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Development of Mixed Matrix Anion-Exchange Membranes from Chemically Modified Phenol-Formaldehyde Resin for Electrochemical Systems

Moly P P[1], Ambily K J[2], Jeena C B[3], Elsa P J[4]
[1]Department of Chemistry, Little Flower College (Autonomous) Guruvayur, Kerala, India
[2]Department of Chemistry, Mercy College Palakkad Kerala India
[3]Department of Chemistry, Sree sankara College, Kalady, Kerala India
[4]Department of applied science and humanities, Royal college of engineering and technology Akkikavu Thrissur, Kerala India
Emails: *piusmoly@gmail.com[1], ambilykj@gmail.com[2], jeenabalakrish@gmail.com[3], elsapjose@gmail.com[4]*

Abstract

Anion exchange membranes (AEMs) play vital role in electrochemical applications. Conventional synthetic methods for AEMs are using reagents like chloromethyl methyl ether which is highly carcinogenic. Here, we are presenting a safe, simple, and cost-effective method for the fabrication of AEM. Phenol–formaldehyde prepolymer on condensation with guanidine was used as the anion exchange material and it was then dispersed in polyvinyl chloride (PVC) and membrane fabrication was done by solution casting method. This approach completely eliminates the usage of carcinogenic materials and enables uniform membrane fabrication. This was confirmed by FT-IR spectroscopy. Thermogravimetric analysis (TGA) which showed thermal stability up to 150°C, which suggests that the membrane is appropriate for real-world applications. Scanning electron microscopy (SEM) showed an even and smooth surface of the membrane. AC impedance measurements demonstrated a significant increase in ionic conductivity with an increase in ion-exchange material content. The membrane exhibited an ionic conductivity of 65 mScm^{-1}at room temperature in 2M NaOH solution. The improved thermal stability, high ionic conductivity, and environmentally friendly synthesis make this method an interesting alternative to traditional AEM fabrication methods, which can have applications in energy storage and conversion devices.

Keywords: *Anion Exchange Membranes; Eco-Friendly Synthesis; Impedance Study; Ionic Conductivity; Phenol–Formaldehyde Resin.*

1. Introduction

Modern clean energy technologies are crucial for addressing global energy and environmental challenges by reducing dependance on fossil fuels and allowing sustainable energy usage. Devices such as fuel cells, solar cells and wind turbines convert renewable resources into electricity. Newly developed batteries are ensuring efficient energy storage and delivery [1] (Madhuranthakam et al., 2024). Anion exchange membranes (AEMs), essential in several of these equipment. Membranes are often developed by chemically modifying base polymers like poly (phenylene oxide) or poly (aryl ether sulfone ketone) to impart ionic conductivity (Arunkumar et al., 2023) (Sheng et al., 2020) [2] [3]. In most methods ion-exchange groups are attached to polymer membranes via chloromethylation followed by quaternization with trimethylamine (TMA)(Liu et al., 2018), forming quaternary ammonium (QA) groups. But these QA groups are undergoing degradation when exposed to strong alkaline conditions due to Hofmann elimination, reducing membrane chemical stability [4] (Vega et al., 2010). Conventional anion exchange membranes (AEMs) also usually exhibit low ionic conductivity, restricting their practical efficacy. Literature shows that researchers have developed AEMs functionalized with guanidinium groups, which offer superior stability in strong alkaline medium and higher ionic conductivity due to the high basicity and resonance stabilization of the guanidinium moiety (Sajjad et al., 2015) [5]. With a Pka of 13.6, guanidine generates a greater concentration of mobile hydroxide ions than TMA, thereby enhancing membrane conductivity. The synthesis of the first plastic by polymerization of phenol and formaldehyde invented Baekeland in 1910, and its ion-exchange properties were later discovered by Adams and Holmes in 1935 (Brydson, 1995) [6]. By the 1940s, phenol-formaldehyde (PF)-based ion-exchange membranes were employed in electrodialysis and desalination applications. These membranes were typically synthesized via polycondensation of phenol, sodium phenol sulfonate, and formaldehyde in alkaline condition, followed by curing on reinforcing substrates such as glass fiber. Anion-exchange membranes were also developed using phenylenediamines, phenol, and formaldehyde, though their durability was limited. Over recent decades, high-performance polymers have been developed for membrane applications, with PVC rising importance due to its tenacity, chemical stability, and processability (Demirel et al., 2017) [7]. PVC-based membranes are widely used in battery separators, ultrafiltration, and proton exchange membranes (PEMs). Enhanced membrane performance has been reported for PVC blends with EVA (An et al., 2003), sulfonated PVC, zwitterionic polymers, Fe_2O_3 composites [8] (Demirel et al., 2017), and polycarbonate (PC)(Allan et al., 2015). The present study aims to develop anion-exchange resins by chemically functionalizing PF resins with guanidinium groups. This was achieved by condensing phenol and formaldehyde under basic conditions, followed by reaction with guanidine hydrochloride and excess formaldehyde. The resulting resins were blended with PVC in N-methyl-2-pyrrolidone (NMP), and membranes were fabricated via solution casting and solvent evaporation [9].

