Preparation and Characterization of Biopolymer Electrolyte Membranes Based on LiClO$_4$-complexed Methyl Cellulose as Lithium-ion Battery Separator

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Highlights:
- utilization of lithium-ion batteries for energy storage;
- biopolymer electrolyte providing the ability to replace synthetic polymer electrolyte;
- mechanical and thermal properties of MC-based biopolymer electrolyte are sufficient to meet the requirements of lithium-ion batteries separator.

Abstract. The polymer electrolyte membrane is a main component of lithium-ion batteries (LiBs), serving as separator and electrolyte. In this work, we prepared biopolymer electrolyte (BPE) membranes of lithium perchlorate (LiClO$_4$)-complexed methyl cellulose (MC). Methyl cellulose (MC), a cellulose derivative, has attractive properties for use as biopolymer electrolyte. The bulkier anion size of lithium salt (LiClO$_4$) significantly enhances the performance of biopolymer electrolyte (BPE) membranes. The fabricated biopolymer electrolyte (BPE) membranes were characterized by FTIR, EIS, tensile tester, XRD, SEM and TGA. Biopolymer electrolyte membranes with various weight percentages of LiClO$_4$ salt (0%, 5%, 10%, 15%, and 20%) were prepared using a simple solution casting technique. Incorporation of 10% weight of LiClO$_4$ into the MC-based host polymer was selected as optimum condition, because this yielded good conductivity ($3.66 \times 10^{-5}$ S cm$^{-1}$), good mechanical properties (tensile strength 35.97 MPa and elongation at break 14.47%), good thermal stability (208.4 to 338.2 °C) as well as ease of preparation and low cost of production. Based on its characteristics it can be stated that the 10% LiClO$_4$-complexed MC membrane meets the requirements as a candidate separator for lithium-ion battery application.

Keywords: biopolymer electrolyte; lithium-ion batteries; methyl cellulose; lithium perchlorate; separator.

1 Introduction

Fossil fuels as the main energy source are limited in their amount and in their application due to their impact on the environment, such as the increase of
pollution and global warming caused by emissions from burning fossil fuels, leading to the greenhouse effect [1-3]. To find ways to convert to alternative energy sources, studies on electrochemical conversion and storage devices such as fuel cells, redox flow, alkaline ion batteries have been conducted. Lithium-ion batteries (LIBs) are very attractive as energy storage devices when replacing fossil fuels as energy source. For the two last decades, LIB technology has been applied to fields such as communication technology (for example in smartphones, tablets, digital cameras), information technology (for example in laptop computers) and transportation (for example in electric vehicles) [1,4-5]. It is predicted that global LiB consumption will reach $56 billion in 2024 the compound annual growth rate (CAGR) will reach 10.6% from 2016 to 2024 [6].

<table>
<thead>
<tr>
<th>Table 1 Minimum requirements of polymer-electrolyte membranes for Li-ion application [7].</th>
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<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Ionic conductivity</td>
</tr>
<tr>
<td>Tensile strength</td>
</tr>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Thermal stability</td>
</tr>
</tbody>
</table>

LIBs have excellent properties such as a long life cycle, high energy density, and rechargeability [7]. The polymer electrolyte membrane, as separator, is one of the main components of LIBs. It consists of salt-doped macromolecules conducting ions to significantly increase the conductivity [8-9]. However, the application of solid polymer electrolytes (SPEs), as both LIB separator and electrolyte to replace liquid electrolytes and organic solvents, still has drawbacks, especially their low ionic conductivity, resulting in low performance [10-11]. The minimum requirements of polymer-electrolyte membranes for LiB applications can be seen in Table 1. Some commercial synthetic polymers that have been developed as host polymers, polyethylene (PE), polypropylene (PP) [12] and polyvinylidene fluoride (PVDF) [13], introduce environmental problems, because they are not decomposable in nature, are difficult to prepare and their cost of production is high. Examples are: polymethyl methacrylate (PMMA) [14], polyacrylonitrile (PAN) [15] and polyethylene oxide (PEO) [16].

