

## **SUMMARY AND CONCLUSIONS**

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The present investigation was carried out to prepare metal oxide (filler) nanoparticles and to evaluate the performance of composite microporous polymer electrolyte by addition of synthesized filler nanoparticles. Composite microporous polymer electrolytes have enhanced the electrochemical properties such as ionic conductivity, interfacial stability, lithium ion transference number, electrochemical stability and discharge capacity of the lithium ion battery. PVdF-HFP was chosen as a host polymer matrix due to high ionic conductivity at elevated temperature, excellent mechanical strength as well as electrochemical stability.

For the preparation of composite microporous polymer electrolytes, nanoscale inorganic fillers such as  $\text{CeO}_2$ ,  $\text{ZnO}$  and  $\text{MgO}$  obtained by polyol mediated thermolysis process were used. The synthesized metal oxides fillers have been dispersed into the PVdF-HFP polymer matrix to get the composite microporous polymer membranes by conventional phase inversion method. These composite microporous polymer membranes were immersed in 1M  $\text{LiClO}_4$  (EC/DMC, 1:1 v/v ratio) electrolyte solution to get composite microporous polymer electrolytes which enhances the physical and electrochemical properties. There is a need to identify the optimum filler content of the polymer matrix. The optimized filler concentration was used to make further improvement on composite microporous polymer electrolytes by preferential polymer dissolution process, where the removal of PVP from the polymer blend matrix has greater influence on the formation of uniform microporous structure and also the properties of polymer electrolyte.

The significant goals of the present work are to prepare the metal oxide nanoparticles and then composite microporous polymer electrolytes using the prepared metal oxides and are characterized.

Metal oxides such as CeO<sub>2</sub>, ZnO and MgO were prepared by polyol mediated thermolysis (PMT) process and characterized by the following studies:

- ✓ Thermogravimetric analysis/Differential thermal analysis (TG/DTA) was carried out to know the thermal behaviour of metal oxide precursors.
- ✓ X-ray diffraction (XRD) analysis was carried out to find out crystalline nature of the metal oxides.
- ✓ Brunauer-Emmett-Teller (BET) method was used to know the specific surface areas of the nanoscale metal oxides
- ✓ Scanning electron microscopy studies were used to find out surface morphology of the materials.
- ✓ Transmission electron microscopy (TEM) was used to identify the particle size of the synthesized products.

Prepared composite microporous polymer membranes/electrolytes were characterized by the following studies:

- ✓ Thermal behaviour of composite micro porous polymer membranes (obtained by both conventional phase inversion and preferential polymer dissolution methods) was studied by differential scanning calorimetry (DSC) analysis.
- ✓ Prepared composite microporous polymer membranes were used to find out the porosity, solution uptake and solution leakage percentage of the membranes.

- ✓ Ionic conductivity of composite microporous polymer electrolytes was studied using ac-impedance spectroscopic method.
- ✓ Electrochemical stability of the polymer electrolyte membranes was carried out by linear sweep voltammetry (LSV) technique.
- ✓ Interfacial stability of composite microporous polymer electrolytes was carried out using ac-impedance spectroscopic method.
- ✓ Transference number of composite microporous polymer electrolytes was determined by using the chronoamperometry and ac-impedance methods.
- ✓ The electrochemical charge-discharge behaviour of the composite microporous polymer electrolytes obtained by preferential polymer dissolution method was studied by fabricating a cell with the configuration of MCMB/LiCoO<sub>2</sub> using galvanostatic method in the range of 3.0V to 4.2V at C/2 rate and was compared with the composite microporous polymer electrolyte obtained by the conventional phase inversion method to suggest the best method to obtain composite microporous polymer electrolytes.

