Received: 15 February 2021 | Revised: 7 June 2021 | Accepted: 8 June 2021

DOI: 10.1002/er.6983

REVIEW PAPER

INTERNATIONAL JOURNAL OF ENERGY RESEARCH WILEY

A review of alkaline solid polymer membrane in the application of AEM electrolyzer: Materials and characterization

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Funding information
Universiti Kebangsaan Malaysia, Grant/Award Number: MI-2019-023

Summary

Electrochemical water splitting is one of the practical systems for green hydrogen production. This hydrogen processing is sustainable by the use of a water electrolysis cell known as an electrolyzer. In recent decades, the alkaline electrolyzer and the proton exchange membrane electrolyzer have entered the advanced commercial level for the hydrogen processing industry. Unfortunately, both techniques have many crucial issues, such as the handling of hydrogen, large structure, and expensive materials needed during the construction of the cell. Anion exchange membrane (AEM) electrolyzers have been recommended to address the worst of previous electrolyzer types due to the ability to use non-platinum and non-Nafion membrane materials, high hydrogen storage density, and the ability to build compact micro-cells on a large cell scale. A solid polymer alkaline membrane is a key component that influences the efficiency of the AEM electrolyzer, which reacts as an anion exchange membrane (AEM membrane). AEM membrane serves as an anode and cathode separator, ion transfer pathway, and electron flow barriers. This review paper explores polymeric materials and the characterization of an alkaline solid polymeric membrane used in an AEM electrolyzer. Several polymeric membranes that have been investigated by researchers for this application have been discussed. Critical characterizations such as ion exchange capability, ionic conductivity, chemical and mechanical stability, and cell performance durability are comprehensively addressed to guide future research and development in an alkaline solid polymeric membrane for application in an AEM electrolyzer.

Highlights

- An overview of materials and characterization assessment of alkaline solid polymeric membrane in AEM electrolyzer is discussed.
- The progress of polymeric materials for alkaline solid polymeric membrane modification in the AEM electrolyzer is presented.

- Critical characterization of the alkaline solid polymeric membrane is described, including the ion exchange capacity, ionic conductivity, chemical and mechanical stability, and durability of cell performance.

KEYWORDS

AEM electrolyzer, AEM membrane, alkaline solid polymeric membrane, hydrogen production, polymeric materials

1 | INTRODUCTION

In the 19th century, the reliance on fossil fuels in human activities became more pronounced to satisfy the rising oil demand. Many modern machines used to implement this technological revolution need large-scale electricity generation.[1,2] Besides, the increase of vehicle usages, such as buses, trucks, and automobiles, tends to raise fossil fuel demand. Furthermore, the availability of fossil fuels is abundant and sufficient to meet the needs of customers worldwide. Many countries rely on fossil fuels as their principal source of income. The utilization of fossil fuels has significantly assisted in the modernization of human life. Unfortunately, there are serious negative repercussions for the consumption of fossil fuels. The release of harmful gases into the atmosphere resulting from burning fossil fuels to generate energy is a significant problem that cannot be halted. For example, nitrogen oxide emission, sulfur dioxide, carbon dioxide, and carbon monoxide from everyday sediment usage and industrial power plants are hazardous to the atmosphere. It may also exacerbate respiratory conditions, such as lung cancer and asthma.[3,4] Besides, the chemical reaction between the nitrogen oxide and the sulfur oxide released along with water, oxidants, and gases in the atmosphere would create acid rain. Acid rain production can occur, resulting in disruptions to habitats such as water pollution and damage to animals and crops. Therefore, the alternative energy resources approach is desperately needed to reduce fossil fuels' use to mitigate the environmental crisis.[5,6]

Hydrogen is one of the most promising fuel alternatives to fossil fuels. Hydrogen is a versatile fuel, which is quickly becoming an important energy resource to fulfill global demand. When hydrogen generates energy, it can be categorized as a zero-carbon fuel.[7,8] For example, hydrogen has been used in fuel cell systems as a fuel, such as in alkaline fuel cells (AFCs), proton exchange membrane fuel cells (PEMFCs), and solid oxide fuel cells (SOFCs). In practice, PEMFCs and SOFCs have commercialized as public utilities such as buses and trucks. Meanwhile, AFCs have also been used to generate energy for spacecraft release.[9,10] There are various advantages to using hydrogen as a source of energy. All the fuel cell types have produced water and heat during the consumption in a fuel cell system during the conversion of hydrogen fuel into energy. The use of hydrogen energy in fuel cell system has a remarkable ability to reduce air pollution compared to the conventional technologies, which is used in the combustion process of fossil fuels and produces the greenhouse gases. Thus, hydrogen in fuel cells can be classified as a green technology to produce energy resources.[11,12] Besides, hydrogen has a high energy density. It can supply three times the amount of power as most fossil fuel sources due to the high efficiency of hydrogen energy conversion through the fuel cell system. In addition, the non-toxicity properties of hydrogen have contributed to a human-friendly and environmentally safe benign. If the hydrogen burns, no harmful byproducts are released into the air.[13,14]

In fact, the enormous energy resources of hydrogen can be found all around us. Thus, hydrogen is considered a renewable energy source since it can be produced and processed in a continuous series on a large scale from various sources. For example, natural gas reform, coal and biomass gasification, and green liquid fuels reform are some of the different processing methods that can be used for hydrogen production. From the complex mechanism until as simple as the mechanism of water splitting can be used to produce hydrogen. Electrolysis is one of the practical ideas used to generate hydrogen from water as a renewable resource.[15,16] Through an electrolysis process, water is split into hydrogen and oxygen using electricity in an electrochemical process. Hydrogen reduction occurred in the cathode, whereas oxygen oxidation occurred in the anode. All the redox activities are conducted in the electrolysis cell, known as an electrolyzer.[17,18] In the manufacturing of hydrogen fuel, the electrolysis method offers numerous benefits. Electrolyzers are available in various system sizes, from the lightweight size in micro-scale to large-scale configuration size. A few electrolyzer units can be manufactured for the micro-scale application due to the simplicity of the cell that consists of few components and does not require an external compartment or moving parts. For huge applications, such as power plant generation resources, electrolyzer units can be attached to the extensive open processing processes linked directly to renewable or other non-greenhouse energy generation resources.[19,20]

Besides, the production of hydrogen is very pure up to >99.999% and produced in a non-polluting manner. It is very ideal for fuel cell consumption in high fuel concentration. Besides, without any delay in fuel processing, hydrogen can be generated directly via the electrolyzer unit. It can be placed anywhere, not like a solar cell requiring areas of high sunlight intensity.[21,22] In addition, an electrolyzer unit can be integrated with another power source system in various applications such as stationary, portable, and transportation to provide reliable energy supplies over a long period. For example, an electrolyzer can be used in conjunction with other power generation such as solar and wind turbine during the intermittent period to provide energy to the system on a continuous condition.[23,24] In addition, electrolyzers can alleviate the problem of some power generation systems that only run for a limited amount of time, such as wind turbines that only work when it is windy. As a result, the electrolyzer system can replace existing holes in order to improve power generation systems such as wind turbines. Moriarty and Honnery[25] explored the potential of integration of electrolyzer and wind turbines. Hence, this system has a high capability to overcome the energy demand problem, although the weather-change route occurred.

1.1 | The type of commercial electrolyzer

Like the fuel cell system, the electrolyzer can be manufactured with a unipolar or bipolar configuration design. For an alkaline electrolyzer, the unipolar electrolyzer cell typically uses liquid electrolyte in an alkaline aqueous solution medium. Meanwhile, the proton exchange membrane (PEM) electrolyte consumption is used as a separator of pair electrodes for the PEM electrolyzer in the bipolar configuration. For an alkaline electrolyzer, potassium hydroxide is used as the liquid electrolyte. While for PEM, the electrolyzer is used as the solid polymeric membrane. The main electrolyzer component is similar to fuel cell technology, in which the main features are electrode and electrolyte. Nowadays, both of these electrolyzers have now reached the commercial, industrial market level, allowing them to manufacture hydrogen on a massive scale for global consumption.