In trying to overcome these problems some researchers have used natural polymer sources as polymer electrolyte membrane material, such as starch, cellulose, carrageenan, chitosan, pectin, chitin, lignocellulose, agarose, etc., also known as biopolymer electrolytes [17-22]. Biopolymer electrolytes meet the main requirements of an LIB separator, such as high ionic conductivity, low cost, excellent dimensional properties, and good mechanical properties [23]. Different approaches to produce good polymer electrolyte membranes have been...
investigated, among others: using dopants, plasticizers [24-25], polymer blending [26], or cross-linking [27]. Several researches worked with biopolymer electrolytes such as carrageenan-based [17, 28] cellulose acetate-based [23], chitosan-based [24, 19-22], cellulose-based [29] electrolytes.

Cellulose is the most abundant biopolymer in nature [30] and can easily be modified into its derivatives [31-33]. Cellulose derivatives are very promising biopolymer electrolyte membrane candidates because they have good properties, such as transparency, flexibility and resistance to oil and fat [34]. The advantages of good mechanical properties and thermal stability can replace commercial synthetic materials that have been used previously [29]. Methyl cellulose (MC) is an important cellulose ether [26] besides ethyl cellulose [12], carboxymethyl cellulose (CMC) [4,18] and hydroxyethyl cellulose (HEC) [16].

Methyl cellulose consists of β-(1,4)-glucosidic bonding with methyl substituents in linear chains [35] and has polar groups at the oxygen atoms that function as lone pair electron donors [36]. MC is widely used for various applications in the pharmaceutical, food, agricultural, construction, paint, ceramics, detergent, adhesives, and cosmetics industries among others, due to its excellent properties [26]. Appealing characteristics are biodegradability, non-toxicness, [12,37-40], good mechanical properties [41], ease of film forming [42], and good thermal stability [43].

Because of its appealing properties, MC is promising to be developed into a host polymer as a matrix for biopolymer electrolyte membranes [44-45]. Some works used MC as a host polymer and/or blend/composite agent, for example MC-NH$_4$NO$_3$-PEG for fuel cell application [36], sulfonated poly(ether ether ketone) with methyl cellulose (SPEEEK-MC) for proton exchange membrane [46], methyl cellulose/keratin hydrolysate composite membranes for composite membranes [31] and PE/MC blend microporous membranes as separator in lithium-ion batteries [47].

For lithium-ion batteries, the ionic conductivity of the biopolymer electrolyte membrane is a crucial aspect in order to have high energy density. In liquid systems there is no problem, but there are issues with solid polymers. The ionic conductivity contains contributions from both anions and cations, so ionic conductivity is mostly caused by the mobility of Li$^+$ cations. Thus, lithium salts have also been considered. This is often achieved by choosing anions that easily dissociate from Li$^+$ ions [48].

Lithium salts with low lattice energy are preferred because they have a larger dissociation degree, thus facilitating the transport of Li$^+$ ions [24]. The selection of large (bulky) anions, such as CF$_3$SO$_3^-$ (triflate ions) [49], PF$_6^-$
Biopolymer Electrolyte Membranes Based on LiClO$_4$ has been widely reported to increase ionic conductivity [52]. In this work, we analyzed the effects of the incorporation of LiClO$_4$ salt, which has branched anions, to a commercial MC as the host polymer. LiClO$_4$ has low crystal lattice energy compared to other lithium salts. The total lattice potential energies of LiClO$_4$, $U_{\text{POT}}$ and $U_{\text{POT}}^{\text{BFHC}}$, are 709 and 715 kJ/mol [53]. Its smaller dissociation energy was also a reason to select LiClO$_4$ salt [54].

Study of the incorporation of LiClO$_4$ into MC as host polymer has never been reported previously. An LiClO$_4$-complexed MC biopolymer electrolyte membrane is considered a good matrix as lithium-ion batteries separator. The fabricated biopolymer electrolyte membranes were characterized by FTIR, EIS, tensile tester, XRD, SEM and TGA. The optimum condition was obtained by considering the ionic conductivity and mechanical properties.

