygroscopic oxides (SiO_2/TiO_2), zirconium phosphates $Zr(HPO_4)_2 \cdot nH_2O$, ZrP), zirconium sulphophenylphosphates and heteropolyacids. Furthermore, ionic liquids or phosphoric acid can be a substitute for water due to less volatile properties while under dehydrating ambiance in order to sustain high proton conductivity, for example, $10^{-2} S \cdot cm^{-1}$ [38]. However, Nafion membrane is very expensive with the addition of not having adequate conductivity at a higher temperature of 90°C and near anhydrous condition. It is also not environmentally friendly due to the usage of many chemicals in its fabrication, utilization, and discarding processes [32]. In the DMFC system, the Nafion membrane or perfluorinated PEM cannot be directly used due to the high crossover of methanol that can shorten the lifetime and performance of the fuel cells. The high methanol crossover can be explained by the large channel related to the molecular structure that consists of a large ion group [4].

Currently, Nafion and Nafion-based membrane are the most popular and widely used membranes for applications in proton exchange membrane fuel cell, direct methanol fuel cell, and electrolyzers. It has good proton conductivity and fair thermal stability for operating in temperatures below 80°C. However, Nafion is very costly and permeable to fuel, thus allowing diffusion of anolyte to catholyte. In addition, Nafion also loses its good proton conductivity properties at operating temperatures beyond 100°C [27].

2.1.1.2. Polybenzimidazole

Polybenzimidazole (PBI) refers to multiple units of benzimidazole in the structure of aromatic heterocyclic polymers. PBI has a few advantages as compared to Nafion membrane including good tensile strength, fair chemical stability, and exclusive affinity with polyaryletherketone and some other polymers. **Figure 2** presents the synthesis of PBI polymer.

Although Nafion membrane is very good for processes that operate at temperatures from 20 to 80°C, it is not suitable for high-temperature (HT) applications above 100°C due to poor mechanical stability and the significant decrease of proton conductivity [40]. Polybenzimidazole (PBI) was first used by Wainright in 1995 for high-temperature-polymer electrolyte membrane

(HT-PEM) at 150°C and is a very suitable candidate for any process temperature ranging from 120 to 200°C [35, 41].

However, pristine PBI has very low conductivity when compared to Nafion, which makes it unsuitable as a replacement for Nafion. Researches to improve the proton conductivity of pristine PBI have been carried out by treating the PBI with many inorganic acids via PBI composite membrane synthesis. Sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) act as a synergistic effect of contributor and acceptor in transferring the proton, thus allowing for proton transport through the membrane. Phosphoric acid (H_3PO_4) is more favorable when compared to sulfuric acid (H_2SO_4) due to its superiority with process temperatures greater than 150°C in terms of mechanical strength, improved proton conductivity, and thermal durability [35, 42].

When PBI membrane was doped with phosphoric acid (H_3PO_4), its properties improved including low gas permeability, low methanol vapor crossover, and it did not need any humidification. Despite having the advantage of operating at a higher temperature range above 100°C, the doping process is necessary to reinforce the mechanical stability of the membrane due to standard PBI-like Celazole that has a low-to-medium linear molecular weight with poor mechanical stability and poor oxidative resistance. Following are the advantages of HT-PEM-FC that operates above 100°C: ability to use less expensive nonnoble catalyst like cobalt and iron, improved heat rejection rate, enhanced water management, more robust to impurities, and better electrode kinetics [41].

Hybrid membrane from PBI can be prepared by the addition of inorganic fillers such as silicates, titanium dioxide (TiO_2), zirconium dioxide (ZrO_2), heteropolyacids (HPA), and carbon nanotubes (CNT) [22]. Barium zirconium oxide ($BaZrO_3$) was fabricated as a composite membrane from PBI base according to Hooshyari et al. [43] who also researched on the nanocomposite PEM-ZrO_2 nanocluster that was mixed into a solution cast of 2,6-pyridine polybenzimidazole (2,6,Py-PBI) and doped with phosphoric acid with variations from 0 to 10 wt% of ZrO_2 nanocluster [44].