1.1.1 | Alkaline electrolyzer

In 1789, Troostwijk developed the first design of an alkaline electrolyzer.[26] Alkaline electrolyzer manufacturing has evolved and spread globally as the most advanced industrial electrolysis system technology in the commercial phase. Compared to the other electrolyzers, the alkaline electrolyzer has the lowest cost of development due to the mature level of research and invention.[27] The general schematic diagram of an alkaline electrolyzer is simple, as presented in Figure 1A.[28] The current density of commercial alkaline electrolyzer has achieved approximately around 100 to 400 mA cm^{-2}. The working temperature of the alkaline electrolyzer is between 25°C and 100°C with 1 to 30 Bar of pressure. The optimum range weighs the percentage of liquid electrolyte as an essential parameter to balance ionic conductivity property with corrosion resistance. In practice, 20 to 30 wt% aqueous potassium hydroxides (KOH) solution has been used as a liquid electrolyte to apply alkaline electrolyzer. Asbestos is usually applied to the diaphragm material to react as a barrier to mixing hydrogen and oxygen within the cell to prevent a firing process since all gases are flammable.[29]

The key advantage of an alkaline electrolyzer is the low cost of the metal electrode, such as iron or nickel, which can be used to produce hydrogen gas, which is suspended in an aqueous electrolyte solution. The reaction will begin when the continuous supply of current to the electrodes arrives, and hydrogen and oxygen are released.[30,31] Unfortunately, the main disadvantages of an alkaline electrolyzer are a low rate of effective fuel production for this electrolysis unit, low efficiency of hydrogen production, and a vast compartment of design system sizes for hydrogen storage. Besides, the electrolyte condition in liquid form led to several dangerous situations, such as the nature of the electrolyte that is easy to leak, the high ohm resistance that decreases the current density attainable, and the efficiency of the alkaline electrolyte deteriorates under part-load performance.[32,33] Thus, due to the low fuel storage rate of alkaline electrolyzer, the entire state of high hydrogen permeability has increased hydrogen concentration in the anode. As a result, this operating condition has decreased cell performance.[34,35]

1.1.2 | PEM electrolyzer

A PEM electrolyzer is another type of commercially available electrolysis system. Russell et al[36] developed the first hydrogen production system using the PEM electrolyzer system in 1960. Basically, the PEM electrolyzer's general configuration is similar to the fuel cell system, which is PEMFC. The solid polymer membrane was placed in the middle of the cells and sandwiched between pair electrodes in this bipolar electrolysis unit configuration, as presented in Figure 1B. Compared to the alkaline electrolyzer, the structure of the PEM electrolyzer is simpler, flatter, and more straightforward. The PEM is the important component of a PEM electrolyzer. Usually, Nafion membranes based on perfluorocarbon polymers are

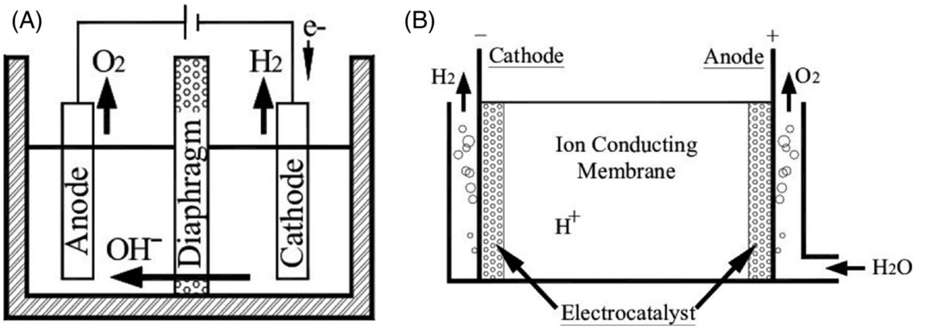

FIGURE 1 Schematic diagram of A, alkaline electrolyzer, B, PEM electrolyzer[28]

commonly used in the application of PEM electrolyzers. The transport of water to the electrode of the anode is the first step in the operating principle of the PEM electrolyzer. The water molecule has released the electron, resulting in the formation of the proton and oxygen. Within the PEM component, the proton diffused to the cathode electrode and reduced the hydrogen. The production of hydrogen is starting.[37,38]

The advantages of a PEM electrolyzer are high purity hydrogen production, the ability to work in high-pressure circumstances, and the ability to store hydrogen fuel rapidly. This electrolyzer has high proton conductivity and impermeability characteristics of hydrogen output compared to the alkaline electrolyzer.[39,40] The use of solid polymeric membrane has a high potential for reacting as an excellent redox reaction barrier and gas separator, allowing for a compact cell construction with a fragile distance between a pair of electrodes and a decrease in the number of moving parts, making the structure easier to maintain.[21,41] Unfortunately, the acid environment of the PEM electrolyzer is critical for the high efficiency of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).[42] At this operating condition, only the most expensive noble metals and their oxides, such as platinum and iridium, could be held in this state and perform flawlessly the redox reaction in an acidic environment containing 10% to 20% of H_2SO_4 with the continuous stable performance.[43] Besides, the consumption of expensive PEM membranes, such as Nafion-based membranes, in the development of PEM electrolyzer has increased the cost of production. Furthermore, the PEM electrolyzer stack materials are more expensive than those used in alkaline electrolyzers. All these issues are the most significant barriers to commercializing the PEM electrolyzer at a low-cost production price, which is restricting their production at the commercial level.[44]

1.2 | Anion exchange membrane electrolyzer

To overcome the disadvantages of an alkaline electrolyzer and a PEM electrolyzer, an alkaline solid polymeric membrane known as anion exchange membrane (AEM) electrolyzer is introduced for use in an electrolyzer system.[16,45] The AEM serves as the core component of the AEM electrolyzer, which is located in the middle of the cell. AEMs have been recognized to apply in various electrolyzers and fuel cells.[46,47] Several studies have investigated the potential of the alkaline solid polymeric membrane because the AEM electrolyzer provides more benefits than the previous electrolyzer systems, PEM, and alkaline. Table 1 lists the advantages and disadvantages of all types of electrolyzers that have been discussed. Thus, the comparison provides the reader with an initial overview of all possible electrolyte systems.

There are several primary advantages to using AEM membrane application in the electrolyzer system for green hydrogen production. For example, the ability to apply a non-noble metal catalyst, such as nickel and copper, in the electrolyzer cell component. Second, a simple electrolyte may be used, such as distilled water or a low concentration alkaline solution, to replace the high corrosive electrolyte. Third, non-expensive polymeric membranes, such as Quaternized polymer-based membranes, may be replaced by high-cost Nafion-based membranes. Next, there is a free interaction between carbon dioxide and AEMs since metal ions can solve this problem. Finally, the AEM electrolyzer did not require a liquid electrolyte with highly corrosive properties. This state would solve the issue of leakage cells and volumetric stability. Besides, the lightweight electrolysis cell in terms of size and weight can be manufactured using the lightweight, thin, and micro-scale AEM membrane. Thus, the low-cost AEM electrolyzer can be manufactured and contributed to the development of stable hydrogen production, increased durability, and increased energy efficiency in stationary, portable, and transportation power generation systems.[48,49]

1.3 | The working principle of the AEM electrolyzer

An AEM electrolyzer is a novel emerging electrolysis system. It has been investigated at many academic and

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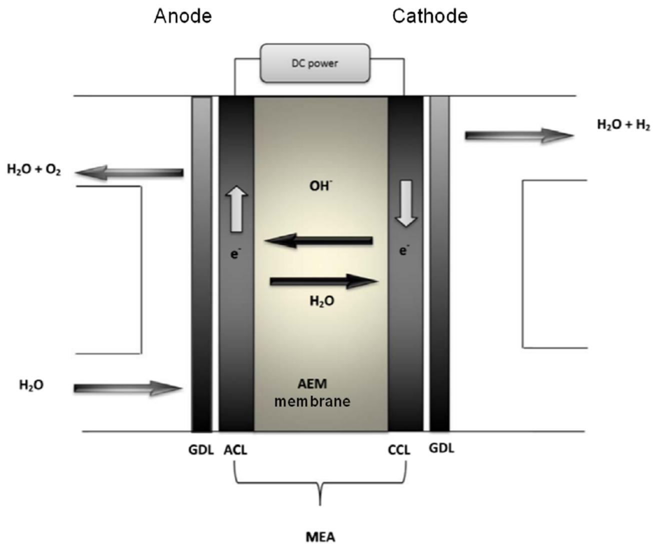
TABLE 1 Lists the benefits and drawbacks of several electrolyzer types