2 Experiment

2.1 Materials and Methods

All materials and solvents were used without further purification. They were: methyl cellulose (Sigma- Aldrich, DS = 1.5-1.9), lithium perchlorate (LiClO$_4$) (Sigma-Aldrich, 99%), and distilled water (Merck, 99%).

![Schematic representation of biopolymer electrolyte (BPE) membrane based on LiClO4-complexed MC preparation.](image)

Biopolymer electrolyte (BPE) membranes of LiClO$_4$-complexed MC were prepared using the solution casting technique as shown in Figure 1. One gram of various MC and LiClO$_4$ salt mixtures was dissolved and stirred in 30 mL distilled
water for 24 h to obtain a homogenous blend. The solution was then cast onto a flat glass surface, evaporated at ambient temperature for 3 to 4 days, continued by storing in a desiccator for 3 to 4 days. Biopolymer electrolyte membranes LiClO$_4$-complexed MC were successfully prepared with LiClO$_4$ salt variation at 0%, 5%, 10%, 15%, and 20% (w/w). All the fabricated biopolymer membranes were not over the maximum standard of the lithium-ion battery separator thickness, i.e. ≤ 25 μm. They were controlled to have the same thickness of 10 μm.

2.2 Characterizations

Biopolymer electrolyte (BPE) membranes of LiClO$_4$-complexed MC were characterized with FTIR (Prestige 21 Shimadzu), electrochemical impedance spectroscopy (EIS, Agilent, type E490A, precision LCR), tensile tester (FAVIGRAPH), diffractometer XRD (Rigasu Smart Lab), scanning electron microscopy (SEM) (Type JEOL-JSM-6510LV), and thermogravimetry analysis (TGA, Linseis, type STA PT 1600) to study infra-red (IR), ionic conductivity, mechanical properties, crystallinities, cross-section morphology and thermal stability, respectively.

2.3 Ionic Conductivity, Tensile Strength and Young’s Modulus Calculation

The ionic conductivity was calculated using Eq. (1) as follow:

\[
\sigma = \frac{l}{R \times A}
\]  

(1)

where \( \sigma \) = ionic conductivity (S cm$^{-1}$); \( l \) = electrode distance (1.5 cm); \( R \) = total resistance (ohm); \( A \) = area (width of electrodes x thickness of membrane = 0.4 cm x thickness).

The tensile strength was calculated by using Eq. (2) as follow:

\[
\text{tensile strength} = \frac{F}{A} = \frac{m \times g}{t \times w}
\]  

(2)

where \( F \) = force (N), \( A \) = unit area (m$^2$), \( m \) = load mass (kg), \( g \) = gravitation force (9.8 kg/m$^2$); \( t \) = thickness of membrane (m); \( w \) = width of membrane (m).

Young’s modulus was calculated by using Eq. (3) as follow:

\[
E = \frac{\text{stress} (\sigma)}{\text{strain} (\varepsilon)}
\]  

(3)

where \( E \) = Young’s modulus (MPa); \( \sigma \) = stress (MPa); \( \varepsilon \) = strain (%).
3 Results and Discussion

3.1 IR Analysis of Biopolymer Electrolyte Membranes Based on LiClO$_4$-complexed MC

The complexation and interaction of polymer-salt in biopolymer electrolyte (BPE) membranes of LiClO$_4$-complexed MC were studied by several wavenumber shifts and vibration modes described by the IR spectra. Figure 2 shows the absorption wavenumber shifts of important groups of the BPE membranes. The LiClO$_4$ displayed some main peaks, i.e. O-H stretching from crystal water at 3431 cm$^{-1}$, the typical peak of LiClO$_4$ at 1635 cm$^{-1}$, and the stretching mode of the ClO$_4^-$ ion at 1085 cm$^{-1}$ [48].

