

Review

Styrene and Its Derivatives Used in Proton Exchange Membranes and Anion Exchange Membranes for Fuel Cell Applications: A Review

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Abstract: The proton exchange membrane (PEM) is a critical component of fuel cells, responsible for controlling the flow of protons while minimizing fuel crossover through its channels. The commercial membrane commonly used in fuel cells is made of Nafion, which is expensive and prone to swelling when in contact with water. To address these limitations, various polymers have been explored as alternatives to replace the costly Nafion membrane. Styrene, a versatile and cost-effective material, has emerged as a promising candidate. It can be modified into different forms to meet the requirements of a fuel cell membrane. The aromatic rings in styrene can copolymerize with hydrophilic functional groups, enhancing water (H₂O) uptake, proton conductivity, and ion exchange capacity (IEC) of the membrane. Additionally, the hydrophobic nature of styrene helps maintain the structural integrity of the membrane's channels, reducing excessive swelling and minimizing fuel crossover. The flexible aromatic chains in styrene facilitate the attachment of hydrophilic functional groups, such as sulfonic groups, further improving the membrane's ion conductivity, IEC, thermal stability, mechanical strength, and oxidative stability. This review article explores the application of styrene and its derivatives in fuel cell membranes, with a focus on proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), and anion exchange membrane fuel cells (AEMFCs).

Keywords: proton exchange membrane fuel cell; anion exchange membrane fuel cells; direct methanol fuel cells; membrane; styrene; polystyrene; styrene derivatives



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1. Introduction

Fossil fuels produce large amounts of pollution, which increases the environmental hazard as well as health issues related to humans and animals. To reduce reliance on fossil fuels, new renewable energy technologies have been developed that are environmentally friendly and safe [1–3]. Moreover, fossil fuels increase global warming when used for power production. New emerging renewable technologies have overcome these drawbacks and replaced fossil fuel usage rapidly [4–6]. These emerging technologies include lithium-ion batteries and fuel cells [7–12]. Moreover, the non-polluted fuels used in these technologies produce clean energy. One of the examples of a new emerging power generation device is a fuel cell, which operates on nontoxic and environmentally friendly fuels. It converts

chemical energy into electrical energy by using oxygen and fuel, and as a product, heat and water are produced. Compared to traditional devices, fuel cells provide high efficiency, are eco-friendly, and provide a continuous supply of energy with an uninterrupted fuel supply. There are several types of fuel cells [13]. Some are listed below while others are detailed in supplementary data.

Fuel cells come in a variety of forms:

- Proton exchange membrane fuel cells (PEMFCs);
- Anion exchange membrane fuel cells (AEMFCs);
- Phosphoric acid fuel cells
- Solid acid fuel cells
- Alkaline fuel cells
- Molten carbonate fuel cells
- Microbial fuel cells (MFCs)
- Solid oxide fuel cells (SOFCs)
- Zinc-Air fuel cells (ZAFCs)
- Direct methanol fuel cells (DMFCs)

Among these fuel cells, proton exchange membrane fuel cells (PEMFCs) are lightweight, high-efficiency power generation devices with a simple structure, making them ideal for transportation and aviation applications [14–16] [Figure 1]. They consist of an anode, cathode, and a separator that facilitates proton flow while preventing fuel crossover [17–19]. PEMFCs are categorized into low-temperature PEMFCs (LTPEMFCs), which use Nafion membranes and operate at 80–100 °C [20–22], requiring full hydration for proton conduction, and high-temperature PEMFCs (HTPEMFCs), which use Polybenzimidazole (PBI) membranes doped with phosphoric acid and operate at 100–160 °C without the need for hydration [23–26]. LTPEMFCs are susceptible to CO poisoning from hydrogen fuel impurities, while HTPEMFCs are more resistant to CO and can tolerate hydrogen with up to 10 ppm CO. Despite their differences, both types offer high power density and efficiency, with HTPEMFCs providing additional advantages in high-temperature and impurity-tolerant operations [27–29].

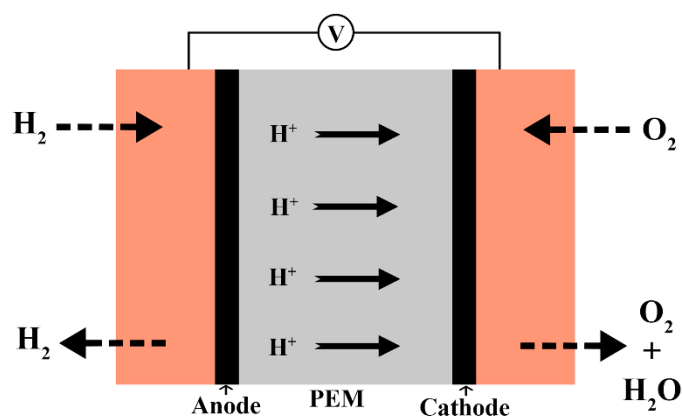


Figure 1. Typical schematic diagram of PEMFC working principle.

The direct methanol fuel cell is another power production device that converts chemical energy produced from methanol fuel to electrical energy. It is simple in design, portable, and used in different transportation and military equipment [30,31]. Methanol fuel offers high energy density, easy storage and handling, and cost effectiveness, making it ideal for fuel cell applications. Its liquid form and compatibility with existing infrastructure simplify its use, while its renewable production potential provides environmental benefits, making it a practical alternative to hydrogen and other fuels. Its structure is similar to PEMFCs

except for fuel [32]. An aqueous methanol solution is supplied to the anode side, where it splits into electrons and protons. Protons in the form of H^+ pass through the membrane while electrons pass through the external circuit. Pure or moist oxygen is supplied to the cathode side, where it combines with protons and electrons. The byproducts are water and extract heat [33]. The type of membrane usually used in DMFC is Nafion. The overall chemical reactions are provided in Table S1.

An anion exchange membrane fuel cell (AEMFC) operates in an alkaline environment, where hydroxide ions (OH^-) move through the membrane, unlike proton exchange membrane fuel cells (PEMFCs) that rely on protons. AEMFCs consist of an anode, cathode, and membrane, and typically operate at 25–90 °C [34], though research is ongoing for high-temperature AEMFCs (>110 °C) [35,36] [Figure 2]. Fuel, such as hydrogen or methanol, is oxidized at the anode, producing water, electrons, and heat, while oxygen at the cathode reacts with water and electrons to form hydroxide ions. Unlike PEMFCs, the ion flow in AEMFCs is reversed, moving from cathode to anode. Hydroxide ion transport occurs via two mechanisms: the Grotthuss mechanism, where OH^- ions “hop” through hydrogen-bonded water molecules, and vehicular movement, where hydrated OH^- ions diffuse through membrane channels. These mechanisms work together, with the Grotthuss mechanism dominating at low hydration and vehicular movement dominating at high hydration. However, challenges such as carbonation, dehydration, and chemical instability in alkaline conditions hinder performance. Optimizing membrane hydration, ion exchange capacity, and temperature is critical for improving AEMFC efficiency and conductivity.

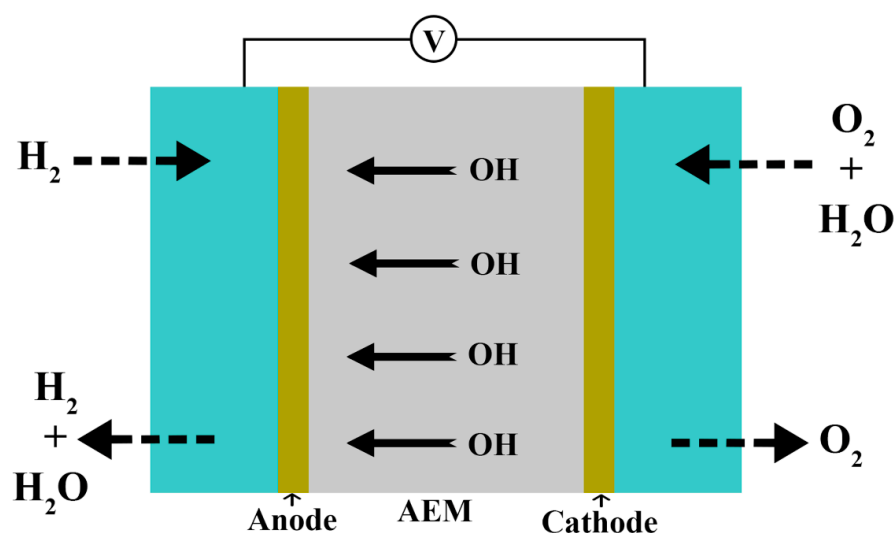


Figure 2. Schematic diagram of an anion exchange membrane fuel cell (AEMFC).

