EXPERIMENTAL DETAILS

CHAPTER-III
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In this chapter, a short description for various processes involved in the preparation of PVdF-co-HFP based micro-porous gel polymer electrolyte membranes and their physical and electrochemical characteristics are presented. Finally, the effect of blending of PMMA with PVdF-co-HFP and the addition of nano-sized ceramic fillers such as ZrO₂ and LiAlO₂ onto PVdF-co-HFP based membrane were also studied.

3.1 MATERIALS USED

- Poly (vinylidene fluoride-co-fluoropropylene) (PVdF-co-HFP) with a number average molecular weight of ~5,00,000 (Aldrich, USA) was dried under vacuum at 70°C for 10hrs.
- Poly (methyl methacrylate) (PMMA) with a number average molecular weight of >3,00000 (Aldrich, USA) was dried under vacuum at 70°C for 10hrs.
- Poly (vinyl alcohol) (PVA) with a number average molecular weight of >50,000 (Aldrich, USA) was dried under vacuum at 70°C for 10hrs.
- Lithium perchlorate (LiClO₄) (Aldrich, USA) was dehydrated at 80°C under reduced pressure.
- Zirconium dioxide (ZrO₂)(Aldrich, USA) with the particle size of <100nm
- Lithium aluminium dioxide (LiAlO₂) (Aldrich, USA) with the particle size of <100nm
- Nano-crystalline LiMg₉.₅₆Mn₉₀.₄₄O₄ powder (Synthesized indogeneously) [1]
- Ethylene carbonate (EC) (E-Merck, Germany)
- Diethyl carbonate (DEC) (E-Merck, Germany)
• N-methyl 2-pyrrolidone (E-Merck, Germany)
• Acetone (E-Merck, Germany)
• Dimethyl formamide (DMF) (E-Merck, Germany)

3.2 PREPARATION OF MICRO-POROUS POLYMER MEMBRANES

The PVdF-co-HFP based micro-porous polymer membranes were prepared using the following processes:

3.2.1 Phase inversion process

The PVdF-co-HFP co-polymer was dissolved in acetone. The resultant viscous solution was spread as a film on a glass substrate using doctor blade [Fig.3.1]. Finally, the polymer film was dried at 50°C in a vacuum oven under 10⁻³ torr pressure for 3h to remove any further traces of acetone. The thickness of the films were obtained in the range of 150-200 μm. The polymer films were immersed in a pool of excess of de-ionized water for 6h to induce phase inversion. The resultant membrane were washed with running water and immersed in a pool of de-ionized water for 24h. The membrane was dried in a vacuum oven at 80°C for 24h [2].

3.2.2 Non-solvent extraction process [3]

The PVdF-co-HFP co-polymer was dissolved in acetone at room temperature. To this, different wt (%) of N-methyl 2-pyrrolidone (NMP) [0, 5, 10, 15 and 20wt %] were added. The resultant viscous solutions were spread as a film on a glass substrate using doctor blade. The polymer blend films were dried at 50°C in a vacuum oven under 10⁻³ torr pressure for 5 hrs to remove any further traces of acetone. The thickness of the films were obtained in the range of 150-200 μm. Then, the polymer film was immersed into pool of excess of deionized water to extract NMP from polymer matrix to generate micro-porous structure. These micro-porous polymer membranes were dried in a vacuum oven at 50°C for >6h.
3.2.3 Novel preferential polymer dissolution process [4, 5]

The PVdF-co-HFP co-polymer was dissolved in DMF. To this different wt (%) of PVA [0, 5, 10, 15 and 20wt (%)] were added. The resultant viscous solutions were spread as a film on a glass substrate using doctor blade. Then, the polymer blend films were dried at 80°C in a vacuum oven under $10^3$ torr pressure for 5h to remove any further traces of DMF. The thicknesses of the films were obtained in the range of 150-200 μm. The prepared cast polymer blend films were immersed in a pool of excess of deionized water at 60°C to dissolve PVA to get micro-porous structure. These micro-porous polymer membranes were dried in a vacuum oven at 80°C in a vacuum oven under $10^3$ torr pressure for >6h.