There are few approaches to enhance the properties of PBI-doped H_3PO_4 membrane, which includes a method of preparing ion cross-linked structures such as a mixture of PBI with sulfonated polyether ether ketone (SPEEK), sulfonated polysulfone, or sulfonated partially fluorinated arylene polyether [38]). In addition, improved PBI-doped phosphoric acid membrane can be synthesized by covalently cross-linked structure or composite/hybrid PBI membrane. In PBI/PA, the proton conductivity is strongly dependent on the acid doping level, which is defined as the number of PA molecules per repeating units of the polymer.

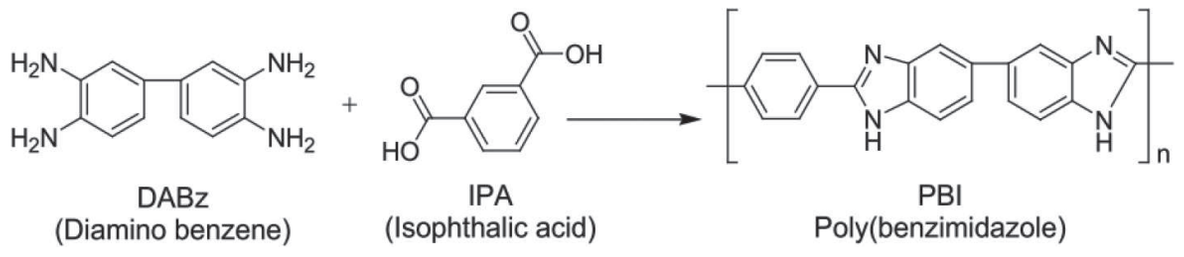


Figure 2. Synthesis of poly(benzimidazole) (PBI) [39].

PBI-based PEM-FC cathode is 70-fold more invulnerable to sulfur content in the air as compared to Nafion®-based PEM-FC cathodes [40]. It is also noted that acid doping in PBI shows a significant effect in the membrane thermal stability and proton conductivities [45]. The proton conductivities of acid-doped PBI membranes were also dependent to the doped acids in the order of $H_2SO_4 > H_3PO_4 > HClO_4 > HNO_3 > HCl$ [45, 46]. Similarly, Oono et al. [47] studied the influence of the phosphoric acid doping level in a PBI membrane by means of immersing the PBI membrane in 85% phosphoric acid solution for 500 min at 20°C and 80 min at 40 and 60°C. Sulfonated PBI showed higher proton conductivity as compared to pristine PBI membrane due to more active acid sites. PBI blending with Nafion, sulfonated polyether, and polyphosphazene were studied to investigate the effect on membrane stability and less permeable to methanol crossover. Moreover, the addition of inorganic fillers enhanced the properties of proton conductivities and physical strength of the modified membrane. However, doping decreased the proton conductivities, but this could be controlled by introducing sulfonated material as reinforcements.

There are numerous methods that have been implemented to enhance the conductivity and stability of PBI membranes, which include membrane fabrication technique for optimization, polymer backbone crosslinking, polymer blending, and creating composite membrane by the introduction of many kinds of organic acids. Factors influencing the proton conductivity of PA-doped PBI and PBI composite membrane are process temperature, acid doping level (ADL), and relative humidity (RH). This was found in PA-doped PBI that had a 5.6 doping level (mole number of H_3PO_4 per repeat unit of PBI) with a conductivity of 6.8×10^{-2} S cm^{-1} and process conditions at 200°C and 5% RH. Moreover, under the similar setting, the PBI composite membrane with 15 wt% of Zirconium Phosphate (ZrP) reported a greater conductivity of 9.6×10^{-2} S cm^{-1} [42]. Nonetheless, the PBI-based membrane still has the disadvantage of poor mechanical properties after doping with a high concentration of acid and poor ability to withstand the long duration of testing [44].

