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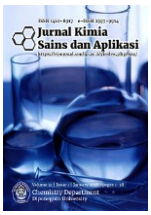

Chitosan/Bentonite Composite Membrane Doped with LiOH as an Electrolyte Candidate for Energy Storage Systems

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Abstract

This study aimed to synthesize and characterize chitosan/poly(vinyl alcohol) (PVA)-based polymer electrolyte membranes modified with bentonite and LiOH using the solvent casting method. The chitosan:PVA composition was varied from 10:90 to 90:10 to evaluate its effects on the physical, mechanical, thermal, morphological, and electrochemical properties of the membranes. Characterization was conducted through thickness, tensile strength, and porosity measurements, as well as Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy (SEM–EDX), Thermogravimetric Analysis–Derivative Thermogravimetry (TGA–DTG), and Cyclic Voltammetry (CV). The results showed that the membrane with a chitosan:PVA ratio of 10:90 exhibited the highest tensile strength of 19.86 MPa, whereas the membrane with a ratio of 30:70 achieved the highest porosity of 20.49%, which facilitated ion transport and enhanced electrochemical performance. FTIR analysis confirmed intermolecular interactions among chitosan, PVA, bentonite, and LiOH through the O–H, N–H, C=O, Si–O, and Li–O functional groups. SEM–EDX analysis revealed that carbon and oxygen were the predominant elements, while calcium, sodium, silicon, and lithium were also detected, consistent with the membrane composition. Cyclic voltammetry demonstrated typical capacitive behavior, with the current response increasing as the scan rate increased. Meanwhile, TGA–DTG analysis indicated gradual thermal degradation, with the primary decomposition occurring between 350°C and 550°C, demonstrating good thermal stability. Overall, the chitosan/PVA–bentonite composite membrane doped with LiOH shows strong potential as an environmentally friendly polymer electrolyte membrane for energy storage applications, particularly lithium-ion batteries.

1. Introduction

The development of modern technology, particularly in portable electronic devices such as smartphones, laptops, digital cameras, and electric vehicles, has significantly increased the demand for energy storage systems that are efficient, environmentally friendly, and capable of delivering high energy density. Batteries play a crucial role in determining the performance of these devices. Among the available energy storage technologies, lithium-ion batteries (LIBs) are considered the most promising due to their high energy density, high power output, and excellent cycling stability. Consequently, LIBs have been widely adopted in applications ranging from small-scale consumer electronics to electric vehicles and medical devices [1, 2].

LIBs operate through electrochemical redox reactions involving the migration of lithium ions between the cathode and anode via an electrolyte. During charging, lithium ions migrate from the cathode to the anode, whereas during discharge, they return to the cathode. Simultaneously, electrons flow through an external circuit to generate electrical energy [3]. Despite

their remarkable advantages, LIBs still face significant challenges related to safety and thermal stability. Conventional polyolefin separators commonly used in LIBs exhibit poor thermal resistance and limited electrolyte wettability, which may compromise battery reliability and safety [4]. Furthermore, improper disposal of spent LIBs poses serious environmental concerns [5]. The main components of a typical lithium-ion battery are illustrated in Figure 1.

To address these challenges, polymer electrolyte membranes have emerged as a promising alternative. In addition to functioning as electrolytes, they also serve as separators between the anode and cathode. Compared with conventional separators, they offer several advantages, including excellent chemical and thermal stability, high flexibility, superior ionic conductivity, low production costs, and the ability to be fabricated into thin films [6]. Moreover, the use of environmentally friendly polymers in PEM fabrication aligns well with the growing emphasis on sustainable energy storage technologies.

Chitosan is a natural biopolymer containing amino ($-NH_2$) and hydroxyl ($-OH$) functional groups, enabling the formation of hydrogen bonds and interactions with ionic species. It is biodegradable, non-toxic, and possesses excellent film-forming ability. However, its relatively low ionic conductivity and limited mechanical stability restrict its direct application as a polymer electrolyte. To overcome these limitations, poly(vinyl alcohol) (PVA) is commonly incorporated because of its excellent film-forming capability, high flexibility, and compatibility with various salts. The interaction between the functional groups of chitosan and PVA forms a stable polymer matrix while enhancing ion migration pathways and improving membrane conductivity [7, 8].

In addition to organic polymers, inorganic fillers such as bentonite have been shown to enhance membrane performance. Bentonite is a layered clay mineral characterized by high cation exchange capacity, large specific surface area, and excellent thermal stability [9, 10]. The incorporation of bentonite can improve the mechanical strength and thermal stability of polymer membranes while facilitating Li^+ transport through its hydrophilic nature and cation intercalation capability [11, 12]. In addition, bentonite contributes to improved membrane morphology by promoting a more uniform pore distribution.