2. Method

Phenol, formaldehyde solution (37%), NMP, guanidine hydrochloride, and ammonia were from Merck (India) and used without further purification. Commercial-grade PVC was obtained from BASF India.

2.1.Synthesis of Anion–Exchange Material

Phenol and 40% formaldehyde were reacted in a 1:2 mole ratio under alkaline conditions (pH 9) and refluxed until a yellow resin precipitated. The resin was dried, ground into a fine powder, dispersed in acetone and reacted with one mole equivalent of guanidine chloride. The reaction mixture was heated at 80 °C for 2 hrs. to induce further condensation.

2.2.Preparation of Anion–Exchange Membrane

Anion-exchange membranes were prepared by solution casting technique by mixing anion-exchange material functionalized with guanidine (10–40 wt.%) and PVC powder in NMP [10]. The suspension was mixed to form a homogeneous mixture and membrane fabrication was done by solution casting technique. membranes were coded as P1, P2, P3, and P4, which contained 10, 20, 30, and 40 wt.% of the functionalized resin, respectively.

2.3.Characterization Methods

Surface morphologies of composite membranes were characterized by SEM analysis. FT-IR spectroscopy was utilized in studying chemical structure and the functional groups within the membrane. Thermal stability of the membranes was tested utilizing TGA. Electrochemical impedance spectroscopy (EIS) was used in the ionic conductivity evaluation of the membranes. All the characterization methods were according to the reference (Moly et al., 2018).

3. Results and Discussion

3.1.Results

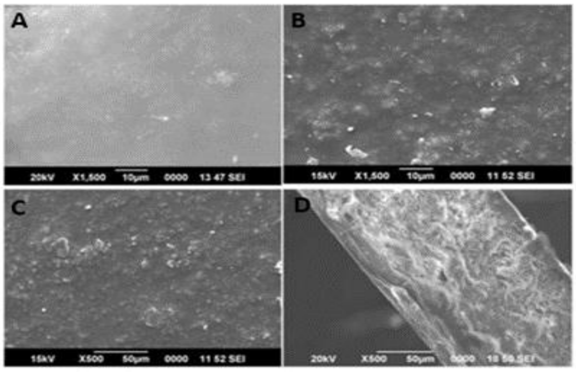

Figure 1 SEM Images of the Membranes: A) PVC B&C) P4 at Various Magnifications D) Layer View of P4