Alkaline electrolyzer	PEM electrolyzer	AEM electrolyzer
Benefits		
• In developed markets, this technology has already been mature. • Exempt from using high-cost catalysts. • The hydrogen production can be done in long-term working conditions. • High capability in the utilization of the megawatt range.	• Excellent cell performance for hydrogen production. • The efficiency of voltage is higher compared to other types. • Dynamic of working condition is operational. • High rapid response in the hydrogen production system.	• Ability to use non-noble metal catalyst such as nickel for hydrogen production. • Can be replaced by the high-cost of electrolyte material like Nafion membrane. • Able to fabricate in the small-scale system. • High operating condition pressure.
Drawbacks		
• The current density is low. • Corrosive condition of liquid electrolyte. • High hydrogen permeability of liquid electrolyte. • Low pressure conditions during cell operation cause problems with hydrogen storage. • The leaking issue of liquid electrolyte is the biggest problem in the alkaline electrolyzer.	• The cost of production of PEM electrolyzer is high due to expensive components of electrode and electrolyte. • The corrosive condition of electrolyte due to high concentration acid applied. • The operating condition only sustained in the below megawatt range.	• Still in the research and development stage. • Only low current density can be applied. • The durability of the cell still does not have a proven study. • Membrane degradation usually happened during the cell operating condition.

industrial research and development levels. The ability of the AEM electrolyzer to be constructed at a minimal cost development and with high efficiency of the hydrogen generation process has attracted the interest of many researchers to investigate this technology.[50,51] In general, an AEM electrolyzer is a type of electrolysis system that uses an alkaline solid polymeric membrane as an AEM membrane. This component allows the electrochemical reaction to complete water splitting and the production of hydrogen.[52] An AEM membrane is located in the middle of the AEM electrolyzer cell, as illustrated in Figure 2. As depicted in Figure 2, the major component of the AEM electrolyzer consists of the gas diffusion layer (GDL), the electrocatalyst layer, and the AEM membrane, as well as the complete electrochemical process of water splitting for hydrogen production.[53] Before understanding the hydrogen production mechanism, it is necessary to understand the AEM electrolyzer component. Every AEM electrolyzer cell is divided into two half-cells with the AEM part in the middle. Each half-cell comprises several components, including the GDL and the electrocatalyst layer, either the anode catalytic layer (ACL) or the cathode catalyst layer (CCL). The bipolar plate component separates each cell when several single cells are used to construct the AEM electrolyzer stack.[53,54]



$$\text{Anode}: \quad 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad E_0 = 0.401\ \text{V}$$

$$\text{Cathode}: \quad 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \quad E_0 = -0.828\ \text{V}$$

$$\text{Overall}: \quad 2H_2O \rightarrow 2H_2 + O_2 \quad E_0 = 1.23\ \text{V}$$

FIGURE 2 Schematic diagram and chemical reaction of AEM electrolyzer[53]

The working principle of the AEM electrolyzer system has started when connecting the external power supply through the electrolysis cell with the electrode to supply direct current (DC) power. Simultaneously, the HER occurs at the cathode, and at the anode, the OER has occurred. The anode side is filled with a dilute alkaline electrolyte solution, such as KOH. There is no solvent solution provided on the cathode side. The presence of water in the cathode side is arisen due to the water permeability from the anode side. Water diffuses to the cathode side via the alkaline solid polymeric membrane. The HER process converts water to hydrogen gas and ion hydroxide by combining electrons and releasing them through the cathode side. The generating hydroxide ion at the cathode has been transferred to the anode side through the alkaline solid polymeric membrane. Finally, the hydroxide ion has been chemically reacted and recombined as water and oxygen via the OER process, with the electrons released to complete the reaction.[55,56] The overall chemical reaction for hydrogen production has been shown in Figure 2.

1.4 | Alkaline solid polymer membrane

The alkaline solid polymeric membrane is a crucial component of the AEM electrolyzer. In practical, the efficiency of the AEM electrolyzer in producing hydrogen is influenced by the characteristics and performance of the alkaline solid polymer membrane as an AEM membrane. The primary function of an alkaline solid polymer membrane is to separate the reactant of anode and cathode, to prevent the migration of electrons inside the AEM electrolyte, and to allow ion hydroxide to diffuse through the cathode to anode.[57,58] To ensure that alkaline solid polymeric membranes can play an essential role in ensuring that AEM electrolyzer cells perform optimally, various crucial features of the alkaline solid polymeric membrane, such as ion exchange capability, ion conductivity, chemical stability, and mechanical stability and thermal stability, must be studied and explored. Unfortunately, only a few publications have been published and highlighted by the AEM electrolyzer as a novel electrolysis technology.

Further research on AEM electrolyzers, specifically for the fabrication of alkaline solid electrolyte membranes, is desperately required to enhance the status of hydrogen production, the stability of the cell component, and the cost of cell manufacture. There have only been a few papers that have been published and highlighted by the AEM electrolyzer as a novel form of electrolysis technology. Further research on AEM electrolyzers, specifically for the fabrication of alkaline solid electrolyte membranes as an AEM membrane, is desperately required to enhance the status of hydrogen production, the stability of the cell component, and the cost of cell manufacture.[59,60]

In this article, the main objective is to highlight the polymeric materials and characterization of the alkaline solid polymeric materials in the application of AEM electrolyzer toward the creation of an alternative AEM electrolyzer with high hydrogen production efficiency. Based on a review of the literature, this article is the first attempt to illuminate the review on the characterization assessment of alkaline solid polymeric membrane as an AEM membrane to apply AEM electrolyzer. The critical characteristics of an alkaline solid polymeric membrane as an effective AEM membrane during the fabrication process are comprehensively discussed, including ion exchange capability, ion conductivity, chemical stability, mechanical, and thermal stability. General characterization assessment methods are typically presented in order to provide some idea for new researchers to begin on their journey in the research and development of AEM electrolyzers.

2 | PROGRESS OF POLYMERIC MATERIALS AS AN ALKALINE SOLID POLYMERIC MEMBRANE IN AEM ELECTROLYZER

Compared to conventional electrolyzers such as alkaline electrolyzers and PEM electrolyzers, there are many advantages that AEM electrolyzers can offer. In order to solve the problems of existing conventional electrolyzer systems, many attempts have been made to research the potential of this system. One aspect that concerns the researcher is developing an alkaline solid electrolyte membrane as an AEM membrane.[61,62] The core components of the AEM electrolyzer are AEM membranes, which are fabricated from alkaline solid polymeric membranes. It is typically synthesized by modifying the polymeric backbone with grafted cationic functional groups to the formed alkaline solid polymeric membrane, which can animate the structure of anion movement.[55] For example, the modification of polyvinyl alcohol (PVA) turned to Quaternized PVA and forming AEM by combining with quaternary ammonium functional groups via the Quaternization process, as presented in Figure 3A.[63,65] Several ion-exchange groups can be grafted to polymeric materials to synthesize the AEM, including —NH3+, —RNH2+, —RN+, =R2N+, and —R3P + —R2S+.[66] This sub-topic will discuss alkaline solid polymeric membranes as AEM membranes that have been developed for AEM electrolyzer applications by commercial organizations and universities. The discussion has included the introduction of polymer materials, polymer material modifications, and studies on other component parameters in AEM electrolyzer cells that contribute to the efficiency of AEM membranes.

2.1 | A-201 polymeric membrane

Currently, the alkaline solid polymeric membrane has been commercialized by Tokuyama Corporation from

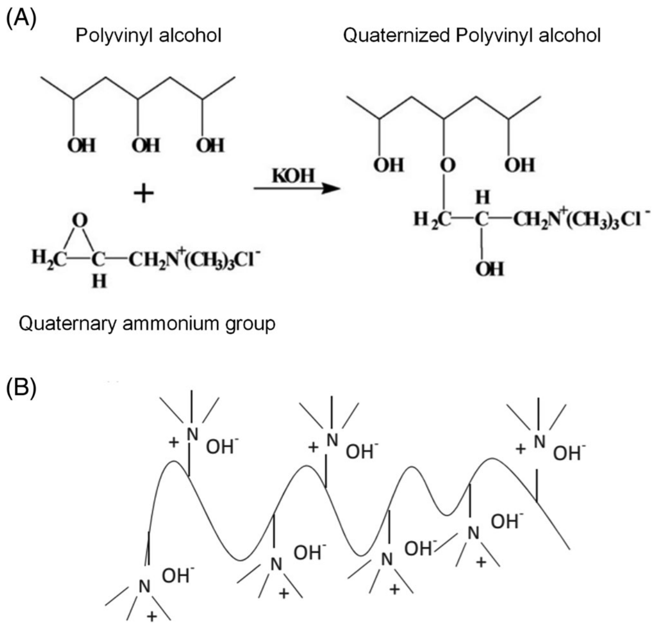


FIGURE 3 A, Illustration of quaternization process of PVA,[63] B, Illustration structure of chemical chain the A - 201 membrane[64]

Japan, known as an A-201 membrane. A-201 membranes are essentially Quaternized-based membranes. As illustrated in Figure 3B, the A-201 membrane contains a high concentration of quaternary ammonium functional groups that are grafted onto a linear hydrocarbon to form the backbone of the polymeric membrane. Thus, the A-201 membrane possesses a high capacity for associated hydroxyl ions to complete the hydrogen production process using the AEM electrolyzer method. By forming a dense network of ionic pathways, the presence of a functional group within the polymer backbone improved ionic conductivity.[64,67] Leng et al[43] fabricated the AEM electrolyzer with the A-201 membrane as an AEM membrane. A current density of AEM electrolyzer achieved 399 mA cm^{-2} at 1.8 V. The platinum black is used as the cathode catalyst, and the iridium oxide is used as the anode catalyst. The AEM electrolyzer system has been sustained for more than 535 hours, as presented in Figure 4A. It is proven that the A-201 membrane is promising to maintain the long-term durability condition and provide low-cost hydrogen production.