The conclusions on metal oxides synthesis are summarized below:

- ❖ The cerium oxide nanoparticles were synthesized at 500°C for 2h by polyol mediated thermolysis process. A typical cubic fluorite structure of cerium oxide was well matched with standard XRD pattern of pure CeO<sub>2</sub> powders. The line broadening of CeO<sub>2</sub> peaks was used to calculate crystalline size by Scherrer equation. The crystal size of cerium oxide was 9.2nm, when the mole ratio of cerium acetate : PVP is 0.1:0.003, and then crystal size became bigger with further increase of PVP mole ratio. Small crystalline particle size of the sample had high surface area of 66.1m<sup>2</sup>/g among all other samples. The ratio

of PVP played a vital role in the specific surface area of the products. HRTEM image of CeO<sub>2</sub> nanocrystalline particles size was ~10nm and no agglomeration was observed over the whole area to confirm the particle size distribution.

- ❖ Crystallization of zinc oxide nanoparticles started at 350°C without impurities, as evident from the TG/DTA analysis. Wurtzite structure of ZnO nanoparticles size was 12.8nm, when the molar ratio of PVP was 0.002 and calcinated at 500°C for 2h as investigated by XRD. It had high specific surface area of 121.2m<sup>2</sup>/g investigated from BET method. As measured by TEM, the average particle size of wurtzite zinc oxide was 14.8, 12.5, 47.2 and 81.3nm at the molar ratio of Zn(II)/PVP is 1:0.001,1:0.002,1:0.003 and 1:0.004 respectively. This may be due to the adverse effect of capping agent at its higher concentration.
- ❖ Cubic structure of MgO nanoparticles was synthesized by polyol mediated thermolysis process using ethylene glycol as a solvent and PVP as a capping agent at different temperatures. Crystalline size of MgO was increased with temperature significantly. MgO had smaller crystalline size of 3.1nm at 500°C, whereas crystalline size of 27.4 and 51.2nm were obtained at the calcination temperature of 600 and 700°C for 2h respectively. High specific surface area of 112.8m<sup>2</sup>/g was obtained at 500°C calcined magnesium oxide nanoparticles. HRTEM image showed that particles size was about 2-5nm with nearly spherical in shape. The average particle size of magnesium oxide was 3.5, 30 and 54 nm obtained from TEM analysis.

To conclude, in PMT process, the combined effect of ethylene glycol and PVP are more important to get the metal oxide nanoparticles with uniform size and shape. The synthesized metal oxide nanoparticles were nearly spherical in shape without agglomeration. The metal oxide nanoparticles (CeO<sub>2</sub>, ZnO and MgO) with high phase purity and high surface area was achieved by calcined at 500°C for 2h by polyol mediated thermolysis.

Comprehensive investigations on physical and electrochemical characterizations of the prepared composite microporous polymer membranes/electrolytes obtained by both phase inversion and preferential polymer dissolution methods were summarized below:

- Synthesized CeO<sub>2</sub> (~10nm, 66.1m<sup>2</sup>/g) nanoparticles were dispersed onto the PVdF-co-HFP to obtain composite micro-porous polymer membranes (PI-CMPM) by phase inversion process. These composite microporous polymer membranes were activated by immersed in 1M LiClO<sub>4</sub> containing 1:1 (v/v) ratio of EC and DMC to obtain composite microporous polymer electrolytes (PI-CMPEs). The ionic conductivity of PI-CMPE depends upon the quantity of liquid electrolyte entrapped and filler concentration in the polymer matrix. The optimum filler content of 8wt% CeO<sub>2</sub> dispersed composite microporous polymer electrolyte reached maximum electrolyte uptake (150%), high porosity (72%), less solution leakage (24%) and high room temperature ionic conductivity (2.531 X 10<sup>-3</sup> Scm<sup>-1</sup>). Activation energy of PI-CMPE (14.86 kJ.mol<sup>-1</sup>) was calculated from the Arrhenius plot. Low Interfacial resistance was observed in CeO<sub>2</sub> filler dispersed composite microporous polymer electrolyte compared to filler free polymer electrolyte membrane. The lithium transference number (t<sub>+</sub>) was 0.64 and the electrochemical stability of PI-CMPE was 4.7V vs Li/Li<sup>+</sup> at room temperature. The initial discharge capacity of MCMB/PI-CMPE/

LiCoO<sub>2</sub> cell showed 140mAh/g and its capacity fading was about 14% at the 50<sup>th</sup> cycle.