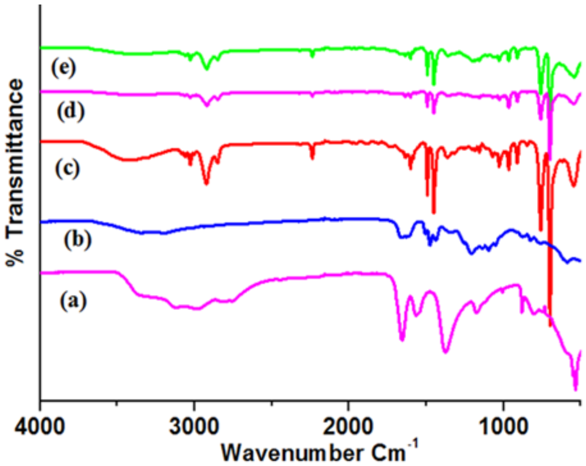

Figure 2 FT-IR data of (a) Guanidine (b) Anion-Exchange Resin (c) PVC (d) P2 (e) P4

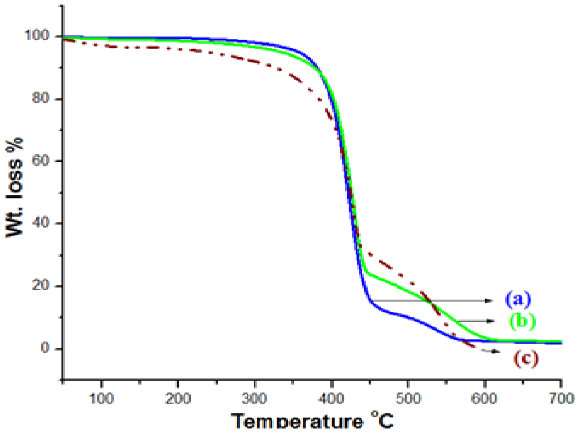

Figure 3 TGA curves for (a) PVC (b) P2 (c) P4

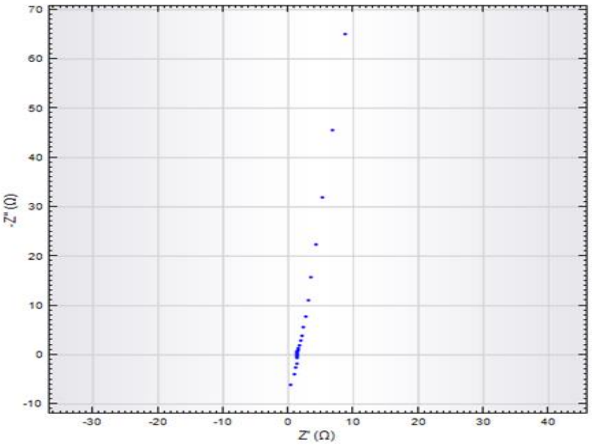

Figure 4 Nyquist Plot for the AEM M4 from AC Impedance Spectroscopy Measurements at Room Temperature

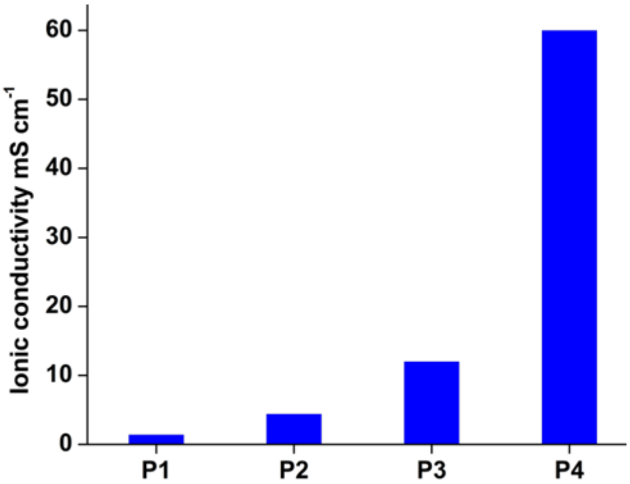

Figure 5 Influence of Ion-Exchange Material Content On the Ionic Conductivity of The AEM

