Lithium Salt Doped Poly(Vinylidene Fluoride)/Cellulose Acetate Composite Gel Electrolyte Membrane for Lithium Ion Battery

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Abstract. In this study, composite gel electrolyte based on Polyvinylidene fluoride (PVDF)/cellulose acetate with the addition of different proportions of lithium nitrate (LiNO\textsubscript{3}) is prepared by a simple casting method. Salt doping effects on gel electrolyte membrane are investigated by scanning electron microscopy, X-ray analysis, DSC, FT-IR and TGA analysis. Salt doped gel electrolyte membrane shows a porous structure with a high uptake of 150\%. Furthermore, with the addition of 20 wt\% salt in the gel electrolyte membrane increase the ion conductivity from $0.21 \times 10^{-3}$ S cm\textsuperscript{-1} to $3.0 \times 10^{-3}$ S cm\textsuperscript{-1} at room temperature after soaking 1M LiPF\textsubscript{6} EC/DEC liquid electrolyte. As compared with PP 2325 separator, pristine PVDF and PVDF/cellulose acetate gel electrolyte membrane, the salt doped PVDF/cellulose acetate membranes exhibit wide electrochemical window and lower interfacial resistance. Composite gel electrolyte membrane with 10 wt\% salt contents possess 100\% capacity retention after 100 cycles at 1C rate as compared to PP 2325 separator which shows only 87\% capacity retention.

1. Introduction

Lithium ion battery with high charge density, long cycling, high thermal stability and high resistible against chemical reactions with electrolyte is highly desirable [1][2]. Lithium ion battery consists of cathode, anode and separator. The separator is the key component which is responsible to enhance the safety of the battery by separating the positive and negative electrode as well as provide a smooth path for the movement of lithium ions. Commercial polyfin separator (PE, PP and PP/PE/PP) Polypropylene (PP), are most widely used separators in lithium based batteries which consist of thickness in the range of 10-25\micron. However, their low thermal stability due to low melting temperature and low ion conductivity due to hydrophobic in nature still make them insufficient for advanced lithium ion batteries (LIBs) [3].

Nowadays, gel polymer electrolyte is a promising candidate as a separator for application of lithium ion batteries due to its high ion conductivity, the capability of holding electrolyte without leakage, chemically inert and electrochemical stable for both electrodes. These properties make it superior to solid
polymer electrolytes and liquid electrolytes [4,5]. Various polymer hosts of gel polymer electrolytes have been studied such as polymethymethacrylate (PMMA)[6], Polyimide [7], polyacrylonitrile (PAN) [8], polyetherimide[9], polyvinylidene fluoride (PVDF) and its copolymers [10,11]. Polyethylene oxide (PEO) [12]. Among them, PVDF holds a special place. PVDF has a strong electron-withdrawing functional group (–C–F) and the high dielectric constant(ε = 8.4) which is beneficial for the larger dissolution of lithium salts and for a higher concentration of charge carriers. But due to its low crystallinity, hydrophobic in nature and low ion conduction provokes it’s application in lithium ion batteries [13].

Cellulose acetate is on the promising derivatives of cellulose which can easily soluble in an organic and polar solvent. CA possess high glass transition temperature, electrically non-conductor and high affinity towards organic electrolyte due to acetyl (C=O) and hydroxyl group (-OH) make it a promising candidate for LIBs [14].

Lithium nitrate (LiNO3) is a low cost lithium salt which is using as a filler and to develop the tunable structure for lithium ion battery separators. Due to its high electronegativity and charge delocalization, it enhances the ion conduction of the membrane and also has a great ability to make complex such as cellulose acetate [15], PVDF[16] etc. In this work, PVDF and cellulose acetate blended gel electrolyte membrane (GEM) is developed which dopes with lithium nitrate in the backbone of cellulose acetate. The effects of lithium nitrate on morphology, ion conductivity and cycling performance of the lithium ion battery were investigated.

2. Experimental

2.1. Materials
Cellulose acetate (CA)[ CAS:9004-35-7] was purchased from Sigma Aldrich , Poly (vinilidene fluoride) (PVDF) keynar 761 was purchased from Alchemy chemical company , N, N-Dimethylformamide (DMF) was purchased from Aladdin, Lithium nitrate [LiNO$_3$] was purchased from Chemical reagent Co. Ltd, The electrolyte 1M LiPF$_6$ solution in EC/DEC solvent which was supplied by MTI corporation.

