

RESEARCH ARTICLE

Synthesis and Characterization of Polyvinyl Alcohol Cross-Linked Mercaptosuccinic Acid Pendant Cardanol-Based Polybenzoxazines Incorporating ZrO₂ Nanoparticles for Proton Exchange Membranes

Janani Jayakumar¹ | Senthil Theerthagiri² | Karikal Chozhan Chinnakkannu³ | Alagar Muthukaruppan^{4,5}  | Dinakaran Kannaiyan¹ 

¹Department of Chemistry, Thiruvalluvar University, Vellore, India | ²Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, Thailand | ³Department of Chemistry, J.J. College of Engineering and Technology, Tiruchirapalli, India | ⁴Polymer Engineering Laboratory, PSG Institute of Technology and Applied Research, Coimbatore, India | ⁵Center for Advanced Materials, PSG College of Arts and Science, Coimbatore, India

Correspondence: Dinakaran Kannaiyan (kdinakaran.tvu@gmail.com)

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ABSTRACT

This study reports on the synthesis of cross-linked networks of cardanol-based polybenzoxazine (MCBZ) having pendant 2-mercaptosuccinic acid with polyvinyl alcohol (PVA) to create hydrophilic polymer membranes. These membranes were further reinforced with varying weight percentages of zirconium oxide nanoparticles (ZrO₂ NPs) for proton transport membrane fuel cell (PEMFC) applications. The nanocomposites were characterized using FT-IR, ¹H NMR, ¹³C NMR, PXRD, FE-SEM, and HR-TEM analyses. Their physicochemical characteristics such as swelling ratio (SR), water uptake (WU), and ion-exchange capacity (IEC) were systematically assessed. Among the prepared nanocomposite membranes, the membrane with 5 wt% ZrO₂-dispersed PVA/MCBZ showed an optimal IEC of 1.5 meq g⁻¹ and a proton conductivity of 1.096 × 10⁻¹ S/cm at 110°C. Arrhenius plots indicated low activation energies, suggesting efficient proton transport through the vehicular mechanism. The stability of membranes was estimated through Fenton's reagent testing at 80°C, which showed minimal chemical degradation. The ZrO₂/PVA/MCBZ membrane demonstrated an improved maximum power density of 0.802 mW cm⁻² at a current density of 2.26 mA cm⁻², surpassing the 0.530 mW cm⁻² achieved by the PVA/MCBZ membrane at 1.19 mA cm⁻². Based on these results, the composite membranes show promising potential as membrane materials for fuel-cell applications.

1 | Introduction

Fuel generation from non-renewable fossil fuels has been essential to the development of human civilization; excessive use of them that far outpaces their natural production rate has resulted in environmental pollution, petroleum crises, and climate change brought on by the release of greenhouse gases. In reply, the Convention on Climate Change of United Nations Framework (UNFCCC)

formed the 2015 Paris Agreement, which aims to keep rises in global temperatures to less than 2°C [1]. This has sped up the development of internal combustion engine substitutes with zero emissions, such as solar cells [2], fuel cells [3], Li ion batteries [4], and hydrogen energy [5]. The performance of the polymer membrane as an electrolyte is critical for proton-exchanging membrane fuel cells (PEMFCs). Nafion membranes are the industry standard owing to their outstanding chemical and physical stability and

high proton conductivity, but they are limited by their high price, poor oxidative stability, and high gas crossover [6]. Also, their ionic conductivity is extremely dependent on hydration, which leads to mechanical failure and a drastic decrease in device performance at temperatures above 100°C [7–9]. The complicated fluorination process and production costs add to their financial disadvantages [10, 11]. Extensive research has been steered toward developing fluorine-free membranes, due to the limitations of Nafion, particularly on sulfonated hydrocarbon polymers such as sulfonated poly(ether ether ketone) (SPEEK) [12, 13], poly(arylene ether ketone)s (SPAEEKs) [14], poly(phenylene sulfide sulfone) (PPSS) [15] and sulfonated polybenzimidazoles [16]. These materials have better mechanical properties, lower production costs, easier processing, and better chemical and thermal stability [17]. However, their practical use is still inadequate due to a recurring trade-off between water swelling and proton conductivity. To overcome these obstacles, modification techniques such as blending, crosslinking, and the creation of organic–inorganic mixed matrix membranes have been investigated due to their minimal swelling behavior; the integration of inorganic particles is especially promising. Another promising approach is to use biopolymers and bio-derived polymers to fabricate proton conducting films at low cost. This research is to use biocompatible polymers such as polyvinyl alcohol and a polybenzoxazine (PBz) synthesized from phytocompound such as cardanol to fabricate PEMs. PBz, a phenolic thermoset resin, has been of great interest among polymer candidates due to its catalyst-free polymerization, excellent flame retardance, improved mechanical and thermal properties, minimal shrinkage upon curing, and flexibility in molecular design. PBz resins offer additional advantages, such as improved flexibility, water resistance, and sustainability when produced from cardanol, a renewable by-product of cashew nut shell liquid (CNSL) [18]. CNSL contains cardol, cardanol, anacardic acid, and 2-methylcardol, as well as alkyl side chains that can be either saturated or unsaturated. Cardanol is an inexpensive, readily available agricultural by-product used in fine chemicals, intermediates, flame retardants, resins, inks, water repellents, stabilizers, and antioxidants [19–21].

A membrane made up of poly(vinyl alcohol)/hexafluoroglutaric acid showed methanol permeability and proton conductivities of 10^{-8} to 10^{-7} cm² s⁻¹ and 10^{-3} to 10^{-2} S cm⁻¹, respectively [22]. Imaan et al. developed a poly(vinyl alcohol)-based zinc oxide (PVA-ZnO) composite proton exchange membrane that demonstrated a low percentage of methanol uptake (17%–21%) and a high percentage of water uptake (WU) (85%–105%), and they reported a transport number of 0.88 and an ion exchange capacity (IEC) of 0.78 meq g⁻¹ [23]. Wong et al. [24] provided further details on the use of Poly(vinyl alcohol) (PVA) centered proton exchange membranes. In this study, ZrO₂/MCBZ/PVA nanocomposite membrane IEC values are increased. Ionic conductivity variations with respect to temperature displayed a closely analogous trend. Over the whole temperature range under investigation (30°C–110°C) and at 95% relative humidity (RH), the 5 wt% ZrO₂/PVA/MCBZ nanocomposite membrane had the best proton conductivity. In Fenton tests, pristine PVA/MCBZ and ZrO₂ NP-incorporated membranes showed noticeably higher breakdown rates, as shown by mass loss. Weight loss was 10.84% for ZrO₂/PVA/MCBZ and 29% for pristine PVA/MCBZ after 30 min. Proceeding, a semi-interpenetrating polymer network is created by dispersing ZrO₂ nanoparticles in a PVA/MCBZ polymer blend at different

ratios (1–5 wt%). This strategy seeks to permit higher doping levels while improving the membranes' physicochemical characteristics and chemical endurance.

In the present work we have synthesized cross-linked networks of cardanol-based polybenzoxazine (MCBZ) having pendant 2-mercaptosuccinic acid with PVA to create hydrophilic polymer membranes. These membranes were further reinforced with varying weight percentages of ZrO₂ NPs for PEMFC applications. The prepared membranes are well characterized, and the results are reported herein.