3.2.Discussion

SEM was employed to study the surface characteristics of the fabricated membranes. Figure 1 presents the SEM image of P4 with uniform and smooth surface of the membrane. This indicates uniform distribution of the anion-exchange material in the PVC matrix. The newly developd membrane showed a thickness of 120 µm in range. Figure 2(a-e) shows FT-IR spectra of (a) Guanidine (b) Anion-exchange resin (c) PVC (d) P2 (e) P4. The above spectra show broad band between 3100-3400 cm^{-1}, which corresponds to stretching vibration of guanidinium N-H bonds and O-H stretching vibrations in the corresponding samples. Band at 1654 cm^{-1} corresponds to coupled vibrations of guanidinium N-H in plane bending vibrations and asymmetric C-N stretching vibrations of guanidinium group. The band at 1198 cm^{-1} is assigned to guanidinium N-H bending vibration. (Sajjad et al., 2014). The anion-exchange material's absorption peak in 3100-3400 cm^{-1} region is weaker, meaning most of the functional groups like –NH_2 provided by guanidine and –OH group of phenol has undergone the condensation reaction with formaldehyde (Antony et al., 2009). The peaks at 1504 cm^{-1} are due to aromatic ring vibration of benzene present in phenol. The band at 1078 cm^{-1}is due to the C-O-C ether linkages formed by condensation reactions with formaldehyde. Spectrum of PVC membrane shows strong bands at 1425 cm^{-1}, 1340 cm^{-1}, 1200 cm^{-1}, 1050 cm^{-1}, and 680cm^{-1}. These correspond to the C-C and C-H, C-Cl vibrations in the PVC polymer (Doi et al., 2019). The band at 1600 cm^{-1}, 1505 cm^{-1} is due to C-C aromatic stretching vibrations of the phenyl group (Wu et al., 2007). The above spectral results confirm successful incorporation of anion-exchange material into the polymer matrix. TGA assessed the membranes' thermal stability as they were heated from room temperature to 700°C at a rate of 10°C per minute under a nitrogen atmosphere. TGA curves for (a) PVC membrane, (b) membrane P2, and (c) membrane P4 are shown in Figure 3 (a-c). The first weight loss stage, which was less than 7%, occurred from room temperature to 350°C in Fig. 3(a-c). This was arising due to the vaporization of absorbed water and the loss of pendant chloride as HCl, leaving residual polyethylene backbone (Zhang et al., 2016). The second weight loss step happened between 420 and 450°C because the polymer backbone was degrading due to heat (Zhang et al., 2016). The third weight loss step, which occurred above 500°C, was also caused by the breakdown of the polymer's backbone. The fact that all membranes showed weight loss of less than 8% below 250°C indicates that the newly developed membrane has good thermal stability. As shown in Figure 4, the Nyquist plot of the fabricated P4 membrane reveals a good ionic conductance of 65 $mScm^{-1}$. Figure 5 displays how the ionic conductivity of the newly developed membrane changes as the content of the ion-exchange material increases. It is clear that the right amount of ion-exchange material helps to improve the conductivity of the composite membranes. Well-dispersed ion-exchange resin creates broader hydrated ion transport networks for anion transfer through the membrane. The high alkalinity of the guanidinium moieties increases the ionic conductivity of the membranes. Hydroxide conduction mainly happens through Grotthus mechanism, allowing it to diffuse through the network of hydrogen bonds present in the membrane.

Conclusion

Here, we used a new and cost-effective method for the development of AEMs having good thermal stability and improved ionic conductivity. This method avoids the use of chloromethyl methyl ether, which is a carcinogenic chemical typically used in the fabrication of AEM. From SEM images of the membranes, it is clear that the surface is uniform and even. The results from TGA analysis indicated that the membranes are stable up to 150°C, making them suitable for applications at high temperature. The AC impedance data showed that the ionic conductivity improved significantly with more ion-exchange resin. This method provides a better option than traditional methods for fabricating AEMs.

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