- Different wt% of PVP (10, 20 and 30wt %) extracted PVdF-HFP-CeO<sub>2</sub>(8wt%) based composite micro-porous polymer membranes were prepared by preferential polymer dissolution process. The extraction of PVP in the composite polymer blend matrix has improved pore configuration, when compared with phase inversion process. From this process, 20 wt% of PVP extracted PD-CMPE showed a maximum porosity of 85% and maximum electrolyte uptake of 216%, which were higher than PI-CMPE. PD-CMPM showed honey-comb like structure with uniform micropores on both top and bottom surface (1-2 $\mu$ m) and less solution leakage (12%). Mechanical strength of PD-CMPE was also maintained nearly (234kPa), when compared with PI-CMPE (284kPa). Hence, PD-CMPE achieved a high ionic conductivity of about  $3.84 \times 10^{-3} \text{ Scm}^{-1}$  at room temperature. An apparent increase in lithium transference number (ca.0.71) was observed with good electrochemical stability of 4.9V Li/Li<sup>+</sup> for 20wt% of PVP extracted PD-CMPE. Moderate change in the impedance spectra was observed before and after dc-polarization studies as in the case of PD-CMPE. MCMB/PD-CMPE/LiCoO<sub>2</sub> cell showed an initial discharge capacity of 143.0mAh/g which was slightly higher than PI-CMPE (140.0mAh/g). The PD-CMPE obtained by this process showed a capacity fading of 8% which was slightly lower than the composite micro-porous polymer electrolyte (PI-CMPE) obtained by the phase inversion process (14%).
- ZnO (12.5nm, 121m<sup>2</sup>/g) nanoparticles were dispersed onto the PVdF-co-HFP to get composite microporous polymer membrane (PI-CMPM) by phase inversion process. The optimum filler content of 6wt% ZnO dispersed PI-CMPM showed sponge like structure with tiny pores and one or two micropores

(1 $\mu$ m) (top surface), but bottom surface had different pore sizes. The PI-CMPM was found to have high degree of porosity (76%), more solution uptake (210%) and less solution leakage (28%). It showed mechanical strength of 243kPa with enhanced ionic conductivity in the range of  $2.73 \times 10^{-3} \text{ Scm}^{-1}$  at room temperature; whereas higher filler concentration (>6wt%) decreased the ionic conductivity due to dilution effect predominates. The enhancement in ionic conductivity of PVdF-co-HFP-ZnO system was attributed to a reduction in degree of crystallinity (28.14%), decrease in activation energy ( $15.70 \text{ kJ.mol}^{-1}$ ) and an increase in the effective mobility of ions. The electrochemical stability of PI-CMPE showed 4.6V vs Li/Li<sup>+</sup>. The lithium-ion polymer cell using PI-CMPE as the separator exhibited discharge capacity of about 137.0mAh/g at C/10 rate. The active material utilization was reduced to about 20% only at 50<sup>th</sup> cycle.

- PVP extracted PVdF-HFP-ZnO(6wt%) based composite microporous polymer membranes were prepared by preferential polymer dissolution process. 20wt% PVP extracted composite microporous polymer membrane (PD-CMPM) exhibited uniform honey-comb like structure with micropores (1 to 2 $\mu$ m) in both top and bottom surfaces. The porosity, electrolyte uptake and solution leakage of PD-CMPM varied with the removal of different wt% of PVP. The PD-CMPM obtained by the extraction of 20wt% PVP showed high electrolyte uptake of 264%, less solution leakage of 14% and porosity of 83%. Optimal removal of PVP enhanced the room temperature ionic conductivity of  $3.55 \text{ mS.cm}^{-1}$ , which showed high interfacial stability than other systems. The temperature dependence of ionic conductivity of this composite micro-porous polymer electrolyte obeys Arrhenius character. This PD-CMPE had minimal activation energy of  $14.09 \text{ kJ.mol}^{-1}$  and its lithium transference number was about ca.0.67. No obvious change in the impedance spectra of the test cell before and after