2 | Materials and Method

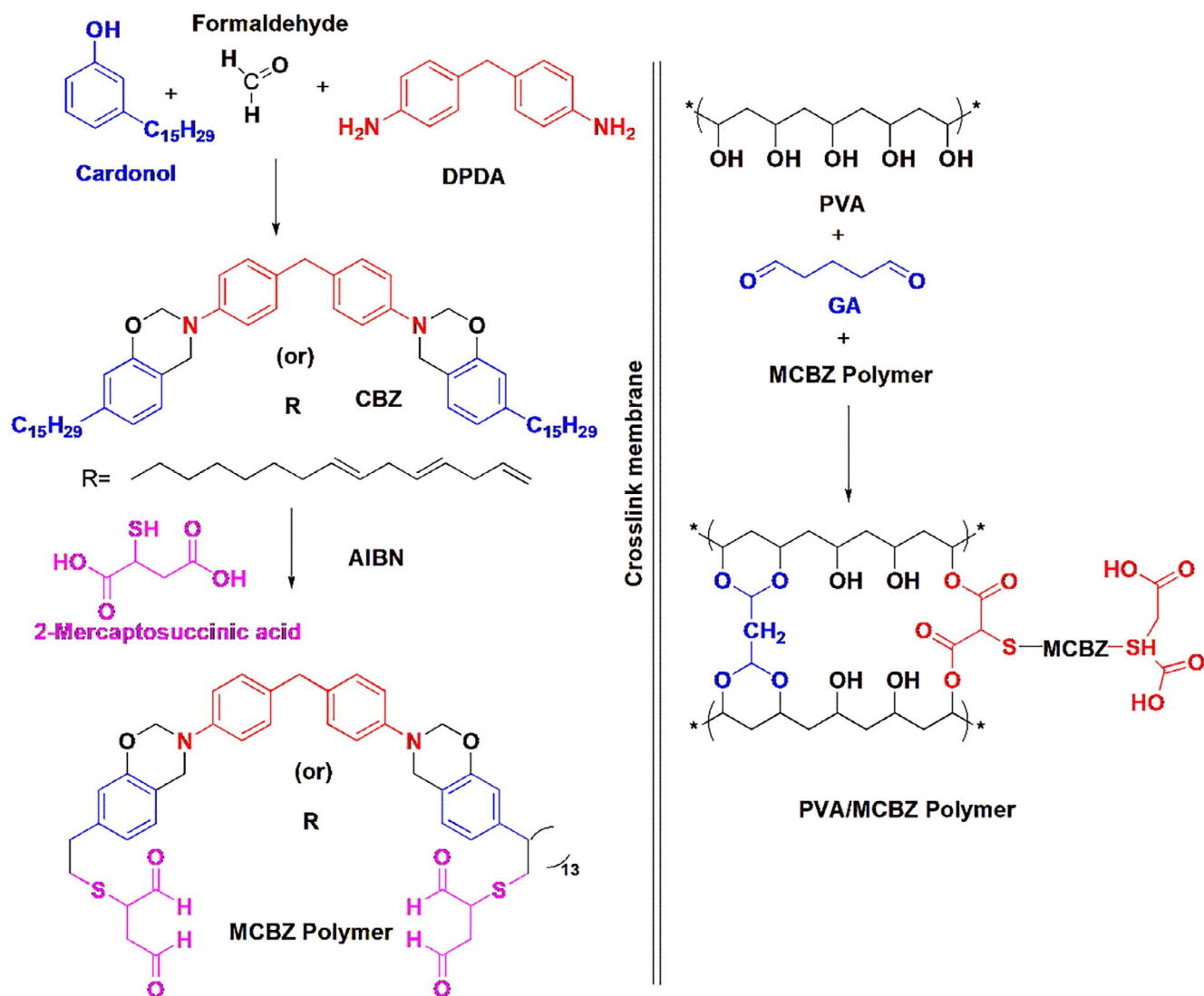
All chemicals and reagents used in this study were of analytical grade and were used as such without further purification. Cardanol was received from Satya Cashew Chemicals Pvt. Ltd., Chennai, Tamil Nadu, India. PVA, tetrahydrofuran (THF), and chloroform were procured from Fisher Scientific, Mumbai, India. Sigma-Aldrich in India supplied paraformaldehyde, zirconium nitrate [Zr(NO₃)₄], sodium hydroxide (NaOH), glutaraldehyde (GA), and dimethyl sulfoxide (DMSO).

2.1 | Preparation of ZrO₂ Nanoparticles

Sol-gel was used to create ZrO₂ NPs at an alkaline pH of 9. The reaction was carried out at 50°C with vigorous mixing at 700 rpm. One molar of zirconium oxide was made by dissolving 33.924 g of Zr(NO₃)₄ in 100 mL of distilled water and stirring the mixture at 50°C at 700 rpm in a magnetic stirrer. To make a layer, 12 g of sodium hydroxide pellets had to be dissolved in 300 mL of distilled water at 50°C with constant stirring [25]. Drop by drop, the Zr(NO₃)₄ solution was added to NaOH while being constantly stirred. The solution turns colorless to milky white when sodium hydroxide is added. The precipitate produced by this process was filtered and purified with distilled water, then dried for several hours at 100°C before being crushed in a manual mill. Finally, the powder was calcined in a muffle furnace for 2 h at 600°C.

2.2 | Preparation of Benzoxazine From Cardanol (CBZ)

Cardanol, paraformaldehyde, and 4,4'-Diaminodiphenyl methane were condensed in a single step to make use of a solvent-free method to create the benzoxazine monomer from cardanol. A 500 mL round-bottom flask with a reflux condenser and magnetic stirrer was filled with cardanol (3.29 g, 0.011 mol), diphenyl diamino methane (2.5 g, 0.065 mol), and paraformaldehyde (0.0695 g, 0.023 mol). The reaction solution was brought to reflux for 5 h at 130°C and 1 h at 85°C. After that, the reaction mixture was permitted to reach room temperature. The organic layer was added to the formerly described reaction mixture. The organic layers were combined, dried with sodium sulphate, and filtered to yield a red oil. Benzoxazine (CBZ) was produced as a black, viscous solid after the solvent was removed at low pressure and the residue was vacuum-dried at 353 K [26].



SCHEME 1 | Schematic representation of cardanol-based benzoxazine (CBZ), mercaptosuccinic acid-functionalized benzoxazine (MCBZ), and the cross-linked membrane.

2.3 | Synthesis of MCBZ

The synthesis of MCBZ followed a previously described literature method [26]. The product was then produced using a thiol-ene process, as shown in Scheme 1. In a typical synthesis, CBZ monomer (1.0 g) and 2-mercaptosuccinic acid (0.357 g) were dissolved in 40 mL of THF. The liquid reaction mixture was then allowed to cool down to room temperature. Upon cooling, the product was precipitated out by slowly adding ice-cold methanol to the reaction mixture with constant stirring. The precipitated product was then filtered off and washed with acetone and de-ionized water to remove unreacted reactants and residual impurities. Finally, the purified product was dried under vacuum to yield a bright yellow powder.

2.4 | Synthesis of PVA Cross-Linked MCBZ Polymer

For the preparation of a homogeneous solution, PVA (2.0 g) and GA (0.2 g) were dissolved in 50 mL of DMSO and stirred at room

temperature for 24 h. The required amount of MCBZ was added, and the mixture was stirred at 80°C for 24 h to ensure uniform mixing. The homogeneous solution was cast onto a Petri dish, and DMSO was evaporated under controlled conditions to obtain the precursor membrane. The resultant membrane was then thermally treated to induce chemical cross-linking between the hydroxyl groups of PVA and the carboxylic acid groups of the MCBZ compound through esterification, as shown in Scheme 1. Further, the PVA chains are cross-linked with the GA, which helped in the preparation of a uniform film during casting and improved the structural stability of the resultant membrane. The cross-linked network was characterized by FT-IR and solvent-swelling analysis.

2.5 | PVA/MCBZ/ZrO₂ Composite Film Preparation

The ZrO₂/PVA/MCBZ nanocomposite membranes were prepared by the solution casting method as shown in Scheme 1. Briefly, 2.0 g of PVA/MCBZ mixture was dispersed in 50 mL DMSO and stirred at 800 rpm. Then ZrO₂ was added at different

concentrations (1, 3, and 5wt%) relative to the polymer matrix. The suspension was stirred at 60°C for obtaining homogenous dispersion of ZrO₂ in the PVA/MCBZ matrix. The suspension was mixed thoroughly and then vacuum degassed under ambient conditions to remove any trapped air bubbles. The degassed suspension was poured into a glass Petri dish and left to dry at 80°C for 48 h to allow gradual solvent evaporation and the formation of a uniform membrane. Thermal cross-linking was carried out by heating the precursor membranes at 100°C, 125°C, 150°C, 175°C, and 200°C for 20 min at each temperature on a hot plate. The resultant thermally treated membranes were used for further characterization.

3 | Physicochemical Properties

3.1 | Ion Exchange Capacity

A classical acid–base titration method was used to quantify the IEC in polymer electrolyte sheets (PEMs). In brief, the dry membranes were soaked in 2 M NaCl for 24 h to exchange H⁺ with Na⁺ ions. The displaced H⁺ ions were then detected using a phenolphthalein indicator after the known volume of the resultant solution was titrated with 0.01 M NaOH. The IEC of PEMs was estimated according to the following equation [27].

$$\text{IEC (meq. g}^{-1}\text{)} \quad (1)$$

3.2 | Water Uptake and Swelling Ratio

Swelling ratio (SR) and WU of PEMs were determined by means of the samples of pristine PVA/MCBZ incorporated with 1, 3, and 5wt% of ZrO₂ nanoparticles. The specimens were initially dried at 80°C for 12 h [28]. The dry weight (W_{dry}) of the samples was calculated before immersion in deionized (DI) water at 60°C for 12 h. After immersion, the wet weight (W_{wet}) was recorded. WU and SR of the PEMs were then determined with the help of Equations (2) and (3):

$$\text{WU} = (W - D) / D \times 100 \quad (2)$$

$$\text{SR} = (L - D) / D \times 100 \quad (3)$$

where W, L and D represents weight and length of wet and dry membranes.

