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Synthesis and characterization of graphene oxide and TiO₂ nano-structures loaded piperazine based sulfonated polybenzoxazines for proton exchange membrane fuel cells

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ABSTRACT

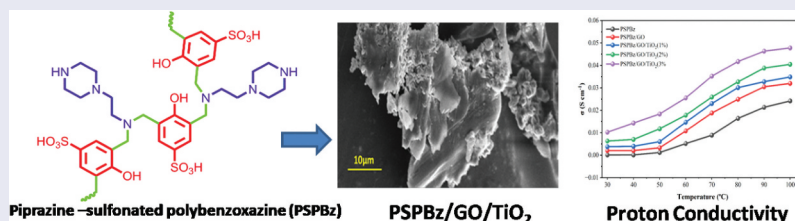
Piperazine-based sulfonated polybenzoxazine (PSPBz)/graphene oxide (GO) composite membranes with 1–3 wt% TiO₂ nanoparticles were developed for proton-exchange membranes (PEMs) applications. These membranes were fabricated using a solvent-casting method, followed by thermal curing to achieve stable cross-linked three-dimensional network structures. The successful formation and structural characteristics of the PSPBz were confirmed using FTIR and NMR spectroscopic analyses. The thermal stability and phase-transition behaviour were investigated through TGA and DSC analyses, respectively, inferred an enhanced thermal stability with a 9.45% char yield. Additionally, SEM analysis ascertained the incorporation of GO and TiO₂ nanostructures within the polymer matrix. A rutile-phase TiO₂ nanoparticles were confirmed by powder x-ray diffraction analysis (PXRD). Among the membranes developed, the PSPBz/GO/TiO₂ 3 wt% nanocomposite membrane exhibited the highest proton transport of 0.0477 S cm⁻¹, considerably surpassing that of the pristine PSPBz membrane. The improved proton-conducting ability is mainly credited to the optimized TiO₂ filler content, which promotes the formation of interconnected proton conduction pathways and facilitates efficient proton transport through the membrane and also the PSPBz/GO/TiO₂ 3 wt% membrane also exhibits better physicochemical properties, including water uptake (WU), swelling ratio (SR), ion exchange capacity (IEC), and chemical stability.

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Introduction

Fuel cells that utilize proton exchange membranes (PEMs) represent an effective and environmentally friendly technology for converting chemical energy into electrical energy without generating hazardous emissions. These cells can recover up to 90% of the heat produced while operating at high efficiencies of 40–60% [1]. Nafion, known for its stability and strong proton conductivity, has been widely employed as a proton exchange membrane. The unique structure of Nafion facilitates efficient proton transfer. However, Nafion has high costs, tends to swell and lacks functionality at certain temperatures. To enhance their performance, fillers and nanocomposites can be incorporated [2]. Significant efforts have been made over time to develop sulfonated polymers and ionic liquid-modified systems. The addition of polybenzoxazine to silica gel has improved mechanical stability, resulting in the formation of durable and efficient materials for various engineering applications [3].