The mechanism in proton conductivity for PA-doped PBI membrane enables PA to transfer the proton contrary to water which helps to increase the temperature span of fuel cell membranes. This is not possible for membranes like Nafion or other sulfonated membranes in an anhydrous condition, which relies heavily on water for proton H^+ movement. However, there is the possibility of PA being detached from the PA-doped PBI membrane if the temperature of the system decreases below 100°C due to water condensation that is forced out of the PA from the membrane. Apart from that, the detached PA can lead to corrosion in the fuel cell system of PA-doped PBI in fuel cell that can chemically deteriorate at operation temperature of 150–200°C, which is crucial in diminishing the poisoning effect to the anode catalyst due to carbon monoxide generation [48]. Titania, TiO_2 and zirconia, and ZrO_2, which are categorized as inorganic fillers can be integrated into the modification of composite PA-doped PBI-based membrane by enhancing the hydromechanical characteristics. This is achieved due to improvement in the proton conductivity and stability of PBI-based membrane in PA-doped medium [44]. Summary of PBI improvement techniques from several types of research is illustrated in **Table 2**.

Previous studies of PBI polymer have demonstrated that PBI derivatives, the 2OH-PBI polymer (dihydroxy function groups), have formed the phosphate linkages between the hydroxyl

No.	Methods	References	Remarks
1.	Optimization of membrane fabrication techniques	[35, 49]	Improvements were found limited demonstrating weakness in mechanical strength when highly loaded with acid and poor endurance when tested for a long term [50]
2.	Crosslinking of polymer backbone	[51–55]	
3.	Blending with other polymers	[56–58]	
4.	Forming a composite structure by incorporation of various inorganic acids	[22, 26, 42, 59]	
5.	Designing composite PA doped PBI-based membranes using ceramic nanoscale and mesoscale fillers such as Titania and Zirconia	[60, 61]	Nanoscale ZrO_2 filler and the accompanied membrane casting is challenged by agglomeration and precipitation [62]
6.	Adding more nitrogen atoms to the polymer molecule structure to enhance acid retention.	[60]	Development of pyridine-polybenzimidazole (Py-PBI), which provides an additional pyridine ring capable of boosting the interaction with PA [60, 63–65]

Table 2. Summary of PBI improvement techniques.

groups of the PBI backbone during polymerization in poly (phosphoric acid) in the cross-linking process. However, the increase in proton conductivity is not translated into better performance of fuel cell. Instead, Pt alloy that has been used as catalysts turned out to give better results, which was 0.49 A/cm^2 at 0.6 V and 0.69 V at 0.2 A/cm^2 with operation temperatures at 180°C and pressure of 1 atm in H_2/air environment [66].

2.1.1.3. Polyether ether ketone

Today, Victrex is the leading manufacturer of PEEK polymer in the world. The sulfonation process for its PEEK membrane is introduced using sulfonic acid groups (SO_3H) via alteration or polymerization of sulfonated monomers onto the backbone structure of the polymer. The hydrophilic nature of the PEEK polymer is developed from the accumulation of sulfonic acid groups. It has been reported that the membranes developed the carrier for proton charge as the consequences of the segregation of the sulfonic acid groups and proton conductivity with the help of water movement in PEEK hydrated state [27]. This is supported by the fact that polymer with aromatic rings like polyether ether ketone (PEEK), polybenzimidazoles (PBI), polyoxadiazole, polysulfone (PSf), and polyimides can contribute to cheaper production cost and deliver sufficient physicochemical properties [67].

