Improvement of ionic conductivity of titanium dioxide incorporated PVDF-HFP/cellulose acetate electrolyte membrane

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Abstract. This work aims to improve the lithium ion conductivity by incorporating titanium dioxide (TiO$_2$) in Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) and Cellulose acetate (CA) electrolyte membrane. The morphology of the prepared membrane was observed using Scanning Electron Microscope (SEM) and the ability of the membrane to uptake liquid electrolyte was also tested. The SEM results show that the electrolyte membrane has porous, interconnected network but the addition of TiO$_2$ resulted in a reduction in porosity. Despite reduced porosity, the electrolyte uptake of PVDF-HFP+CA+TiO$_2$ is the highest among others with value up to 287.5%, this increase is due to the improvement in the amorphous phase. The ionic conductivity increases by 21.29% compared to PVDF-HFP electrolyte membrane with the addition of TiO$_2$. The generation of more mobile lithium ion and prevention of crystallization of polymer through Lewis acid-base reaction leads to improvement in ionic conductivity.

1. Introduction
Considering the remarkable energy density, lightweight and long cycle life of Lithium-ion batteries (LIB)[1], they had gained an unprecedented significance in both scientific and industrial field. Since the employment of LIB as the power sources in electronic devices such portable telecommunication devices and also hybrid electric vehicles rapidly accelerating, the desire for superior quality batteries in term of performance and longevity has been increased.

The separator is the crucial aspect of the battery that always has been overlooked. Gel polymer electrolyte (GPE) could resolve some fundamental issues associated with the volatile organic liquid electrolyte such as fire or explosion due to short circuit and overheated of batteries[2]. GPE reported has better ionic conductivity compared to the solid-state electrolyte at the same time possess better safety features than the liquid electrolyte. GPE entraps the electrolyte molecules in their pores to avoid leakage while aiding the mobility of ions. It was generally agreed that the amorphous regions are mainly involved in ionic conduction rather than the crystalline region. Liquid electrolyte with suitable plasticizer used to form GPE will increase the size and number of the amorphous region due to adsorption which eventually will form a percolative pathway of connected amorphous regions for fast ionic conduction[3].

Recently, PVDF-HFP has drawn huge attention as a promising material for GPE because it has lesser crystallinity compared PVDF, thanks to the amorphous hexafluoropropylene (HFP) monomers. PVDF-
HFP has high dielectric constant ($\varepsilon = 8.4$), facilitating a higher concentration of charge carriers [4] and strong electron withdrawing group (C-F) which lead to wider electrochemical stability[5]. The crystalline VdF units give the mechanical integrity to the PVDF-HFP electrolyte while the amorphous region entraps the liquid electrolyte, allocate more free volume for mobile cations. Blending or incorporation of other additives such as nanoparticles and other polymers into PVDF-HFP to further improve ionic conductivity is a common practice in the fabrication of polymer electrolyte. As stated in table 1, core-shell structured SiO$_2$(Li$^+$) powder was added to PVDF-HFP to produce an electrolyte membrane with better ionic conductivity than PVDF-HFP[6]. Capacity retention and initial discharge capacity also improved with the addition of SiO$_2$(Li$^+$) up to 20 wt. %. Table 1 shows the contribution of various additives in improving the performance of the PVDF-HFP electrolyte membrane.

Cellulose constituents are the most abundant, renewable polymer source available today and many researchers have been extensively interested in cellulose-based LIB especially cellulose-based separator/electrolyte[7, 8]. Cui et al. showed that the addition of CA in PVDF membrane increases the amorphous structure of separator which is beneficial for electrolyte uptake[9]. Cellulose acetate has some interesting physical and chemical property that meet the requirement of LIBs electrolyte. CA has a low thermal conductivity, good electrical insulation and the presence of polar functional groups (C=O and C-OH) in CA can provide the polymer with high affinity towards lithium ion and plasticizing solvents[10, 11].