- dc-polarization was seen. PD-CMPE showed the maximum electrochemical stability of 4.8V vs Li/Li<sup>+</sup>. The lithium-ion polymer cell using PD-CMPE as the separator exhibited discharge capacity of about 140.0mAh/g at C/2 rate. The active material utilization was reduced to about 13.4% at 50<sup>th</sup> cycle.
- Synthesized MgO (3.5nm, 112.8m<sup>2</sup>/g) nanoparticles were dispersed onto the PVdF-co-HFP to obtain composite micro-porous polymer membranes (PI-CMPE) by phase inversion process. The optimized filler content of 8wt% MgO dispersed PI-CMPE exhibited the ionic conductivity of 5.20 x 10<sup>-3</sup>Scm<sup>-1</sup> at room temperature and its corresponding membrane crystallinity, porosity and electrolyte uptake were 22.76%, 81% and 215% respectively. The higher ionic conductivity of PI-CMPE was attributed to the higher number of effective charge carriers and decreased surface/volume ratio of the polymer network. The temperature dependence of ionic conductivity was explained on the basis of Arrhenius model. It exhibited low activation energy of 11.51kJ/mol<sup>-1</sup> and low interfacial resistance of 484Ωcm<sup>2</sup> with the storage time of 720h, which is due to good adhesion between composite polymer membrane and the lithium electrode. Lithium ion transference number was about 0.69 and its corresponding initial interfacial resistance and steady state interfacial resistance were determined by ac-impedance analyzer before and after the chronoamperometry technique. Linear sweep voltammetry was used to find out the oxidation peak around 4.9V vs Li/Li<sup>+</sup>. The MCMB//LiCoO<sub>2</sub> cell with PI-CMPE delivered the initial capacity of 140.0mAh/g at room temperature during cycling process and retained almost 86% of its initial capacity at 50<sup>th</sup> cycle.
  - Effect of PVP removal (10, 20 and 30wt% PVP) in PVdF-HFP -MgO(8wt%) composite polymer blend matrices was studied by preferential polymer dissolution process. The composite micro-porous polymer electrolyte obtained by preferential polymer dissolution process(PD-CMPE) showed enhanced ionic

conductivity ( $7.63\text{mS}\cdot\text{cm}^{-1}$ ) rather than the conventional phase inversion method (PI-CMPE). 20wt% PVP extracted PD-CMPE showed uniform honeycomb like structure with higher uptake of electrolyte (359%) solution. The PD-CMPE had higher porosity and less solution leakage, when compared with the PI-CMPE. The activation energy calculated from the Arrhenius plot. The 20wt% PVP extracted PD-CMPE showed less activation energy value of  $10.35\text{kJ}\cdot\text{mol}^{-1}$ . It is due to increase in the charge carrier. The highly ordered uniform microporous network enhanced the lithium-ion transference number of PD-CMPE, obviously in the range of 0.69 to 0.76 when the porosity of membrane increased from 81% to 93%. In addition, interfacial resistance reduced from  $484\Omega\text{cm}^2$  (PI-CMPE) to  $369\Omega\text{cm}^2$  (PD-CMPE) which is due to the change in adhesion between the electrolyte and electrode. The process achieved initial capacity of about  $145.0\text{mAh/g}$  and its capacity loss is 6.2% at 50<sup>th</sup> cycle which was much better than all other studied composite microporous polymer electrolytes. Hence, the preferential polymer dissolution process is an effective and the best process for the preparation of composite micro-porous polymer electrolytes (PD-CMPEs) rather than the conventional phase inversion process.

To conclude, the composite micro-porous polymer electrolytes obtained by the preferential polymer dissolution method (PD-CMPE) are proven to have superior characteristics than the composite micro-porous polymer electrolytes obtained by the conventional phase inversion method. Among various composite micro-porous polymer electrolytes, PVdF-HFP -MgO(8wt%) based PD-CMPE could be used as a promising candidate for high voltage rechargeable lithium-ion polymer batteries even at higher operation temperatures.

## **FUTURE SCOPE OF THE STUDY**

The PMT process will be further extended to the synthesis of metal oxide nanowires and its influence onto the PVdF-HFP based microporous polymer electrolytes is to be studied. The continuation of this study will go further into details concerning the applicability of composite microporous polymer electrolytes at higher operation temperatures for high voltage (>4.5V) Li-ion batteries.