Pure methyl cellulose (MC), as reference, has some important absorption groups, such as O-H stretching, C-H stretching, CH$_3$, C-C ring stretching, C-O-C stretching, and OCH$_3$ at 3450.65; 2933.72; 2837.28; 1654.92; 1070.49 and 947.04 cm$^{-1}$, respectively. These bands are similar to those from a previous report [29]. However, the LiClO$_4$-complexed MC biopolymer electrolyte membrane showed no significant wavenumber shift compared to pure MC as reference. No change in wavenumbers means that no strong interaction between MC and LiClO$_4$ occurred.

Figure 2 IR spectra of (a) pure MC and $x$LiClO$_4$-complexed MC, $x$: (b) 5%, (c) 10%, (d) 15%, (e) 20%.
3.2 Ionic Conductivity of Biopolymer Electrolyte Membranes Based on LiClO$_4$-complexed MC

The motion of the polymer backbone is influenced by the glass transition temperature ($T_g$) of the system, free volume availability, salt concentration, fillers and plasticizers, which affect the free volume of the polymer [48]. The ionic conductivity of the biopolymer electrolyte membranes of the LiClO$_4$-complexed MC are depicted in Table 2, showing an increase of ionic conductivity as the concentration of LiClO$_4$ salt increased. In this work, the ionic conductivity was mainly affected by the LiClO$_4$ salt concentration. The highest ionic conductivity was obtained for the BPE membrane with 20% LiClO$_4$ salt.

<table>
<thead>
<tr>
<th>Biopolymer electrolyte membranes</th>
<th>Ionic Conductivity, $\sigma$, (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure MC</td>
<td>1.36 x 10$^{-5}$</td>
</tr>
<tr>
<td>5% LiClO$_4$-complexed MC</td>
<td>1.66 x 10$^{-5}$</td>
</tr>
<tr>
<td>10% LiClO$_4$-complexed MC</td>
<td>3.66 x 10$^{-5}$</td>
</tr>
<tr>
<td>15% LiClO$_4$-complexed MC</td>
<td>7.57 x 10$^{-5}$</td>
</tr>
<tr>
<td>20% LiClO$_4$-complexed MC</td>
<td>3.94 x 10$^{-5}$</td>
</tr>
</tbody>
</table>

The five variations of LiClO$_4$ incorporation (0, 5, 10, 15, 20%) released 1.36 x 10$^{-5}$; 1.66 x 10$^{-5}$; 3.66 x 10$^{-5}$; 7.57 x 10$^{-5}$ and 3.94 x 10$^{-5}$ S cm$^{-1}$, indicating that the Li-ion conductivities were of the order -5 after LiClO$_4$ incorporation, which is a good ionic conductivity for biopolymer electrolytes. Based on the data, it can be seen that at 20% of LiClO$_4$ incorporation, the ionic conductivity decreased due to ion-pair formation causing ion aggregation. However, the pure MC membrane in this work exhibited better ionic conductivity than in a previous report [36], i.e. 3.08 x 10$^{-11}$ S cm$^{-1}$. After a while, the LiClO$_4$-complexed MC showed sufficient ionic conductivity, proving it to be a better matrix compared to the others. The results were better than for biopolymer electrolyte membranes based on PMMA-LiClO$_4$-DMP-CeO$_2$ (7.3 x 10$^{-6}$ S cm$^{-1}$) [55], MC-NH$_4$NO$_3$ (2.10 x 10$^{-6}$ S cm$^{-1}$) [36] and also PVA-NH$_4$CH$_3$COO (1.1 x 10$^{-6}$ S cm$^{-1}$) [56] without plasticizer. Improvement of ionic conductivity has been carried by utilization of plasticizers [36] and ionic liquids [43, 50].