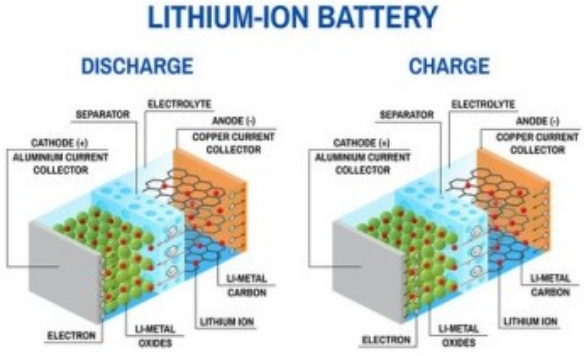


Figure 1. Lithium-ion battery parts [11, 13]

Lithium hydroxide (LiOH) was incorporated as the lithium-ion source to enhance membrane ionic conductivity. As a strong base that undergoes complete ionization, LiOH increases the concentration of lithium ions within the polymer matrix. Previous studies have demonstrated that chitosan/LiOH membranes exhibit improved flexibility, reduced hygroscopicity, and enhanced electrochemical properties [3, 14]. The integration of LiOH into the chitosan/PVA–bentonite composite is therefore expected to produce membranes with superior mechanical, thermal, and electrochemical performance.

In chitosan-based systems, the alkaline nature of LiOH may partially deprotonate the $-NH_3^+$ groups while strengthening the coordination interactions between Li^+ ions and electron-donating functional groups, such as the $-OH$ and $-NH_2$ groups present in both chitosan and PVA. These interactions are evidenced by FTIR spectra showing the appearance of Li–O absorption bands at 425–458 cm^{-1} and shifts in the O–H/N–H stretching bands, indicating the coordination of Li^+ ions with oxygen- and nitrogen-containing functional groups within the polymer matrix. Therefore, LiOH serves not only as a lithium-ion source but also as a modifier of the membrane's chemical environment, thereby facilitating more efficient ion transport pathways.

Compared with commonly used lithium salts such as $LiPF_6$ and $LiClO_4$, LiOH offers several practical advantages for biopolymer-based systems. Lithium hexafluorophosphate is highly sensitive to moisture and can decompose to produce corrosive hydrofluoric acid, whereas lithium perchlorate presents safety concerns because of its strong oxidizing properties. In contrast, LiOH remains stable in the aqueous/acetic acid medium employed during the solvent casting process, making it more compatible with hydrophilic chitosan/PVA systems. Furthermore, because this study emphasizes the development of environmentally friendly membranes, LiOH represents a more sustainable and cost-effective alternative to organofluorine lithium salts.

In this study, LiOH performs a dual function in this study: (1) as a source of Li^+ ions to improve membrane ionic conductivity and (2) as a basic additive that promotes intermolecular interactions and ion coordination within the chitosan/PVA–bentonite matrix, thereby influencing membrane flexibility, morphology, and electrochemical performance [7, 9, 11].

Previous studies have explored various strategies for improving polymer electrolyte membranes, including the incorporation of bentonite into poly(vinylidene fluoride) (PVDF) to enhance crystallinity [15] and the combination of hydroxyethyl cellulose with bentonite to improve electrophilic properties [16]. However, studies investigating chitosan/PVA composite membranes modified simultaneously with bentonite and LiOH remain limited. This combination has considerable potential to produce polymer electrolyte membranes with enhanced mechanical properties, high ionic conductivity, improved thermal stability, and well-controlled morphology.

Therefore, this study focuses on the synthesis and characterization of chitosan/PVA-based polymer electrolyte membranes modified with bentonite and LiOH using the solvent casting method. The membranes were characterized by thickness, tensile strength, and porosity measurements, as well as Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy (SEM–EDX), Thermogravimetric Analysis/Derivative Thermogravimetry (TGA/DTG), and electrochemical analysis using cyclic voltammetry (CV). The findings are expected to contribute to the development of environmentally friendly polymer electrolyte membranes with enhanced mechanical properties, controlled morphology, superior electrochemical performance, and potential applications in next-generation lithium-ion batteries.

The membranes were synthesized using the solvent casting method, which involves dissolving the polymer and other raw materials in a suitable solvent, followed by homogeneous mixing before film formation [17]. One of the primary advantages of solvent casting is its ability to produce membranes with highly uniform thickness compared with other fabrication techniques. In this process, the spreading device plays a critical role in achieving a homogeneous thickness profile. Extensive theoretical studies have been conducted to optimize the hydrodynamic profile required for uniform film casting. Because the process is governed by laminar flow, solvent casting produces films with low intrinsic molecular orientation and minimal thickness variation. Depending on the viscosity of the casting solution, desired film thickness, and processing rate, slot-die or doctor-blade casting techniques may also be employed. Another significant advantage of solvent casting is its ability to accommodate substantially higher solid contents than extrusion processes, reaching up to approximately 95 wt.% [18].