3.3 | Oxidative Stability

The pristine and polymer nanocomposite membrane specimens were evaluated for oxidative stability. The pristine and polymer nanocomposite films were dried in a hot air oven at 60°C for 6 h, and the dry weight of the specimens was noted. After that, the sample sheets were submerged in the Fenton's solution (3% H₂O₂ + 2 ppm FeSO₄), and the solution was maintained at 80°C for 24 h. The membrane's stability was evaluated based on the rupture time and remaining weight. The values were calculated from the following Equation (4) [29].

$$\text{OS (\%)} = \frac{F}{I} \times 100 \quad (4)$$

3.4 | Proton Conductivity

The proton conductivity of the membranes was determined by electrochemical impedance spectroscopy (EIS) using a two-electrode configuration with a Bio-Logic SP-200 potentiostat. The membrane samples were sandwiched between the two electrodes, and their impedance responses were recorded over the selected frequency range at temperatures from 30°C to 110°C under 95% RH conditions. The EIS measurements were carried out in a frequency range of 1–10 kHz with an AC voltage amplitude of 50 mV. The membrane resistance was extracted from the impedance spectra. The proton conductivity was calculated as:

$$\sigma \text{ (S cm}^{-1}\text{)} = L / (RA) \quad (5)$$

where σ is the proton conductivity (S cm^{−1}), L is the thickness of the membrane (cm), R is the resistance of the membrane (Ω), and A is the effective electrode area (cm²).

3.5 | Tensile Strength and Elongation at Break

The tensile testing is done according to ASTM standards with three specimens per sample in a Universal Testing Machine. Environmental Condition maintained is 23°C ± 1°C and 50% ± 5% RH; Test Speed 5 mm/min.

4 | Result Discussion

4.1 | FT-IR Analysis of ZrO₂/CBZ/MCBZ Monomers

FTIR spectroscopy analysis is shown in Figure 1a,c (A, B), including the enlarged view. The Zr–O–Zr vibration is responsible for absorption bands in the range of 600–1633 cm^{−1}. Figure 1a (A) FTIR spectra of ZrO₂ NPs calcined at 600°C. The Zr–O–Zr region exhibits a sharp absorption, suggesting that zirconia bonding was significantly impacted by the synthesis technique [30]. The absorption band between 2923 and 3425 cm^{−1} stretches and bends to the O–H vibrational link, indicating the existence of water in the sample. Figure 1a (B) presents an explanation of the structures and the ring-closure reaction of the main amino group with phenolic OH in the presence of paraformaldehyde, resulting in the production of benzoxazine monomers based on cardanol [31]. The band at 1236 cm^{−1} is due to the asymmetric oxazine ring stretch C–O–C; the characteristic benzoxazine ring vibration is observed at 812 cm^{−1} (frequently diagnostic), aromatic C=C stretches at 1514 cm^{−1}, and residual N–H (if unreacted amine is present) at 3589 cm^{−1} should be weak or non-existent for a fully converted monomer. The absorption band at 2917 cm^{−1} corresponds to cardanol's aliphatic C–H side chain. The aliphatic C–H stretch of the long side chain has strong bands in the 2360–3000 cm^{−1} region. Aromatic C–H stretch: A weak band located just over 3000 cm^{−1}. In Figure 1a (C), the benzoxazine ring in the MCBZ monomer is at 917 cm^{−1}, while the stretching vibration of –SH (thiol) is 2500–2600 cm^{−1}. Figure 1b shows the FTIR spectra of PVA/MCBZ (black) and ZrO₂/PVA/MCBZ (red). The broad band from 3200 to 3500 cm^{−1} results from O–H stretching, and the bands from 2920 to 2850 cm^{−1} are due to aliphatic C–H stretching. Characteristic bands in

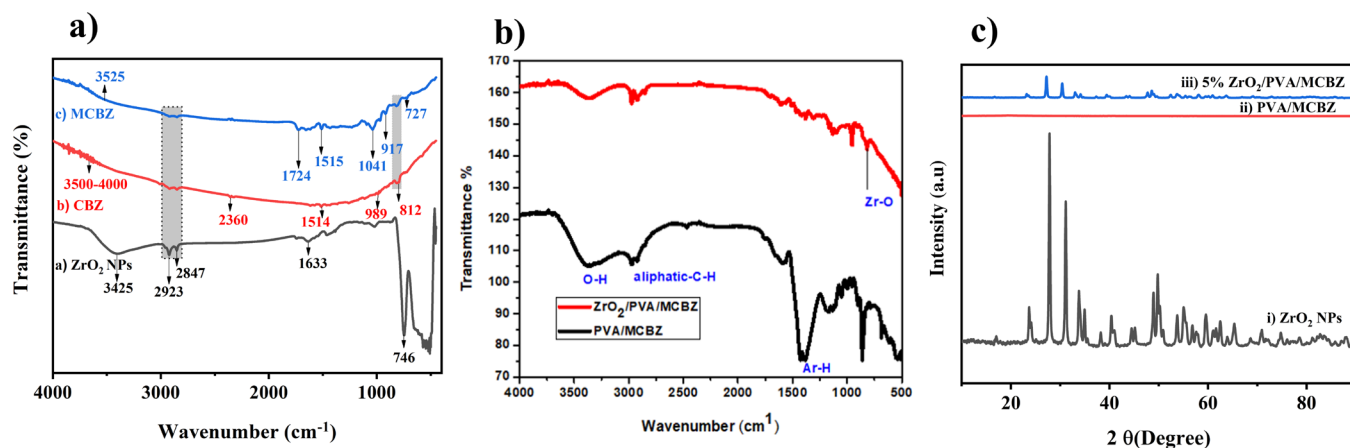


FIGURE 1 | (a) FT-IR analysis of ZrO₂ NPs, CBZ, and MCBZ. (b) FT-IR analysis of PVA/MCBZ and ZrO₂/PVA/MCBZ 2. (c) FT-IR Analysis of PVA/MCBZ, ZrO₂/PVA/MCBZ.

the 1600–1500 cm⁻¹ and 1250–1000 cm⁻¹ regions arise from aromatic C=C and C–O–C/C–O/C–N vibrations, respectively. Importantly, the ZrO₂/PVA/MCBZ membrane shows a new band at about 700 cm⁻¹, which is attributed to Zr–O vibrations, confirming the existence of ZrO₂ in the polymer matrix.

4.2 | P-XRD Analysis

The XRD patterns of the virgin polymer membrane, ZrO₂ nanoparticles, and 5 wt% ZrO₂ nanocomposite membrane are shown in Figure 1c. The XRD pattern of ZrO₂ shows sharp and well-defined peaks confirming its crystalline structure. The pristine membrane shows a broad diffraction halo, indicating the amorphous nature of the membrane [32]. The successful incorporation of ZrO₂ nanoparticles is confirmed by the presence of the amorphous halo of the polymer matrix together with the characteristic diffraction peaks of ZrO₂ in the 5 wt% nanocomposite membrane. The decreased intensity and slight broadening of the ZrO₂ peaks in the nanocomposite suggest good dispersion of the nanoparticles in the polymer matrix. The lack of any additional impurity peaks indicates the absence of secondary phases and high compatibility of the polymer and filler.

4.3 | ¹H and ¹³C Analysis of Benzoxazine Monomer and Polymer

¹H and ¹³C analysis of benzoxazine monomer and polymer were publicized in Figure 2. (i) CBZ: The protons of the phenyl/benzoxazine aromatic rings were represented by numerous signals in the aromatic area at δ 7.11–6.53 ppm. The Ar–CH₂–N methylene protons were detected at δ 4.99–4.42 ppm, but a distinctive oxazine methylene –O–CH₂–N– resonance showed up as two signals at δ 5.33–5.22 ppm. The long aliphatic chain methylene protons echoed widely between δ 2.70–1.18 ppm, followed by further benzylic and aliphatic methylene signals at δ 3.82–3.40 ppm. The terminal methyl group exhibited a triplet at δ 0.80 ppm [33]. The proton environments predicted for the benzoxazine-based compound are consistent with the general pattern of the spectrum.

(ii) ¹H NMR (MCBZ): the signals at 7.20–6.75 (m, Ar–H, 4H) due to benzoxazine aromatic protons; 5.10–4.45 (m, 4H) due to OCH₂–N and N–CH₂–Ar of benzoxazine rings; 4.30–3.70 (m, 4H) is due to CH–OH and CH₂–S from mercaptosuccinic acid units/benzylic-type protons adjacent to O/N; 3.60–3.20 (m, 6H), are from aliphatic methylenes adjacent to O/N; 2.95–2.50 (m, 4H), is due to CH₂ groups with long cardanol alkyl chains, and 2.20–1.8 H also from the protons of aliphatic long chain.