2. Structure of Nafion and Its Proton Conduction Mechanism

The materials for proton exchange membranes are selected on the basis of high ion conductivity, mechanical strength, chemical stability, low gas permeability and effective water management, high protection from fuel crossover and being environmental friendly. Moreover, polymer membrane materials should exhibit both hydrophilic and hydrophobic properties. The hydrophilic part of the polymer membrane absorbs water, while the hydrophobic part blocks the permeability of hydrogen and oxygen [37,38]. PEM materials must be chemically inert to prevent degradation under exposure to $-OH$ and $-OOH$ radicals. Perfluorosulfonic acid-based membranes provide both hydrophobic and hydrophilic properties in membranes. Its hydrophobic perfluorinated backbone supports the membrane in terms of chemical and mechanical stability, while the hydrophilic pendant chain in the membrane is responsible for water intake, which promotes ion cluster formation [39]. Various

types of perfluorosulfonic acid (PFSA) membranes, such as Nafion 117 and 212, are commercially available [40]. Thick membranes like Nafion 117 (183 μm) offer high resistance to fuel crossover, while the thin Nafion 212 membrane provides high ionic conductivity but is more prone to fuel permeability. Due to their thermally sensitive nature, these membranes cannot operate above 80 $^{\circ}\text{C}$, making them suitable for low-temperature fuel cells. Moreover, its high proton conductivity, chemical stability, and mechanical strength somehow fulfill the criteria of membranes used in fuel cells [41]. The DuPont company manufactured the first PFSA-based membrane for fuel cells, which consists of Nafion. Nafion consists of a backbone of Tetrafluoroethylene (TFE) copolymer and a perfluoro vinyl ether pendant chain. The Nafion membrane delivers high proton conductivity of more than 0.1 S cm^{-1} to 0.13 S cm^{-1} at a temperature of 80 $^{\circ}\text{C}$ under 100% relative humidity (RH). The Nafion membrane can sustain stable power for over $60 \times 10^3\text{ h}$ [42,43]. The ion conduction in the Nafion membrane is based on Grotthuss and vehicular mechanisms [44]. The protons generated by the oxidation and reduction process in the fuel cells combine with water present in the Nafion to make hydronium ions (H_3O^+). These hydronium ions combine with additional water molecules to form larger hydrated complexes, such as H_5O_2^+ and H_5O_3^+ . These ions travel through the free water available in the membrane. Protons move as part of larger hydrated complexes (e.g., H_3O^+ , H_5O_2^+ , H_5O_3^+) through the membrane by diffusion. This movement is called a vehicular mechanism. Moreover, in the Grotthuss mechanism, protons hop on sulfonic groups in the membrane and jump from one group to the other group through electrostatic attraction [45].

3. Deficiencies of Existing Membrane Materials Used in Fuel Cells

Despite Nafion's high mechanical strength and chemical stability, it experiences some drawbacks, such as high swelling and loss of water under high temperature, which lowers the conductivity [46]. Different companies, such as Solvay and Dow Company, introduce membranes that contain high conductivity, low swelling, and high thermal stability as compared to Nafion membranes. On the other hand, fillers such as Titania, silica, and alumina, have been applied to modify the Nafion membrane, but the cost of production increases due to expensive Nafion material [47–49]. Moreover, anion exchange membranes (AEMs) used in AEMFCs face several critical deficiencies that hinder their performance and durability. These include low hydroxide ion conductivity, which results in higher ohmic losses, and poor chemical stability due to the degradation of cationic groups (e.g., quaternary ammonium) in high-pH environments [50]. AEMs are also highly sensitive to CO_2 , leading to carbonation, which reduces ionic conductivity and forms precipitates that further degrade performance. Mechanical instability, caused by swelling and shrinkage during hydration cycles, and limited thermal stability at elevated temperatures exacerbate these issues. Additionally, water management is challenging, as AEMFCs require precise hydration to maintain conductivity without flooding [34,51]. These deficiencies, combined with the limited commercial availability of high-performance AEMs, pose significant barriers to the widespread adoption of AEMFCs. Researchers are actively exploring solutions, such as developing chemically stable cationic groups, hybrid membranes, and advanced materials, to overcome these challenges and improve the viability of AEMFCs for clean energy applications [52].

Several polymers with high glass transition temperatures, good ionic conductivity, and high resistance to fuel crossover and swelling are being used in research and commercial applications. These polymers are often combined with ceramics and nanomaterials to enhance the properties of polymer membranes for fuel cells. To further refine and tune the membrane structure, polymer chains are grafted [53–56] or block copolymers are introduced [57–59]. Examples of these polymers used in fuel cell membranes (PEMFCs,

DMFCs) include PBI [60–62], Polyether ether ketone (PEEK) [63–65], PSF [66–68], and PVDF [69–71]. On the other hand, in an AEMFC, the membrane materials are different from proton exchange membranes because it conducts hydroxide ions rather than protons $[H^+]$. The common materials used in making AEMs are hydrocarbon-based materials: Polyphenylene Oxide (PPO) [72–74], Polyaryletherketones (PAEK) [75–77], Polybenzimidazole (PBI) [78–80], fluorinated materials such as modified PVDF [81–83], nanoparticles [84–86], ionic materials [87–89], and quaternary ammonium functional groups [90–92]. The key parameters are explained in the Supplementary Materials.

4. Properties of an Ideal PEM

For the stability and long life of fuel cells, the membrane should meet the following properties [38,40,93]:

- High mechanical strength and stable porous structure.
- High ion conductivity (usually greater than 0.1 S cm^{-1}) at the required temperature;
- Be electrically insulated to prevent short circuiting.
- High chemical stability against harsh reactive impurities in fuel cells such as radicals, hydrogen peroxide (H_2O_2), and other agents.
- High tensile strength and durability. Withstand high pressure and maintain structural integrity during hydration and dehydration cycles.
- High protection from fuel crossover.
- High resistance against temperature and ensure thermal stability when operating at high temperature without melting or shrinkage
- The membrane materials should be economical and readily available for manufacturing.
- The membrane should be nontoxic, renewable in nature, and sustainable.

5. Properties of an Ideal AEM

An ideal AEM has the following properties:

- The membrane should have high ionic conductivity to facilitate the efficient transport of hydroxide ions (OH^-) from the cathode to the anode.
- The membrane should be an electronic insulator to prevent short-circuiting within the fuel cell.
- The membrane must be chemically stable in high pH environments (typically $pH > 13$) to withstand the alkaline conditions in AEMFC.
- The membrane should resist degradation from oxidative and reductive environments, especially at the electrodes.
- The membrane should have sufficient mechanical strength to withstand the mechanical stresses during cell assembly and operation.
- The membrane should maintain its shape and size under varying conditions of humidity and temperature to prevent delamination or cracking.
- The membrane should be stable at elevated temperatures (typically up to $80\text{--}100^\circ\text{C}$) to ensure efficient operation and to accommodate the heat generated during fuel cell operation.
- The membrane should have low permeability to gases (H_2 and O_2) to prevent crossover, which can lead to mixed potentials and reduced fuel cell efficiency.
- The membrane should maintain adequate hydration to ensure high ionic conductivity without becoming overly swollen, which can compromise mechanical integrity.
- The membrane should facilitate the transport of water produced at the cathode to the anode to maintain proper hydration levels.
- The membrane should be cost effective to produce, as high costs can be a barrier to commercialization.

- The membrane should have a long operational life to reduce the need for frequent replacements, contributing to overall cost effectiveness.
- The membrane should have good interfacial compatibility with the electrodes to ensure low contact resistance and efficient ion transfer.
- The membrane should adhere well to the electrodes to prevent delamination and ensure long-term stability.
- The membrane should be made from non-toxic materials to ensure safety during handling and disposal.
- The membrane should be made from sustainable or recyclable materials to minimize environmental impact.
- The membrane should be easy to fabricate into thin, uniform layers to ensure consistent performance across the fuel cell.
- The membrane should be scalable to large-area production to meet the demands of commercial applications.

In recent years, there has been a growing trend toward eliminating fluorine-containing compounds, such as perfluorosulfonic acid (PFSA) membranes, in electrochemical applications due to environmental and health concerns associated with per- and polyfluoroalkyl substances (PFAS). These “forever chemicals” are persistent, bioaccumulative, and potentially toxic, prompting stricter regulations and a push for more sustainable alternatives. Styrene derivatives have emerged as promising candidates for anion exchange membranes (AEMs) in anion exchange membrane fuel cells (AEMFCs), offering advantages such as lower environmental impact, cost effectiveness, and tunable chemical properties. Unlike PFSA, styrene-based polymers can be synthesized from more benign and abundant materials, aligning with the broader goal of developing greener energy technologies. This shift not only addresses regulatory and ecological challenges but also opens new avenues for improving the performance and sustainability of AEMFCs.

6. Styrene

Styrene (chemical name: phenylethene) is an organic compound with the molecular formula C_8H_8 . It is a colorless to slightly yellow, oily liquid with a sweet smell at low concentrations but a sharp, unpleasant odor at higher levels. Styrene is an important industrial chemical and serves as the precursor to polystyrene and various other copolymers [94]. Its unique structure, consisting of a benzene ring and a vinyl group, makes it highly reactive and suitable for polymerization. Its international union of pure and applied chemistry (IUPAC) name is ethenylbenzene, the molecular formula is styrene ($C_6H_5CH=CH_2$), and the molar mass is $104.15 \text{ g mol}^{-1}$. The structure of styrene consists of a benzene ring (C_6H_6) which provides aromaticity. As shown in Figure 3, a vinyl group ($CH=CH_2$) is attached to the benzene ring. The double bond in the vinyl group makes styrene reactive, especially in polymerization reactions, where the unsaturated vinyl group bonds to other styrene molecules to form long polymer chains. A diagram of the styrene structure is given below.

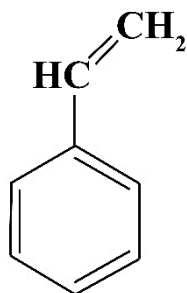


Figure 3. Chemical structure of styrene.