2. Experimental

2.1. Materials and Equipment

The equipment used in this study included standard laboratory glassware, an analytical balance, a hot plate magnetic stirrer, an oven, a thickness gauge, a tensile strength tester, a cyclic voltammetry (CV) system, a Fourier Transform Infrared Spectrometer (FTIR), a Scanning Electron Microscope equipped with Energy Dispersive X-ray Spectroscopy (SEM–EDX), a Thermogravimetric Analyzer (TGA), and personal protective equipment (PPE).

The materials used were bentonite, chitosan, poly(vinyl alcohol) (PVA), lithium hydroxide (LiOH), glacial acetic acid (CH_3COOH), glycerol, and distilled water.

2.2. Bentonite Preparation

A total of 250 g of bentonite was dispersed in 1 L of distilled water in a 2 L beaker and stirred continuously for 2 h. The suspension was then allowed to stand for 24 h. After sedimentation, the bentonite suspension was filtered and dried in an oven at 110°C for 2 h. The dried bentonite was subsequently ground and sieved through a 100-mesh sieve before use [19].

2.3. Synthesis of the Polymer Electrolyte Membrane

The polymer electrolyte membranes were synthesized using the solvent casting method with a total polymer mass of 2 g. Chitosan was dissolved in 100 mL of 2% (v/v) glacial acetic acid, while PVA was dissolved separately in 100 mL of distilled water. The chitosan-to-PVA weight ratios investigated were 10:90, 30:70, 50:50, 70:30, and 90:10.

The two polymer solutions were combined and stirred using a magnetic stirrer on a hot plate at 60°C for 3 h until a homogeneous solution was obtained. Subsequently, glycerol (20 wt.%), LiOH (20 wt.%), and bentonite (30 wt.%), calculated based on the total polymer weight, were added to the polymer mixture. The resulting suspension was further stirred at 40°C for 1 h until homogeneous. The homogeneous casting solution was then poured onto a glass plate and dried in an oven at 80°C for 8 h to obtain the polymer electrolyte membrane [5].

2.4. Thickness Measurement

The membrane thickness was measured using a Lorentzen & Wettre thickness gauge. For each membrane sample, thickness measurements were taken at five different locations, and the average value was reported.

2.5. Tensile Strength Test

The tensile strength of the polymer electrolyte membranes was evaluated to determine their mechanical resistance under a gradually applied static load. The tensile strength was defined as the maximum stress sustained by the membrane before fracture.

2.6. Porosity Measurement

Good ionic conductivity and efficient charge–discharge performance in lithium-ion batteries strongly depend on the electrolyte wettability of the separator. An ideal separator should rapidly absorb the electrolyte and retain it throughout battery operation to maintain high ionic conductivity. The wettability of the separator is closely related to its material properties and porosity [14]. Membrane porosity plays an important role in facilitating ion transport within polymer electrolyte membranes. The porosity of the membranes was determined using the gravimetric method according to Equation 1.

$$Porosity\ (\varepsilon) = \frac{W_b - W_k}{A \times t \times d} \times 100\% \quad (1)$$

Where, W_b is the weight of the wet membrane (g), W_k is the weight of the dry membrane (g), A is the membrane surface area (cm^2), t is the membrane thickness (cm), and d is the density of the immersion liquid ($g\ cm^{-3}$) [4].

2.7. Cyclic Voltammetry (CV)

The electrochemical properties of the polymer electrolyte membranes were evaluated using CV. CV is a widely used electrochemical technique for investigating the electrochemical behavior of various materials, including battery separators and polymer electrolytes.

The resulting cyclic voltammograms provide valuable information on the charge-storage characteristics, ion-transport behavior, and electrochemical stability of the membranes, thereby enabling assessment of their suitability for battery applications [4].

2.8. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was employed to identify the functional groups present in the synthesized membranes and their constituent materials, thereby confirming successful membrane formation [20]. FTIR operates by measuring the absorption of infrared radiation corresponding to the vibrational modes of chemical bonds within the material. The positions and intensities of the absorption bands provide information on the molecular structure and interactions among membrane components. FTIR analysis was performed to verify the presence of characteristic functional groups and to evaluate intermolecular interactions resulting from membrane synthesis [4].

2.9. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

The surface morphology and microstructure of the polymer electrolyte membranes were characterized using SEM. In addition, EDX was conducted to determine the elemental composition and elemental distribution within the membranes. The combined SEM–EDX analysis provided comprehensive information regarding the morphological characteristics and chemical composition of the synthesized membranes.