Pavel et al[57] developed an AEM electrolyzer with an A-201 membrane and a non-platinum catalyst as an electrode. They used low-cost material such as $CuCoO_x$ to synthesize the anode using co-precipitation, and nickel-based nanostructured CeO_2-La_2O_3 material uses the deposition-precipitation process as a cathode. The A-201 membrane had a high-performance cell component, which had a good water uptake of up to 30%. It also achieves a high ion exchange power and ion conductivity of 1.8 mmol g^{-1} and 12 mS cm^{-1}, respectively. Besides, the A-201 membrane has been proven to be cell-sustainable up to approximately 1000 hours with high chemical and mechanical stability, as shown in Figure 4B. Ahn et al[68] modified the membrane electrode assembly based on the A-201 membrane with the low-cost nickel catalysts. With a low amount of nickel catalysts on carbon powder, the direct electrodeposition method was applied on both sides of the electrode to create the electrode membrane assembly for the AEM electrolyzer. Figure 4C presented a cell configuration photograph of setting up a single cell of the AEM electrolyzer. This indicates that the AEM electrolyzer can be designed on a small scale and is ideal for portable and transport applications.

2.2 | Fumasep polymeric membrane

Another commercially available alkaline solid polymeric membrane for use in AEM electrolyzers is FUMATECH BWT GmbH's fumasep FAA-3-based membrane.[69,70] Among the types of Fumasep based membranes commonly used are fumasep FAA-3,[69] fumasep FAA-3-50,[70] fumasep FAA-3-Br,[70] and fumasep FAA-3-PK-130.[71] In essence, the fumasep FAA-3-based membrane comprises polyketone or polypropylene, both of which are composed of polymeric materials. This low-cost AEM membrane was modified with quaternary ammonium groups to enable it to function in alkaline systems. Lim et al[72] investigated the fumasep FAA-3-PK-75 as an AEM portion for this electrolysis cell type. They are testing the optimal parameter state for the membrane electrode assembly. It was stated that the pressing process during the sandwich process, the torque of the single-cell assembly, the fuel feed system, and the operating temperature had a strong effect on the output of the AEM electrolyzer. This poly ketone-based polymeric material showed the highest results with 1 A cm^{-3} at 1.8 V when optimizing the manufacturing process applied. Carbone et al[73] applied the FAA-3-50 as an alkaline solid polymeric membrane in AEM electrolyzer. The specific membrane-electrodes assembly based on this membrane with $NiMn_2O_4$ as an anode catalyst has been fabricated. The AEM electrolyzer durability can sustain their performance with limited degradation until 1000 hours.

In addition, researchers have attempted to compare the performance of fumasep-based membranes to that of A-201 membranes. Vincent et al[53] compared the membranes of Fumasep FAA-3 and Fumasep FAA-3-PP-75 with the A-201 membrane. The final results obtained indicate that the fumasep AEM is comparable to the

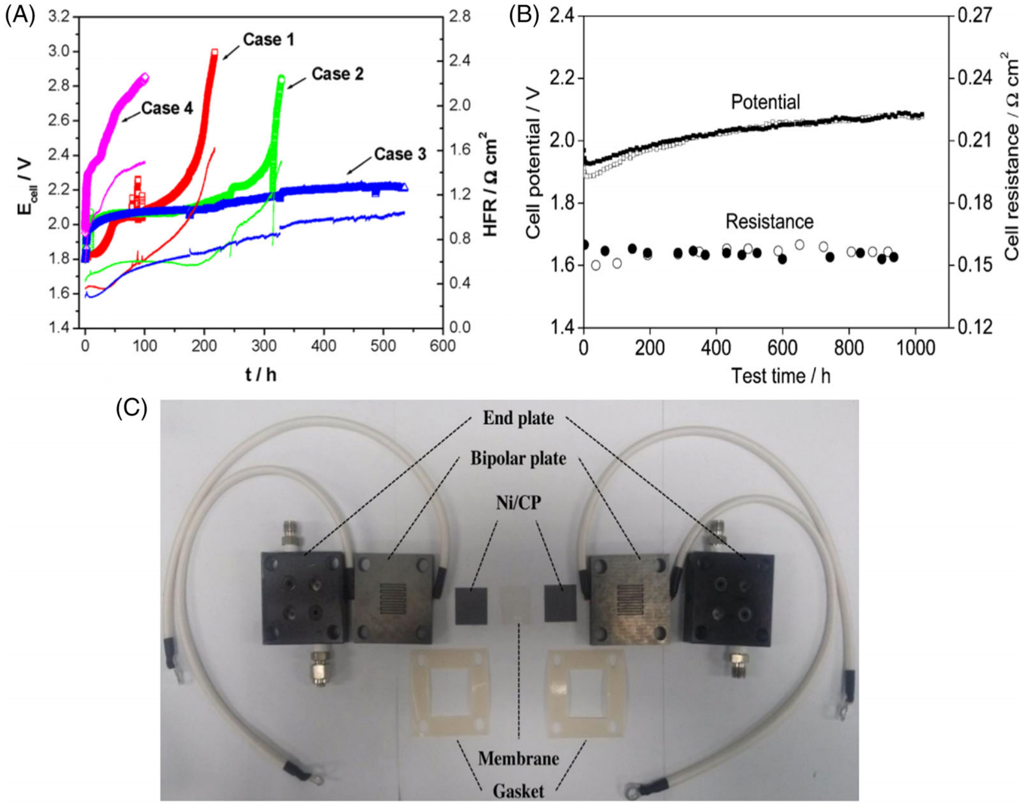


FIGURE 4 A, Cell voltage via A-201 membrane has been sustained more than 500 hours,[43] B, cell voltage via A-201 membrane with non-platinum based catalyst has been maintained approximately until 1000 hour,[57] C, Optical image of AEM electrolyzer cell configuration with A-201 membrane as an alkaline solid polymeric membrane[68]

AEM developed by Tokuyama corporation and can be further developed in the future. Graphene-based materials also have been explored in order to enhance the performance of fumasep based membranes. Ion-Ebrasu et al[74] introduced graphene-based materials to be modified with the Fumion FAA-3 in NMP (10%) solutions via the Doctor-Blade (DB) method. The 3-dimensional structure of graphene beneficial to enhance the electrochemical performance of fumasep based membrane in terms of ion exchange membrane and conductivity at 80°C.

2.3 | Polysulfone membrane

There are numerous polymeric materials, which have been explored in the application of AEM electrolyzer as an alkaline solid polymeric membrane. For example, polysulfone has been introduced in the fabrication of AEM components for alkaline electrolyzer system. As an organic polymer, polysulfone is commonly used in electrochemical applications as a fuel barrier on all sides due to the high durability of the chemical and thermal properties.[75,76] Parrondo et al[77] utilized polysulfone to fabricate the alkaline solid polymer membrane to apply AEM electrolyzer. They tried to modify the chloromethylated within the backbone of polysulfone with several cationic functional groups. They used three functional groups, which are quaternary benzyl-1-methylimidazolium, quaternary benzyl quinuclidine-1-azaoniumbicyclo-[2.2.2]-octane, and quaternary benzyl-trimethylammonium. Based on the ionic conductivity, polysulfone modification with quaternary benzyl-trimethylammonium showed the highest chloride ion form performance. Meanwhile, Xiao et al[78] modified the polysulfone with a quaternary ammonium functional group to evaluate this polymeric material's performance in an alkaline medium. By sandwiched with non-precious metal catalysts such as nickel, iron, and molybdenum, the membrane electrode assembly of AEM electrolyzer based on polysulfone showed a high potential to sustain for an extended period of hydrogen production.