Major properties of styrene are given below in Table 1.

Table 1. General characteristics of styrene.

Characteristics	Physical State	Density (ρ)	Boiling Point (°C)	Melting Point (°C)	Solubility
Values	Colorless/light yellow	0.91	145	−30 °C	Water: 0% Organic solvents (alcohol, ether, etc.): 100%

7. Derivatives of Styrene

- 1. Polystyrene (PS)
- 2. Styrene Oxide
- 3. Styrene-Butadiene Rubber (SBR)
- 4. Alpha-Methylstyrene
- 5. Styrene-Acrylic Copolymers
- 6. Divinylbenzene (DVB)
- 7. Styrene Maleic anhydride (SMA)
- 8. Benzaldehyde
- 9. Poly(styrene-b-butadiene-b-styrene) (SBS)

8. Common Uses of Styrene and Its Derivatives

Styrene is a versatile and widely used monomer in industrial chemistry, playing a critical role in the production of fiberglass-reinforced plastics [95], construction materials like EPS and XPS insulation [96,97], lightweight foam products for packaging and disposable items [98], durable adhesives and coatings [99–101], high-performance paints and inks [102,103], and medical devices such as lab equipment and drug delivery systems [104–106]. It is also essential in electronics for its insulating and shock-absorbing properties [107,108]. Despite its widespread use, it is toxic in nature. However, styrene is used in fuel cell membranes through advanced engineering and material science to ensure safety and performance. It is typically incorporated into copolymers, such as sulfonated styrene-based polymers, which provide excellent proton conductivity and thermal stability—key properties for proton exchange membranes (PEMs). Styrene is chemically stabilized, crosslinked, or encapsulated within a robust polymer matrix to prevent leaching and minimize exposure risks. Manufacturing processes are tightly controlled, adhering to strict safety and environmental regulations, while the sealed operating environment of fuel cells further reduces potential hazards. Although styrene offers cost effectiveness, durability, and high performance in fuel cell applications, ongoing research focuses on developing safer alternatives to further mitigate risks.

This review article covers the whole aspect of styrene and its derivatives for the application of different types of fuel cells as a material for membrane manufacturing. Firstly, the introduction of different types of fuel cells is explained along with their working principle. Membranes are critically studied, including their types, materials, and ion conductivity mechanisms. In addition to their functions, different types of membranes, such as PEM and AEM, are discussed in detail for PEMFCs, DMFCs, and AEMFCs. Furthermore, different types of uses of styrene and its copolymer are discussed in detail along with their application in the future. The recently published research on styrene use in membrane material is explained in the end with the conclusion and future advancement on styrene-related membranes.

9. Application of Derivatives of Styrene in Membrane of Fuel Cells

9.1. Polystyrene

Polystyrene is one of the derivative of styrene also known as synthetic polymer and it is made from a monomer of styrene. It is widely used in plastic and also present in the form of solid and foam. It is lightweight, rigid in nature, clear or white in color, and easy to mold into any shape. It contains better mechanical strength but is brittle and easy to break when stress is applied. It is hydrophobic in nature and dissolves in solvents like acetone. Its melting temperature is 115 °C and its density is greater than 1000 kg m⁻³ [109]. It has wide application including in fuel cells. Its synthesis is possible on a laboratory level. Huang and his colleague scientists [110] synthesized a polystyrene-contained PE solution and mixed it with different amounts of dual functional graphene oxide in order to make polymer composite membrane for DMFCs. The graphene oxide functionalized with sulfonic and phosphonic groups. A strong π - π interaction between fillers and polymers developed defects free and smooth of the surface of the membrane which facilitated the protection from fuel crossover and the value shrunk to 18.42×10^{-7} cm² s⁻¹. Moreover, the presence of dual functional groups on the composite membrane surface facilitates proton transport through the membrane via vehicular and Grotthuss mechanisms, resulting in increased proton conductivity. The exchange of functional groups further enhances the ion exchange capacity (IEC) of the membrane due to the abundance of sulfonic and phosphonic groups on the composite membrane. The high proton conductivity and enhanced IEC create efficient pathways for the membrane to function effectively in fuel cells, enabling the composite membrane to deliver a power density of 78 mW cm⁻² at 25 °C.

Styrene is also copolymerized with other polymers to transfer its properties, making the membrane more suitable for fuel cell applications. Saxena and his colleague scientists [111] prepared a composite membrane consisting of sulfonated poly(styrene-co-maleic anhydride), poly(ethylene glycol), and silica. PEG was added in the composite membrane with the different amounts of silica nanoparticles. The role of PEG is to adjust the spacing between chemically connected polymer chains and silica nanoparticles, fine-tuning the ionic channels in the membrane. When tested for ion conductivity and IEC, the modified membrane showed no significant advantage over commercial Nafion membranes but exhibited higher mechanical strength. The tortuous pathways in the modified membrane reduce methanol permeability, with values lower than those of the commercial Nafion 117 membrane when tested at temperatures ranging from 30 °C to 70 °C. The improved thermal stability, low swelling, and high protection from fuel crossover represents that the membrane is able to apply in a DMFC fuel cell.

Polystyrene can be easily modified with sulfonic groups, enhancing its hydrophilic properties [112]. Grafting polystyrene sulfonic acid onto nanoparticles is a common practice to enhance the compatibility of nanoparticles with polymers in composite membranes. Moreover, polystyrene grafting further enhances fuel crossover resistance and improves proton conduction in the composite membrane. Shukla and his colleague scientists [113] used covalent grafting to make polystyrene-modified graphene oxide nanoplatelets. Then, the polystyrene sulfonic acid-grafted graphene oxide was mixed with SPEEK polymer to make composite membrane. The barrier attributes of modified graphene nanoplatelets act as a shield against methanol crossover and reduce its value to 5.57×10^{-7} cm² s⁻¹. Moreover, the hydrophilic functional groups of SPEEK and polystyrene sulfonic acid-grafted graphene oxide attract more water molecules, and the interactions between these functional groups within the membrane capture and retain water, further boosting proton conductivity. With 0.15 wt.% modified graphene oxide nanoplatelets, the composite membrane shows a proton conductivity value of approx. 73 mS cm⁻¹. With taking advantage of minimum fuel crossover and high proton conductivity, the composite membrane shows a

power density value of 170 mW cm^{-2} which is more than that of the pristine SPEEK membrane [110 mW cm^{-2}] and 50% higher than that of the commercial Nafion 117 membrane [80 mW cm^{-2}]. Moreover, the composite membrane is able to deliver stable performance up to 100 h of working in a fuel cell.

In another example, Shalaby and his colleague scientists [114] synthesized SSA and grafted it with cellulose acetate materials. Afterwards, it was converted into membrane by solution casting method [Figure 4a]. Grafting SSA onto cellulose acetate in the membrane increase its thermal stability, mechanical strength, and oxidative stability. The hydrophilic functional groups of polystyrene and cellulose acetate absorb more water molecules, and their interactions strengthen the interior walls of the channels, reducing swelling. High water uptake in the modified cellulose acetate membrane results in high proton conductivity and IEC. As a result, the modified membrane with 1.5 wt.% SSA shows low methanol permeability ($5.514 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$), proton conductivity (4.77 mS cm^{-1}), membrane selectivity of $8.65 \times 10^3 \text{ S s cm}^{-3}$, and peak power density of 24.6 mW cm^{-2} , respectively [Figure 4b]. This high power density stems from the membrane's unique architecture, where the sulfonated polystyrene grafts provide efficient proton-conducting pathways, while the cellulose acetate matrix acts as a barrier to methanol crossover. The shallow ohmic region slope further confirms low membrane resistance, aligning with the high proton conductivity data.

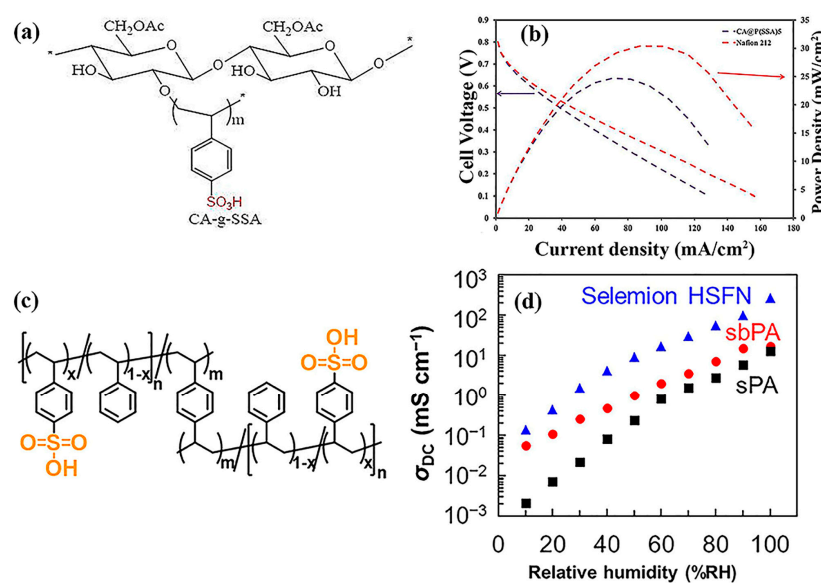


Figure 4. (a) Chemical structure of polystyrene grafted cellulose acetate. (b) Polarization curves for CA@P(SSA)5 grafted membrane and Nafion® 212. (c) Sulfonated crosslinked polystyrene (Selemon HSFN). (d) Relative humidity dependence of conductivity of sbPA (red circles), sPA (black squares) at 80 °C temperature [114,115].