2.10. Thermogravimetric Analysis (TGA)

The thermal stability of the polymer electrolyte membranes was evaluated using TGA to investigate their thermal decomposition behavior as a function of temperature. Thermal stability is an important parameter for ensuring the safe operation of lithium-ion batteries [5]. TGA measurements were performed over a temperature range of 25–600°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere [6].

3. Results and Discussion

3.1. Thickness Test

The thickness measurements of the polymer electrolyte membranes are presented in Table 1. The thickness measurements of the chitosan/PVA polymer electrolyte membranes modified with bentonite and LiOH revealed noticeable variations among the different membrane compositions. As shown in Table 1, the thickness values were 13.9, 17.4, 13.5, 13.7, and 14.6 µm for Variations 1–5, respectively. Among all samples, Variation 2 (30:70 chitosan:PVA) exhibited the greatest thickness, reaching 17.4 µm.

The increased thickness of Variation 2 can be attributed to the balanced chitosan/PVA composition, which likely produced a casting solution with higher viscosity due to enhanced interactions between the polymer matrix and the bentonite filler. The increased viscosity reduced the mobility of the casting solution during film formation, thereby limiting film thinning. Furthermore, the higher viscosity slowed solvent diffusion and evaporation, promoting the early formation of a surface skin layer that restrained further shrinkage during drying. The incorporation of bentonite, particularly its montmorillonite component, may also have contributed to solvent retention and increased the solid content of the casting solution, thereby minimizing dimensional contraction during solvent evaporation. The combined effects of increased viscosity, slower solvent evaporation, and higher solid content enabled the membrane to retain a greater final thickness than the other membrane compositions [21].

3.2. Tensile Strength

Tensile strength reflects the mechanical performance of the polymer electrolyte membrane. The tensile strength of the synthesized membranes is presented in Figure 2. Membrane variation 1 (chitosan/PVA 10/90%) exhibited the highest tensile strength (19.86 MPa), followed by Variation 2 (16.93 MPa), Variation 3 (14.08 MPa), Variation 4 (11.86 MPa), and Variation 5 (8.12 MPa). These results indicate that the chitosan/PVA composition strongly influences the mechanical properties of the membrane.

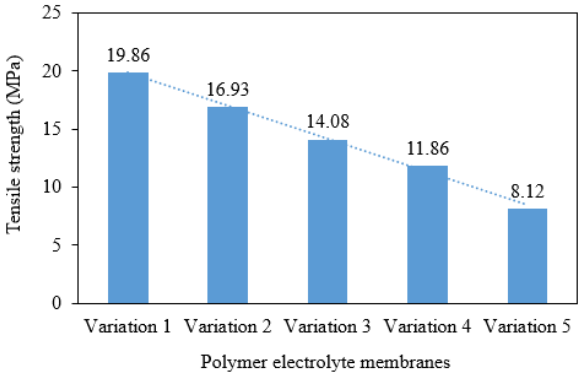
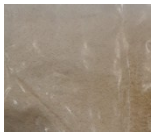
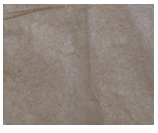


Figure 2. Tensile strength of the polymer electrolyte membranes

Table 1. Thickness of the synthesized polymer electrolyte membranes

Sample	Variation 1 (10:90)	Variation 2 (30:70)	Variation 3 (50:50)	Variation 4 (70:30)	Variation 5 (90:10)
Result					
Thickness (µm)	13.9	17.4	13.5	13.7	14.6

The superior tensile strength of Variation 1 can be attributed to the formation of a homogeneous polymer network resulting from effective intermolecular interactions among the $-NH_2$ and $-OH$ groups of chitosan, the hydroxyl groups of PVA, and the bentonite filler. PVA possesses excellent film-forming ability and flexibility, enabling the formation of a dense and continuous polymer matrix that effectively transfers applied stress throughout the membrane. Consequently, the membrane exhibits improved mechanical integrity and higher tensile strength [4].

The progressive decrease in tensile strength from Variation 1 to Variation 5 indicates a transition from a compatible polymer blend to a less compatible system as the chitosan content increased. At the optimum composition (Variation 1), strong hydrogen bonding between chitosan and PVA formed a compact, continuous network that distributed mechanical stress uniformly. Such structures are typically characterized by smooth, homogeneous, and defect-free surfaces, as observed in SEM micrographs. Previous studies have likewise reported that chitosan contents of approximately 15–30 wt.% provide optimum compatibility and maximum tensile strength due to enhanced intermolecular interactions [20].