2.2. Experimental
The schematic diagram was shown in Figure 1. PVDF and Cellulose acetate polymer (ratio 4:1) was dissolved into DMF solvent at 70 °C for 1h. After a homogeneous solution, certain amounts of lithium nitrate was added into a solution and further stirred for 23 h at 70 °C. Then the solution was cast on a Teflon plate and dried at 50 °C to form composite gel electrolyte membrane. After drying, the solid electrolyte membrane was activated in a liquid electrolyte (Figure 1). The different weight percent salt (0, 10, 20,) containing electrolyte membrane was designated by M$_1$, M$_{10}$, M$_{20}$ and pristine PVDF membrane. The thickness of the samples was set to 128-134 μm. Note that a further increase of lithium salt amount from 20 wt% makes the membrane mechanically weak. For comparison purpose, pristine PVDF, PVDF/cellulose acetate (M$_1$) commercial Celgard PP 2325 separator was dipped into electrolyte separately.

2.3. Preparation of cathode electrode
The Lithium iron phosphate based cathodes were made by blade coating method in which 80 % cathode material, 10 % black carbon and 10 % PVDF in NMP solvent were mixed together by stirring for 12 h. Then the slurry was cast on the plain aluminum sheet attached on a clean glass plate. Then these sheets were dried for 12 h under vacuum at 120 °C temperature. After heating, aluminum sheet cut into a disc of 14 mm diameter. The lithium disc of 16 mm diameter was selected as an anode.

2.4. Characterizations
The surface of composite gel electrolyte membranes with and without salt were examined by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan), and samples were sputter-coated with gold before characterization.
The liquid electrolyte uptake was obtained by immersing the salt doped gel polymer electrolyte membranes in 1M LiPF₆ EC+DEC electrolyte for 2h. The surface electrolyte was gently removed by filter paper. The liquid electrolyte uptake was calculated by the following formula.

Electrolyte Uptake = \( \frac{W_w - W_d}{W_d} \times 100 \) \hspace{1cm} (1)

Where \( W_d \) is the weight of the dry membrane and \( W_w \) is the weight of the membrane after immersing into the liquid electrolyte. To confirm the readings, 5 pieces of each sample were tested and the mean value was taken.

Fourier transform infrared (FT-IR) spectra of the samples were recorded using IR/Nicolet 6700 Fourier transform infrared spectrometer in the range of 600~4000 cm\(^{-1}\). Differential scanning calorimetry (DSC) characterization was performed using Differential scanning calorimeter (DSC 8000) by Perkin Elmer under a nitrogen atmosphere from 50 to 200 °C at a heating rate of 10 °C min\(^{-1}\). X-ray diffraction (XRD) patterns were recorded using out using a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (1.540 Å) in the 2θ range between 5 and 85 ° at 5° per min.

The ionic conductivities of S-GPEs were measured with blocking-type cell, in which the S-GPE was sandwiched between two stainless steel (SS) electrodes. Impedence data were obtained from AUTOLAB PGSTAT302N using frequency range from 1 to 10\(^5\) Hz and potential amplitude of 5 mV. The ionic conductivity was obtained by the following equation.

\[ \text{Ion conductivity} (\lambda) = \frac{T}{R \times A} \times 100 \] \hspace{1cm} (2)

Where T and A represent the thickness and the area of the circular shaped membrane sample, and R corresponds to impedance resistance.

For activation energy calculation, ion conductivity was measured from 30 to 90 °C temperature. The following formula was used to get the activation energy value.

\[ \text{Activation energy} (E_a) = - \text{slope} \times R \] \hspace{1cm} (3)

Where slope value was obtained from a graph using origin (version 8.5) and R is the universal gas constant which has a value of 8.31416 KJ mol\(^{-1}\).
Linear sweep voltammetry (LSV) was measured by sandwiching the gel electrolyte membrane sample between stainless steel electrode (working electrode) and lithium metal (Reference electrode) with a potential range of 0.2–6.0 V (vs. Li/Li⁺) at a scanning rate of 5 mV s⁻¹.

The salt Li/S-GPE/LFP cells were tested on Neware Charge-Discharge testing equipment at 25 °C temperature. The cells were cycled in the voltage range of 3.0–4.2 V at different charge densities (0.2 to 8C rate) and for 100 cycles at 1C rate.