Very broad downfield resonances and/or broad signals between 10.5 and 11.5 ppm were found and attributed to exchangeable –COOH/–OH protons. Chemical shift ranges and multiplicities are provided as observed; assignments were established based on expected connectivity and comparison to benzoxazine and cardanol resonances found in the literature [34]. The successful formation of the targeted MCBZ structure is confirmed by the characteristic signals in the ¹³C NMR spectrum of MCBZ that correspond to carboxylic carbonyl carbons (~170–175 ppm), aromatic carbons (115–160 ppm), benzoxazine methylene carbons (~50–90 ppm), and aliphatic chain carbons (20–45 ppm).

4.4 | FE-SEM and HR-TEM Analysis of the Pristine Polymer and Nanocomposite Membrane

Field-emission scanning electron microscopy (FE-SEM) was employed to investigate the surface and cross-sectional morphologies of the pristine PVA/MCBZ and ZrO₂/PVA/MCBZ composite membranes, and the corresponding images are presented in Figure 3a–f. The pristine PVA/MCBZ membrane was incorporated with 5 wt% ZrO₂ nanoparticles to fabricate the composite proton exchange membrane. The top-view and cross-sectional FE-SEM images of the pristine PVA/MCBZ and ZrO₂/PVA/MCBZ membranes are shown in Figure 3a,b,d,e, respectively. As shown in Figure 3a,d the pristine PVA/MCBZ membrane shows a smooth and uniform surface. No cracks or pinholes are visible on the PVA/MCBZ membrane, which indicates that the pristine PVA/MCBZ membrane forms a good film. In contrast, the ZrO₂/PVA/MCBZ composite membrane has a surface that contains well-distributed nanoparticles inside the polymer matrix. However, the ZrO₂/PVA/MCBZ composite membrane also shows some clumping of those

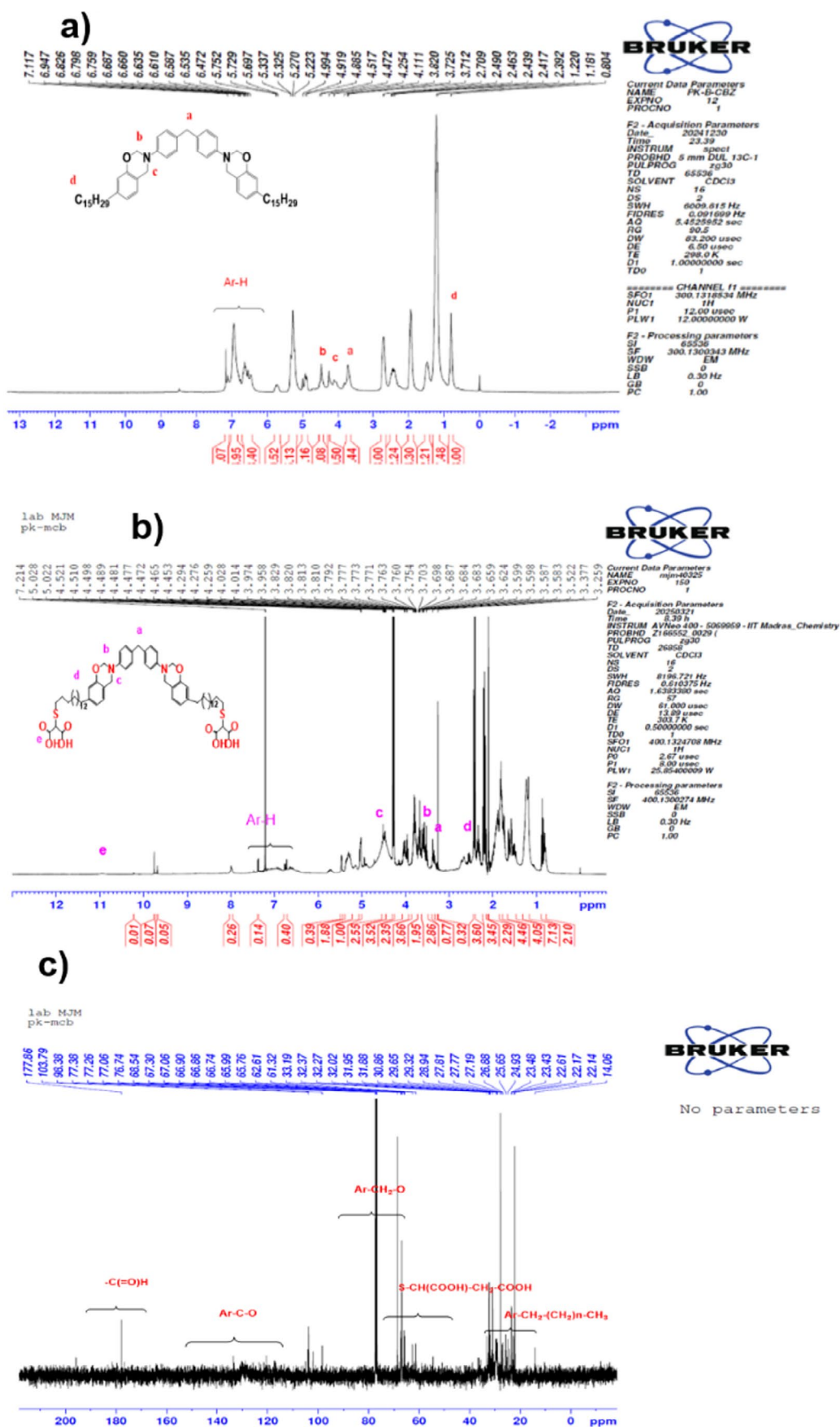


FIGURE 2 | Proton NMR spectra of (a) CBZ and (b) MCBZ. (c) ^{13}C spectrum of MCBZ.

particles. The cross-sectional picture of the PVA/MCBZ membrane (Figure 3e) displays a fairly smooth and compact structure. The ZrO_2 /PVA/MCBZ composite membrane (Figure 3e) shows an uneven cross-section because the ZrO_2 nanoparticles are mixed in and sometimes cluster together inside the polymer matrix [35]. EDX spectra of the PVA/MCBZ membrane and ZrO_2 /PVA/MCBZ composite membrane are presented in Figure 3c,f. These spectra confirm the presence of carbon, oxygen, sulfur, and zirconium elements. The detection of zirconium in the membrane proves that ZrO_2 nanoparticles have

been successfully added into the PVA/MCBZ polymer matrix. The distribution of nanoparticles appears to be mostly even across the membrane, with some areas showing localized clustering. This suggests that the filler integrates into the polymer matrix. Adding nanoparticles to the PVA/MCBZ matrix leads to an increase in ion-exchange capacity and proton conductivity. The way ZrO_2 integrates into the system fits well with the data obtained from XRD analysis. This implies that ZrO_2 may help in moving protons efficiently when the membrane is in a hydrated state.