To date, previous studies have shown that alteration of PEEK polymer properties can replace Nafion membrane in PEM-FC and DEMFC systems. Significant mechanisms are critically used to prepare the PEM from PEEK like PEEK electrophilic sulfonation (S-PEEK), S-PEEK and nonfunctional polymers blending, and S-PEEK heteropolycompounds with polyetherimide doping with organic acids [27]. Therefore, it is crucial to regulate the degree of sulfonation (DS) as it is affecting the thermochemical stability of PEEK membranes by keeping the DS low [68]. It has been reported that the workability of proton exchange membranes

from sulfonated polyether ether ketone (SPEEK) are strengthened by unaltered silica (SiO_2) and altered silica (SiO_2–SO_3H) nanoparticles. The characterization of sulfonated membranes includes the degree of sulfonation (DS), water uptake, and thermostability properties. The SiO_2 fusion elevates the degree of hydrophilic tendency, hence admitting a higher degree of water retention that promotes better route for proton transfer. However, we can observe that there is a decrement of the proton conductivity. The steady synergy of –SO_3H/-SO_3H within SiO_2-SO_3H and SPEEK chains results in ion cross-linked membrane framework which balances the reduction in proton conductivity. The SPEEK/SiO_2-SO_3H membrane with nanoparticles fillers has the ability to function as a competent PEM from the performance study conducted for fuel cell application [69].

3. Electrolyzer technologies

The chemical reaction equation for an electrolyzer is presented in Eq. (1):

$$2CuCl(s) + 2HCl(aq) \rightarrow H_2(g) + 2CuCl_2(aq) \quad (1)$$

The Atomic Energy of Canada Limited (AECL) has succeeded in generating hydrogen from the above step using CuCl/HCl electrolyzer and suggesting an alteration to the existing CuCl cycle [70, 71]. The operating parameters, appropriate membrane selection, and electrochemical cell's scheme are important factors to be tackled in order to have a functional electrolyzer. AECL has tested and determined that the CuCl electrolyzer needs to have these characteristics [72]:

i. Optimum pressure 24 bar, temperature range 70–80°C

ii. 0.1 A cm^{-2} of current density

iii. 0.6–0.7 V range of cell voltage

iv. 1.23 V of reversible cell potential

v. 75% of potential conversion

vi. 0.5 M CuCl and 11 M HCl as recommended concentration for operation

vii. ΔH = 93.76 kJ/mol [71]

Research conducted by Naterer et al. confirmed that the CuCl/HCl electrolysis reaction rate enhances with the increment of reaction temperature and the concentration of CuCl [72] and greater current density at 80°C when compared to 25°C for the same cell voltage [17]. The schematic diagram of proton exchange membrane (PEM) water electrolysis cells is presented in **Figure 3**. The solid polymer electrolyte that conducts proton ion is sandwiched between two electrodes to construct a membrane electrode assembly (MEA). The MEA is submerged in pure water (18 μ cm) and the proton movement stays within the membrane's boundary.

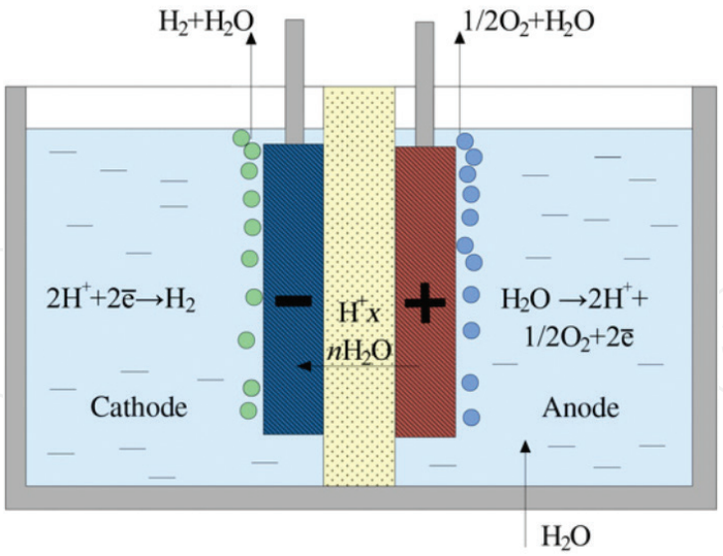


Figure 3. Schematic diagram of PEM electrolysis cell [33].