Dispersion of nanofillers such as SiO$_2$[12], TiO$_2$[13], Al(OH)$_3$[9] and ZrO$_2$[14] in polymer electrolyte has been widely reported. These metal oxides act as solid plasticizer to prevent crystallization/reorganization of the polymer chain and enhance ionic mobility and dissociation through Lewis acid-base interaction between the fillers and polar groups of polymer or fillers and the ionic species[15, 16]. Shi and He investigated about Lewis acid-base properties of PVDF-HFP polymer and showed that PVDF-HFP is the strongest Lewis acid polymer compared to polycarbonate (PC), PANI and polymethyl methacrylate (PMMA) and polyvinyl chloride(PVC)[17]. Lithium ion which is one of the strongest Lewis acids could have a strong interaction with PVDF-HFP through Lewis acid-base interaction thus it will restrict the transference of lithium ion in the polymer. The inclusion of inorganic nanoparticles in PVDF-HFP cause the inorganic fillers to interact with the Lewis basic site of polymer and suppress Li$^+$-F thus lead to enhancement of lithium ionic transport [18]. Nanoparticle especially TiO$_2$ has a high dielectric constant of 100 and acidic nature [19]. Researchers have been reported that these properties could promote dissociation of the LiPF$_6$ salt and adsorb PF$_6^-$ anions through Lewis acid-base interaction, hence generating more mobile lithium ions[20, 21].

In this study, we chose PVDF-HFP as the main polymer, CA as the copolymer and TiO$_2$ as nanofiller. The effect of nanoparticle addition to PVDF-HFP and CA polymer electrolyte was investigated. The polymers were blended together with the nanoparticles and fabricated using immersion precipitation technique. The effect of TiO$_2$ to PVDF-HFP+CA electrolyte membrane in term of the electrolyte uptake, porosity, crystallinity and ionic conductivity was investigated.

**Table 1.** Ionic conductivity, transference number, porosity and electrolyte uptake of PVDF-HFP electrolyte membrane with various additive.

| Polymer Electrolyte | Anode/ Cathode | Ionic conductivity at 25, mS.cm$^{-1}$ | Transference number | Porosity (%) | Electrolyte uptake (%) | Ref |
|---------------------|----------------|----------------------------------------|---------------------|--------------|------------------------|-----|
| P(VDF-HFP)-PE: LiPF$_6$-EC-DMC-EMC-DEC | Lithium metal: LiFePO$_4$ | 1.01 | - | 95.6 | 216 | [22] |
| P(VDF-HFP)-PANI-GO: LiPF$_6$-EC-DMC | Lithium metal: LiFePO$_4$ | 66.4 | 0.30 | 88.7 | 367.6 | [23] |
2. Experimental

2.1. Materials
The main host polymer PVDF-HFP and CA which used as copolymer were obtained from Modern Lab Chemicals Sdn. Bhd. N-Methyl-2-Pyrrolidone (NMP) and acetone were also purchased from Modern Lab Chemicals Sdn. Bhd and used as solvents without further purification. Distilled water was used as non-solvent. TiO₂ particles (1-150 nm) were purchased from Modern Lab Chemicals Sdn. Bhd. N-butanol used in the porosity test was obtained from Modern Lab Chemicals Sdn. Bhd. The liquid electrolyte was LiPF₆ (1M) in 1:1 [(EC):(DMC)] and obtained from MTI corporation. Table 2 shows the composition of the gel electrolyte membrane.

Table 2.: The composition of electrolyte membranes.

| Electrolyte membrane | PVDF-HFP (wt. %) | CA (wt. %) | TiO₂ (wt. %) |
|----------------------|-------------------|------------|--------------|
| PVDF-HFP             | 15                | -          |              |
| PVDF-HFP+CA          | 12                | 3          | -            |
| PVDF-HFP+CA+TiO₂     | 12                | 3          | 1            |