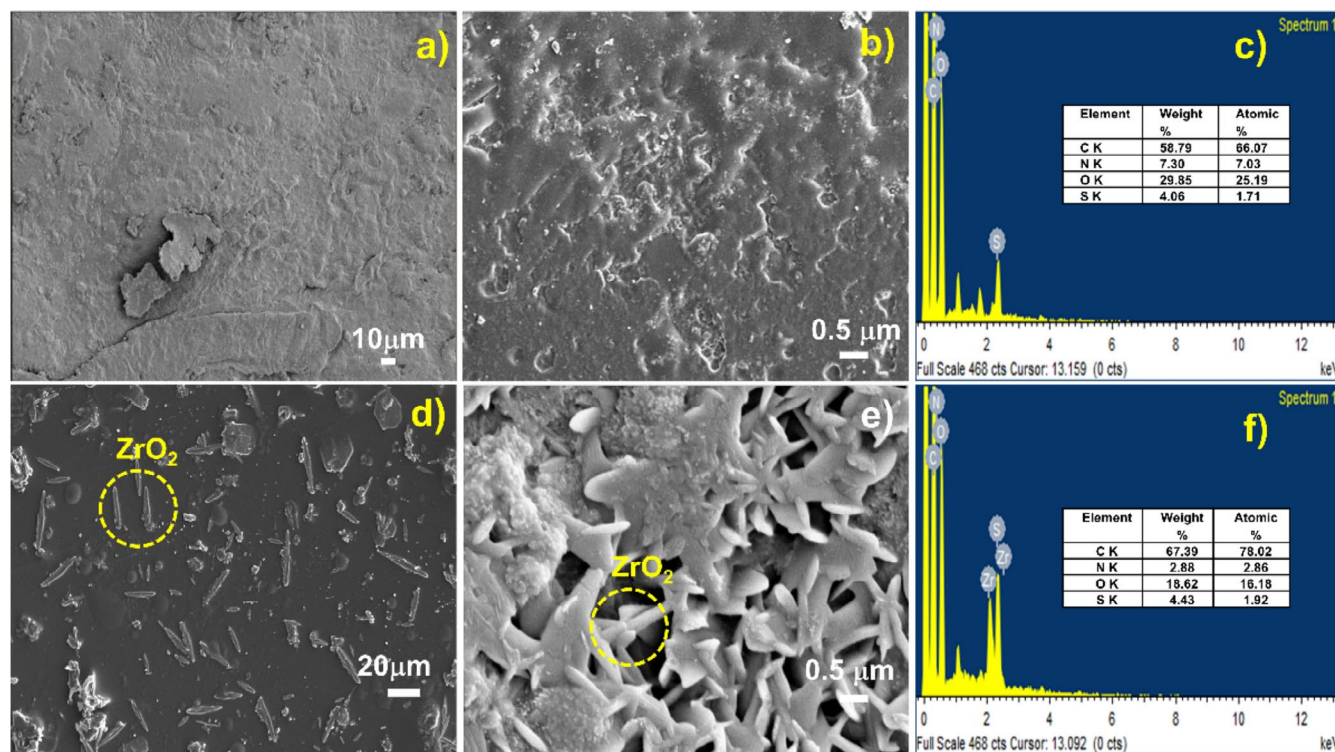


FIGURE 3 | FE-SEM and EDX analyses of the membranes: (a, d) top-view FE-SEM images of the pristine and composite membranes, (b, e) cross-sectional FE-SEM images of the pristine and composite membranes, and (c, f) EDX spectra of the pristine and composite membranes.

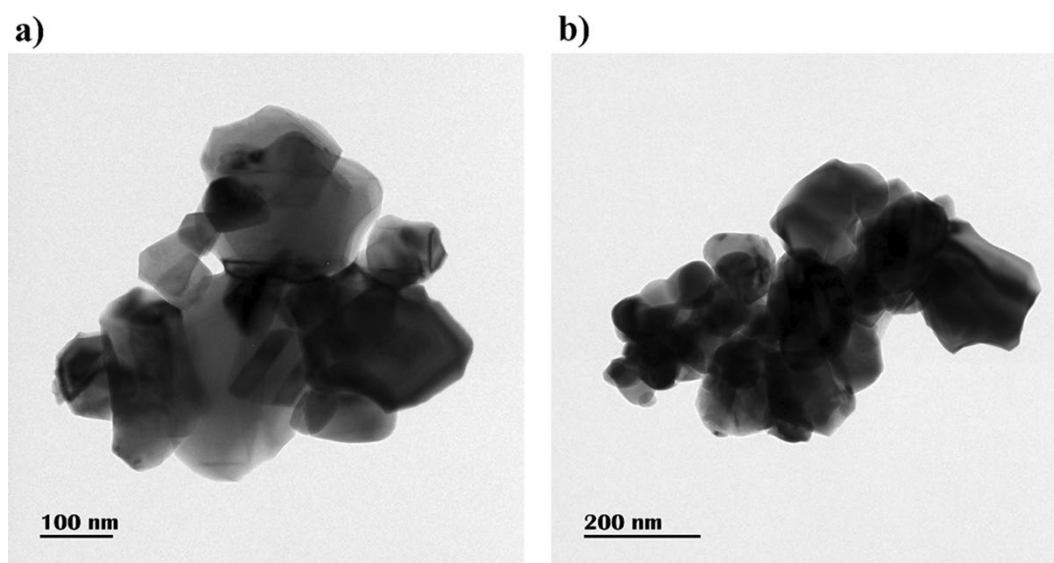


FIGURE 4 | HR-TEM images of ZrO_2 nanoparticles.

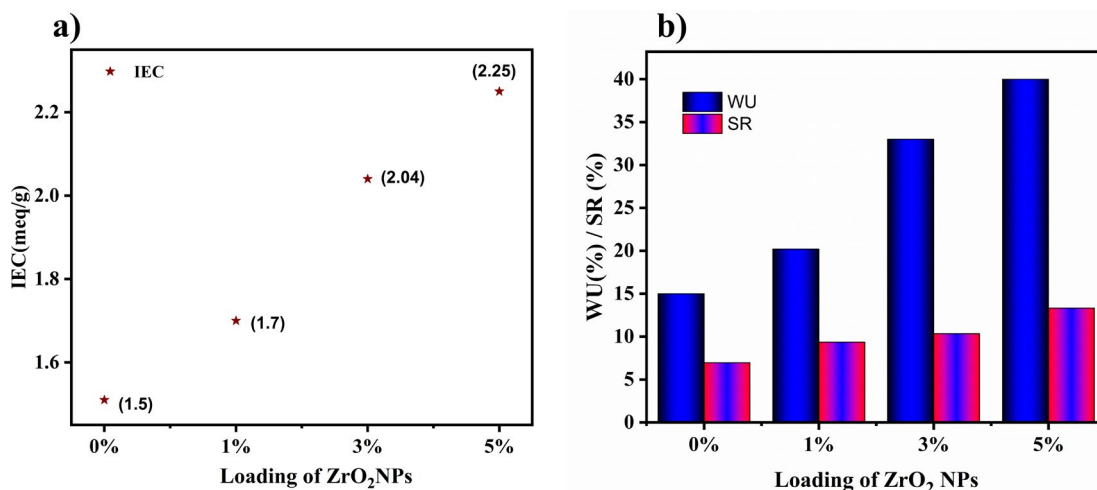


FIGURE 5 | (a) IEC, and (b) WU and SR of pristine and composite membranes.

Figure 4 represents TEM micrographs of the as-synthesized ZrO₂ nanoparticles at different magnifications. The images show nanosized particles, irregular to quasi-spherical in morphology and strongly tending to agglomerate. The particles are intimately linked. Nanoscale ZrO₂ exhibits strong interparticle interactions and a high surface energy, leading to aggregation. The TEM results demonstrate the effective production of ZrO₂ nanoparticles with a heterogeneous and aggregated shape.

4.5 | IEC, Swelling Ratio and Water Uptake

IEC for nanocomposite membranes, as shown in Figure 5a, is to some extent superior to that of the pristine membrane. This suggests a possible increase in ion conduction channels within the nanocomposite membranes due to the incorporation of ZrO₂ additive particles, resulting in a slight increase in IEC compared to the plain membrane. SPAAKs/TiO₂ composite membranes have also been prepared within our research group [36]. In contrast to their IEC values, the hydrophilic ZrO₂ nanoparticles in the PVA/MCBZ membrane cluster network enhanced WU for each nanocomposite sample (Figure 5b). Arumugam et al. [37] WU and IEC of ZrO₂/PAPEI/PVA nanocomposite membranes exhibited similar behavior. ZrO₂/PA-PEI/PVA nanocomposite membranes showed improved WU and IEC, credited to the nanoparticles' hydrophilic nature and membrane voids. The effects of the addition of ZrO₂ on the SR and WU of ZrO₂/PVA/MCBZ composites are significant (Figure 5b) [38]. The SR and WU show a gradual increase with the increase in ZrO₂ content, which can be attributed to a more hydrophilic polymer matrix and increases in free volume. The higher SR values than WU indicate an increase in the dimensional expansion related to water absorption and the effective interaction between ZrO₂ particles and the polymer network. Figure 5b shows the SR and WU of ZrO₂/PVA/MCBZ composites with 0–5 wt% ZrO₂ loadings. The WU rises from 15% to 40% across the same composition range, demonstrating improved water retention with increasing ZrO₂ content, whereas the SR progressively

increases from roughly 7% for the pristine membrane to 13% at 5 wt% ZrO₂ loading.