3.3 PREPARATION OF MICRO-POREUS GEL POLYMER ELECTROLYTE MEMBRANES

The resultant micro-porous polymer membranes were activated by soaking in 1M LiClO$_4$ containing EC and DEC (1:1 v/v ratio) for 18h to get the micro-porous gel polymer electrolyte membranes.

3.4 EFFECT OF BLENDING OF PMMA WITH PVdF-co-HFP IN THE DEVELOPMENT OF MICRO-POREUS POLYMER BLEND ELECTROLYTE MEMBRANES

A novel preferential polymer dissolution process was chosen to prepare micro-porous polymer blend membrane. By using this process, the effect of blending of PMMA with PVdF-co-HFP in the development of micro-porous polymer blend electrolyte membrane was studied as follows:

3.4.1 Preparation of PVdF-co-HFP-PMMA based micro-porous polymer blend electrolyte membranes

1:1 (wt/wt) ratio of PVdF-co-HFP co-polymer and PMMA were dissolved in a mixture of solvent such as DMF and acetone. To this, different wt (%) of PVA [0, 5,
10, 15 and 20wt (%) were added. The resultant viscous solutions were spread as a film on a glass substrate using doctor blade. Then, the polymer blend films were dried at 80°C in a vacuum oven under $10^{-3}$ torr pressure for 5h to remove any further traces of DMF. The thicknesses of the films were obtained in the range of 150-200 μm. Then, the polymer film was immersed into pool of excess of deionized water to dissolve PVA from polymer blend matrix to generate micro-porous structure. These micro-porous polymer blend membranes were dried in a vacuum oven at 80°C for >6h. The resultant micro-porous polymer blend membranes were activated by soaking in 1M LiClO₄ containing 1:1 (v/v) ratio of EC and DEC for 18h to get the micro-porous polymer blend electrolyte membranes.

3.5 EFFECT OF ADDITION NANO-SIZED CERAMIC FILLER ONTO PVdF-co-HFP MATRIX IN THE DEVELOPMENT OF MICRO-POOROUS NANO-COMPOSITE POLYMER ELECTROLYTE MEMBRANES

Here also a novel preferential polymer dissolution process is chosen to prepare micro-porous nano-composite polymer membrane. By using this process, the effect of nano-sized ceramic filler such as ZrO₂/LiAlO₂ onto PVdF-co-HFP in the development of micro-porous nano-composite polymer electrolyte membranes was studied as follows:

3.5.1 Optimization of nano-sized ceramic filler content onto a PVdF-co-HFP based polymer matrix

First, the PVdF-co-HFP co-polymer was dissolved in acetone. To this, different wt (%) of nano-sized ceramic filler such as ZrO₂/LiAlO₂ [0, 2, 4, 8 and 10wt (%)] were added. The resultant viscous solutions were spread as film on a glass substrate using doctor blade. Then, the nano-composite polymer films were dried at 50°C in a vacuum oven under $10^{-3}$ torr pressure for 6h to remove any further traces of acetone. The thickness of the films were obtained in the range of 150-200 μm.
Finally, the resultant nano-composite polymer films were subjected into differential scanning calorimetric analysis (DSC) to optimize the ceramic fillers content onto a PVdF-co-HFP based polymer matrix.

3.5.2 Preparation of PVdF-co-HFP- ZrO₂/LiAlO₂ based micro-porous nano-composite polymer electrolyte membranes

The optimized composition ratio of PVdF-co-HFP with nano-sized ceramic filler (ZrO₂/LiAlO₂) were taken and dissolved in DMF. To this different wt (%) of PVA [0, 5, 10, 15 and 20wt (%)] were also added. The resultant viscous solutions were spread as films on a glass substrate using doctor blade. These resultant nano-composite polymer films were dried at 80°C in a vacuum oven under 10⁻³ torr pressure for 6h to remove any further traces of DMF. The thickness of the films were obtained in the range of 150-200 µm. The prepared cast nano-composite polymer films were immersed in a pool of excess of deionized water at 60°C to dissolve PVA to get micro-porous structure. These micro-porous nano-composite polymer membranes were dried in a vacuum oven at 80°C under 10⁻³ torr pressure for >6h. Finally, the micro-porous nano-composite polymer membranes were activated by soaking in 1M LiClO₄ electrolyte solution containing 1:1 (v/v) ratio of EC and DEC for 18h to get the micro-porous nano-composite polymer electrolyte membranes.