In Figure 3, a Nyquist plot, the decrease of impedance indicates that the ionic conductivity increased. LiClO$_4$-complexed MC had a low impedance value ($Z$) compared to pure MC. The existence of LiClO$_4$ shortened the $Z'$ axis, which means a decrease of the cross-section resistance of the membrane. The Bode plot in Figure 4 explains that the ion diffusion mechanism in the membrane was confirmed by the presence of Warburg impedance, which forms at 45° [57]. A
The ions are proposed to move by either the segmental motion of the backbone or a hopping mechanism where lithium ions ‘jump’ from one transit site to vacant neighboring ones [58]. In Figure 5 it can be seen that the Li⁺ cations coordinate with polar sites of the MC and/or cellulose (atom O), while the ClO₄⁻ anions interact with the methyl group (-H/CH₃). The consequence of this complexity is the disruption of the strongest supramolecular hydrogen bonds between the
cellulose and methyl cellulose/cellulose polymer chains, thus causing diffusion of Li\(^+\) ions between AGUs (as discussed in detail below).

Figure 5 shows a proposed mechanism of inter-hydro-glucose (AGU) Li\(^+\)-ion hopping due to the incorporation of LiClO\(_4\) salt into the host polymer of the MC matrix. The polar sites of the MC and/or cellulose interacting with Li\(^+\) cations, especially on O-6, are more likely disrupted compared to O-2 and O-3, which are more affected by the AGU steric rings. The LiClO\(_4\) salt concentration increases the coordination between Li\(^+\) and O ions (MC and/or cellulose).

![Figure 5](image)

**Figure 5** Proposed mechanism of MC-LiClO\(_4\) complex and hopping Li\(^+\) ions: the curved red (\(\rightarrow\)) arrows depict the possibility of Li\(^+\) ions hopping through the MC backbone, while the broken lines (\(-\rightarrow\)) represent ion–dipole interactions between the Li\(^+\) ions as well as ClO\(_4^-\) ions and the polar functional groups of the MC structure.

Meanwhile, the ClO\(_4^-\) anions coordinate with –H atoms and/or -CH\(_3\) groups from MC and/or cellulose, resulting in a weaker hydrogen bond between the MC and/or cellulose polymer chains. This condition is adapted from a previous work [28]. The weakness of the hydrogen bond affects the decreasing degree of crystallinity of the MC so that the diffusion of Li\(^-\) ions is made easier. This
Biopolymer Electrolyte Membranes Based on LiClO$_4$

The phenomenon is similar to cellulose and its derivative dissolution process [59]. The segmental motion of methyl cellulose also affects the Li$^+$-ion inter-chain distribution. The segmental motion increases the effect of decreasing rigidity or increasing elastic mechanical properties. This explanation relates to the increase of amorphous regions of methyl cellulose incorporating LiClO$_4$ into the matrix.

### 3.3 Mechanical Properties of Biopolymer Electrolyte Membranes Based on LiClO$_4$-complexed MC

The mechanical properties are important parameters to find the best condition for the polymer electrolytes. The mechanical strength of the LiClO$_4$-complexed MC biopolymer electrolyte membranes was measured with a Favigraph tensile tester with the following settings: load cell = 100 cN and test speed = 10 mm/min.

Table 3 shows that LiClO$_4$ incorporation decreased the tensile strength and tended to increase the elongation at break, which means that the membranes became more flexible [60]. The elongation at break pattern contrasts with the tensile strength. A lower tensile strength results in a higher elongation at break percentage [19]. The interesting mechanical properties of BPE membranes of MC are because it has good tensile strength, so that it meets the mechanical requirements for Li-ion battery application (~30 MPa) [7]. The tensile strength produced was sufficient according to the lithium-ion battery separator standard. The tensile strength of LiClO$_4$-complexed MC for all LiClO$_4$ variations was better than that of biopolymer electrolyte based on MC/keratin (27.8 MPa) [60].