4.6 | Proton Conductivity

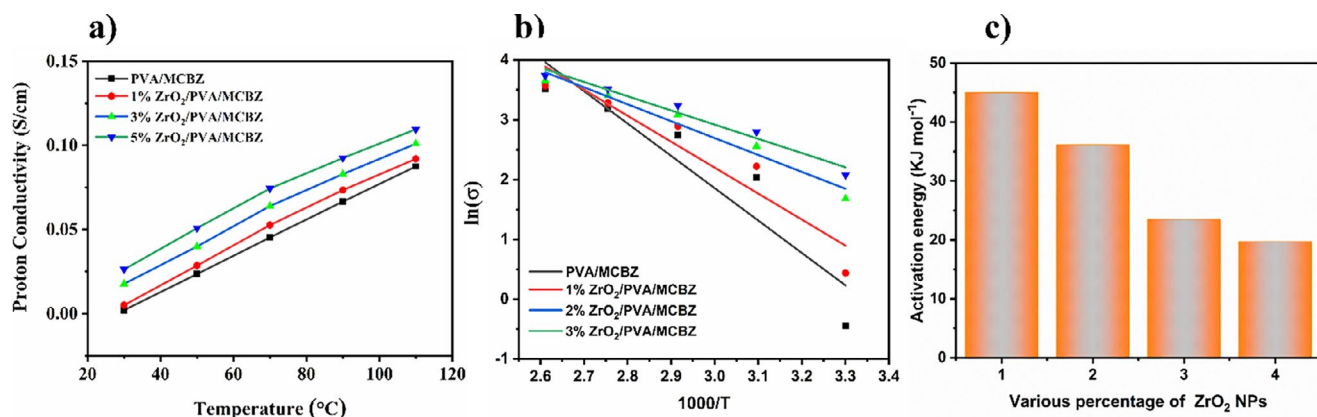
Figure 5a demonstrates a growth in ionic conductivity of the composite films at a temperature range of 30°C–110°C, under hydrated (95% RH) conditions. Dinakaran et al. [39] and Sun-Ju Song et al. [40] observed a closely related tendency for ionic conductivity with respect to temperature. The 5 wt% ZrO₂/PVA/MCBZ nanocomposite membrane showed the highest proton transport in the entire temperature range studied (30°C–110°C) at 95% RH. The conductivity of the pristine PVA/MCBZ reached a maximum of S/cm, and the conductivity of 5 wt% ZrO₂ composites reached a maximum of S/cm with the increase in temperature, which is higher than the pristine PVA/MCBZ membrane (Figure 5a). At 30°C, the proton conductivities of the pristine PVA/MCBZ, 1 wt% ZrO₂/PVA/MCBZ, 3 wt% ZrO₂/PVA/MCBZ, and 5 wt% ZrO₂/PVA/MCBZ membranes were and S/cm, respectively. These values gradually increased with temperature, reaching maxima of and S/cm at 110°C [41, 42]. Proton conductivities are slightly higher at 95% RH, consistent with higher WU that limits vehicular (H₃O⁺ diffusion) and Grotthuss (proton hopping) mechanisms. The enhanced conductivity at high ZrO₂ loading (5 wt%) arises from synergistic contributions of ZrO₂ nanoparticles and polymer matrix. A comparison of proton conductivity of the ZrO₂/PVA/MCBZ membranes with literature data is given at Table 1.

4.6.1 | Arrhenius Plots

Figure 6b,c reveals a strong positive correlation between proton conductivity and temperature, governed by the activation energy (E_a) for proton migration through the membrane. The slopes of the Arrhenius plots and corresponding activation energies (E_a) in electron volts (eV) are presented in Figure 6b. Activation energies were converted to kJ/mol using the factor eV = 96.485 kJ/mol. Table 2 lists values for pristine PVA/MCBZ and ZrO₂-incorporated nanocomposites under 95%

TABLE 1 | Comparison of proton conductivity of the ZrO₂/PVA/MCBZ membranes with literature data.

S. no	Name of the composite membrane	Proton conductivity (S/cm)	Temperature (°C)	References
1	MPPO-1.0 wt%ZrO ₂	8.77×10^{-2}	80°C	[43]
2	PBI4N(ZrO ₂) _{0.231} (H ₃ PO ₄) ₁₃	1.04×10^{-1}	80°C	[44]
3	GNS/SnO ₂ @SPEEK	1.96×10^{-1}	80°C	[21]
4	MoS ₂ /GNS@SPAE/DPDA	2.5×10^{-2}	110°C	[45]
5	SPEEK/SZ	6.87×10^{-2}	120°C	[46]
6	Nafion/ZrO ₂ 8wt%	8.68×10^{-2}	80°C	[47]
9	ZrO ₂ /PVA/MCBZ	1.096×10^{-1}	110°C	Present work

**FIGURE 6** | (a) Proton conductivity of pristine and ZrO₂/PVA/MCBZ composite membrane, (b) Arrhenius plot of pristine and ZrO₂/PVA/MCBZ composite membrane, and (c) activation energy of polymer and nanocomposite membrane.**TABLE 2** | The polymer and polymer nanocomposite membrane values of the physicochemical properties, proton conductivity, and activation energies.

S. no	PVA/MCBZ polymer/ZrO ₂ NPs	IEC (meq/g)	WU (%)	SR (%)	PC (S/cm)	Activation energy (kJ mol ⁻¹)
1	Pristine	1.5	15	6.97	8.75×10^{-2}	44.98
2	1%/PVA/MCBZ	1.7	20.2	9.37	9.20×10^{-2}	36.10
3	3%/PVA/MCBZ	2.04	33	10.34	1.01×10^{-1}	23.50
4	5%/PVA/MCBZ	2.25	40	13.33	1.09×10^{-1}	19.75

Abbreviations: IEC, ion exchange capacity; PC, proton conductivity; SR, swelling ratio; WU, water uptake.

RH, which is higher to enhance proton conduction at elevated humidity. Proton conduction mechanisms dictate these values. The Grotthuss and vehicle mechanisms, followed in the benzoxazine-based PVA/MCBZ membranes, rely on proton hopping via hydronium ions (H₃O⁺) and typically exhibits of 14–40 kJ/mol. The ZrO₂ nanocomposite membranes followed this path with values very close to this range (Figure 6c; Table 2). In the Grotthuss (hopping) mechanism protons create H₃O⁺ by connecting to lone-pair electrons, on water molecules allowing fast movement of charge without moving water molecules (Figure 7). By contrast, the vehicular mechanism involves H₃O⁺ diffusion through the polymer matrix, producing hydronium ions, hydrates, and oxidized species. Both mechanisms require sufficient water content, with higher RH promoting their efficiency and reducing.

4.7 | TGA Analysis

Figure 8a shows the TGA profiles of the pristine polymer and ZrO₂-containing nanocomposite membranes. All samples display three distinct mass-loss regions. The first, at 98°C–99°C, is associated with the evaporation of adsorbed water, followed by the loss of residual solvent at 190°C [48]. The pronounced mass loss between 232°C and 480°C is assigned to the decarboxylation of –COOH groups, accompanied by CO₂ evolution [49]. Above 480°C, the organic matrix progressively thermally decomposes, leaving the thermally stable ZrO₂ phase as inorganic residue [50]. The inorganic ZrO₂ phase is suggested by the higher residual mass of 28.1 wt% at 800°C observed for the nanocomposite. The pristine polymer retained 10% of its initial mass, whereas the nanocomposite retained 39.62%, confirming the increased inorganic

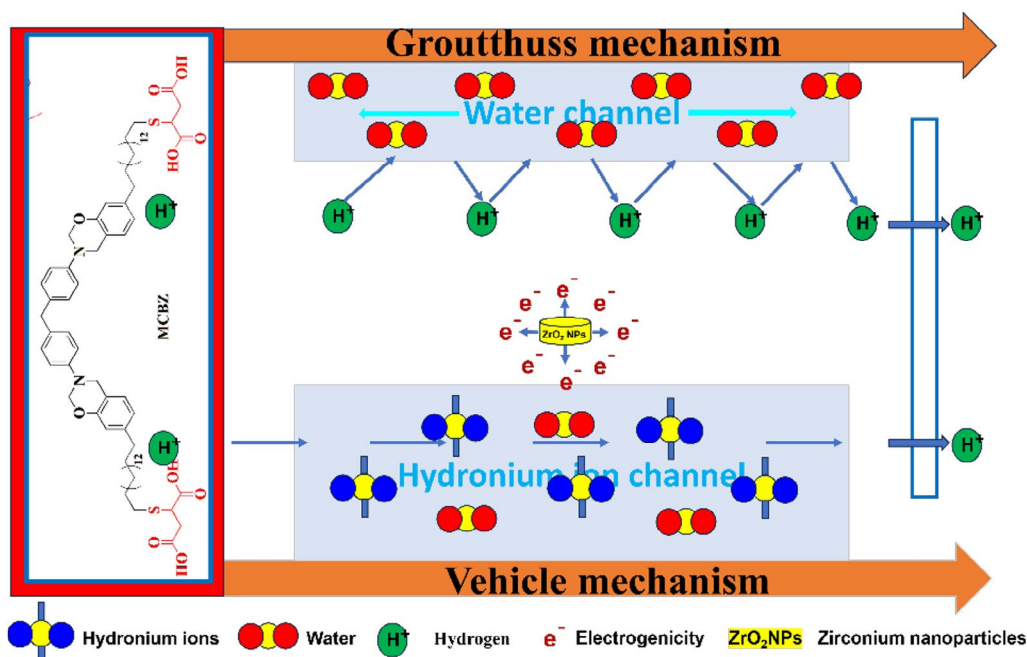


FIGURE 7 | Proton transport mechanism of composite membrane.