3.6 PHYSICAL CHARACTERIZATIONS

3.6.1 Scanning electron microscopy analysis

The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination of the micro-structural characteristics of solid objects. The primary reason for the SEM usefulness is the high resolution which can be obtained when bulk objects are examined. SEM observations of the polymer films/membranes were carried out with Au coated vacuum ion sputter by liquid hydrogen method. SEM studies were carried out with JOEL-scanning electron
microscope (JSM-35CF) to find out the surface morphology of polymer films/membranes [Fig.3.2].

3.6.2 Determination of porosity [6]

The porosity (P) was determined by weighing the micro-porous polymer membranes with and without 1-butanol and using the following equation,

\[
P = \frac{m_a/\rho_a}{m_a/\rho_a + m_p/\rho_p}
\]  

(1)

Where \(m_a\) is the micro-porous polymer membrane weight after impregnation with 1-butanol, \(m_p\) is the micro-porous polymer membranes before impregnation with 1-butanol, \(\rho_a\) and \(\rho_p\) are density of 1-butanol and the dried micro-porous polymer membrane respectively.

3.6.3 Swelling study [6]

Swelling behaviour of the micro-porous polymer membranes were studied inside the glove box. The extent of swelling (Sw) of micro-porous polymer membranes were determined to investigate its dependence on micro-porous structure. The percentage of swelling was determined by using the following equation:

\[
Sw = \left(\frac{W - W_o}{W}\right) \times 100
\]  

(2)

Where, \(W_o\) is the weight of dried membrane and \(W\) is the weight of swelled membrane.

3.6.4 Differential Scanning calorimetry analysis (DSC)

DSC experiments of micro-porous polymer electrolyte membranes were carried out using a Dupont-DSC analyzer (Model TA-2000) over a temperature range of 0°C to 200°C at a scan rate of 10°C/min under N₂ atm. The dry samples were
Fig. 3.2 Scanning electron microscopy
sealed in Al crucible inside the glove box. The sealed samples were taken out from the glove box at the time of DSC experiments. The thermograms were base line corrected and calibrated against Indium metal.

The crystallinity of the micro-porous polymer electrolyte membranes were calculated based on the following equation from the DSC curves [7].

\[ X_c (\%) = \left( \frac{\Delta H_m}{\Delta H^{\Phi_m}} \right) \times 100 \quad (3) \]

Where, \(\Delta H^{\Phi_m}\) is the crystalline melting heat of pure PVdF (104.7 J/g), \(\Delta H_m\) is the heat of fusion of PVdF-co-HFP based micro-porous polymer electrolyte membrane. It can be calculated from the integral area of the base line and each melting curve.

3.6.5 XRD-analysis

The X-ray diffraction patterns were recorded with a JOEL - X-ray diffractometer (JDX-8030) [Fig.3.3] using nickel filtered Cu-Kα radiation at a scanning rate of 10° / min to examine the nature of the crystallinity with respect to EC, DEC and LiClO₄ in the polymer network.