The lowest tensile strength of 20% LiClO$_4$-complexed MC still meets the minimum LIB separator standard. The decrease in tensile strength after LiClO$_4$ incorporation indicates that LiClO$_4$ can deconstruct the power of hydrogen bonding supramolecular of methyl cellulose. This condition was further explained in crystallinity studies of LiClO$_4$-complexed MC biopolymer electrolyte membranes [60]. To understand the elastic and flexible plastic properties of the LiClO$_4$-complexed MC biopolymer electrolyte, analysis of the Young modulus was conducted. Young’s modulus can explain stiffness or rigidity: a high modulus means high rigidity. However, a high Young modulus is different from resistance to breaking [61].

In Table 3 we can see a trend in Young’s modulus that describes the relationship between stress and strain. The elastic properties commonly indicate that when the stress increases, the strain decreases and vice versa. Figure 6 shows that LiClO$_4$ incorporation from 0 to 10% (w/w) exhibited elastic properties, but above this trend the Young modulus decreased with increasing elongation. The phenomenon of stress and strain increasing simultaneously is called the elastic property. Liao [62] reported that highly mobile polymer chain segments, in turn, make the
toughness increase. Based on this explanation, both pure MC and LiClO$_4$-complexed MC biopolymer electrolyte have microcrystalline polymer characteristics, a combination of flexibility and dimensional stability [61].

**Table 3** Tensile Strength, Elongation at Break and Young Modulus of LiClO$_4$-complexed MC biopolymer Electrolyte Membranes

<table>
<thead>
<tr>
<th>Biopolymer electrolyte membranes</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Young’s Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure MC</td>
<td>54.08</td>
<td>8.06</td>
<td>490.41</td>
</tr>
<tr>
<td>MC-5% LiClO$_4$</td>
<td>38.73</td>
<td>8.9</td>
<td>323.00</td>
</tr>
<tr>
<td>MC-10% LiClO$_4$</td>
<td>35.97</td>
<td>14.47</td>
<td>159.16</td>
</tr>
<tr>
<td>MC-15% LiClO$_4$</td>
<td>34.97</td>
<td>30.87</td>
<td>60.95</td>
</tr>
<tr>
<td>MC-20% LiClO$_4$</td>
<td>31.73</td>
<td>24.75</td>
<td>84.47</td>
</tr>
</tbody>
</table>

**Figure 6** Tensile strength, elongation at break (%), Young’s modulus at various weight percentages of LiClO$_4$ (w/w).

These properties are desirable for forming and applying an elastic film (biopolymer electrolyte membranes) compared to elastomer properties that have dimensional instability and are able to bounce back. In this work, determining the optimum conditions was conducted by considering ionic conductivity, mechanical properties, and cost of production of the BPE membranes with MC-LiClO$_4$. The 10% LiClO$_4$-complexed methyl cellulose is considered the best material due to its good ionic conductivity of 3.66 x 10$^{-5}$ S cm$^{-1}$ with outstanding mechanical properties (35.97 MPa stress, 14.47% elongation) and low cost of production. Although the incorporation of 15 and 20% LiClO$_4$-complexed MC showed the best ionic conductivity, a higher concentration of LiClO$_4$ increases the cost of production.
3.4 Crystallinities of Biopolymer Electrolyte Membranes Based on LiClO₄-Complexed MC

Methyl cellulose has some diffraction peaks at ~7.8°; 13.4°; 20° and 21° correlated to Miller indices (001), (100), (012), (102) [20]. Meanwhile, according to Quiroz, methyl cellulose-based films gave an amorphous-crystalline structure, especially at high intensity (2θ = 8°), which is the crystalline structure of a trimethyl glucose repeating unit [63,64]. Viera et al. state that 2θ = 8° indicates an increase in interplanar distance compared to native cellulose [65,66]. Meanwhile, a broad peak around 2θ = 21.5° [63] represents the van der Waals force [67]. A weak peak around 12.64° indicates a more hydrated structure, which disappears in the MC powder [68]. As is well known, the structure of a microcrystalline polymer generally consists of crystalline and amorphous regions [61]. Intermolecular hydrogen bonding is the most dominant in facilitating MC microcrystalline properties.