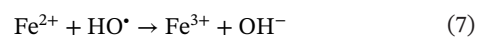
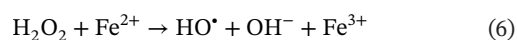
residue after ZrO_2 incorporation. Despite this difference, the similar degradation profiles indicate that ZrO_2 incorporation does not markedly change the overall thermal-degradation behavior of the polymer matrix. Figure 8b also shows a zoomed-in view of the TGA profiles in the range of 100°C – 250°C , which clearly shows the superior thermal stability of both the pristine and composite films in this critical low-temperature regime. The DSC profiles of pristine PVA/MCBZ membrane and the composites filled with ZrO_2 are shown in Figure 8c. A broad thermal transition is observed for the original membrane, while the ZrO_2 -containing membranes exhibited a more obvious exothermic event at about 201°C – 203°C . The corresponding enthalpy increases markedly upon incorporation of ZrO_2 , indicating a change in the thermal response of the PVA/MCBZ matrix. The similar peak temperatures for the 1 and 3 wt% composites suggest that ZrO_2 incorporation modifies the magnitude rather than the nature of this thermal event. These changes may arise from polymer ZrO_2 interfacial interactions; however, the DSC data alone do not establish crystallization or crosslinking as the underlying process. Therefore, interpreted the observed exothermic transition as a modification of the thermal behavior of the polymer matrix following ZrO_2 incorporation. Table 3 DSC data show that when ZrO_2 loading increases, the exothermic peak temperature (T_p) gradually shifts toward higher temperatures. When 1 and 5 wt% ZrO_2 are added, the T_p rises to 201°C and 203°C , respectively, while the pristine PVA/MCBZ membrane shows an exothermic peak at 191°C . This change shows that adding changes how the PVA/MCBZ matrix reacts to heat and delays the heat caused reaction. The connection, between nanoparticles and the polar parts of the polymer matrix is what causes the higher temperature at which the process starts. These connections can stop the polymer chains from moving and make the membrane more stable when it is hot. The modest increase in T_p from 201°C to 203°C at increasing ZrO_2 loading indicates that after the first loading, ZrO_2 's impact diminishes.

4.8 | Mechanical Properties of PVA/MCBZ Blended Film and ZrO_2 /PVA/MCBZ 5 Wt % of Membranes

The mechanical properties of the membranes shown in Table 4 indicate that the tensile strength, approximately 23 MPa, does not change significantly with the inclusion of ZrO_2 nanoparticles in the PVA/MCBZ matrix [50]. However, the elongation at break decreases from 16% to 14.92%, indicating that the nanocomposite membrane is slightly rigid due to the presence of inorganic ZrO_2 . These observations imply that the ZrO_2 reinforcement improves the ductility of the membrane without deteriorating its mechanical strength [51].

4.9 | Role of the Fenton Test in the PEM Chemical Stability

Oxidative stability is one of the major factors to determine the long-term durability of the PEMs in fuel cells. The Fenton test is a fast ex-situ method for evaluating the chemical degradation of the prepared polymer and polymer nanocomposite membranes [52]. The results of the Fenton test on the studied membranes are presented in Table 5. The Fenton solution generates free radicals in an aqueous medium by the interaction of Fe^{2+} and H_2O_2 , as described by Haber and Weiss. During the reaction, Fe is oxidized from Fe^{2+} to Fe^{3+} and vice versa, catalyzing the decomposition of H_2O_2 , as depicted in Equations (6–10). Several unstable intermediate species, such as free radicals, are formed and attack the vulnerable sites of the ZrO_2 /PVA/MCBZ membrane structure.



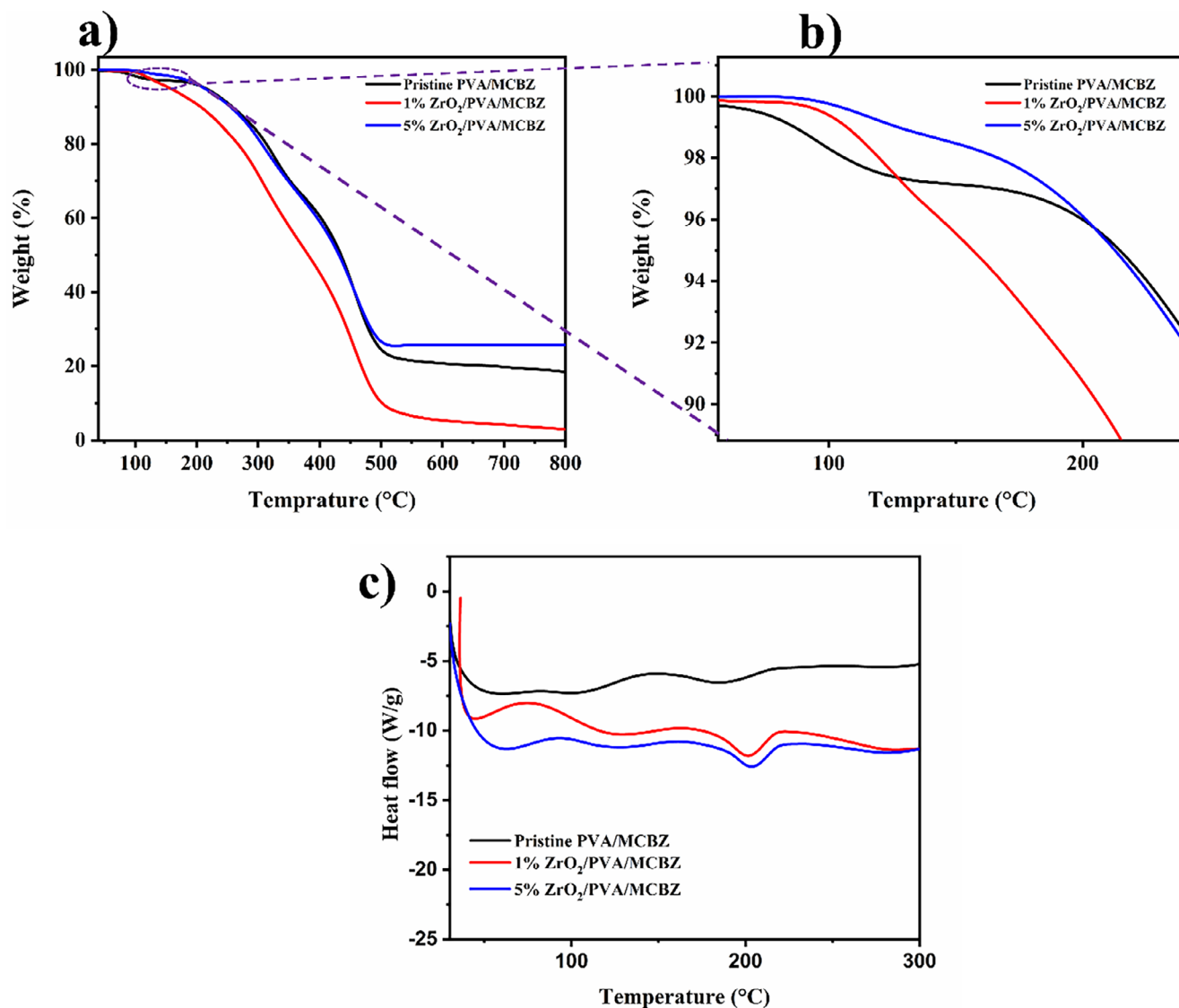


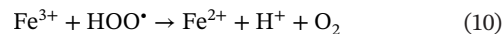
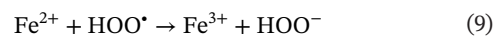
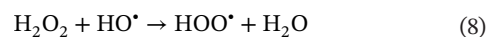
FIGURE 8 | (a, b) TGA thermograms of pristine and ZrO₂/PVA/MCBZ composite membranes, (c) DSC of ZrO₂/PVA/MCBZ composite membranes.

TABLE 3 | DSC peak enthalpy (ΔH) of MCBZ and ZrO₂/PVA/MCBZ composite membranes.

Sample	ZrO ₂ loading (wt%)	Exothermic peak, T_p (°C)
PVA/MCBZ	0	191
ZrO ₂ /PVA/MCBZ	1	201
ZrO ₂ /PVA/MCBZ	5	203

TABLE 4 | Mechanical properties of PVA/MCBZ blended film and ZrO₂/PVA/MCBZ 5 wt% of membranes.