2.4 | Poly (vinyl benzyl chloride) membrane

Poly (vinyl benzyl chloride) has been investigated as an alkaline solid polymeric material in AEM electrolyzer. Poly (vinyl benzyl chloride) is produced through the free radical polymerization process of 4-vinyl benzyl chloride or a mixture of 3- and 4-vinyl benzyl chloride.[79,80] Coa et al[81] have studied poly (vinyl benzyl chloride) as polymeric materials to produce alternate AEMs in the electrolysis system. The alternative AEM based on poly (vinyl benzyl chloride) showed good ionic conductivity performance, which increased to 27 mS cm^{-1} from 16 mS cm^{-1} when the operating temperature rose to 60°C in the ambient condition. The increase in operating temperature is useful for lowering the ohm resistance. Faraj et al[82] prepared the blend of AEM based on the low-density polyethene (LDPE) and poly (vinyl benzyl chloride) via a UV-induced grafting method. The cationic functional group has been grafted onto LDPE to optimize the structure of AEM. At 60°C, the highest ionic conductivity has shown 25 mS cm^{-1}. The modification of polymeric materials sustained until 500 hours with 460 mA cm^{-2} of current density and the cell voltage only significantly increased by 6 mW per day.

2.5 | Polystyrene membrane

There are also efforts to develop AEM components using other polymeric materials. Polystyrene is also a promising polymeric material to use as an alkaline solid polymer membrane in an alkaline AEM electrolyzer. Polystyrene is a well-known synthetic aromatic hydrocarbon polymer that is used as plastics. The uniqueness of polystyrene is clear, challenging, and easy to modify based on our application requirements.[83,84] Joe et al[85] introduced polystyrene as an alkaline solid polymer membrane with the nickel-based electrode to fabricate the AEM electrolyzer. With only water consumption, the AEM electrolyzer shows a high current density at the high operating temperature. To enhance the performance of polystyrene in the AEM electrolyzer, graphene oxide has been introduced in the cell component of single-cell. The presence of graphene oxide motivated the catalytic activity of the reactant, which increase the ionic conductivity.

2.6 | Other polymeric membranes

Two quaternary ammonium-tethered aromatic polymers have been explored as an AEM in alkaline electrolyzer by Park et al[86] The biphenyl-based membrane and the poly(triphenylene)-based membrane have been synthesized via the super-electrophilic acid-catalyzed Friedel-Crafts polycondensation by modifying the quaternary ammonium functional groups. The composition of both membranes exhibited good chemical stability until 60 days in an alkaline atmosphere. Besides, Park et al[87] proposed the low-cost polymeric materials for the application of AEM electrolyzer, which is poly (vinyl alcohol) (PVA). PVA is widely used in energy applications such as fuel cells and electrolyzer due to the unique properties of this polymeric material to be modified chemically and physically. N3-butyl imidazolium-based AEMs blended with PVA have been prepared for the AEM electrolyzer. This membrane has performed with outstanding electrochemical performance and high ionic conductivity. Table 2 summarizes the advantages and disadvantages of polymeric materials that have been applied to fabricate as an AEM component in an alkaline AEM electrolyzer. All the primary characterization assessment of the AEM component is discussed comprehensively in the challenges and advances section following ion exchange capacity, ionic conductivity, chemical and mechanical stability, and durability of cell performance.

3 | CHARACTERIZATION ANALYSIS OF ALKALINE SOLID POLYMERIC MEMBRANE

In practical, many cell condition parameters influence the efficiency of the AEM electrolyzer. For example, the operating temperature, the pressure applied to the cell, and humidity of the cell environment. Figure 5 shows a general illustration of the configuration development of the AEM electrolyzer system. Starting with the membrane electrode assembly (MEA) fabrication, a single-cell is manufactured using the hot-pressing process, which sandwiches the pair of electrodes with the AEM membrane. The single-cell is the main component of the AEM electrolyzer. Thus, the process of MEA fabrication is a critical stage in maintaining optimal characterization and avoiding degradation of the AEM membrane within a single-cell for the application of the AEM electrolyzer. Thus, several essential steps must be determined during the MEA fabrication, including identifying the appropriate parameters for the polymer material being used, such as the suitable operating temperature, the required pressure necessary, and the duration needed for the process assembly. Then, the single cell is connected with the current collector plate to complete the electrolysis cell and linked to the external energy source for the activity of the hydrogen production system. This configuration is an essential step in ensuring that the structure and characterization of the AEM can be preserved in such a manner that the AEM electrolyzer cell can be used.[72] The alkaline solid electrolyte membranes characterization and performance as an AEM membrane is the most critical factor that must be engaged seriously to develop the high-efficiency system of AEM electrolyzer. The ideal feature

TABLE 2 Advantages and disadvantages of alkaline solid polymeric membrane

AEM	Advantages	Disadvantages
Tokuyama A-201	• High conductivity in an alkaline atmosphere. • Low-cost production. • Can be performed in thin-film structure and minimizes the cell structure.	• Requires high concentration of alkaline condition, which leads to corrosive properties to cells. • High possibility of incorporation of carbonate inside the membrane
Fumasep	• Good electrochemical properties. • Low membrane resistances. • Compact structure polymeric membrane.	• Limitation of ion exchange diffusion. • Low mechanical stability.
Polysulfone	• Biopolymer materials. • High mechanical strength. • High thermal stability of the polymeric membrane.	• Low ionic exchange capacity and ionic conductivity. • Low water uptake due to high hydrophobic properties.
Poly (vinyl benzyl chloride)	• Low cost of polymeric materials. • Easy to modify in chemical process or physical process.	• Low capabilities to diffuse the ionic transfer within the polymeric membranes.
Polystyrene	• High chemical stability. • Easy to modify chemically. • Can stand in high thermal and pressure.	• Low ionic conductivity. • Low water uptake. • Non-degradable leads to climate change.
Poly (vinyl alcohol)	• High tendency to form thin-film. • Easy to modify chemically and physically. • Low-cost and biodegradable.	• Low ionic exchange capacity and ionic conductivity. • High swelling ratio.

of an efficient AEM membrane in the electrolyzer application, including high conductivity of ion hydroxide, increased capabilities to react as an obstacle from electron and fuel diffusion, and excellent stability properties of the chemical and mechanical.[53,57] Table 3 described the general characterization requirement and description of the AEM membrane. The characterization of AEM membrane has been discussed in detail in the following sub-topic.

3.1 | Ion exchange capacity and ionic conductivity

In electrochemical energy systems, the primary characteristic that should be evaluated is an ion exchange capacity. This property presented the ability of ionic transfer within the alkaline solid polymeric membrane. This property is highly influenced by the ionic conductivity of the AEM membrane, affecting the performance of electrolyzer cells. The high charge density of cation functional groups promotes ionic movement within the structure of the AEM membrane. The classical titration method is appropriate for evaluating the ion exchange capacity of the AEM membrane.[49,88] An increase in the number of cation functional groups grafted onto the polymeric matrix's main chain backbone. This modification is advantageous because it incorporates a hydrophilic structure into the matrix structure of the AEM membrane. In addition, this is beneficial for facilitating water absorption by the vehicle mechanism during ionic diffusion within the matrix structure. Similarly, the presence of cation functional groups is a mechanism for transporting ions via the Grotthuss mechanism.[89,90] Hence, this condition will enhance the ion exchange capacity of the AEM component. Figure 6A presented the illustration lattice structure of the Mg-Al layered double hydroxides-based membrane as an AEM component for an alkaline electrolyzer.[91] The Mg-Al layered double hydroxides-based membrane exhibits an excellent rhombohedral structure that facilitates ionic movement within the AEM component. Each host layer is composed of Mg^{2+} that has been substituted with Al^{3+} and functionalized with hydroxyl groups. Water molecules can be bound within the free space of the crystalline structure, which is critical for the vehicle's mechanism.[92,93] Faraj et al[82] claimed that the high density of functional group grafted into the polymeric membrane would increase the conductivity properties of AEM. As presented in Figure 6B, the addition of functional groups to polyvinyl benzyl chloride through the use of quaternary ammonium sites. Thus, this site can be used to increase the ionic exchange capacity of the AEM membrane.