In contrast, excessive chitosan incorporation adversely affects the membrane structure. Because chitosan is more rigid and less flexible than PVA, increasing its proportion disrupts the continuity of the PVA-rich matrix and promotes the formation of chitosan-rich domains, microvoids, and weak interfacial regions. Previous SEM studies have shown that higher chitosan contents produce rougher, more heterogeneous membrane surfaces, indicating phase separation and poor interfacial adhesion [21]. These structural defects act as stress concentration sites, hindering uniform stress distribution and making the membrane more susceptible to mechanical failure. Consequently, the tensile strength decreases with increasing chitosan content.

3.3. Porosity Test

The porosity of the polymer electrolyte membranes is strongly influenced by the membrane composition, particularly the chitosan-to-PVA ratio and the incorporation of bentonite and LiOH. The porosity results for the synthesized membranes are presented in Figure 3. The porosity measurements revealed considerable differences among the membrane compositions. Variation 1 exhibited a porosity of 19.46%, Variation 2 showed the highest porosity of 20.49%, followed by Variation 3 (11.40%) and Variation 4 (8.25%), whereas Variation 5 exhibited 0% porosity. Among all samples, Variation 2 produced the most porous membrane, indicating that this composition promoted the formation of a more interconnected porous structure capable of facilitating electrolyte uptake and ion transport.

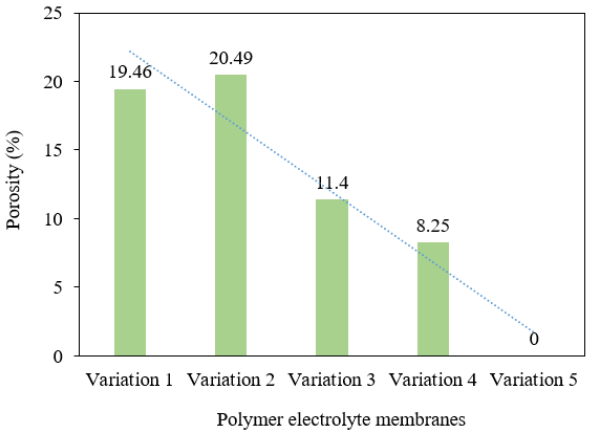


Figure 3. Porosity of the polymer electrolyte membranes

The superior porosity of Variation 2 can be attributed to the balanced chitosan/PVA ratio, which likely promoted better compatibility between the polymer matrix and the bentonite filler during membrane formation. This favorable interaction facilitated the development of a well-distributed pore network while preventing excessive pore collapse during solvent evaporation. In contrast, increasing the chitosan content beyond the optimum composition produced denser membrane structures with fewer interconnected pores. The higher rigidity of chitosan and the stronger intermolecular hydrogen-bonding interactions within the polymer matrix restricted pore formation, resulting in the marked reduction in porosity observed in Variations 3–5. The absence of measurable porosity in Variation 5 suggests that the membrane became highly compact, thereby limiting electrolyte penetration.

Overall, these findings demonstrate that the chitosan-to-PVA ratio plays a critical role in controlling membrane porosity. An appropriate pore structure is essential for achieving a balance between mechanical strength and electrochemical performance in polymer electrolyte membranes. Higher porosity generally enhances electrolyte uptake and facilitates lithium-ion transport by providing interconnected pathways for ion migration, thereby reducing internal resistance and improving battery performance [4].

3.4. Cyclic Voltammetry (CV)

The CV results for Variation 2 of the polymer electrolyte membrane are presented in Figure 4. Based on the three CV curves, the nearly rectangular, loop-shaped profiles without distinct redox peaks indicate that the electrochemical behavior of the membrane is predominantly governed by capacitive effects, specifically electric double-layer capacitance (EDLC), rather than by Faradaic redox reactions. This behavior is commonly observed in polymer-based materials and polymer electrolyte membranes.