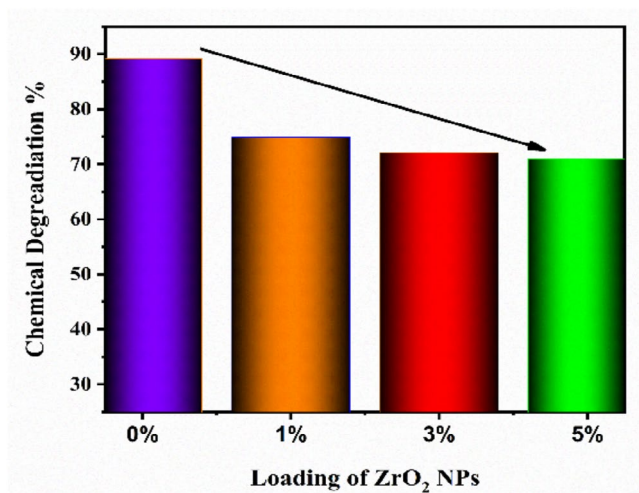
S. no	Sample	Tensile strength (MPa)	Elongation (%)
1	PVA/MCBZ	1.59	16.0
2	5% ZrO ₂ /PVA/MCBZ	15.19	14.92



PEMFC operation generates peroxide radicals that damage the membrane. The ZrO₂/PVA/MCBZ membrane shows enhanced chemical stability due to the strong interfacial interactions between the surface of ZrO₂ and COOH functional groups of the polymer, which could limit polymer-chain mobility and enhance the polymer-nanoparticle interface. The pristine PVA/MCBZ membrane showed much higher degradation than the ZrO₂-incorporated membrane during the Fenton test. After 30 min, the mass loss was 29% for pristine PVA/MCBZ while only 10.84% was observed for the ZrO₂/PVA/MCBZ membrane (Figure 9), indicating the enhanced resistance of the nanocomposite membrane to oxidative degradation. Moreover, the dispersed ZrO₂ nanoparticles can increase the tortuosity of diffusion pathways for oxidative species, thus hindering their penetration into the polymer matrix and inhibiting chemical degradation.

TABLE 5 | Chemical stability study of various percentages of ZrO_2 /PVA/MCBZ composite membranes.

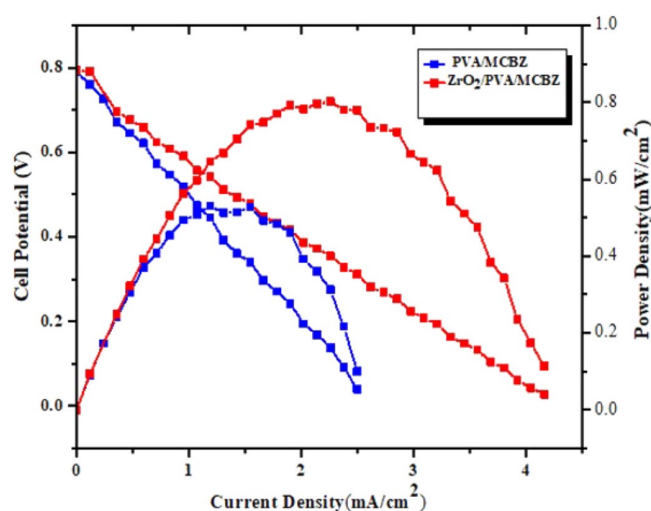
Loading of ZrO_2 NPs	Dimension (cm)	Volume (mL)	Degradation %
0%	1 × 1	100	89 ± 16
1%	1 × 1	100	74 ± 89
3%	1 × 1	100	72 ± 13
5%	1 × 1	100	71 ± 1

**FIGURE 9** | Chemical stability study of pristine and ZrO_2 /PVA/MCBZ composite membrane.

The polymer network has sulfur-based parts. These parts can help stop damage caused by radicals. They make the polymer less likely to break down because of oxygen. They also make the polymer more stable when it is in Fenton conditions. The enhanced durability of the ZrO_2 -containing membrane also represents the favorable effect of the inorganic phase on oxidative resistance and potential fuel-cell durability. Table 5 shows the volume of solution, membrane dimensions, and the percentage mass loss of the membranes with different ZrO_2 loadings after chemical degradation.

5 | Possible Mechanism of Hydroxyl Radical Attack on PVA/MCBZ Matrix

In the working conditions of PEMFC, highly reactive oxygen-centred radicals produced during the Fenton reaction, especially hydroxyl ($\cdot\text{OH}$) and hydroperoxyl ($\text{HOO}\cdot$) radicals, can attack potential sites in the PVA/MCBZ polymer matrix, such as hydroxyl groups in the PVA backbone, decarboxylation sites in the carboxylic acid/mercaptosuccinic-acid segments, and aromatic and benzoxazine groups. These oxidative attacks can lead to sulfur oxidation, chain scission, decarboxylation, and degradation of the cross-linked network, which may eventually result in a decrease in the mechanical integrity and durability of the membrane. The introduction of ZrO_2 nanoparticles can alleviate oxidative degradation by virtue of strong interfacial interactions

**FIGURE 10** | Polarization and Power density curves of PVA/MCBZ and ZrO_2 /PVA/MCBZ.

with the polymer, enhanced hydrogen-bonding interactions, and increased tortuosity of diffusion pathways for reactive species. These effects may impede the diffusion of oxidative species and enhance the structural stability of the polymer network. Therefore, a PVA/MCBZ/ ZrO_2 nanocomposite membrane exhibits improved oxidative stability and durability and is a good candidate for proton exchange membrane fuel cell applications.

5.1 | Fuel Cell Performance

The fuel-cell performance of the prepared membranes was evaluated using a membrane electrode assembly (MEA) with an active area of 8.41 cm^2 . Gas diffusion layer (GDL) paper was employed as the electrode backing layer, with Pt/C catalyst loadings of 0.35 mg cm^{-2} at the anode and 0.55 mg cm^{-2} at the cathode. The MEA was assembled and compressed at a torque of 3 N m . The electrochemical performance of the acid-treated membranes was evaluated from their polarization and power-density characteristics. The polarization measurements were performed at room temperature and atmospheric pressure with the flow rates of hydrogen and oxygen of 100 and 75 mL min^{-1} , respectively. The cell voltage was recorded as a function of current density, and the corresponding power density was calculated from the product of cell voltage and current density. Figure 10 compares the polarization and power-density characteristics of the prepared membranes under the same operating conditions. The performance of the fuel cell was considerably improved by adding ZrO_2 , compared to the PVA/MCBZ membrane. The maximum power density of the PVA/MCBZ membrane was about 0.530 mW cm^{-2} at a current density of 1.19 mA cm^{-2} , whereas for the ZrO_2 /PVA/MCBZ membrane the maximum power density was significantly higher at about 0.802 mW cm^{-2} at 2.26 mA cm^{-2} . Thus, the maximum power density was increased by about 51% by the addition of ZrO_2 , while the current density at maximum power was increased by about 90%. The improved performance may be attributed to improved proton transport and/or membrane-electrode interfacial characteristics by adding ZrO_2 . These results indicate that the ZrO_2 /PVA/MCBZ membrane has improved electrochemical performance in the ambient operating conditions investigated. A comparison

TABLE 6 | The values of current density and peak power density of literature studies are compared with the present work.

Membranes	Current density	Peak power density	Temperature	References
PVA/PVP-BaZrO ₃ , 1 wt%	0.201 A cm ⁻²	0.282 W cm ⁻²	70°C	[53]
PVA/IC-sulfated ZrO ₂ , 7.5 wt%	0.150 A cm ⁻²	0.76 W cm ⁻²		[54]
Nafion/S-ZrO ₂	0.189 A cm ⁻²	0.183 W cm ⁻²	60°C	[55]
ImPS/ZrO ₂ , 10 wt%	0.640 A cm ⁻²	0.270 W cm ⁻²	50°C	[56]
5 wt%-ZrO ₂ /MCBZ	0.226 A cm ⁻²	0.802 W cm ⁻²	60°C	Present work

of the result obtained in the present work and the literature data is presented in the Table 6.

6 | Conclusion

Hydrophilic polymer membranes were synthesized by cross-linking cardanol-based benzoxazine (CBZ) with 2-mercaptosuccinic acid (MCBZ) via radical polymerization. ZrO₂ NPs were added in varying percentages to optimize these membranes for PEMFCs. The outcome of zirconia nanoparticle loading on the physicochemical and electrochemical properties of recast PVA/MCBZ membranes was investigated. The synthesized polymer and nanoparticles were characterized using FE-SEM and XRD. The nanocomposite membranes (ZrO₂-1, 3, 5 wt%/PVA/MCBZ) were synthesized through the solution casting method. The prepared composite membranes were characterized by proton conductivity, IEC, SR, WU, and oxidative stability. The results showed that nanocomposite membranes absorbed more water than the pristine membrane. It was observed that the proton conductivity increased significantly, proportionally to the rise in the quantity of ZrO₂ NPs and temperature. SEM images revealed a homogeneous structure in the pristine membrane and good nanocomposite incorporation within the polymer matrix. The ZrO₂/PVA/MCBZ membrane demonstrated an improved maximum power density of 0.802 mW cm⁻² at a current density of 2.26 mA cm⁻², surpassing the 0.530 mW cm⁻² achieved by the PVA/MCBZ membrane at 1.19 mA cm⁻². These results show that composite membranes have potential as membrane materials for fuel-cell applications.

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The authors have nothing to report.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

No data were used to support this study.

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