The ionic exchange capacity of an alkaline solid polymer membrane is the most crucial characterization that influences ionic conductivity performances. In practice, the high current density performance of the AEM

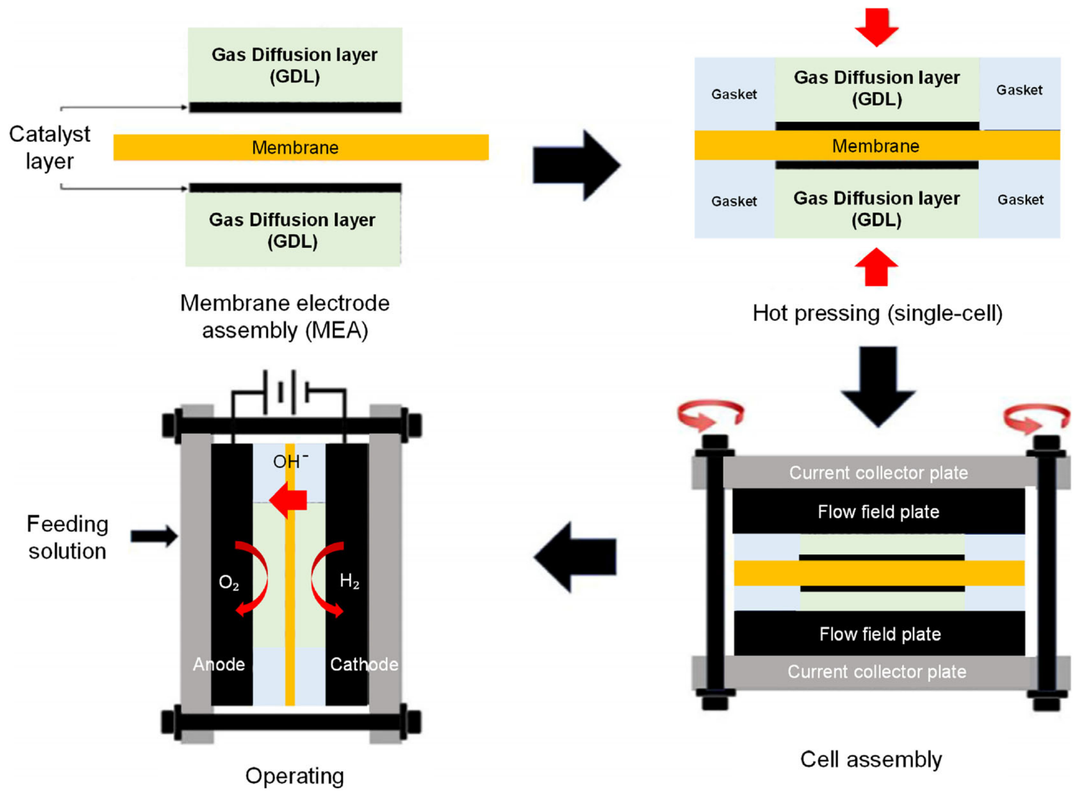


FIGURE 5 Illustration of AEM electrolyzer development, as reproduced from Lim et al[72]

TABLE 3 General characterization of AEM membrane

Properties	Description
Ionic exchange capacity and Ionic conductivity	• The AEM membrane must be 0.01 to 0.1 S cm^{-1} of ionic conductivity with low ohmic resistance.
Chemical and mechanical stability	• The AEM membrane should exhibit air and fuel stability. The electrolyte is inert from a chemical reaction. • Mechanical stability is essential to avoid cell degradation. Thus, the membrane should have high-water stability.
Durability of cell performance	• Must have long-term performance stability and sufficient in the AEM membrane mismatch.

electrolyzer genuinely depends on the high ionic conductivity of alkaline solid polymer membrane condition with low ohmic resistance.[94] As a pioneer commercialized AEM membrane, the A-201 membrane has been recorded. The maximum ionic conductivity raises to 12 mS cm^{-1} at the ambient condition.[64] Generally, the AEM has a high ionic conductivity with a high charge density within the alkaline solid electrolyte membrane structure. The polymeric backbone modification with augmenting the cation functional group will provide a wide hydrophilic area within the polymeric system to absorb the water and diffuse the hydroxyl ion. Increasing the ionic conductivity is helpful for vehicle mechanisms. The cation functional group's presence will augment the ionic pathway within the polymeric structure for the hopping mechanism, which increases ionic conductivity.[95,96] Besides, the alkaline solid polymer membrane's excellent morphology is a significant parameter for the high efficiency of the AEM component. The strong homogeneous distribution of the matrix polymer with the filler is crucial for the hydrophilic and hydrophobic balancing regions to increase ion conductivity and become a strong reactant separator. Figure 7A has shown the excellent morphology of the AEM component based on the Mg-Al layered double hydroxide membrane. The Mg-Al layered double hydroxide membrane formed a dense and compact structure without any porous area. This morphology has been observed to serve good ion conductivity, which is 7.75 m S cm^{-1}. In practice, this membrane also has reacted as a good fuel barrier due to the good morphology of the AEM component.[91]

Another solution to improve the efficiency of ion conductivity is by increasing the operating temperature of

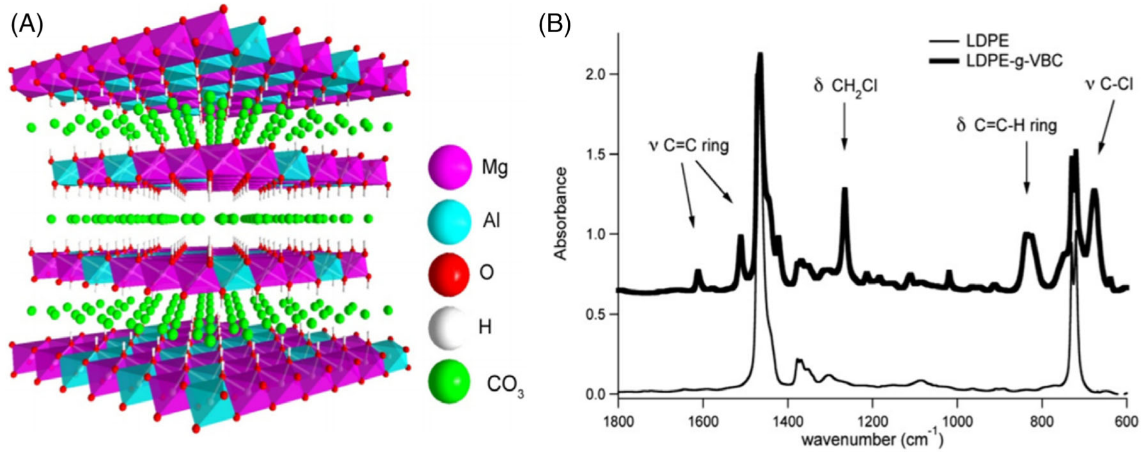


FIGURE 6 A, The lattice structure illustration of Mg-Al layered double hydroxides based membrane,[91] B, The presence of functional group within the polymeric membrane after the modification[82]