The efficiency of a PEM cell is dependent on the current density during operation. While a higher current density is crucial to cut down the start-up cost, a lower current density is needed to cut down the cost of operation. Both factors have to be taken into consideration [33]. Different types of electrolytes can be deployed in an EL cell: an alkaline electrolysis (AEL) cell works with a basic liquid electrolyte. In a proton exchange membrane (PEM) EL cell, an acidic ionomer—a process often called solid polymer electrolysis (SPE)—is used, and a high-temperature (HT) EL cell has a solid oxide as the electrolyte. The schematic diagram of the alkaline electrolysis cell is presented in **Figure 4**.

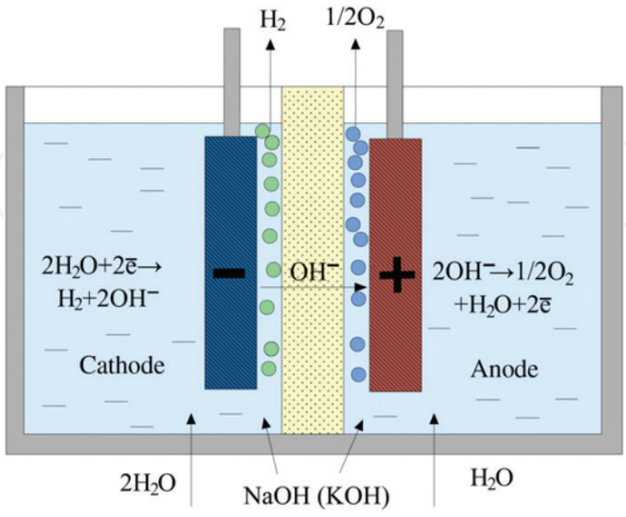


Figure 4. Schematic diagram of the alkaline electrolysis cell [34].

Technology	Advantages	Disadvantages
Alkaline electrolysis	Technology: oldest and well established	Current density: low
	Cost: cheapest and effective	Degree of purity: low (crossover of gases)
	Catalyst type: Noble	Electrolyte: liquid and corrosive
	Durability: Long term	Dynamics: low dynamic operation
	Stacks: MW range	Load range: low for partial load
	Efficiency: 70%	Pressure: Low operational pressure
	Commercialized	
PEM electrolysis	Current density: high	Technology: new and partially establish
	Voltage efficiency: high	Cost: high cost of components
	Load range: Good partial load range	Catalyst: noble catalyst
	System design: compact	Corrosion: acidic environment
	Degree of purity: high gas purity	Durability: comparatively low
	Dynamics: high dynamics operation	Stack: Below MW range
	Response: rapid system response	Membrane: limited and costly
		Commercialization in near term
High-temperature steam electrolysis	Efficiency: 100%	Technology: in laboratory phase
	Thermal neutral efficiency >100% with hot steam	Durability: low due to high heat, ceramics
	Catalyst: Nonnoble	System design: bulk system design
	Pressure: High-pressure operation	

Table 3. A comparison between alkaline, PEM, and high-temperature electrolysis [73–75].

To ensure a sufficiently high ionic conductivity, every electrolyte requires minimum temperatures. The upper temperature limit is determined mostly by the stability of the cell materials and components. More details are provided in later in this chapter.

Currently, three most used electrolysis technologies are being used. A comparison between alkaline, PEM, and high-temperature electrolysis is presented in **Table 3**.

4. Conclusion

In this chapter, hydrogen production from membrane electrolysis is discussed in detail. Hydrogen production from membrane water splitting technologies possesses great potential as a sustainable hydrogen source. Previous research focused mainly on Nafion-based membrane, but with the advancement in the research, a better and cheaper membrane can be used without compromising on the output of hydrogen production. Composite membrane provides better performance in terms of durability, heat resistance, hydrogen production, and purity.

Acknowledgements

The authors would like to express appreciation for the financial support provided by the Ministry of Higher Education Malaysia under the Universiti Putra Malaysia project number 9452000 GP-IPM Putra Grant and Universiti Teknologi Malaysia project number 03G10 Flagship Research University Grant.

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