Membranes containing phosphonic groups can be easily synthesized using polystyrene as a monomer due to its hydrophobic nature. As an example, Nakayama and his fellow scientists [115] synthesized a poly(4-(p-styryl)-1-butanephosphonic acid) (sbPA) polymer and diethyl 4-(p-styryl)-1-butanephosphonate which afterwards converted into membrane for PEFC [Figure 4c]. During the synthesis process, the diethyl 4-(p-styryl)-1-butanephosphonate monomer was treated with a phosphonic acid along with an alkylene spacer as a crosslinking agent. Through polymerization, sbPA polymer was synthesized containing phosphonic groups by alkylene spacer. The final step involved deprotection of the alkyl protecting group containing phosphonic acid ester. Due to high molecular mobility, the sbPA polymer membrane with an alkylene spacer exhibits a thermal stability

temperature of 170 °C, while the thermal stability of the sbPA polymer membrane with an alkylene spacer reaches 218 °C. However, TGA results show that the sbPA polymer membrane begins to degrade at approximately 180 °C, which is higher than the operating temperature of current PEFCs (100–150 °C under low humidity conditions). Moreover, the sbPA-based polymer membrane shows no irreversible weight loss, indicating that the membrane containing phosphonic groups or polystyrene begins to degrade only at temperatures up to 400 °C. With hydrophilic groups, the sbPA polymer membrane with spacer shows conductivity around 1.1 mS cm^{−1} at a temperature of 120 °C [Figure 4d] and under 20% RH which are two times higher values than sbPA polymer membrane without spacer.

Gadim and his colleague scientists [116] developed a membrane using bacterial cellulose and PSSA polymer using radical polymerization of sodium 4-styrenesulfonate, and in this process, PEGDA was used as a crosslinking agent to bind two polymers. Afterwards, the hybrid polymer was converted into acid form by sulfonation process. The results show that bacterial cellulose nanofiber make a network in the membrane and provide mechanical strength to the structure of the membrane. When tested at a high temperature of 140 °C, the membrane structure is sustained while at this temperature, Nafion or pure PSSA polymer have membrane meltdown. The sulfonic groups on the membrane form an ionic cluster and help to create ionic channels for a smooth pathway. Ultimately, the IEC capacity of the modified membrane containing PSSA and PEGDA in an amount of 83 wt.% reaches a value of 2.25 mmol g^{−1} for a composite with 83 wt.% PSSA/PEGDA. Moreover, through plane ion conductivity, it delivers a value ranging from approximately 0.042 S cm^{−1} to 0.1 S cm^{−1} when tested under a humidity value from 60% to 98% relative humidity (RH) at a temperature of 94 °C. These conductivity values are higher than values of Nafion or PSSA polymer membrane. These results demonstrate that this kind of multidimensional modified membrane shows great potential for the application in electronic devices such as PEMFC, DMFC, and AEMFC.

To further enhance the properties of polystyrene sulfonic acid, its copolymerization of hydrophilic polymers has been studied, such as in PVP and imidazole. The resulting copolymer is easily soluble in organic solvents, facilitating the production of physically and electrochemically stable membranes. For example, Ye and his colleague scientists [117] synthesized poly(styrene sulfonic acid-co-vinylpyridine) or NaSS-4VP by free radical polymerization and converted it into membrane by crosslinking with haloalkyl. The membrane exhibits high strength and flexibility due to interaction between sulfonic groups of polystyrene sulfonic acid and nitrogen groups of pyridine. Moreover, the acid-base interactions within the membrane enhance its thermal and oxidative stability. The synthesized polymer membrane exhibits reduced swelling and a stable porous structure at high temperatures, ensuring long-term durability and efficient proton conduction during fuel cell operation. Ultimately, an amount of 90.3% crosslinked polymer membrane shows a proton conductivity value of 71 mS cm^{−1} at a temperature and RH value of 30 °C and 90%, respectively, which are superior to that of the Nafion 117 membrane. However, the presence of more free water in the membrane increases methanol crossover, with values 16% higher than those of the Nafion 117 membrane under the same conditions. Despite high fuel crossover, the synthesized polymer membrane exhibits a selectivity value of 3.38×10^5 S cm^{−3} s which is five times superior to that of the Nafion 117.

In another example, Panawong and his colleagues [118] synthesized a poly(styrene sulfonic acid-co-1-vinylimidazole-co-styrene) terpolymer through traditional free radical polymerization and mixed it with PVC in order to obtain a polymer blend membrane. The sulfonic acid groups of polystyrene and the imidazole groups of vinylimidazole provide a strong mechanical structure through their interactions, while the hydrophobic nature of

polystyrene ensures long-term structural stability. The membrane exhibits high thermal and oxidative stability but lower water uptake and proton conductivity as the amount of polystyrene-based synthesized polymer increases. Under hydrated conditions, the polymer blend membrane with 1:1:4 synthesized polymer and PVC contents shows a proton conductivity value of $7.8 \times 10^{-5} \text{ S cm}^{-1}$.

Kang and his colleague scientists [119] synthesized a fibrous mat as an anion exchange membrane which consists of styrene-co-vinylbenzyl chloride-co-acrylonitrile copolymer by electrospinning technique using organic reaction blend. The unique phase modification of the membrane is responsible for its high ion conductivity. Moreover, the hydrophilic groups in the modified nanofiber mat result in a high water uptake, low swelling, and high IEC as the chemical composition of the organic blend in the membrane changes. With the ration of 3:5:2 of styrene-vinylbenzyl chloride-acrylonitrile, the modified membrane shows an ion conductivity value of 214 mS cm^{-1} at a temperature of 80°C . With its superior properties, the modified anion exchange membrane retains up to 94% of its ion conductivity after soaking in 1 M potassium hydroxide (KOH) solution for 72 h. A summary of these studies is provided in Table 2.

Table 2. Polystyrene-based membranes for application in fuel cells.

Types of Materials	Types of Fuel Cell	Ion Conductivity (mS cm^{-1})	Current Density (mA cm^{-2})	Power Density (mW cm^{-2})	Ref.
styrene-co-vinylbenzyl chloride-co-acrylonitrile copolymer	AEMFC	214	-	-	[119]
poly(styrene sulfonic acid-co-1-vinylimidazole-co-styrene)	PEMFC	7.8×10^{-2}	-	-	[118]
NaSS-4VP	PEMFC	71	-	-	[117]
SSA/cellulose acetate	DMFC	4.77	-	24.6	[114]
Polystyrene/graphene oxide	DMFC	73	-	170	[113]
Polystyrene/PE/graphene oxide	DMFC	-	-	78	[110]

In conclusion, polystyrene, a synthetic polymer derived from styrene monomers, is widely used in various applications, including fuel cells, due to its lightweight, rigid, and moldable nature. However, its brittleness and hydrophobic characteristics limit its direct use. To overcome these limitations, polystyrene is often modified or combined with other materials to enhance its properties. For instance, Huang et al. [110] synthesized a polystyrene-based composite membrane with dual-functional graphene oxide, which improved proton conductivity and reduced methanol crossover in direct methanol fuel cells (DMFCs). Similarly, Saxena et al. [111], developed a composite membrane using sulfonated poly(styrene-co-maleic anhydride), poly(ethylene glycol), and silica, which exhibited high mechanical strength and low methanol permeability, making it suitable for DMFCs.

Polystyrene can also be sulfonated to enhance its hydrophilic properties, as demonstrated by Shukla et al. [113], who grafted polystyrene sulfonic acid onto graphene oxide and combined it with SPEEK to create a composite membrane with high proton conductivity and low methanol crossover. This membrane outperformed both pristine SPEEK and commercial Nafion 117 membranes in terms of power density.

These advancements highlight the potential of polystyrene-based membranes in fuel cell applications, offering improved performance, durability, and cost effectiveness compared to traditional materials like Nafion. By leveraging modifications such as sulfonation,

copolymerization, and nanocomposite formation, polystyrene-based membranes can address key challenges in fuel cell technology, contributing to the development of sustainable energy solutions.

9.2. Polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS)

SBS is another type of thermoplastic polymer derived from styrene, known for its flexibility and good durability. Despite these qualities, SBS is not directly used in fuel cells due to its low conductivity and chemical resistance. To enhance its properties, researchers functionalize it with hydrophilic groups. As an example, Tian and his colleague scientists [120] prepared an AEM membrane by using a crosslinking and post-functionalization method. Crosslinking and polymerization are achieved by application of UV rays which opens the rings available on an SBS polymer and develop a connection with bromoalkyl groups [Figure 5a]. Crosslinking reduces excessive water uptake and swelling, maintaining mechanical integrity while ensuring sufficient hydration for ion transport. These bromoalkyl groups are converted into quaternary ammonium (QA) groups through a reaction with trimethylamine (TMA). The study optimizes IEC to balance high ion conductivity with mechanical stability and controlled swelling, achieving values typically in the range of 1.5–2.5 meq. g^{−1}. Higher IEC enhances conductivity by increasing the number of ion-exchangeable groups but can also lead to excessive water uptake and swelling. The dual-functional epoxide groups in the polymer enable simultaneous quaternization (for high IEC) and crosslinking (to mitigate swelling and improve mechanical strength). As a result, the modified membrane contains hydrophilic side chains and PB blocks which provide support to mechanical strength. The modified SBS-based membrane contains long hydrophilic chains that enhance ionic clustering and create ionic channels for improved ion transport [Figure 5b,c]. The results show that with tune parameters of modified membrane, the hydroxide conductivity increases more than 100 mS cm^{−1} when tested at a temperature of 80 °C. Moreover, it exhibits better toughness, mechanical strength, and high alkaline stability in 1 M NaOH solution at 80 °C for 500 h.