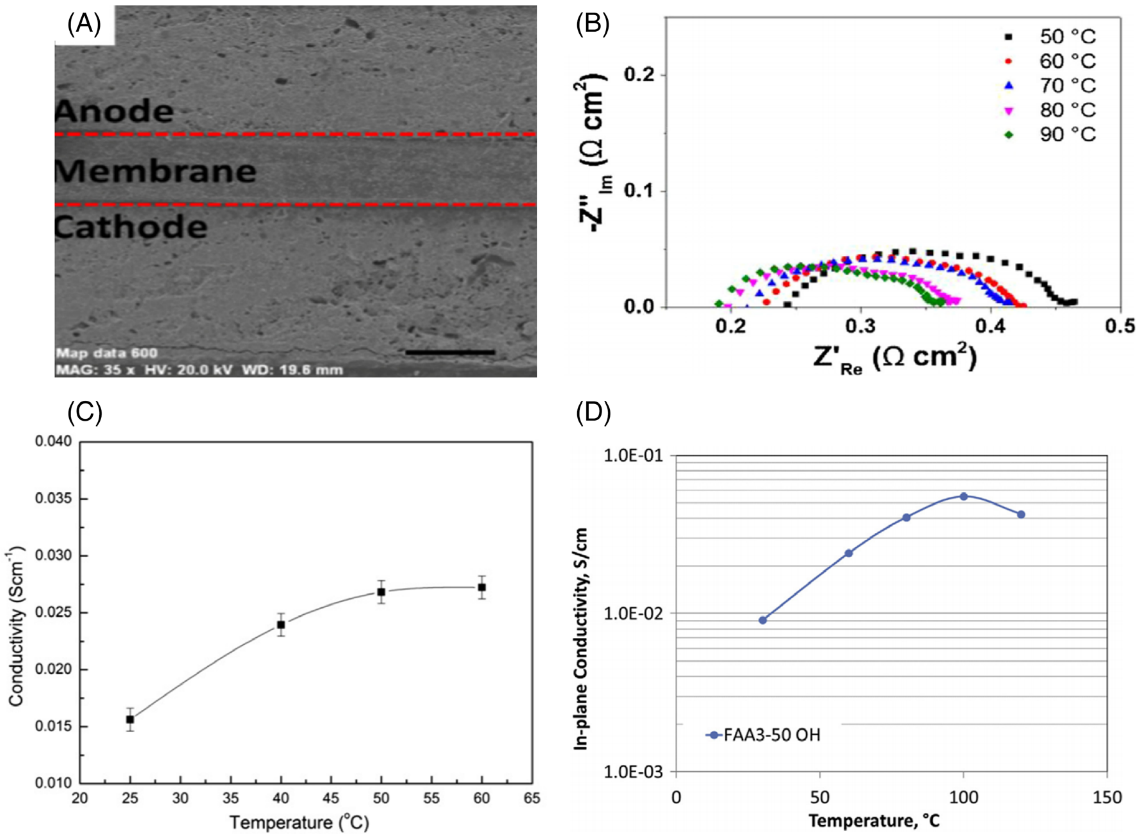


FIGURE 7 A, The morphology of Mg-Al layered double hydroxides membrane with the pair of the electrode,[91] B, the EIS Nyquist plots of AEM electrolyzer with Fumasep FAA-3-PK-75 membrane,[72] C, the ionic conductivity of the polyvinyl benzyl chloride-based membrane,[81] D, the ionic conductivity of fumasep FAA-3-50[73]

the cell. Electrocatalytic operation and electrochemical reactions are accelerated at high temperatures, and ion hydroxyl diffusion is much faster than ambient conditions. This condition is an excellent justification to strengthen ion conduction's hopping process, although hydrogen bonding strength has been diminished.[97] Lim et al[72] discussed that increasing cell operating temperature from 50°C to 90°C had improved ionic conductivity efficiency. Based on the Nyquist plot shown in Figure 7B, the increased cell operating temperature has made the improvement in the kinetics of ionic conduction and electron transfer due to the reduction of ohmic resistance from 0.239 Ω cm^2 to 0.185 Ω cm^2 and polarization resistance from 0.219 Ω cm^2 to 0.171 Ω cm^2. Besides, the current density rose to 0.983 A cm^{-2} with a cell voltage of 1.8 V as the cell's operating temperature increased to 90°C. Cao et al[81] also recognized that an increase in cell temperature would improve the ionic conductivity of the polyvinyl benzyl chloride-based membrane, as presented in Figure 7C. When the temperature increased from 25°C to 60°C, the AEM component's ionic conductivity rose to 2.7 mS cm^{-1} due to improved ionic kinetic energy. However, every alkaline solid polymeric membrane has an endpoint of temperature rise, which helps increase membrane conductivity. Excessive temperature rise will cause deterioration of ion conductivity performance due to the absorption condition of AEM, which will be degraded in high temperature, as presented in Figure 7D has shown that the ionic conductivity of the Fumasep FAA-3-50 based membrane decreased when the operating temperature exceeded 100°C.[73]

3.2 | Chemical and mechanical stability

The chemical stability of AEM is a solid characterization to obtain the high performance and sustainability of alkaline solid polymeric membrane. In practice, most AEM is prone to low chemical stability.[98] Commonly, the critical issue with AEM is a nucleophilic attack on the cation functional groups. Besides, the reaction of Hoffmann elimination on the cation functional groups also caused the chemical degradation of AEM due to the displacement of CH_3 by OH^- Both issues lead to the degradation of AEM performance due to the reduced concentration of the number of anion-exchange groups, which negatively affects ionic conductivity efficiency.[99,100] Figure 8A shows the alkaline degradation mechanism of alkaline solid polymer membrane by the nucleophilic attack and Hoffmann elimination, which reduces mechanical stability and ionic conductivity.[101] Therefore, the fabrication of an alkaline solid polymer membrane with a strong interaction between the matrix polymer and the cation functional group is critical to producing high chemical stability properties. For example, the synthesized biphenyl-based membrane and the poly(triphenylene)-based membrane by Park et al[86] successfully formed the excellent interaction between matrix polymer and the quaternary ammonium functional groups. After the alkaline stability test for 60 days, both polymeric membranes still maintain the interaction between the polymer backbone and functional groups, although the condition is within 1 M NaOH at 95°C.

The Fenton reagent test is typically used to determine the chemical stability of the alkaline solid polymer membrane. For example, Ayers et al[94] observed the degradation of the AEM after 5 hours of cell performance. Three results at one and a half hour intervals during the Fenton reagent test. Physically, the AEM appears stable and remains as expected, but with the use of FTIR and Raman spectroscopy, as presented in Figure 8B. Roughly, the importance of cationic functional groups has been missing. This has demonstrated that polymer degradation has arisen between the polymer backbone and the cationic functional groups. Thus, the performance of the AEM electrolyzer has been reduced. Nevertheless, this result shows the high ability of AEM components to survive in high alkaline atmosphere conditions.

Another critical parameter for developing high-performance AEM is balancing the properties of ion conductivity and mechanical stability. The cation functional group's high density can improve the ion conductivity, but the mechanical stability of the AEM appears to be degraded due to extra water absorption. The hydroxide attack can readily occur, which decreases ion conductivity and mechanical stability.[53] Therefore, the mechanical properties are an essential characteristic of AEM that must be determined during the alkaline solid polymer membrane fabrication. Usually, the tensile strength, Young modulus, and elongation at the break of the polymeric membrane have been evaluated to understand the AEM component's mechanical stability.[102,103] Wu et al[104] studied the mechanical properties of AEM components in terms of tensile strength, Young modulus, and elongation at break of the polymeric membrane. By using the Quaternized poly (DMAEMA-co-TFEMA-co-BMA) (QPDTB) based membrane, the mechanical properties have shown 7.629 MPa of tensile strength, 0.229 GPa of Young's modulus, and 45.8% of elongation at break, as presented in Figure 9A. The modification of pure poly (DMAEMA) with the cation functional groups has been successfully enhanced the mechanical properties of AEM and increased the ionic conductivity. The modification of the commercial membrane with the other synthetic polymer is also a promising technique for improving the AEM component's mechanical stability. For example, the fabrication of polybenzimidazole and fumasep FAA-3 based membrane obtains the blend membranes for AEM electrolyzer. This blend membrane has shown the increment of the mechanical stability of the commercial membrane and maintained for 4 weeks to undergo a mechanical test period through the tensile strength analysis, as presented in Figure 9B.[69]

3.3 | Durability of cell performance

Although the modification of the current alkaline solid polymeric membrane has increased the ionic conductivity