3. Results and discussions

Table 1. Uptake, ion conductivity values and related resistance values for composite gel electrolyte

| Sr. no. | Ion conductivity (mS cm⁻¹) at 25 °C | Electrolyte uptake (%) | Resistance (ohm) | Eₐ Kj mol⁻¹ |
|---------|-----------------------------------|------------------------|------------------|------------|
| Pure PVDF | 0.21                              | 55                     | 30.36            | 10.03      |
| M₀       | 1.17                              | 107.33                 | 5.50             | 7.87       |
| M₁₀      | 1.56                              | 136                    | 3.99             | 6.42       |
| M₂₀      | 3.0                               | 150                    | 2.24             | 4.693      |
| Celgard  | 0.57                              | 120%                   | 2.51             | 7.53       |
| 2325     |                                   |                        |                  |            |

Solution casting method usually creates a flexible, high quality mechanically strong film. The morphology of the PVDF membrane along with cellulose acetate blend and lithium salt doped polymers blended membrane is shown in Figure 2a-d. The results show that PVDF and PVDF/cellulose acetate membrane possess dense top layer with irregular pores shape due to the high affinity of PVDF and DMF solvent [Figure 2(a, b)] [17]. Lithium salt disrupts the polymer chain due to high dissociation with polymers and creates a porous structure which is beneficial for high electrolyte uptake and high ion conductivity [Figure 2(c, d)].

The electrolyte uptake was measured by immersing the gel electrolyte membrane in 1M LiPF₆ EC: DEC solvent. Table 1 shows that the electrolyte uptake values for pristine PVDF, PVDF/cellulose acetate and Gel polymer membrane with 10 wt% and 20 wt% salt contents are 50%, 107.33%, 139% and 150% respectively. The reason behind low uptake of PVDF is due to dense and less porous structure which does not contribute to the absorption of electrolyte [18]. The salt dopes gel electrolyte membrane exhibits high electrolyte uptake as compared to pristine PVDF, PVDF/cellulose acetate and commercial PP 2325 separator because of its good computability with electrolyte and possesses porous structure which holds the electrolyte.
To check the interactions between lithium nitrate, cellulose acetate and PVDF FT-IR spectroscopy were applied. Figure 3(a) shows FT-IR bands of pristine PVDF, PVDF/cellulose acetate (M1), 10 and 20% salt doped membrane (M10, M20). The bands 908, 1030, 1219, 1371, and 1736 cm$^{-1}$ represent CH$_2$ rocking, C–O–C stretching, C–O stretching, CH$_2$ bending, and C=O symmetric stretching, respectively. The change in intensity of the peaks represents the successful introduction of the salt in the polymers complex. The band at 3420 cm$^{-1}$ observe after addition of lithium salt which is due to moisture absorbed by lithium nitrate due to its hygroscopic nature [19]. Moreover, the stretching of the carbonyl group at 1749 cm$^{-1}$ is due to strong intermolecular interaction between the oxygen atom of the carbonyl group and lithium ion which result salt polymer complex [20]. The FT-IR results show no extra bands appear with the addition of salt which indicates that there is no chemical interaction between salt and polymers blends.

The crystallinity of the gel electrolyte membrane is measured by XRD pattern. Figure 3(b) shows the XRD peaks of pristine PVDF, PVDF/cellulose acetate (M1), 10 and 20% salt doped PVDF/cellulose acetate membrane. The peaks at 2$\theta$=18.3°, 20.2° and 25.6° represent pristine PVDF membrane and peaks at 2$\theta$= 16.3° and 22.5° are the diffraction peaks of the Cellulose acetate. After addition of lithium nitrate LiNO$_3$, the intensity of the peaks substantially decline which indicates the successful dissociation of salt with polymers blend and also an indication of increment in amorphous nature of gel electrolyte membrane by decreasing the crystallinity of the gel electrolyte membrane.

To further analysis the crystallinity change in gel polymer electrolyte membrane, DSC analysis was employed. DSC is a thermal analysis technique to measure the heat flow which passes in or out of the sample as a function of temperature while the sample is experienced controlled temperature.

Figure 3(c) shows DSC curves of the Pristine PVDF, PVDF/cellulose acetate (M1) and salt doped membranes. The values of heat of fusion and melting temperature of polymer blends and salt doped membranes are listed in table 2. The Table 1 shows that, with the addition of cellulose acetate and salt amounts, the melting temperature shifts from 172.2 °C to 167.5 °C and heat of fusion decline from 42.57
J. g\(^{-1}\) to 24.27 J. g\(^{-1}\), which indicates the successful formation of polymers and salt complex. The results also show that the addition of lithium salt creates free volume and amorphous region in the PVDF matrix.