3.7 ELECTROCHEMICAL CHARACTERIZATIONS

3.7.1 AC-impedance measurements

In the present study, the bulk conductivity was evaluated from complex impedance plots. The experimental arrangement used for the conductivity cell setup is shown in Fig. 3.4. Conductivity measurements were performed by sandwiching the micro-porous polymer electrolyte membranes in between two stainless steel electrodes using HIOKI -LCR meter (Model 3522-50) [Fig.3.5] over a frequency range of 1mHz - 100kHz at a scan rate of 1mV/sec with various temperatures ranging from 298K to 353K. \(Z\) and \(\varepsilon\) values were measured using the impedance analyzer. \(Z\cos \varepsilon\) ((Z real) and \(Z\sin \varepsilon\) (Z img) values were calculated. The value of
Fig. 3.3 X-ray diffractometer
Fig. 3.4 Conductivity cell setup for polymer electrolyte
Fig. 3.5 Conductivity measurement setup along with HIOKI-LCR meter
resistance $R$ was found to be the intercept of the x-axis. The ionic conductivity was calculated using the formula

$$\sigma = \frac{d}{RA}$$

(4)

Where $\sigma$ is ionic conductivity (Scm$^{-1}$), $d$ is thickness of the film, $R$ is the resistance of the film and $A$ is the area of the film.

3.7.2 DC-polarization studies

The measurement of lithium ion transference number ($t_+$) was suggested by Bruce et al [8, 9]. Briefly, a well sealed symmetrical Li/polymer electrolyte/Li test cell was assembled in a glove box and tested by combining the ac impedance method and the dc polarization method using EG&G Electrochemical Analyzer (Model-6310) [Fig.3.6] to determine the transference number, ($t_+$) which can be calculated using the following equation:

$$t_+ = \frac{I_s (\Delta V - I_0 R^0)}{I_0 (\Delta V - I_s R^s)}$$

(5)

Where $\Delta V$ is the applied dc-potential difference, $I_0$ and $I_s$ represent the initial and steady state currents flowing through the test cell respectively. Finally, $R_0^0$ and $R_s^s$ represent the initial and steady state resistance of the interface respectively. In this study, the membrane area is ca.1.5cm$^2$, and the applied dc-potential difference is 10mV. The resistance needed in Eq.5 was estimated from the impedance spectra obtained in the frequency ranging from 1mHz to 100kHz.

3.7.3 Linear sweep voltammetry technique

The electrochemical stability of micro-porous polymer electrolyte membranes was evaluated with cell featuring a stainless steel (SS) as working electrode and lithium as counter and reference electrodes by linear sweep voltammetry at 25°C using an EG&G Electrochemical analyzer (Model-6310) [Fig.3.7] in the scan rate of 1mV/sec was performed to study the system under investigation. The cell was
Fig. 3.6 EG&G Electrochemical analyzer for DC-polarization
assembled in a glove box [Fig.3.7] under argon atmosphere.

3.7.4 Dielectric spectroscopic studies [10]

The frequency dependence of dielectric permittivity was performed by sandwiching the micro-porous polymer electrolyte membrane between two stainless steel electrodes using HIOKI-LCR meter (Model-3532) over a frequency range of 40Hz – 5MHz at room temperature.

3.7.5 Charge-discharge studies

Carbon and LiMg$_{0.10}$Mn$_{1.90}$O$_4$ were employed as negative and positive electrodes respectively. A typical composite cathode consisted of the mixture of cubic spinel type LiMg$_{0.10}$Mn$_{1.90}$O$_4$ powder, acetylene black and Teflon binder in the 85:10:5 weight ratio. The above composite material is mixed with alcohol. The Teflon and acetylene black was used to provide good electrical conductivity as well as mechanical toughness between active grains. The above mixture was pressed in die onto an expanded aluminum micro grid at a pressure of 5 tons/cm$^2$ using hydraulic press. This procedure yields circular pellet electrodes of 18mm diameter. The pellets were then dried at 120°C in an oven. Carbon was used as anode invariably for all the compounds. The cells consist of Carbon/MPPEM/ LiMg$_{0.10}$Mn$_{1.90}$O$_4$ were assembled in a dry box under argon atmosphere. The galvanostatic charge-discharge studies were performed with in the voltage range of 3.2V - 4.8V at C/10 rate using WonA Tech – Battery cycle life tester [Fig.3.8].
Fig.3.7 Glove box
Fig. 3.8 WonA Tech-Battery cycle life tester