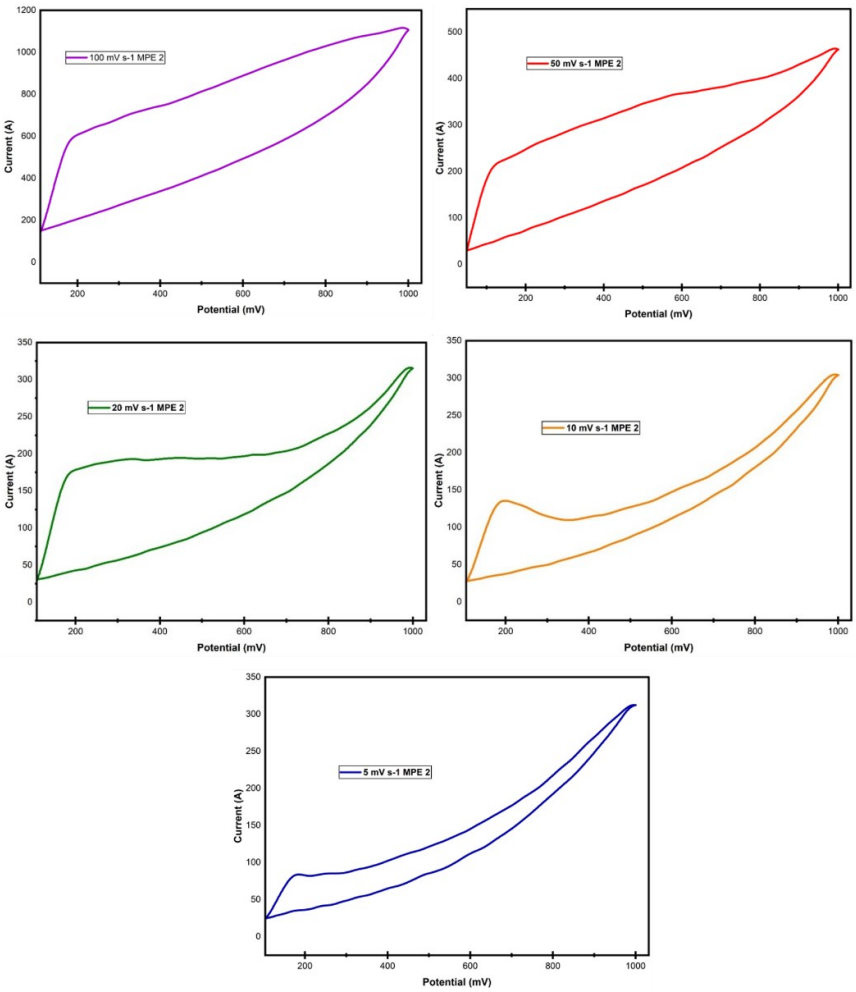


Figure 4. Cyclic voltammograms of polymer electrolyte membrane variation 2

As the scan rate increased from 20 to 50 and 100 mV s^{-1}, the current response increased significantly, indicating that the current is strongly dependent on the scan rate. In theory, this behavior is consistent with the Randles–Ševčík equation, in which the peak current increases with the square root of the scan rate in diffusion-controlled systems. However, in predominantly capacitive systems such as this membrane, the increase in current is more closely associated with greater charge accumulation in the electric double layer at higher scan rates.

Furthermore, the relatively unchanged shape of the CV curves at different scan rates indicates that the electrochemical mechanism remains stable despite changes in the scan rate. The slight difference between the forward and reverse scans (hysteresis) suggests the presence of internal resistance (IR drop) or partially irreversible charge-transfer kinetics, which are commonly observed in polymer-based materials or electrodes with limited conductivity. At the lower scan rate of 20 mV s^{-1}, ions have more time to diffuse and interact with the electrode surface, resulting in a response that is closer to equilibrium. In contrast, at the higher scan rate of 100 mV s^{-1}, ion diffusion becomes more limited, leading to an increased current response but a less uniform charge distribution, which may cause slight distortion of the CV curve.

Overall, these results indicate that the membrane exhibits predominantly capacitive behavior with contributions from internal resistance and charge-transfer kinetics. The electrochemical performance is strongly influenced by the scan rate, where increasing the scan rate increases the current response while also enhancing non-ideal effects within the system [22].

3.5. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR results of the polymer electrolyte membranes are presented in Figure 5, while the corresponding functional groups and absorption wavenumbers are summarized in Table 2. The FTIR spectra of the bentonite–chitosan–LiOH polymer electrolyte membranes (MPE 1 to MPE 5) indicate the presence of chemical and physical interactions among the membrane components, as evidenced by the positions and slight shifts of the characteristic absorption bands. The broad absorption band in the range of 3261–3266 cm^{-1}, corresponding to the O–H and N–H stretching vibrations, indicates the formation of hydrogen bonds between chitosan and PVA, as well as possible interactions with the hydroxyl groups of bentonite. The slight shifts observed among the membrane variations suggest changes in the strength of these hydrogen-bonding interactions resulting from differences in membrane composition.

