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Structural, morphology and ionic conductivity studies on compositeP(S-MMA)-ZrO_2 Polymer electrolyte for Lithium Polymer battery

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Abstract: In the present study, the composite material ZrO_2 has been prepared using NH_3 and Na_2CO_3 as precipitation agents, via co-precipitation technique. The as prepared ZrO_2 has been characterized using XRD, FE-SEM, FTIR analyses. The ZrO_2composites were used as filler in the parent polymer electrolytes based on P(S-MMA)-$LiClO_4$by solution casting techniques. Electrical, structural and functional analyses of P(S-MMA) based polymer electrolytes comprising ZrO_2 were studied and the results are reported. The incorporationZrO_2 filler greatly enhanced the ionic conductivity and other electrochemical properties of P(S-MMA) based polymer electrolytes.
Key words- P(S-MMA); ZrO_2; $LiClO_4$.

Introduction and Experimental

The rapid development of new technologies such as cell phone, notebook PC, and electric vehicle (EV) has promoted research aimed at improving battery performance with special effort devoted to Lithium batteries [1]. Numerous methods have been reported for improving characteristics of polymer electrolytes such as cross-linking, incorporation of organic solvents and fillers, etc., An attempt has been made to study the effect of addition of ZrO_2 in PS-MMA based SPEs for various compositions using conventional solution casting technique. Towards attaining good properties of filler, ZrO_2 was prepared laboriously by co-precipitation method using NH_3 and Na_2CO_3 as precipitating agents. Based on the properties of as-prepared optimized filler, the various compositions of composite polymer electrolytes were prepared.

The ZrO_2fillers were synthesized by co-precipitation method using 0.2M Zr $(NO_3)_2.3H_2O$ and Na_2CO_3 or NH_3 as precipitation agent [2]. The prepared composites of different weight ratio were added into the optimized P(S-MMA)-$LiClO_4$ as dopant salt by solution casting technique.

Results and discussion

In order to determine the thermal property of the ZrO_2precursors, the calcinations temperatures were fixed as 700 and 900 °C for NH_3 and Na_2CO_3 as a Precipitation agent respectively. Fig 3.1.A shows the TG curves of the precursors of ZrO_2 whose precipitation agents are NH_3 and Na_2CO_3. X-ray diffraction pattern and IR Spectra of the as prepared ZrO_2 filler using NH_3 and Na_2CO_3 as precipitation agents are represented in Fig.3.1 (B & C).

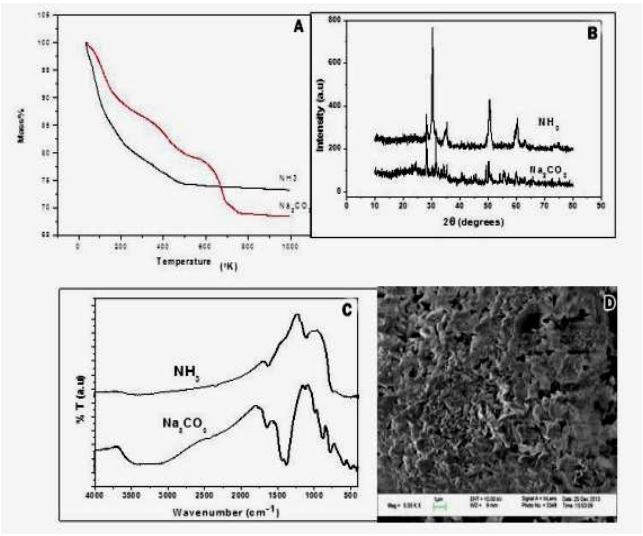

Fig.3.1 (A)TG curves (B) XRD patterns and **(C)** FT-IR spectra of ZrO_2 precursors when NH_3 and Na_2CO_3 are used as precipitation agents. D) SEM image of ZrO_2 Precursors when Na_2CO_3 as precipitation agent.