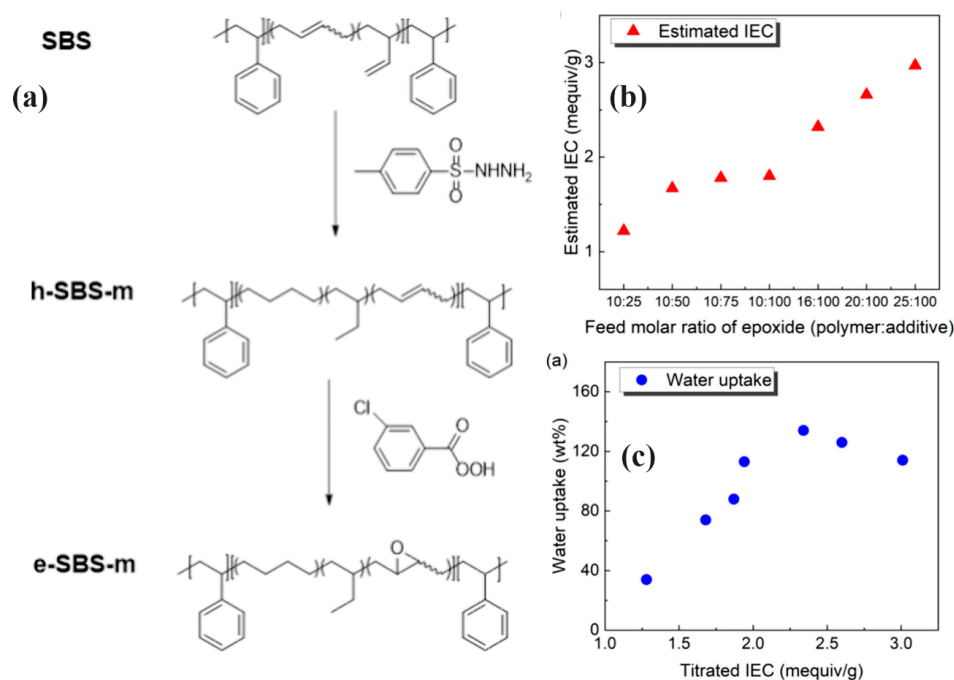


Figure 5. (a) Schematic diagram of preparation of SBS, h-SBS-m, e-SBS-m; (b) approximated IEC of SEBS-based membrane; (c) graph between IEC vs. water uptake value of SEBS-based membrane [120].

Turan and his colleagues [121] prepared hydrogenated h-SBS triblock copolymer-based membranes by a series of chemical reactions including a thiol-ene click reaction containing polybutadiene with 6-mercapto-1-hexanol. Afterward, the remaining bonds were hydrogenated by a brominating reaction of alcohol groups. In the end, a substitution of TMA was carried out for complete formation of copolymer. The amount of functional groups contain 50% carbon single bonds and double bonds are controlled by controlling the thiol-ene click reaction. H-SBS polymer membrane modified with TMA and 24% functionalized groups exhibits an IEC and -OH ion conductivity of 1.83 meq. g^{-1} and 93 mS cm^{-1} , respectively, when tested at a temperature of 80°C . The results show that the hydroxide ion conductivity and IEC remain stable when modified membrane is preserved under a 1 M NaOH solution at a temperature of 80°C for 4 weeks. Moreover, the modified SBS-TMA membrane provides a strong mechanical strength, less swelling under water and humid conditions, a minimum water uptake, and stable ion conductivity when tested at 80°C temperature. These properties prove that the modified SBS-TMA membrane with additional functional groups are a good candidate for the application of AEMS as compared to rigid SBS polymer membrane.

9.3. Styrene-Ethylene-Butylene-Styrene (SEBS)

SEBS is a polymer produced by the hydrogenation of SBS. During functionalization, this method provides protection from a side reaction in the non-aromatic double bonds. SEBS exhibits good flexibility and chemical inertness. However, its use as a membrane in fuel cells is limited due to its tendency to swell and low tensile strength. Various attempts have been made to use SEBS as an AEM by introducing ion-conducting head groups. These efforts have resulted in AEMs with high ionic conductivity due to excellent phase separation, despite relatively low IEC values. SEBS can also be easily copolymerized with other styrene-based polymers, enhancing the physical and electrochemical properties of membranes. In one of the examples, Bhavani and colleagues [122] synthesized modified SEBS by live anion copolymerization with polystyrene and 1,4-butadiene units. 1,4-butadiene become part of the membrane materials, while polystyrene high contents provide high mechanical strength to the membrane. With 70% PS, the modified membrane shows IEC and proton conductivity values of 3.37 mmol g^{-1} and 190 mS cm^{-1} when tested at a temperature of 80°C [Figure 6a–d]. Figure 6e,f demonstrates the alkaline stability and fuel cell performance of the synthesized poly(styrene-*b*-(ethylene-co-butadiene)-*b*-styrene) anion exchange membrane (AEM), showcasing its practical viability. The figure includes polarization and power density curves, where voltage and power output are plotted against current density. The polarization curve reveals three key regions: an initial voltage drop due to activation losses at low current densities, a linear decline from ohmic resistance (dominated by the membrane), and a sharp drop at high current densities caused by mass transport limitations. Moreover, the modified membrane is able to attain a power density value of nearly 1000 mW cm^{-2} with a current density value of 2.09 A cm^{-2} when tested in H_2/O_2 single cell assembly at a temperature of 80°C . The results show that the modified SEBS anion exchange membrane is able to apply commercial fuel cells [Figure 6e,f].

The presence of styrene allows for the sulfonation of SEBS, making the membrane more hydrophilic and enhancing its ability to attract water molecules. As an example, Bhavani and his fellow colleagues [123] synthesized sulfonated SEBS and crosslinked it with glutaraldehyde of different amounts from 2 to 10%. Glutaraldehyde acts as a crosslinking agent which favors the dimensional stability of the prepared membrane. The modified membrane shows a high proton conductivity value of 10 mS cm^{-1} at a temperature of 25°C . The modified sulfonated membrane shows power density values of 68 mW cm^{-2} and 58 mW cm^{-2} with a current density value of 200 mA cm^{-2} for a

crosslinked glutaraldehyde amount of 2 and 10%, respectively, when assembled with 2 M concentration of methanol solution at 25 °C. Moreover, the sulfonated modified membrane resists high methanol crossover due to its blocking effects. Ultimately, the methanol crossover value from $16.22 \text{ cm}^2 \text{ s}^{-1}$ to $11.89 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ could pass through modified membrane which is much lower than the commercial Nafion 117 membrane whose value is $35.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

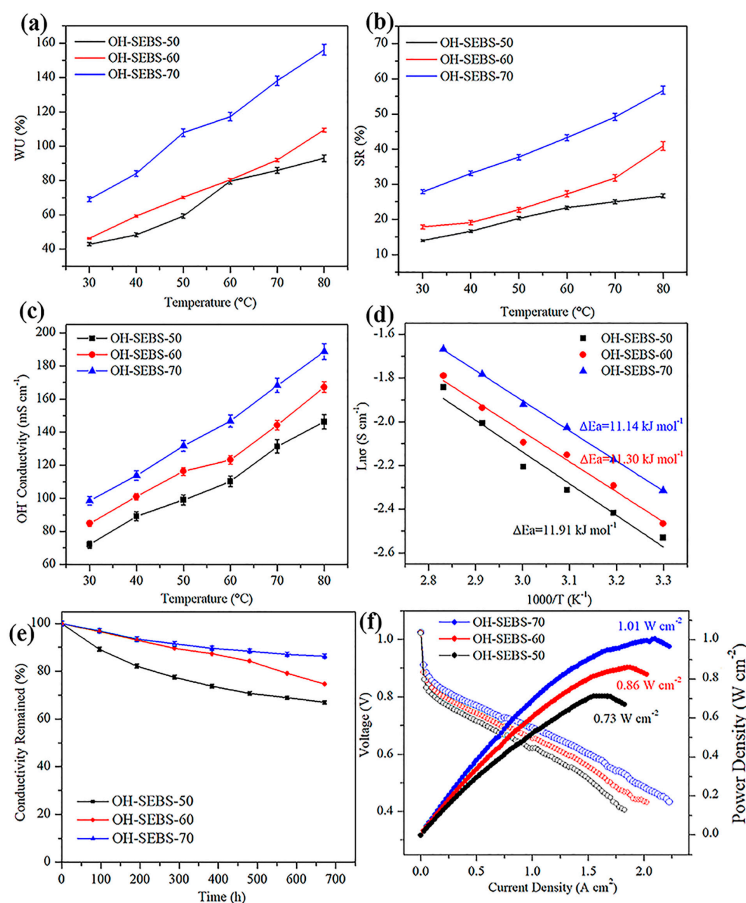


Figure 6. (a) Graphs of different temperature vs. (a) water uptake (b) swelling ratio (c) hydroxide conductivity; (d) temperature dependence graphs of different SEBS-based membranes from 50 to 70%; (e) ion conduction retention for AEM after dipping in NaOH solution of concentration 2 M at a temperature of 60 °C for different time intervals; (f) performance curves consist of SEBS-based membrane with different amounts [122].