Table 2. DSC characterization values of composite electrolyte membranes

| Sample Name       | Pristine PVDF | M\(_1\)  | M\(_{10}\) | M\(_{20}\) |
|-------------------|---------------|----------|------------|------------|
| \(T_m\) (°C)     | 172.2         | 170      | 169        | 167.5      |
| \(\Delta H_f\) (J. g\(^{-1}\)) | 42.57         | 38.44    | 34.57      | 24.27      |
| Crystallinity (%) | 35            | 24       | 16         | 11         |

TGA curves of Pristine PVDF, PVDF/cellulose acetate (M\(_1\)) and salt doped composite electrolyte membrane is shown in the Figure 3d shows that the Pristine PVDF membrane decomposes at 470.5.0°C with 60% weight loss. The PVDF/cellulose acetate decomposes into two stages. In one stage the decomposition occurs at 334°C with the weight loss of 18.5% which is due to decomposition of cellulose acetate while in the second stage the decomposition occurs at 483.2 °C with 80% weight loss. After the addition of salt, decomposition occurs at 487.2 °C which is also the decomposition temperature of lithium nitrate.

![Figure 3](image_url)

**Figure 3.** (a) FT-IR spectra profile of PVDF/cellulose acetate membrane and 20 wt% salt doped gel electrolyte membrane (b) XRD curves of composite gel electrolyte membrane with and without salt dope. (c) DSC curves of Pristine PVDF, PVDF/cellulose acetate, M\(_{10}\) and M\(_{20}\) salt doped gel electrolyte membrane. (d) TGA curves of pristine PVDF, PVDF/cellulose acetate (M\(_1\)) and salt doped gel electrolyte membranes.

The Results demonstrate that the salt doped composite electrolyte membrane decomposition temperature is higher than pristine PVDF and PVDF/cellulose blend.
Cellulose acetate is easily soluble in electrolyte due to high solubility in organic solvents such as ethyl methyl carbonate (EMC) and polycarbonate (PC) [21]. To test the stability of the gel electrolyte membrane containing cellulose acetate, it dips into the electrolyte solution for 2 and 24h as shown in Figure 4(a-d). The results show that there is no distortion of membrane due to the electrolyte which confirms strong hydrogen bonding exists between PVDF and cellulose acetate and gel electrolyte membrane can be used as a separator for lithium ion battery.

The results also show that the salt does not influence the hydrogen bonding between cellulose acetate and PVDF. Figure 4(d) shows that even after 24h remain in the electrolyte, the gel electrolyte membrane is flexible enough to bear the pressure inside a coin cell without structure damage.

Generally, the ionic conductivity in conventional battery separator is achieved due to the continuous pathways developed by the absorbed liquid electrolyte within the interconnected pores of the membrane. The porous structure is one of the important factors in determining the ionic properties of an electrolyte in a separator. Also of importance, the ionic conductivity of a porous membrane undoubtedly depends on the conductivity of the electrolyte embedded in the pores of the membrane. Figure 5(a) shows AC impedance of different GEM. The ion conductivity values of pristine PVDF, pristine PVDF/cellulose and membrane with 10 wt% and 20 wt% lithium nitrate are 0.21, 1.17, 1.56, and 3.00 mS cm⁻¹ which is higher than the previous research [22]. The enhanced ion conductivity of salt doped gel electrolyte membrane is due to high electrolyte uptake and adhesion towards electrode which reduces the interfacial resistance. Salt doped gel electrolyte membrane still contains high electrolyte uptake as compared to commercial PP separator (0.57 mS cm⁻¹). Figure 5(b) shows the Arrhenius plots of the ion conductivity for gel electrolyte membrane with and without salt doping. With increasing temperature ion conductivity increase
which shows that the curves exactly obeys the polymer electrolyte Arrhenius behavior [23][24]. Table 1 shows that the activation energy ($E_a$) values for Pristine PVDF, PVDF/cellulose acetate ($M_o$), commercial PP 2325 separator and salt doped composite electrolyte membrane with 10 and 20% salt are 10.03 KJ mol$^{-1}$, 7.83 KJ mol$^{-1}$, 6.42 KJ mol$^{-1}$ and 4.693 KJ mol$^{-1}$ respectively which calculated from the formula is given in the reference [25]. The activation energy values of Pristine PVDF and PVDF/cellulose acetate ($M_o$) is high because they expanded during heating and create free volume for the migration of ions through their polymer structure[26]. By combining the salt with gel electrolyte membrane, the expansion of the polymer cease which results in low activation energy.