Research aimed at increasing fuel cell endurance has focused on enhancing PEMs through the use of nanomaterials. Titanium dioxide nanocomposite membranes have been shown to improve thermal stability and proton conductivity (PC). Additionally, graphene derivatives have facilitated further proton transfer; these membranes enhance water retention across different temperatures and allow for fuel permeability. The development of hybrid structures has resulted in excellent interfacial capabilities. Overall, PEMs incorporating nanocomposites demonstrate significant potential for long-lasting and highly efficient fuel cell applications [4]. Benzoxazine matrices have garnered extensive research attention owing to their structural and tunable properties. Furthermore, bio-based benzoxazines have exhibited remarkable mechanical strength and thermal stability for high-performance applications [3,5–7]. Recent investigations into polybenzoxazine-based energy storage devices have revealed that polymer blending and hydrogen bonding can improve flexibility and electrochemical behaviour, making them suitable for next-generation applications [8–11]. An advanced rubber-based benzoxazine incorporated with nanofillers, for instance graphene, multi-walled carbon nanotubes (MWCNTs) and MoS_2 , has demonstrated enhanced mechanical strength and durability for electronic applications. Both benzoxazine and polybenzoxazine (PBz) are recognized for their high thermal stability, flame retardancy, low shrinkage and excellent mechanical properties. Various modifications, including silicone elastomer blends [12] and nanocomposites [13] have been implemented to improve interfacial adhesion, toughness and oxidation resistance. Due to their favourable dielectric constant and dimensional stability, PBz materials have found widespread use in electronic packaging, printed circuit boards (PCBs), communication substrates and high-performance engineering applications. Recent studies have reported the development of polybenzoxazine-based composites reinforced with conductive fillers, like Ketjen Black, which exhibited improved electrical conductivity [14]. Recently, several non-fluorinated acid-functionalized polymer membranes have been reported: the hyper-branched sulfonated poly(arylene aliphatic ketones) (HB-SPAAK) [15], poly(aryl-aliphatic ethers) (PA-APAAEs) [16], ceria nanoparticle-dispersed polyvinyl alcohol/sulfonated polybenzoxazine (CeO_2 @PVA/poly S-BZ) [17], poly(vinyl alcohol)/epoxy resin/3-aminopropyl triethoxysilane (PVA/Ep/APS/ SnO_2) [18], (GO@PA/TT-DPDA) [19], Ce-MOF/SPEEK [20] and sulfonated polyphenylenesulfide sulfone (sPPSS) loaded with titania-graphene (TiO_2 -GNS) [21], SPEEK-SBz [22], cross-linkable sulfonated polymer through Diels-Alder reaction [23], poly(SHS-ddm) [24], SPSU/PSU/PBz-m [25], pore-filling membranes using sulfonated poly(arylene ether sulfone)s (SPAES) within cross-linked polybenzimidazole/polybenzoxazine matrices [26], Electrospun sulfonated polybenzoxazines nanofibers [27], sulfonated urethane-crosslinked polybenzoxazine (PUBZx) [28], which serve as alternatives to Nafion membranes and the incorporation of nanofillers enhancing proton conductivity, thermal stability, water retention, and chemical durability of PEMs. A vanillin-based benzoxazine has been noted for its long-term stability [29]. Nitrogen-doped porous materials derived from benzoxazine through ring-opening polymerization and molten salt treatment in air have shown excellent performance as electrode materials [30]. For practical composite applications, graphene oxide is synthesized via the Hummers method for large-scale production. Beyond carbon nanotubes (CNTs) and graphene derivatives, carbon nanostructures have gained increasing attention. Benzoxazine resin, noted for its high thermal stability and char-forming ability, has made it as a capable precursor for advanced carbon materials in energy storage, catalysis and structural applications [31]. Polymer-derived porous carbons are valued for their excellent conductivity and tunable porosity [32]. The sustainable conversion of thermosetting resins into carbon-based materials presents a challenge. Among various methods, laser-induced graphene (LIG) facilitates the formation of porous membranes [33]. Chutayothin and Ishida et al. [34] previously studied the molecular structure and thermal stability of a secondary amine employed in a piperazine-based Mannich polymer made by polycondensing p-cresol, formaldehyde, and piperazine, in which the piperazine moiety forms part of the main polymer chain. In the current study, the sulfonic acid groups serve as the primary proton-conducting sites, whereas piperazine is employed as side-chain functionality in the sulfonated benzoxazine structure. The incorporation of piperazine into the framework of benzoxazine has the potential to enhance the polarity and hydrophilicity of the polymer that is produced as a result. This, in turn, can facilitate the retention of water and the formation of uninterrupted proton-transport channels inside the membrane. The tertiary amine functionalities that are present in the structure of

piperazine have the potential to provide additional proton-accepting sites and to enable acid-base interactions with sulfonic acid moieties. This might potentially assist in the creation of interconnected proton-conducting routes.

In the present work, a phenolic precursor containing a $-SO_3H$ group, an amine (aminoethylpiperazine) and paraformaldehyde was synthesized through Mannich condensation to obtain a sulfonic acid-functionalized benzoxazine monomer. This was subsequently polymerized by a thermal ring-opening reaction to obtain a functionalized polybenzoxazine network. The stability and proton sources of the polymer matrix were further enhanced by the addition of graphene oxide and TiO_2 nanofillers. The resultant materials were evaluated for their morphology, proton conductivity, and functional performance using appropriate analytical methods. The degradation behaviours of the prepared membranes were assessed through TGA and DSC analyses. The crystalline phase and crystal structure of the TiO_2 nanoparticles were confirmed by powder X-ray diffraction (PXRD) analysis. In addition, water uptake, swelling ratio, and chemical stability were studied to ascertain the physicochemical properties of the membranes suitable for PEMFC applications.