Shi and his fellow colleagues [124] used one derivative of styrene to make another derivative of styrene. In the article, two types of SBS named SEBS 1301 and SEBS1401 were chosen, containing 87% 1,4 butadiene. These types were converted into SEBS-based AEMs through methods such as hydrogenation, quaternization, alkalization, and chloromethylation. The results show that the membrane shows a high mechanical strength which is a result of physical self-crosslinking provided by poly(ethylene-co-butylene). The membrane's crystallinity reaches 20% at 80 °C after hydrogenation of the 1,4-butadiene units, improving ion transport pathways. On the other hand, the crosslinked polystyrene in the membrane forms high ion clusters due to its hydrophilic nature. With improved crosslinking and hydrophilic groups, the membrane reduces swelling to 12%. Moreover, AEM shows values of water uptake and hydroxide conductivity of approximately 80% and $81 \times 10^{-3} \text{ S cm}^{-1}$ at a temperature of 80 °C. The polystyrene availability in the membrane enhances the ion exchange capacity value and its value reaches 1.48 mmol g^{-1} when tested with SEBS1401 based AEM. When tested in AEMFC, the membrane with SBS1401 delivers

a power density and current density values of 320 mW cm^{-2} and 860 mA cm^{-2} , respectively. This proves that the SEBS-based AEM results indicate that the proposed method can develop high-performance SEBS-based AEMs, suitable for fuel cell applications.

In another example, Dai and his colleague scientists [125] prepared a triblock copolymer of SEBS-based AEM for AEMFC using Poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene) (PSBEBS) for crosslinking and functionalization purpose. SEBS was first converted into chloromethylated SEBS, then quaternization and crosslinking with tertiary amines were carried out. The $-\text{CH}_2$ spacer group alters the membrane's morphology and improves ionic channels. Thus, the ionic conductivity of SEBS-based membranes improves, and as the spacer group length increases from $-\text{CH}_2$ to $-\text{CH}_{12}$, methanol permeability decreases, confirming its effectiveness. The spacer groups in the modified membrane also increase strength by tightening the polymer chains. Moreover, these changes greatly improve the membrane's chemical and thermal stability. The properties of the synthesized membrane are further improved by adding nanoparticles such as graphene oxide. With 0.5% graphene oxide, the modified membrane shows ion conductivity value and selectivity values of $2.0 \times 10^{-2} \text{ S cm}^{-1}$ and $7.6 \times 10^4 \text{ S s cm}^{-3}$ at a temperature of 60°C which shows its superior resistance against methanol permeability.

Wang and his colleague scientists [126] synthesized the polymer copolymerized with SEBS to make AEM for fuel cell application. Two polymers named *p*-triphenylpiperidine and 1,1,1-trifluoroacetone were synthesized and attached to a fluorine group in their polymer chains which boost the phase separation [Figure 7a]. Moreover, the addition of fluorine helps in the construction of ionic channels within the membrane and further improves the ion conductivity. The results show 5, 10, and 15% PTP contents in the polymer studied. The fluorine contents in the AEM increase the dimensional stability and mechanical strength of the membrane. Poly(triphenylpiperidine) (PIP) cations in the membrane improve the hydroxyl ion conduction in the membrane and hydrophobic phase in the membrane protects from the fuel crossover. As a result, the membrane shows a more stable structure and protects against changes that happen during increasing temperature [Figure 7b,c]. The SEBS-based membrane with 15% PTP shows a tensile strength value and elongation of 38.79 MPa and 183.09% at a temperature of 80°C and relative humidity value of 100%. With better ionic channels, the membrane shows an ion conductivity value of $102.02 \text{ mS cm}^{-1}$ at a temperature of 80°C [Figure 7b]. When alkaline stability is tested, the SEBS-based membrane shows only 6.23% ion conductivity declining under a 2 M NaOH solution and for a time period of 1400 h. [Figure 7d]. The results show that the SEBS-based membrane shows a power density value of $247.86 \text{ mW cm}^{-2}$ which depicts its great potential in the application of AEMFCs [Figure 7e].

PAP polymers with an ether-free polymer back chain are attracted by scientists nowadays to make membranes for AEMs due to its high ion conductivity and alkaline stability. Despite high conductivity, the drawbacks such as low mechanical strength and weak phase separation restrict its direct usage in electronic devices. Some researchers try crosslinking different forms of PAP with SEBS to further enhance its physical and electrochemical properties. As an example, Min and his colleague scientists [127] prepared membrane with the crosslinking of PBB polymer with SEBS polymer using their different ratios for changing the crosslinked degree. The modified membrane with 40% degree of crosslinking shows a young's modulus and elongation values of 486 MPa and 70%, respectively. Moreover, due to the hydrophilic nature of SEBS, the membrane delivers an ion conductivity value in the range from 72.28 to $146.25 \text{ mS cm}^{-1}$ with maximum captured water contents and boosted structure. With high mechanical strength and conductivity, the membrane shows a power density value of 1042 mA cm^{-2} with a voltage value of 1.8 V. The results also show that when tested, the alkaline stability of the membrane for 720 h. and at 2 M KOH for a

temperature of 80 °C, it retains a conductivity value of 99%. For oxidative stability, it is also able to sustain the conductivity value up to 98% when tested for a time period of 120 h. and at a temperature of 60 °C.

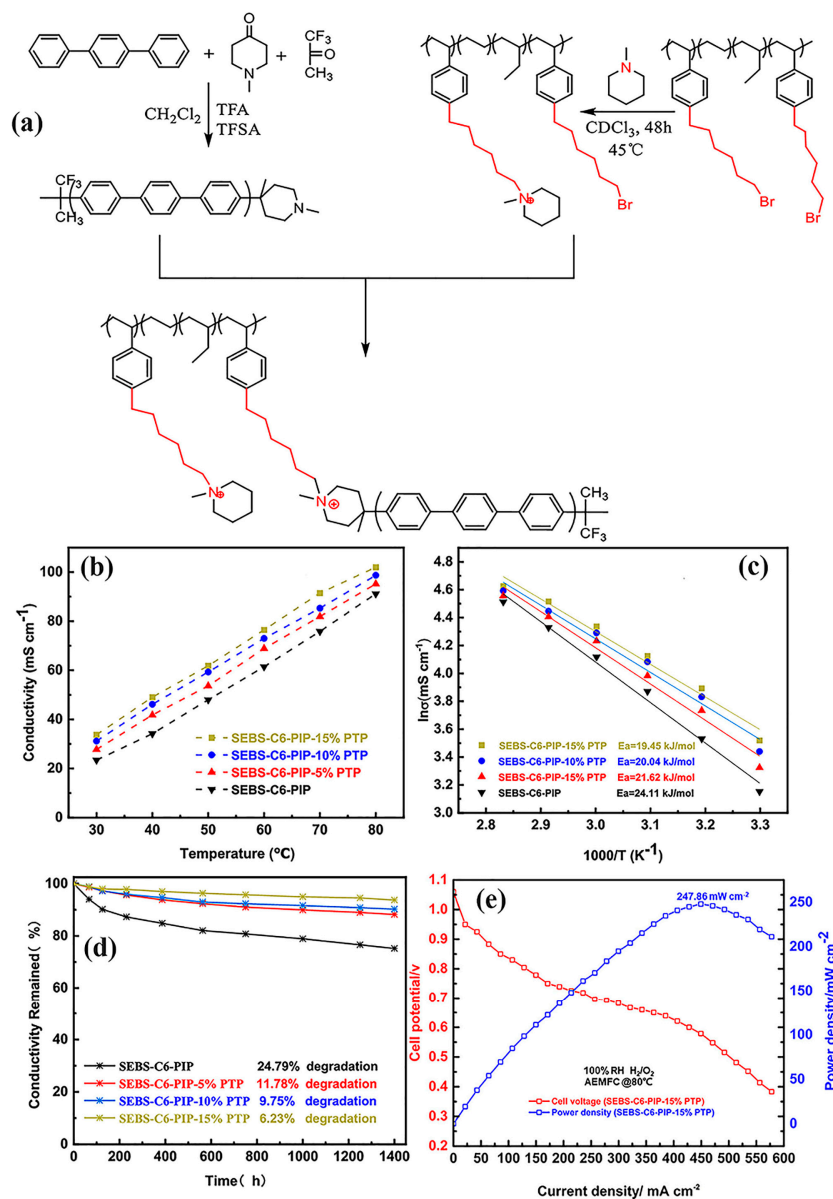


Figure 7. (a) Schematic diagram of synthesis of PTP-based membrane containing SEBS. (b) Temperature vs. ionic conductivity and (c) temperature dependence Arrhenius curve for synthesized SEBS-based PTP membranes [126] (d) ion conductivity retention against time (e) current density vs. cell potential.