![Diffractogram of biopolymer electrolyte (BPE) membranes: (a) pure MC; (b) 10% LiClO₄-complexed MC; (c) 15% LiClO₄-complexed MC and (d) 20% LiClO₄-complexed MC.](image)

Figure 7 shows both pure MC and LiClO₄-complexed MC diffractograms of MC-10% LiClO₄, MC-15% LiClO₄ and MC-20% LiClO₄. All patterns show Miller indices but with different intensity and a small 2θ angle. The presence of LiClO₄ weakens inter- and intramolecular hydrogen bonds, which were detected by the decreased intensity of the main peaks. The decrease of peak intensity correlates
to an increase of the amorphous regions and the decrease of crystallinity by doping salt incorporation [69].

Hodge et al. [69] interpreted a correlation between the intensity of the peak and the degree of crystallinity. The decrease of crystallinity contributes to Li-ion migration and segmental motion of the polymer chain (methyl cellulose in this case), improving the ionic conductivity, as explained by Hongting et al. [70]. This crystallinity study explained that the presence of LiClO$_4$ salt compromised the production of advantageous properties such as toughness and ionic conductivity. However, with more LiClO$_4$ incorporation (more than 15% LiClO$_4$), recrystallization will occur, causing the ionic conductivity to decrease, as shown in Table 2.

3.5 Morphology of Biopolymer Electrolyte Membranes Based on LiClO$_4$-complexed MC

LiClO$_4$ salt incorporation in the host polymer of pure MC causes an increase in the number of pores. The surface morphologies of pure MC membrane and 10% LiClO$_4$-complexed MC are shown in Figure 8. From Figure 8 a significant difference between both samples can be seen. The 10% LiClO$_4$-complexed MC has a sparse cross-section morphology, while pure MC has a dense and smooth cross-section morphology. If it is correlated to the decrease of the crystallinity index, the LiClO$_4$-complexed MC has more pores than pure MC, facilitating ion migration.

![Figure 8](image)

**Figure 8** Cross-section morphology images of (a) pure MC; (b) 10% LiClO$_4$-complexed MC.

The existence of more pores and a rougher surface improves the ionic conductivity caused by the increase of amorphous regions [71]. The bulky size of the ClO$_4^-$ anion of salt is responsible for creating sparse Li-ion diffusion, thus
exhibiting high ionic conductivity. Intermolecular hydrogen bonding is the most dominant, giving the MC microcrystalline properties.

### 3.6 Thermal Properties of Biopolymer Electrolyte Membranes Based on LiClO$_4$-complexed MC

The thermal decomposition of pure MC and 10% LiClO$_4$-complexed MC biopolymer electrolytes was studied by thermogravimetry analysis (TGA), as shown in Figure 9. There are several stages in MC degradation, i.e. humidity of water and small molecule removal until reaching stability at 153.41 °C. The MC starts to decompose at 297.3 °C until reaching stability at 381.9 °C. A decrease of the onset degradation temperature happens as a consequence of LiClO$_4$ incorporation into the MC membrane. The 10% LiClO$_4$-complexed MC biopolymer electrolyte showed a lower decomposition temperature than the pure MC biopolymer, although it is still sufficient for normal lithium-ion battery application [48].

![Thermogram of biopolymer electrolyte membranes: (a) pure MC and (b) 10% LiClO$_4$-complexed MC.](image)

Figure 9 shows the removal of humidity happened until reaching stability at 82.73 °C. The presence of moisture is necessary for the polymer electrolyte to distribute Li$^+$-ions easier through the interchain polymer. The 10% LiClO$_4$-complexed MC started to decompose at 208.4 °C and the offset decomposition temperature was 338.2 °C. Similar to the crystallinity study, the presence of LiClO$_4$ can deconstruct and disturb the inter-chain interaction of methyl cellulose, contributing to the increase of amorphous regions, which facilitates the moving
of Li-ions. A summary comparison of the thermal stability of pure MC and 10% LiClO$_4$-complexed MC can be seen in Table 4.