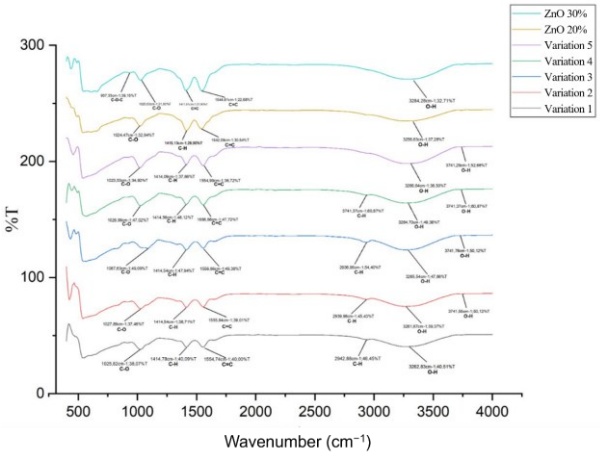


Figure 5. FTIR spectra of the polymer electrolyte membranes

Table 2. Functional groups and corresponding wavenumbers

Functional group	Wavenumber (cm^{-1})				
	MPE 1	MPE 2	MPE 3	MPE 4	MPE 5
O-H	3262	3261	3265	3264	3266
N-H	3262	3621	3265	3264	3266
Aliphatic C–H	2942	2939	2936	2941	2940
Amide II (C=O)	1554	1555	1556	1556	1554
$-CH_3$	1414	1414	1414	1414	1414
C-O	1025	1027	1045	1026	1023
Al-O	545	539	563	569	543
Si-O	545	539	563	569	543
Li-O	545	425	435	447	458

The absorption band at 2936–2942 cm^{-1} is attributed to the stretching vibration of aliphatic C–H groups and remains relatively unchanged across all membrane variations, indicating that the polymer backbone remains stable. The band at approximately 1554–1556 cm^{-1}, assigned to the amide II (C=O) vibration of chitosan, also shows only minor changes, suggesting that the chemical structure of chitosan is preserved while indicating possible interactions between the carbonyl groups and Li^+ ions through electron-pair coordination.

The absorption band at 1414 cm^{-1}, corresponding to the bending vibration of the $-CH_3$ group, remains constant for all membrane variations, indicating that the methyl groups are not significantly affected by changes in membrane composition. In the 1023–1045 cm^{-1} region, assigned to the C–O stretching vibration, a slight shift is observed, particularly for MPE 3 (1045 cm^{-1}), suggesting interactions between the hydroxyl groups of the polymer matrix and the silicate structure of bentonite.

The absorption bands at 539–569 cm^{-1}, attributed to Al–O and Si–O vibrations, confirm the presence of the bentonite mineral structure within the polymer matrix. In addition, the appearance and gradual shift of the Li–O absorption band in the 425–458 cm^{-1} region provide evidence for the successful incorporation of LiOH into the membrane. The variation in the Li–O band position among the membrane samples indicates differences in the interaction or coordination of Li^+ ions with oxygen-containing functional groups in the polymer matrix and bentonite.

Overall, the FTIR results confirm that no new functional groups were formed during membrane synthesis. However, intermolecular interactions, particularly hydrogen bonding and Li^+ ion coordination, occurred among chitosan, PVA, bentonite, and LiOH, contributing to differences in the structure and properties of the membranes with varying compositions.

3.6. Scanning Electron Microscopy/Energy Dispersive X-ray (SEM-EDX)

The surface morphology and elemental composition of Variation 2 of the polymer electrolyte membrane were analyzed using SEM–EDX. The SEM images are presented in Figure 6, while the elemental composition obtained from the EDX analysis is summarized in Table 3. The SEM–EDX analysis of the polymer electrolyte membrane (MPE) Variation 2 showed that carbon (33.99 at%) and oxygen (54.48 at%) were the dominant elements. This result is consistent with the chemical composition of the chitosan/PVA matrix, which contains abundant hydroxyl, amino, C–O, and C–O–C functional groups. The presence of calcium (10.40 at%) confirms the incorporation of Ca-montmorillonite bentonite, while sodium (0.47 at%) and silicon (0.27 at%) were detected in smaller amounts as constituents of the bentonite mineral. These findings indicate that the bentonite used in this study is predominantly the calcium type.