Wang and his colleague scientists [128] synthesized the SEBS-based membrane by using Friedel–Crafts acylation and a ketone reduction reaction. A long alkyl chain was introduced onto styrene to resist the formation of cations and promote the resistance of alkaline. These are the base materials used for the membranes. SEBS-C6-Br is the brominated form of SEBS, and SEBS-C6-MDA is the membrane after modification with caged double cations. An SEBS-grafted group of cations attracts more water and increases the ion conductivity of the membrane. The graph shows the water uptake percentage of the membranes with different TPIP crosslinking percentages (0%, 10%, 15%, 20%). Water uptake is crucial for ion conductivity in AEMs, as it facilitates the transport of hydroxide ions [Figure 8a,b]. The grafted cations contain a large hindrance property which

protects the membrane from degradation when hydroxyl groups attach to it. On the other hand, membrane containing SEBS-crosslinked photon-induced photopolymerization (TPIP) enhances the resistance against swelling and mechanical strength [Figure 8c]. The graph in Figure 8c illustrates the swelling ratio of the membranes under different TPIP crosslinking percentages. With 15% TPIP, the SEBS membrane containing cations delivers an ionic conductivity value of 86.76 mS cm^{-1} at a temperature of 80°C . Moreover, its tensile strength value and elongation reaches 18.75 MPa and 395.9% , respectively. With these enhanced properties, the modified membrane is able to deliver a stable alkaline fuel cell performance for 2200 h. with just a 20.81% degradation rate at a temperature of 80°C under 2 M NaOH solution. and alkali stability [Figure 8d]. With 15% TPIP, the modified SEBS membrane is also able to deliver a power density and current density values of 221 mW cm^{-2} and 460 mA cm^{-2} , respectively. The results show that the membranes are able to be applied in the field of fuel cells [Figure 8e].

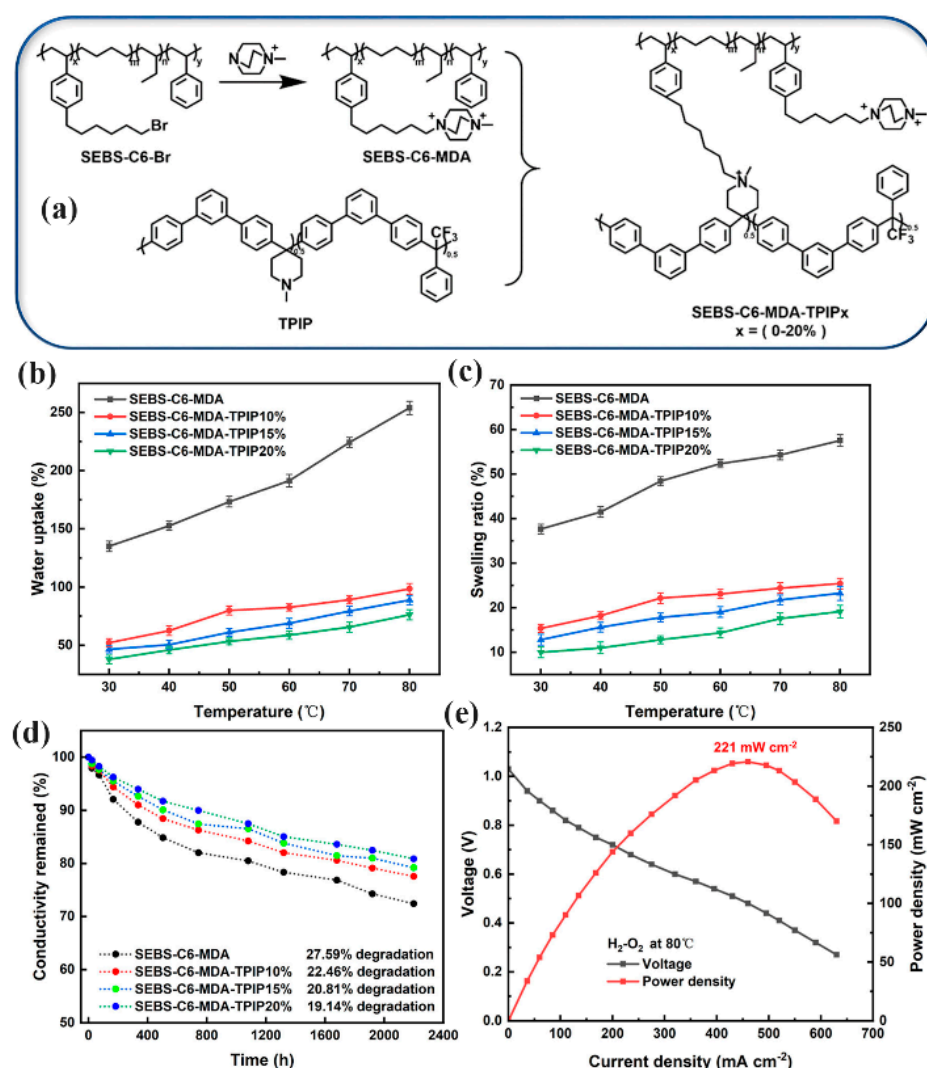


Figure 8. (a) Schematic diagram of synthesis of SEBS membrane based on TPIP from 0 to 20%. Graphs of temperature vs. (b) water uptake (%) (c) swelling ratio (%); (d) graphs of time vs. ion conductivity retention of different SEBS membranes; (e) graphs of current density vs. voltage vs. power density values [128].

The crosslinking method is generally required to attach one polymer with another polymer for enhancing physical and electrochemical properties of AEMs. However, in some cases, the application of crosslinking agent greatly changed the properties of membrane

which it unsuitable for application in fuel cells. The research approach by the scientist nowadays is to apply the crosslinking method without a crosslinking agent which minimizes the damage of polymer physical structure and maximizes the properties such as mechanical strength, reduced swelling, and ion conductivity. As an example, Sung and his colleague scientists [129] synthesized the membrane composed of PPO polymer and SEBS polymer by crosslinking method without crosslinker. By using this approach, the resultant membrane has a thinness in nature and a thickness of 10 μm can be achieved. Moreover, the modified membrane is able to provide a high tensile strength and elongation of 34.3 MPa and 91.6%, respectively. The hydrophilic nature of the SEBS develops ionic channels and promotes absorption of water contents to help maximize the ionic clusters. Ultimately, the hydroxide ion conductivity value of the modified membrane is high under a relative humidity value of 95% and allows the membrane in fuel cells to achieve high efficiency. When the MEA is assembled with a modified membrane, the fuel cell is able to deliver a stable performance for a time period of 300 h at a temperature of 60 $^{\circ}\text{C}$. The fuel cell with modified membrane is also able to deliver a power density value of 405 mW cm^{-2} . These results are superior to the commercially available membrane which proves that the modified membranes are compatible and applicable for AEMFCs.

SEBS (styrene-ethylene-butylene-styrene) has been extensively explored for fuel cell applications due to its flexibility, chemical inertness, and ability to be modified for enhanced performance. In proton exchange membrane fuel cells (PEMFCs), SEBS is often sulfonated to improve hydrophilicity and proton conductivity, making it effective for applications like direct methanol fuel cells (DMFCs) where reduced methanol crossover is critical. For anion exchange membrane fuel cells (AEMFCs), SEBS is functionalized with ion-conducting groups or copolymerized with other polymers to achieve high hydroxide conductivity and excellent phase separation. Crosslinking SEBS with materials like polystyrene, fluorine-containing polymers, or nanoparticles further enhances its mechanical strength, thermal stability, and ion conductivity. These modifications enable SEBS-based membranes to deliver stable performance, resist swelling, and operate efficiently under high temperatures and low humidity. Overall, SEBS is a versatile material that, through various chemical and structural modifications, has proven to be a promising candidate for both PEMFCs and AEMFCs, offering a balance of durability, conductivity, and cost effectiveness.

9.4. Poly(Styrene Acrylonitrile) [SAN]

Poly(styrene acrylonitrile) (SAN) is a copolymer of styrene used for making proton exchange membranes (PEMs) due to its high mechanical and chemical stability, as well as its sheet-forming ability. According to research, the conductivity of sulfonated SAN polymer reaches a value of $10^{-2} \text{ S cm}^{-1}$ [130]. When SAN is sulfonated, its conductivity further improves, positively impacting the overall efficiency of the fuel cell. As an example, Silva and his colleague scientists [130] sulfonated the poly(Styrene-Co-Acrylonitrile) (PSAN) by treating the pure PSAN with H_3PO_4 followed by dipping it in a mixture of CH_2Cl_2 and sulfuric acid. The modified membrane was dried in a vacuum oven for further use. The results show that the conductivity of the PSAN/ H_3PO_4 membrane is in between $10^{-9} \text{ mS cm}^{-1}$ and $10^{-5} \text{ mS cm}^{-1}$. However, when the doping of acid increases in the membrane, conductivity increases but it is still not applicable in fuel cells. Post-sulfonation with sulfuric acid attaches sulfonic groups to the polystyrene chains, forming covalent bonds. The water uptake of the modified membrane shows a value of 45.7%. Ultimately, the ion conductivity boosts and reaches a value of 1 mS cm^{-1} at room temperature and 10 mS cm^{-1} at a temperature of 80 $^{\circ}\text{C}$. A summary of these articles is given in Table 3.