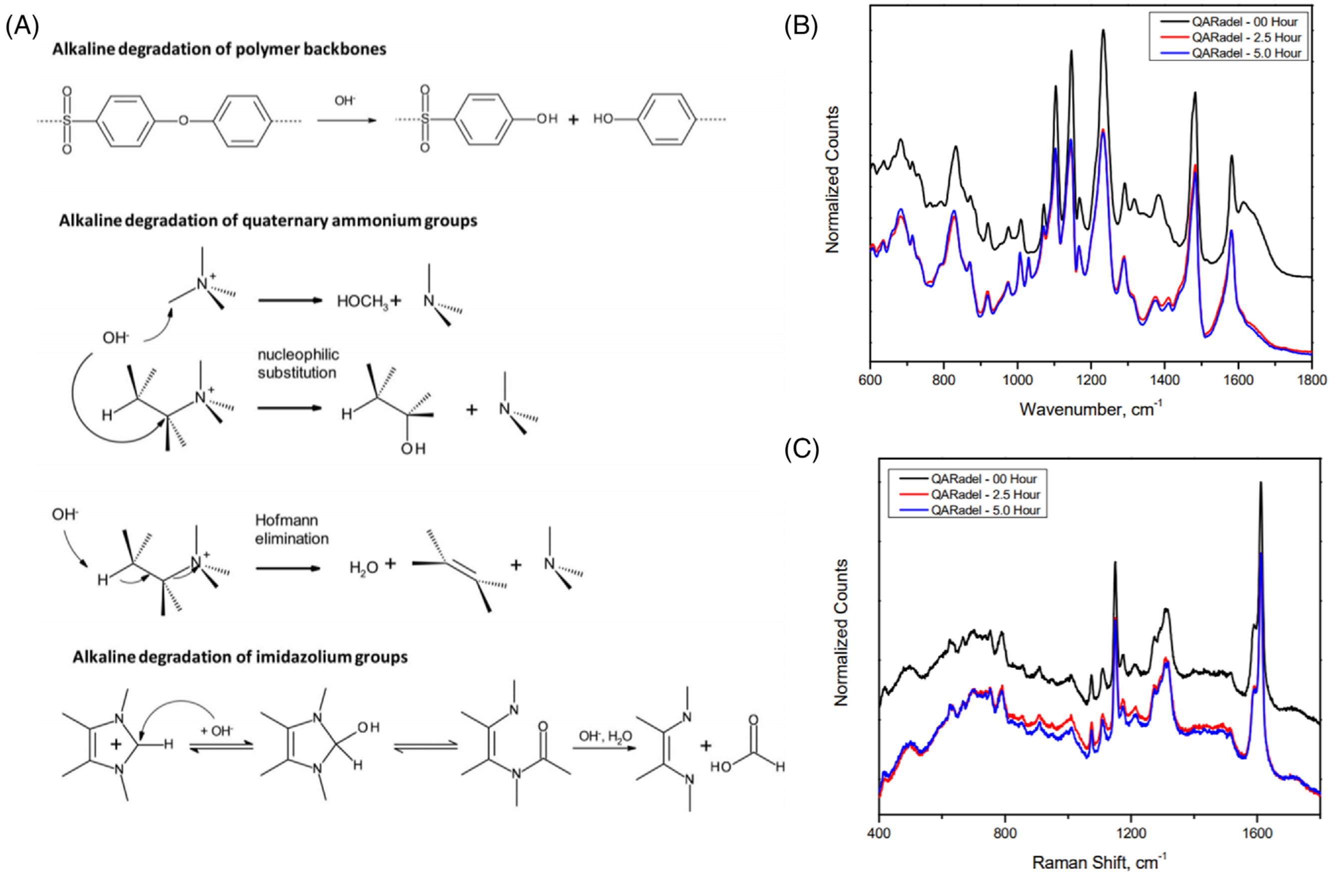


FIGURE 8 A, The mechanism of alkaline degradation of alkaline solid polymer electrolyte,[101] B, the FTIR and C, Raman spectroscopy of AEM, after Fenton test [94]

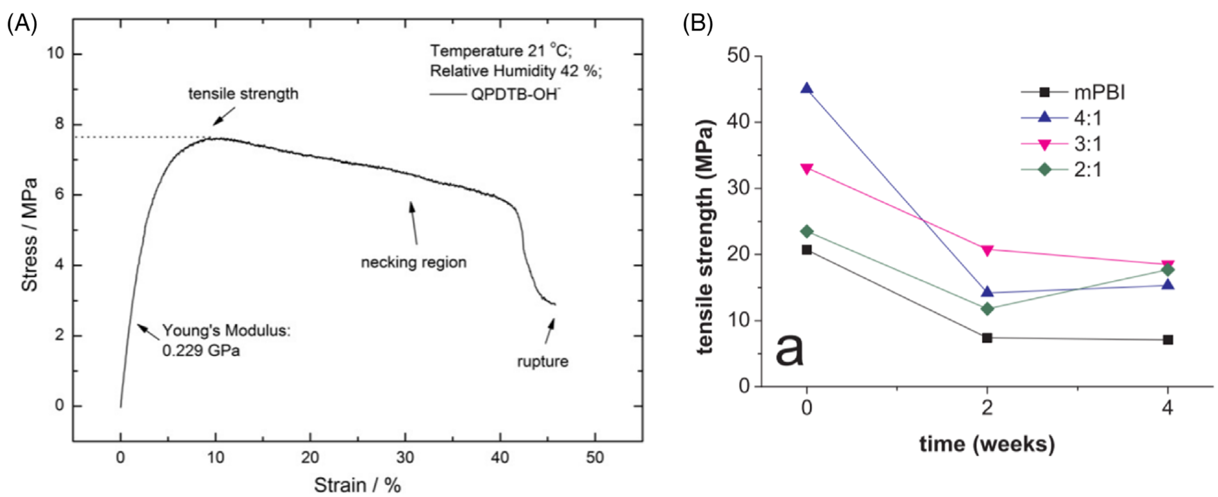


FIGURE 9 A, The mechanical properties of QPDTB based membrane,[104] B, the tensile strength analysis for blend membrane[69]

properties, one of the most challenges to commercializing AEM electrolyzer is to provide the high sustainable durability of the alkaline solid polymeric membrane.[77] The durability of the AEM electrolyzer cell efficiency is strongly dependent on the stability of the alkaline solid polymer membrane in the alkaline atmosphere. The practical measure for evaluating the AEM's stability is to observe the condition of the voltage cell when the current density constant is supplied. The voltage difference reflection shall be calculated whether the AEM is compatible with this application in a stable condition. In reality, the rise in voltage reading has been confirmed that the AEM is in an unstable state. Commonly, the instability of AEM is rooted in the degradation of the cationic functional group or the polymer chain backbone. One of the studies has been proved that the commercial membrane of Tokuyama corporation, which is the A-201 membrane, could be sustained for 600 hours at 100 mA cm^{-2} at 50°C.[105]

Several polymeric materials have been proposed to find the best durability performance of an alkaline solid polymeric membrane. AEM based on polysulfone has shown good stability during cell performance. At 400 mA cm^{-2}, the constant current density still can be remained until 6 hours. However, the cell voltage raised to 2.4 V from 1.6 V. This condition indicated the degradation of the polymer backbone of polysulfone and the deterioration of the functional group due to the interruption of carbon dioxide attacking during the operating cell condition.[77] Xiao et al[78] modified the polysulfone with the quaternary ammonium functional group. At 70°C, they reported the cell voltage stabilized until 8 hours in the range of 1.8 to 1.85 V.

4 | SUMMARY AND PERSPECTIVES

AEM electrolyzer is recognized as a renewable energy resource system with a high ability to supply ultra-pure hydrogen (>99.999%). This system is categorized as a green energy system due to energy production done without any non-polluting manner, which uses the water-splitting process to produce hydrogen and oxygen when the electricity is supplied. Besides, hydrogen production can be processed at any time and at any appropriate location, in which hydrogen can be directly used or stored. In practice, the fuel cell is the most suitable application to be directly used by the hydrogen generated from the electrolyzer unit. This system has the potential to reduce the manufacturing cost of the high-pressure cylinder gas method. Although the AEM electrolyzer has a high potential to provide hydrogen fuel as a future energy resource, many problems need to be resolved to build a real system. In this article, the characterization assessment of the alkaline solid polymeric membrane as an AEM component has been comprehensively discussed to provide the best performance of the AEM electrolyzer for green hydrogen production. Several important characterizations have been described, including ion exchange capacity, ionic conductivity, chemical and mechanical stability, and cell performance durability. Many works still must be done to find the best alternative of alkaline solid polymer membrane as an AEM for AEM electrolyzer. There are numerous research perspectives that can be proposed in the future to find the potential alkaline solid polymer electrolyte for AEM electrolyzer:

- The main challenge for developing the system of the AEM electrolyzer with the high efficiency of the operating condition is to discover the most promising polymeric materials to fabricate the alkaline solid polymer membrane.
- Superior ionic conductivity performance of alkaline solid polymer electrolyte is required by shortening ionic diffusion within polymeric materials in order to reduce the ohmic resistance effect. In parallel, the reactant crossover in the alkaline solid polymer electrolyte must be minimized to avoid the mix potential effect.
- The introduction of various functional groups into the alkaline solid polymer electrolyte is an excellent solution for increasing ionic conductivity due to the extra ionic routes that improved the ionic exchange capacity of the polymeric membrane. Furthermore, the presence of a functional group grafted into the polymer backbone improves the chemical and mechanical stability of alkaline solid polymer electrolytes.
- Finally, the ability of alkaline solid polymer electrolytes to sustain the operating cell of the AEM electrolyzer is critical. Thus, to execute the good durability properties of an alkaline solid electrolyte membrane, the ideal condition of the alkaline atmosphere in an AEM electrolyzer must be identified.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support given to this work by Universiti Kebangsaan Malaysia (UKM) under Grant of Modal Insan with grant No: MI-2019-023.

DATA AVAILABILITY STATEMENT

Data openly available in a public repository that issues datasets with DOIs.

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How to cite this article: Zakaria Z, Kamarudin SK. A review of alkaline solid polymer membrane in the application of AEM electrolyzer: Materials and characterization. *Int J Energy Res*. 2021;45(13):18337–18354. https://doi.org/10.1002/er.6983