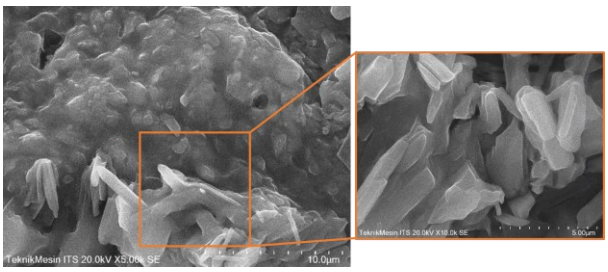


Figure 6. SEM images of polymer electrolyte membrane variation 2

Table 3. Elemental composition of MPE variation 2 obtained by EDX analysis

Element	Atomic (%)
C	33.99
O	54.48
Na	0.47
Li	0.22
Si	0.27
P	0.17
Ca	10:40

Ca-bentonite and Na-bentonite differ in their cation exchange characteristics, which can influence their performance as fillers in polymer electrolyte membranes. In Na-bentonite, the monovalent Na^+ ions are more easily hydrated, resulting in a more expanded interlayer structure that facilitates cation exchange and Li^+ migration. In contrast, Ca-montmorillonite contains divalent Ca^{2+} ions that produce stronger interlayer interactions and a more compact structure with lower swelling. As a result, Li^+ diffusion within Ca-bentonite is relatively more restricted, although the membrane benefits from improved mechanical stability and structural integrity. Therefore, while Na-bentonite is generally more favorable for applications requiring high ionic conductivity, Ca-bentonite offers better structural stability and may serve as an effective filler for improving membrane durability [23].

3.7. Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG)

The thermal stability of Variation 2 of the polymer electrolyte membrane was evaluated using TGA and DTG. The TGA and DTG curves are presented in Figure 7. Based on the TGA (blue curve) and DTG (red curve) results, the membrane exhibits a gradual mass loss with increasing temperature, indicating that thermal decomposition occurs in several stages. In the first stage, between approximately 30°C and 100°C, with a DTG peak at 66°C, the membrane undergoes a mass loss of approximately 12%. This initial weight loss is attributed to the evaporation of free and bound water within the membrane. The hydrophilic nature of PVA and the hygroscopic properties of LiOH promote moisture absorption, making this stage primarily a physical dehydration process rather than chemical degradation.

The second stage occurs in the temperature range of approximately 150–300°C, with a DTG peak at 253°C, where the membrane experiences a mass loss of about 15%. This stage corresponds to the onset of the thermal degradation of PVA, involving polymer chain scission and the elimination of –OH groups. This degradation may be accompanied by the formation of double bonds through an intramolecular dehydration mechanism, indicating the beginning of chemical decomposition of the polymer structure.

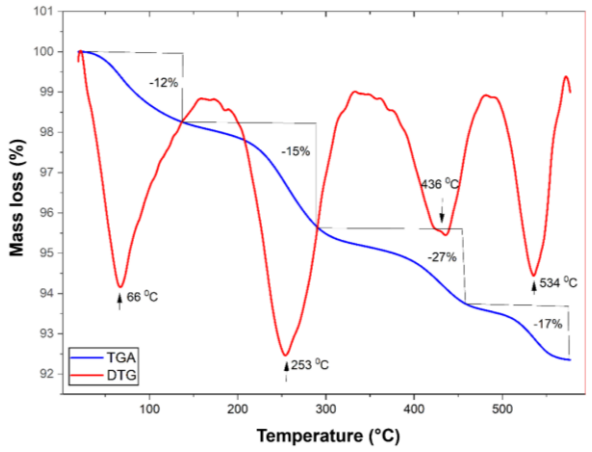


Figure 7. TGA and DTG results of MPE Variation 2

In the third stage, occurring between 350 and 450°C with a DTG peak at 436°C, a more pronounced mass loss of approximately 27% is observed. This stage is associated with further degradation of the polymer backbone and the formation of carbonaceous residues. The presence of LiOH may also influence the thermal stability and degradation mechanism of the membrane in this temperature range. The final stage occurs at approximately 500–550°C, with a DTG peak at 534°C, where an additional mass loss of about 17% is recorded. This stage corresponds to the decomposition of the carbonaceous residues formed during the previous stage. At these elevated temperatures, LiOH may also undergo transformation into other compounds, such as Li_2O, contributing to the observed weight loss.

Overall, the TGA and DTG results indicate that the polymer electrolyte membrane undergoes multi-step thermal degradation and exhibits relatively good thermal stability up to approximately 200°C. Above this temperature, significant degradation of the polymer structure occurs, indicating that this temperature represents an important operational limit for its application as a polymer electrolyte membrane [24, 25].

4. Conclusion

A chitosan/PVA–bentonite composite membrane doped with LiOH was successfully synthesized using the solvent casting method and demonstrated potential as a polymer electrolyte membrane for lithium-ion battery applications. Among the membrane variations, Variation 1 exhibited the highest tensile strength of 19.86 MPa, while Variation 2 showed the greatest thickness (17.4 µm) and the highest porosity (20.49%), indicating better potential for supporting ion transport. FTIR, SEM–EDX, CV, and TGA–DTG analyses confirmed the presence of intermolecular interactions among the membrane components, predominantly capacitive electrochemical behavior, and good thermal stability up to approximately 200°C, with the major degradation occurring between 350 and 550°C. Overall, the results demonstrate that the synthesized chitosan/PVA–bentonite membrane doped with LiOH is a promising, environmentally friendly polymer electrolyte membrane for lithium-ion battery applications.

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