From the XRD pattern it is confirmed that the as-prepared samples are ZrO_2 with the monoclinic structure which is in agreement with the JCPDS 781807. However, all the peaks are in very good agreement with the standard for the sample prepared while using Na_2CO_3 as precipitation agent than the other one. Using the Scherer's relation the crystalline domain size was determined as 110 nm. The IR spectra of ZrO_2 crystalline samples show various stretching frequencies around 740 and 500 cm^{-1}[3], which are attributed to Zr-O_2-Zr asymmetric Zr-O stretching vibrations. These peaks are shifted to 780 and 499 cm^{-1}respectively confirms the formation of ZrO_2inNa_2CO_3 based ZrO_2 samples. Fig. 3.1 Dshowed that the SEM image of Na_2CO_3based ZrO_2 particles; most of the particles are found to have hexagonal structure with needle shape. The particle size is estimated as 294nm for Na_2CO_3based ZrO_2 and has uniform morphology. It reveals that ZrO_2 filler aiding in the formation of amorphous phase into the parent polymer matrix.The XRD pattern, (Fig.3.2 (a)) shows few intense peaks like 2θ=28.3, 31.6° which shows the monoclinicstructure of ZrO_2 filler. [JCPDS:78-1807]. Also two intense peaks at 2θ=13.1 and 22.9° which reveal the hexagonal structure for$LiClO_4$ [JCPDS: 30-0751]; these intensity are comparatively low while incorporating ZrO_2 in the parent polymer electrolyte. Actually, the intensity of bare electrolytes is reduced while incorporating the ceramic fillers as contradict one. This may be caused the complete dissociation of inorganic salt (which is acting as a dissociating agent) in to the polymer matrix which leads to the amorphous nature. The OH stretching vibration of PS-PMMA around 3500cm^{-1} is shifted in between 3533-3650 cm^{-1} in the complexes (Fig.3.2). The vibration peaks at 2990 and 2940cm^{-1} are ascribed to the asymmetric and C-H stretching of the absorption peak of PS-MMA. The characteristic vibration peak appearing at940$cm^{-1}$is assigned to per chlorate anion that is shifted to 960 cm^{-1}in the complexes. The characteristic peaks of Zr-Ostretching and Zr-O_2-Zr asymmetric modes are appeared at 500and 740 cm^{-1}.The addition of new peaks, shifting of peaks and absence of peaks in the complexes ensures the complexation had taken place between PS-MMA and $LiClO_4$ and ZrO_2 filler composites polymer electrolytes. In the present work, ZrO_2 concentration has been varied as (3, 6, 9 and12)wt% on the bare P(S-MMA)-$LiClO_4$electrolyte. The parent electrolyte exhibits the conductivity of $6.8\times10^{-7}Scm^{-1}$ at 303 K. While incorporating the ZrO_2 filler, conductivity enhances two orders of magnitude at 303 K. The temperature dependent ionic conductivity plots are shown in Fig 3.3 in the temperature range 303-353K. The conductivity of the electrolyte increases with the increase of temperature. Also it is clear that the conductivity increases upon the addition of ceramic filler up to 9 wt%; further addition of ZrO_2 makes the conductivity dips down.The same trend was obtained for our previous studies on PVdF-PEMA based composite gel polymer electrolyte and for PEO based composite polymer electrolyte [4]. For all complexes, the conductivity increases with increase of temperature and this can be rationalized by free volume model. The curvature of the plots indicates that ionic conductivity seems to obey

Arrhenius relation, which describes that ion transport in polymer electrolytes is dependent on polymer segmental motion. The activation energy of the system varies within the range 0.14 to 0.37 eV. It reveals that highly conducting sample possesses lesser activation energy.

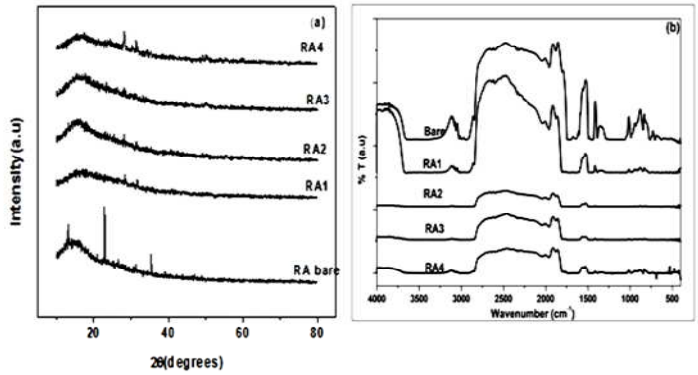

Fig.3.2 (a) XRD patterns and **(b)** IR spectra of bare PS-MMA-$LiClO_4$ and 3 (RA1), 6 (RA2), 9 (RA3) and 12 wt% (RA4) of ZrO_2 based polymer electrolytes.

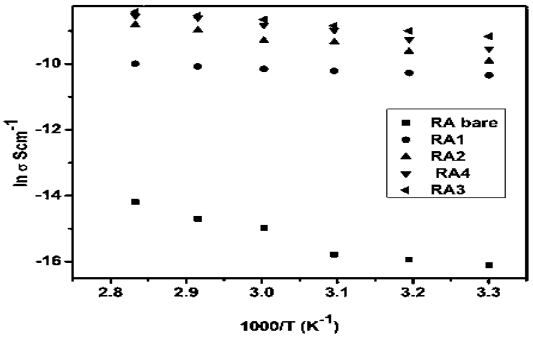

Fig.3.3 Temperature dependent ionic conductivity plots of P(S-MMA) (80)-$LiClO_4$ (20) + ZrO_2 (bare, 3, 6, 9, 12) wt% based electrolytes in the temperature range 303-353K.

Conclusion

The ZrO_2 filler were synthesized by co-precipitation method using Na_2CO_3 and NH_3 as precipitation agents. The as-prepared samples were ZrO_2 with the monoclinic structure which is in agreement with the JCPDS 781807. The 3, 6, 9 and 12 wt% of ZrO_2 was dispersed in to P(S-MMA) (80)-$LiClO_4$(20) polymer matrix by solution casting method. P(S-MMA) (80)-$LiClO_4$ (20)-9wt% ZrO_2 exhibits maximum ionic conductivity 2.2 $\times 10^{-4}$ Scm^{-1}at 303K. The ionic conductivity of composite polymer electrolytes increases in two orders of magnitude on the bare polymer electrolyte. The activation energy varies between .14 to .37 eV.

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