Table 3. SEBS-based membrane for application in fuel cells.

Types of Materials	Types of Fuel Cell	Ion Conductivity (mS cm ^{−1})	Current Density (mA cm ^{−2})	Power Density (mW cm ^{−2})	Ref.
SBS-TMA	AEMFC	100	-	-	[120]
h-SBS	AEMFC	93	-	-	[121]
SEBS-PS	-	190	2.09	1000	[122]
SPSEBS-glutaraldehyde	DMFC	10	200	68/56	[123]
SEBS-PEB	AEMFC	81	320	320	[124]
Amine-SEBS	AEMFC	20			[125]
PTP-SEBS	AEMFC	102.02			[126]
PBB-SEBS	AEMFC	146.25	-	-	[127]
SEBS-PTPIP	AEMFC	86.76	460	221	[128]
PPO-SEBS	AEMFC	-	-	405	[129]
PSAN/H ₃ PO ₄	PEMFC	10	-		[130]

10. Conclusions and Future Perspective

Styrene-based polymers have emerged as promising candidates for PEMs and AEMs in fuel cell applications due to their tunable chemical structure, cost effectiveness, and ease of functionalization. Their hydrophobic backbone combined with the ability to introduce hydrophilic sulfonic acid groups enables these materials to achieve the critical balance between proton conductivity, mechanical stability, and fuel barrier properties. Advances in copolymerization techniques, such as the incorporation of fluorinated and aromatic units, have further improved their performance in terms of proton conductivity, oxidative stability, and durability under operating conditions. Despite these advantages, challenges such as water management, thermal stability, and susceptibility to oxidative degradation hinder the large-scale adoption of styrene-based PEMs and AEMs. Styrene starts melting at a temperature in the range of 100–125 °C which makes it unsuitable for HTPEMFC or SOFC operating temperature greater than 600 °C. At high temperatures, styrene-based membrane not only loses structural stability but also creates pollution due to toxic and corrosive environments such as the presence of hydrogen, oxygen, or steam. Ultimately, after the chain break of styrene, it pollutes the fuel cells which deteriorates the overall performance of the fuel cell. Moreover, achieving high proton conductivity at low relative humidity and elevated temperatures remains an area of ongoing research. While styrene-based PEMs and AEMs exhibit significant potential, their performance still lags behind commercially available membranes like Nafion in critical parameters, particularly in terms of long-term durability and operational efficiency under demanding conditions. Moreover, AEMs face low hydroxide ion conductivity, high ohmic losses, and poor chemical stability due to the degradation of cationic groups (e.g., quaternary ammonium) in high-pH environments.

Future improvements for styrene-based PEMs and AEMs of fuel cells are given below.

10.1. Material Optimization

There are critical issues such as low hydrophilic groups or the weak strength of styrene-containing groups that do not support membranes to work at a high efficiency. The research is focusing to incorporate more hydrophilic functional groups [-SO₃H, -PO₃H, acrylic acid groups, etc.] by using a crosslinking agent or without using a crosslinking agent, radical polymerization, chemical grafting technique, etc., which further enhance the absorption of water helpful in PEMFC and DMFC ion conduction property. As discussed in the section

on “recent advances of styrene in fuel cell”, there is an advantage of high structure stability when functional groups attach with styrene without a crosslinking agent. In AEMFCs, styrene-based membrane functionalized with quaternary ammonium groups $[-NR^{4+}]$ makes it suitable to conduct hydroxide $[-OH]$ conduction instead of protons. Another method of boosting the water contents and ion conductivity of styrene-based membranes is to introduce units such as fluorine and ionic liquids which remove membrane dryness and help in creating ionic channels. Moreover, its high thermal stability make membrane able to work at a high temperature.

10.2. Advanced Fabrication Techniques

The solution casting method is a cost-effective method and is commonly used at the laboratory level but it possesses some drawbacks such as difficulty in adjusting structure tuning, uniform thickness, and particle dispersion in case of composite membrane. Moreover, its durability and mechanical strength are also challenging to achieve. Research focuses on advanced techniques in the field of fuel cells to develop membranes such as the electrospinning method, layer-by-layer method, and 3D printing method. The layer-by-layer method allows for membrane preparation on a nanoscale level and it is based on the formation of membrane by depositing different charged layers on each other. This method has the flexibility of creating membranes with designed ionic pathways. The electrospinning method also allows the researcher to form membranes with multiple functional groups with a high possibility of water retention and enhanced ion conduction [131]. Three-dimensional printing is another method to develop membrane in which different patterns can be achieved within membranes which facilitate ion conduction, enhance water management, favors IEC, and enables high mechanical strength and power density [132]. The attachment of block copolymers with membranes is another efficient method to improve the ion conduction in the membrane. The crosslinking of two polymers in the membrane improves the mechanical strength of the membrane and generate self-healing properties in the membrane to adjust in the chemical polluted environment. Despite these techniques, the recent research focuses on using AI techniques to optimize the property of materials used in the membrane of fuel cells.

10.3. Hybrid and Composite Membranes

Hybrid and composite membranes represent a significant advancement in fuel cell technology, addressing the limitations of traditional single-polymer membranes by combining the strengths of different materials. Hybrid membranes are created by blending two distinct polymers, which helps to mitigate the deficiencies of the primary polymer while enhancing its overall physical and electrochemical properties. For example, combining a polymer with high proton conductivity but poor mechanical strength with another polymer that offers robust mechanical stability can result in a membrane that excels in both aspects. This synergistic effect improves the membrane's performance in fuel cells, making it more durable and efficient under varying operating conditions.

In another approach, composite membranes are developed by incorporating hydrophilic nanoparticles or inorganic fillers, such as metal-organic frameworks (MOFs), silica, alumina, or titania, into a primary polymer matrix like styrene. These additives significantly enhance the thermal and mechanical properties of the membrane, making it more resistant to high temperatures and mechanical stresses. Additionally, the hydrophilic nature of these nanoparticles improves the membrane's water absorption capability, which is crucial for maintaining high ion conductivity, especially in proton exchange membranes (PEMs). The retained water molecules facilitate the transport of protons, thereby boosting the membrane's overall electrochemical performance.

By integrating the advantages of both organic and inorganic components, hybrid and composite membranes offer a versatile and promising pathway for developing next-generation fuel cells. These membranes not only exhibit improved thermal stability, mechanical strength, and ion conductivity but also demonstrate enhanced durability and reduced fuel crossover, making them suitable for a wide range of applications, from automotive fuel cells to stationary power systems. The ability to tailor the properties of these membranes by adjusting the composition and concentration of the additives further expands their potential for optimizing fuel cell performance. As a result, hybrid and composite membranes are poised to play a critical role in advancing fuel cell technologies, contributing to the development of more efficient, cost-effective, and sustainable energy solutions.

10.4. Sustainability and Green Chemistry

Developing bio-derived styrene monomers or exploring recyclable styrene-based PEMs could significantly reduce the environmental impact of these materials, aligning them with circular economy principles.

10.5. Durability Enhancement

The chemical and physical stability of styrene-based PEMs can be improved through crosslinking, incorporation of antioxidants, and tailoring polymer backbones to resist oxidative and hydrolytic degradation.

10.6. Practical Application in Future Newly Created Fuel Cells

The most demanding fuel cells are direct methanol fuel cells and solid oxide fuel cells in which styrene-based PEM should apply to check the quality of the membrane such as a low-methanol crossover property and boost stability.

10.7. Performance Check and Validation in Real-World Applications

Extensive in situ testing under practical operating conditions, such as varying temperatures, humidity levels, and load cycles, will provide critical insights into the long-term performance and reliability of styrene-based proton exchange membranes (PEMs) and anion exchange membranes (AEMs). These tests are essential to evaluate how these membranes withstand real-world challenges, including thermal cycling, mechanical stress, and chemical degradation, which are common in fuel cell applications. By simulating dynamic operating environments, researchers can identify potential failure mechanisms, optimize membrane formulations, and develop strategies to enhance durability and efficiency. Additionally, testing under extreme conditions, such as high temperatures or low humidity, will help determine the operational limits of styrene-based membranes and ensure their suitability for diverse applications, from automotive fuel cells to stationary power systems.

By addressing these future directions, styrene-based PEMs and AEMs hold the potential to revolutionize fuel cell technologies, making them more cost effective, durable, and sustainable. Their development could significantly reduce the reliance on expensive perfluorinated polymers like Nafion, lowering the overall cost of fuel cell systems. Furthermore, the tunable chemical structure of styrene-based membranes allows for the incorporation of functional groups that enhance proton or hydroxide ion conductivity, mechanical strength, and chemical stability. These advancements could enable the widespread adoption of fuel cells in various sectors, including transportation, portable electronics, and renewable energy storage. By contributing to the development of clean energy solutions, styrene-based membranes could play a pivotal role in the global transition towards decarbonization and a sustainable energy future, helping to mitigate climate change and reduce dependence on fossil fuels.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/batteries11040134/s1>, Table S1: Chemical Reactions in fuel cells.

Author Contributions: M.R.A.: writing—review and editing, conceptualization; A.Z.: methodology, investigation; H.S.: visualization, formal analysis; K.D.: data curation, validation; M.T.A.: software; Q.X.: supervision, resources, project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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