Experimental section

Chemicals

Aminoethyl Piperazine (AEP) was obtained from Lancaster Chemicals, with a purity level of 98%. P-hydroxybenzene sulfonic acid was procured from Tokyo Chemical Industry (98%), paraformaldehyde (96%) was sourced from Sigma-Aldrich Chemicals Pvt. Ltd, and methanol was acquired from Rankem Chemicals. Deionised water was used throughout the studies. Sodium hydroxide (NaOH) was obtained from Avra Synthesis, exhibiting 98% purity. Sodium chloride (NaCl 98%), ferrous ammonium sulphate (FAS 98%), hydrogen peroxide 30% (H_2O_2), sodium Nitrate ($NaNO_3$ 99%) and phenolphthalein chemicals were sourced from SDFCL Limited. Potassium permanganate ($KMnO_4$ 99%) and graphite powder (98%) were purchased from Lobachemie. The graphene oxide (GO) was synthesized using the Hummers method, and TiO_2 is sourced from SRL Limited. Dimethyl sulfoxide (DMSO) acquired from SDFCL Limited. Ethyl acetate was acquired from Avra Synthesis, with 99% cleanliness.

Methods

Synthesis of 3-(2-(piperazin-1-yl)-3,4-dihydro-2 H-benzo[e] [1,3] oxazine-6-sulfonic acid from p-hydroxy benzene sulfonic acid (Scheme 1)

AEP 2.22 g (0.0172 mol) and paraformaldehyde 1.03 g (0.0344 mol) were taken in a 250 mL three-necked round-bottomed flask using methanol as a solvent. The contents were stirred at RT for 10 minutes to ensure complete mixing. After weighing and adding up 3 g (0.01722 mol) of p-hydroxybenzenesulfonic acid into the reaction flask, it was continuously stirred for 8 h at 60°C. The reaction completion was monitored using TLC. The light-yellow coloured benzoxazine monomer obtained was isolated using ethyl acetate, dried and its molecular structure was confirmed by NMR spectroscopy [28].

Preparation of graphene oxide

A 500 ml clean beaker was taken and then the graphite powder (3 g) was added, followed by concentrated hydrochloric acid (70 ml), Sodium nitrate (1.5 g) was added while continuously stirring in an ice bath for 1 h then $KMnO_4$ (9 g) was added while being constantly stirred to ensure that the temperature was regulated. The ice bath was removed after the entire addition and the mixture was stirred for an hour at 35°C. After carefully adding 46 mL of deionised water, the reaction mixture was heated at 90°C for 2 h. Thereafter, 100 mL of deionised water was added to the mixture with constant stirring for an hour. 50 mL of hydrogen peroxide (30%) was supplemented to stop the process and eliminate the extra oxidising agent. This resulted in a colour shift, indicating the formation of graphene oxide. Then a 5% HCl solution followed by deionised water was added. Thereafter, the mixture was filtered and dried for 12 h at 40°C, producing a 12 g yield of black GO powder [35].

Conclusion

The PSPBz membranes incorporated with GO and TiO₂ nanoparticles were developed and characterized. ¹H NMR analysis confirms the formation of the PSBz. The membranes prepared showed good thermal stability with efficient film-forming ability. The inclusion of nanofillers contributes to an improved proton conductivity, dimensional stability, chemical stability, and WU. The presence of these GO/TiO₂ inorganic fillers provided additional proton transport pathways and enhanced interactions between the sulfonic acid groups and the polymer matrix, thereby improving proton transport efficiency. Overall, the properties offered by the developed SPBz/GO/TiO₂ (3 wt%) nanocomposite membrane suggest that this membrane can be considered for effective utilization in fuel cells (FCs) construction.

Author contributions

CRedit: **Muthazhagan Ramalingam**: Data curation, Formal analysis, Investigation, Writing – original draft; **Tharangini Umapathy**: Data curation, Formal analysis, Investigation, Validation, Writing – original draft; **Karikal Chozhan Chinnakkannu**: Conceptualization, Data curation, Formal analysis, Methodology, Supervision, Validation; **Alagar Muthukaruppan**: Conceptualization, Methodology, Project administration, Resources, Supervision, Validation, Visualization; **Dinakaran Kannaiyan**: Conceptualization, Methodology, Validation, Visualization, Writing – review & editing.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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