2.2. Gel polymer electrolyte preparation
PVDF-HFP was dissolved in a mixed solvent, NMP and acetone with a weight ratio of 4:1. The polymer solution was under persistent stirring for 24h at 65 °C. After stirring, the solution was degassed and the solution was cast on a clean glass plate. The nascent membrane was left in room condition for 10 minutes before immersed in distilled water. For second polymer electrolyte, CA first added into the mixed solvent and stirred at 65°C. PVDF-HFP added into the solution after CA completely soluble in the solvent. For third polymer electrolyte, TiO₂ first added to the mixed solvent and was sonicated for 2 hours to ensure complete dispersion of nanoparticle in the solvent. After that, CA was added into the solution, followed by PVDF-HFP. The polymer electrolytes were vacuum dried at 90°C for 24h. The dried electrolyte membranes were stored in the glove box with a controlled environment (oxygen and moisture concentration less than 1 PPM). The membranes were immersed in the liquid electrolyte 1M LiPF₆ with (EC):(DMC) for 24 hours to form GPE.

2.3. Characterization
The morphology of the electrolyte membrane was observed under scanning electron microscopy (SEM, TM 3000, Japan). The samples were coated with a thin layer of platinum using sputter coating prior to observation under the microscope. Differential scanning calorimetry (DSC, Perkin Elmer 4000,
USA) is a thermoanalytical technique which carried out to study the crystallinity of the membranes. The test was performed under a nitrogen atmosphere from 30 to 250°C at a 10 °C min⁻¹ heating rate. The crystallinity of the polymer membrane was evaluated based on Eq. (1).

\[
X_C = \frac{\Delta H_m}{\Delta H_{m^0}}
\]  

(1)

where \( \Delta H_m \) and \( \Delta H_{m^0} \) represents the enthalpy of melting of separators and enthalpy of fusion of the repeating unit of a PVDF-HFP perfect crystal of infinite size. The porosity, \( P \) of the separators determined by using the weight method was calculated based on the following Eq. (2):

\[
P(\%) = \frac{(W_n - W_i)/\rho_{n-butanol}}{A \times L} \times 100
\]  

(2)

where \( W_i \) and \( W_n \) are the initial weight of the separator and the weight after immersing in n-butanol for 1 h, respectively, \( \rho_{n-butanol} \) is the density of the n-butanol, \( A \) is the separator surface area and \( L \) is the separator thickness.

The electrolyte uptakes (EU) were measured by soaking the electrolyte for 1 h in the process of the preparation. The EU values were calculated from the Eq. (3):

\[
EU(\%) = \frac{W_u - W_d}{W_d} \times 100
\]  

(3)

where \( W_d \) and \( W_u \) are the weight of the dried and the soaked separator, respectively. The ionic conductivities of GPE were measured by sandwiching it in between two stainless steel electrodes. The electrochemical impedance spectroscopy (EIS) analysis was performed by using Galvanostat/Potentiostat powered by Autolab software at room temperature over the frequency ranging from 1 Hz to 100 MHz with 5 mV of AC amplitude. The bulk resistance, \( R_b \) were obtained through EIS complex graphs and was used in Eq. (4) to find ionic conductivity (\( \sigma \), in S cm⁻¹).

\[
\sigma = \frac{L}{R_b \times S}
\]  

(4)

where \( S \) is the effective surface area of separator disc.

3. Result and discussion

3.1. Morphology structure

Based on figure 1, the PVDF-HFP membrane formed by immersion precipitation method shows an inter-island structure with abundant pores. The mixed solvent, acetone (Boiling point: 56.5°C) and NMP (Boiling point: 203°C) used in this research have a significant difference in evaporation rate. During evaporation, acetone forms in situ pores within the polymer matrix. Simultaneously, PVDF-HFP dissolves in NMP and forms a sturdy organic framework. The interconnected nanopores form 3D ionic transport channels to efficiently transport lithium ion.
While PVDF-HFP+CA also has an interconnected pore network, but it shows a higher pore size compared to the PVDF-HFP membrane. The wider pore of PVDF-HFP+CA is due to the hygroscopic nature of CA. During the evaporation process, the molecular solvent will be replaced by air molecules, air molecule will occupy the empty space left by solvent molecules[26]. Due to the hygroscopic nature of CA, the water absorption become a major factor during the evaporation process, so it will form a membrane with a larger pore size[27]. The presence of TiO$_2$ in the membrane was confirmed with the presence of white patches in the SEM image. However, some pores are filled with TiO$_2$, which validate the porosity test (Figure 3) where porosity value significantly less for the third membrane compared to the previous electrolyte membranes.