<table>
<thead>
<tr>
<th>Bio-polymer electrolyte membranes</th>
<th>Initial thermal decomposition (°C)</th>
<th>Final thermal decomposition (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure MC</td>
<td>297.3</td>
<td>381.9</td>
</tr>
<tr>
<td>10% LiClO$_4$-complexed MC</td>
<td>208.4</td>
<td>338.2</td>
</tr>
</tbody>
</table>

From this explanation it can be concluded that a decrease in crystallinity can affect the thermal stability of polymer electrolyte membranes as a consequence of LiClO$_4$ incorporation. This explanation is also supported by a previous report [72], which states that unstable anions are also able to decrease the thermal stability of polymer electrolytes. This has the benefit of producing appealing properties that are needed in LIBs, both as separator and as solid electrolyte. Although a decrease in thermal stability was observed, this value was still sufficient for LIB application (≥ 150 °C) [7].

Figure 10 shows DTA thermograms of the biopolymer electrolyte membranes, both with pure MC and 10% LiClO$_4$-complexed MC. The water desorption and small molecules are indicated by the endothermic peak of pure MC and 10% LiClO$_4$-complexed MC, i.e. 53.60 °C, 204.14 °C, and 44.82 °C, 109.36 °C, respectively. The endothermic peak of 10% LiClO$_4$-complexed MC was smaller than that of pure MC. The presence of LiClO$_4$ in the membranes can remove water from the matrix and maintain a small amount of humidity. This result is similar to the previous report [67].

A significant difference between the pure MC and the 10% LiClO$_4$-complexed MC is clearly indicated by the endothermic peak, which indicates decomposition of the membrane. The sharp endothermic point of the pure MC at 336.56 °C is higher than that of the 10% LiClO$_4$-complexed MC at 324.42 °C, indicating that the pure MC was more crystalline than the LiClO$_4$-complexed MC. This confirms that the presence of LiClO$_4$ can decrease the intermolecular hydrogen bonding of MC polymers, improving the properties of biopolymer electrolyte membranes [69]. It is interesting to look at the thermal analysis of the membranes. The MC-based biopolymer electrolyte membranes have better thermal properties than commercial polyolefin-based polymer electrolytes such as polyethylene, which decomposes at 130 °C, and polypropylene, which decomposes at 170 °C [16].
The maximum decomposition temperature of the membranes was detected by differential thermal gravimetry (DTG). In Figure 11 it can be seen that the maximum decomposition temperature of pure MC was higher than that of the 10% LiClO₄-complexed MC. The maximum decomposition temperature of pure MC occurred 354.73 °C, while for the 10% LiClO₄-complexed MC it occurred at 299.4 °C.

The maximum decomposition at this point is attributed to depolymerization of the main component of the membranes, i.e. the cellulose derivative chain. Usually, after this point the decomposition rate decreases until a stable condition.
is reached in which carbon residues and inorganic compounds such as LiClO₄ salt remain [73].

4 Conclusion

Biopolymer electrolyte (BPE) membranes based on methyl cellulose were successfully fabricated using a simple solution casting technique, with incorporation of various weight percentages of LiClO₄, i.e. 0, 5, 10, 15 and 20% (w/w). No significant wavenumber shifts caused by LiClO₄ salt coordination to the methyl cellulose host polymer were observed in the IR spectra. The optimum condition of 10% (w/w) LiClO₄-complexed methyl cellulose exhibited an ionic conductivity of 3.66 x 10⁻⁵ S cm⁻¹, a good tensile strength of 35.97 MPa and thermal stability in the range of 208.4 to 338.2 °C. The SEM images showed a large space in the cross-section of LiClO₄ incorporation into the MC, which confirms the increase in amorphous regions. These results meet the minimum standard for Li-ion batteries both as separator and as solid electrolyte. However, its ionic conductivity and other properties need to be enhanced by using plasticizer or ionic liquid.

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