The electrochemical performance of the salt doped gel electrolyte membrane with Pristine PVDF, PVDF/cellulose acetate ($M_o$), salt doped composite gel electrolyte membranes $M_{10}$, $M_{20}$ was investigated with Li anode and lithium iron phosphate (LFP) material as a cathode. Lithium iron phosphate is a very promising candidate with a stable capacity for next generation lithium ion battery applications. Figure 6(c) shows a charge-discharge profile in the potential window of 3.0 to 4.2V at different C rate (0.2C to 8C) using different composite gel electrolyte membrane. In general, the discharge values decrease with increasing charge density due to lithium iron phosphate inside lithium diffusion by extraction/intercalation reaction behavior [30]. PP, PVDF and PVDF/cellulose acetate ($M_o$) exhibit less capacity retention at high charge density while salt doped gel electrolyte membrane possesses high capacity even at high charge density because of their superior ion conductivity, high electrolyte uptake. Figure 6(d) shows a discharge capacity of 10 wt% salt doped gel electrolyte membrane and PP 2325 separator at 1C rate for 100 cycles. The commercial separator shows 88% capacity retention after 100 cycles with 118 mA h g$^{-1}$ initial and

Figure 5. (a) AC impedance spectra of GEM at 25 °C (b) Arrhenius plots of ion conductivities of GEM.

Linear sweep voltammetry (LSV) use to investigate electrical window of separators. Generally, the electrical window for lithium ion battery is limited to 2 to 4.3V. Figure 6a shows that the Pristine PVDF and PVDF-CA ($M_1$) decomposition temperature is 4.5V which is also a decomposition voltage of liquid electrolyte [27]. After addition of salt electrical window increase up to 4.65V, the results show that salt doped gel electrolyte membrane possess good electrochemical stability and can be used as a replacement of commercially available separator in lithium ion battery.

The EIS spectrum is measured by sandwiched the gel polymer electrolyte membrane between two lithium metal. Usually, impedance curves consist of two sections as shown in Figure 6(b). Section one is the straight line in the low frequency range which represents charge transfer resistance ($R_b$) and section two is a semicircular shape which represents the diffusion resistance ($R_i$) [28]. Figure 6(b) shows that the pristine PVDF and PVDF/cellulose acetate($M_o$) contain high interfacial resistance because of the reaction between the F atom of PVDF and electrode during charging and discharging process [29]. After the addition of the lithium salt, the interfacial resistance substantially decline. It is concluded that the salt doped gel electrolyte membranes show soft contact with lithium anode to maintain small interfacial impedance and adoption of volume change in the electrode.

The electrochemical performance of the salt doped gel electrolyte membrane with Pristine PVDF, PVDF/cellulose acetate ($M_o$), salt doped composite gel electrolyte membranes $M_{10}$, $M_{20}$ was investigated with Li anode and lithium iron phosphate (LFP) material as a cathode. Lithium iron phosphate is a very promising candidate with a stable capacity for next generation lithium ion battery applications. Figure 6(c) shows a charge-discharge profile in the potential window of 3.0 to 4.2V at different C rate (0.2C to 8C) using different composite gel electrolyte membrane. In general, the discharge values decrease with increasing charge density due to lithium iron phosphate inside lithium diffusion by extraction/intercalation reaction behavior [30]. PP, PVDF and PVDF/cellulose acetate ($M_o$) exhibit less capacity retention at high charge density while salt doped gel electrolyte membrane possesses high capacity even at high charge density because of their superior ion conductivity, high electrolyte uptake. Figure 6(d) shows a discharge capacity of 10 wt% salt doped gel electrolyte membrane and PP 2325 separator at 1C rate for 100 cycles. The commercial separator shows 88% capacity retention after 100 cycles with 118 mA h g$^{-1}$ initial and
100 mA h g\(^{-1}\) final discharge capacity values while 10 wt% salt doped gel electrolyte deliver 100% capacity retention after 100 cycles with approx. 125 mA h g\(^{-1}\) initial and final discharge capacity values respectively. The superior discharge capacity retention is due to high electrolyte uptake and ion conductivity of salt doped gel electrolyte membrane.

4. Conclusions

Lithium salt doped PVDF/cellulose acetate electrolyte membrane has been developed through the casting method. Due to the high affinity with cellulose acetate and PVDF polymer, lithium salt increased the physical and electrochemical properties of the blended membrane. Due to high affinity towards electrolyte, salt doped electrolyte membrane shows high ion conductivity. Lithium salt doped gel electrolyte possesses good electrochemical window of 4.65V. With 10 wt% salt doping with gel electrolyte membrane provide 100% capacity retention at 1C rate with 100% columbic efficiency. In short, salt doped PVDF/cellulose acetate composite gel electrolyte membrane is a promising candidate as a separator for rechargeable lithium ion batteries.

Acknowledgments

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