**3.2. Porosity and Electrolyte uptake**

Based on figure 2, the porosity of PVDF-HFP+CA+TiO$_2$ membrane is 4.5% lower compared to PVDF-HFP+CA electrolyte membrane. The main reason for this could be the high surface energy of nanoparticle which encourages agglomeration. Although the solution was sonicated and only small amount of TiO$_2$ was used, the agglomeration cannot be prevented fully. In the future, different solvent can be tested for complete dispersion of TiO$_2$ in solution. Usually, higher porosity often associated with higher electrolyte uptake. However, in this case, the electrolyte uptake is highest for the membrane with TiO$_2$. Other than porosity, electrolyte uptake also depends on the crystallinity of polymer and affinity of polymer towards the liquid electrolyte. As discussed in section 3.2., the higher amorphous phase leads to higher absorption of liquid electrolyte. Furthermore, TiO$_2$ improves the affinity of polymer towards the liquid electrolyte. Researchers reported that polar natured nanoparticle could enhance wetting of polymer electrolyte [29, 30].
Figure 2. The electrolyte uptake and porosity of polymer electrolyte membranes.

3.3. DSC analysis
The DSC analysis in figure 3 shows the broad endothermic peaks around 80 °C–160 °C. The broad peak due to coexistence of crystalline phase of PVDF. Kim et al also observed similar results in PVDF-HFP+TiO2 membrane prepared by phase inversion method[18]. They correspond to the broad melting peak to the melting of α-phase (big spherulite) crystals. The area of the melting peak can be calculated and the obtained crystallinity, $X_c$ data of the electrolyte membranes were listed in table 3. Sousa et al reported that crystallinity of PVDF-HFP is in the range of 15%-35% [28], the obtained $X_c$ (31.05%) is well within this range. As expected, the amorphous phase of polymer electrolyte with the addition of TiO2 is highest, approximately the crystallinity reduced by 11.46% than the pristine PVDF-HFP. The reduction in crystallinity confirms the strong interaction between nanoparticle and polymer chain, which forms cross-links via Lewis acid-base interaction with the polar groups, thus obstructing the reorganization of the polymer chains [12].

Figure 3. DSC analysis of polymer electrolyte.
Table 3. The crystallinity data and ionic conductivity of polymer electrolyte membranes.

| GPE            | Crystallinity (%) | Ionic Conductivity (S cm⁻¹) |
|----------------|-------------------|-----------------------------|
| PVDF-HFP       | 31.05             | 2.63E-04                    |
| PVDF-HFP+CA    | 26.46             | 2.97E-04                    |
| PVDF-HFP+CA+TiO₂ | 19.59             | 3.19E-04                    |

3.4. Ionic conductivity

The presence of a more amorphous region in this membrane retain a higher amount of electrolyte compared to other electrolyte membranes. The electrolyte uptake obviously improves the ionic conductivity of GPEs. The polymer chains in the amorphous region are more flexible which promote the segmental motion of the polymer chain which increases the lithium ion conductivity. The addition of TiO₂ improve the amorphous structure of the polymer and provide more mobile lithium ion which contributes to higher ionic conductivity. More free mobile lithium ions were formed due to salt dissociation capacity of TiO₂, their ability to adsorb PF₆⁻ anion [19], broke up the ion-pair clusters (Li⁺···PF₆⁻) that would otherwise have hindered the transport of lithium ions.

4. Conclusion

The presence of TiO₂ nanoparticle in PVDF-HFP+CA membrane reduced the porosity of the electrolyte membrane due to pore plugging phenomena. Although the porosity decreased, the electrolyte uptake of the membrane is better compared to PVDF-HFP and PVDF-HFP+CA. The decline in crystallinity with the addition of TiO₂ cause the electrolyte uptake to increase, thus improve the ionic conductivity.

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