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EFFECTS OF TiO₂ NANO FILLER INCORPORATED POLYMER BLEND ELECTROLYTES FOR LITHIUM BATTERY APPLICATIONS

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ABSTRACT- Hybrid solid polymer Electrolytes of high ionic conductivity were prepared using Poly(ethylene oxide) (PEO)/ Poly(vinyl pyrrolidone) (PVP) / Titanium oxide (TiO₂). These electrolyte films were free standing and dimensionally stable. The increase in amorphous nature of the polymer electrolytes has been confirmed by X-ray diffraction analysis. Ac impedance analysis gives conductivities of the electrolytes. It was found that 12% of the filler added PEO/PVP/LiClO₄/PC complex showed higher ionic conductivity in the order of 10⁻³ S/cm at an ambient temperature. The temperature dependence conductivity seems to obey the VTF relation. TG-DTA and SEM analysis were carried out for the better ionic conductivity polymer electrolyte sample. In future, these polymer electrolytes can be used in Li-ion batteries.

Keywords- [XRD, TG-DTA, SEM, VTF relation.]

1. INTRODUCTION

Lithium micro batteries with lightweight and high power density are of considerable current research interest. Micro batteries can be incorporated into integrated circuits with other electronic elements and have great potential for use in Microsystems, such as smart cards, on-chip power sources, lab-on-chip applications, and portable electronic devices [1]. In Lithium ion battery system, the separator plays a key role with respect to device performance as it prevents short circuits between the electrodes while allowing ionic conduction [2]. A solid polymer electrolyte must meet certain

requirements such as being an electronic insulator, ionic conductor, mechanically strong, dimensionally stable, readily wetted by the electrolyte and chemically resistant to electrolyte and impurity degradation, among others [3]. PEO based polymer electrolyte is of current interest for Li ion batteries due to their easy formation of complex with Li salts, high mobility of charge carriers and stable chemical properties[4]. Lithium solid electrolytes promise the potential to replace organic liquid electrolyte and thereby improve safety of the next generation batteries. One of the challenges for improving the performance of the Li ion batteries for

energy storage is the development of suitable solid electrolytes.

Experimental details

PEO, PVP, the nano sized TiO_2 and the salt LiClO_4 were purchased from Aldrich chemicals (USA) and they were dried under vacuum at 50°C about at 12 hours. The plasticizer propylene carbonate (PC) was used as received. The polymers PEO and PVP with salt LiClO_4 were first dissolved in methanol (CH_3OH) separately and then mixed together. The given amounts of plasticizer were also added into the above polymer salt mixtures. Finally, the nano filler TiO_2 was incorporated into the complex mixture and was stirred continuously about 24 hours for avoiding the fillers aggregation and to ensure the fine mixing. The electrolytes were prepared by the solvent casting technique. The solvent was allowed to evaporate slowly from the complex at 60°C for 6 hours. The composite polymer electrolyte films were harvested and stored in evacuated desiccators.

2. RESULTS AND DISCUSSION

2.1 X-Ray Diffraction Analysis

Figure(1) shows the X- ray diffraction patterns of PEO, PVP, LiClO_4 , TiO_2 and prepared samples with the ratio of 0%, 4%, 8%, 12%, and 16%. The X-ray diffraction pattern of pure Two broad peaks observed at $2\theta = 19.2$ and 23.5° corresponding to the semicrystalline nature of PEO. A peak

appeared at around 22.7° which confirms the amorphous nature of pure PVP. LiClO_4 shows the high intense peaks at angles $2\theta = 21, 23, 27$ and 35° corresponding to the high crystalline nature of ionic lithium salt. The peaks observed at $27, 36$ and 54° reveals the nano sized filler of TiO_2 . The different concentration of TiO_2 (0, 4, 8, 12, 16) as shown such as K0, K1, K2, K3 and K4. . It is observed that without addition of filler (K0) the peaks of LiClO_4 disappeared, this could be due to miscibility and disruption of crystalline structure of lithium salt with the polymer composites. PEO/PVP/ LiClO_4 blend film exhibits three crystalline peaks of PEO, a maximum intensity peak at $19.2, 23.7$ and a relatively less intense peak at 27° . No such well defined sharp peaks attributable to PVP and LiClO_4 could be observed. However on the addition of TiO_2 filler to the polymer blend, it has been observed that, the intensity of the peaks decreases gradually, up to 12% of filler content. The shift and decrease in relative intensity of the peaks suggest that the complexation has occurred between the salt and the polymers [5]. Due to the addition of nanofiller up to 12%, the decrement of intense peaks reveals that this may increase the amorphous nature which can induce greater ionic diffusivity with high ionic conductivity. It is clearly indicated that the sample K4 has relatively high intense peaks which increase the crystalline nature compare to other samples [6].

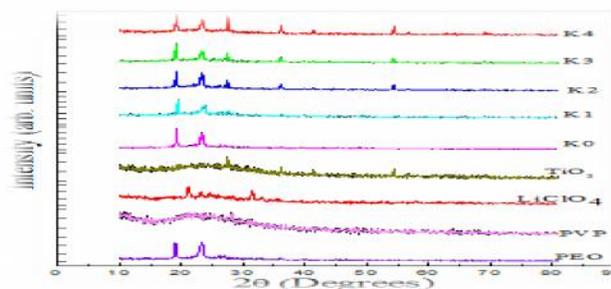


Figure 1- XRD patterns of pure and prepared electrolyte membranes (K0-0 % of TiO_2 , K1-4 % of TiO_2 , K2-8 % of TiO_2 , K3-12 % of TiO_2 , K4-16 % of TiO_2)

2.2. Conductivity measurements

The ionic conductivity of PEO and PVP based polymer electrolytes is calculated from $\sigma = l/R_b A$, where ‘ l ’ the thickness of the film, ‘ A ’ the area of the film and R_b the bulk resistance of the material. Polymer electrolytes with fixed ratios of polymers, salt and plasticizer (PEO (72)–PVP (8) – LiClO₄ (8)–PC (12)) were prepared in order to find the appropriate nanofiller component for lithium battery applications. The ionic conductivity measurements have been carried out on these electrolytes by employing

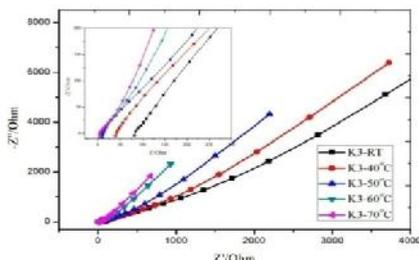


Figure 2- Different temperature complex impedance plot Conductivity of the highest Conductivity sample

variable frequency range from 10 Hz to 1 MHz and temperature range from room temperature to 70°C. Figure.2 shows the complex impedance spectroscopy of the highest conductivity sample at different temperature. The ionic conductivity value for the system with 12% concentration of nanofiller TiO₂ is considered as a maximum conducting combination of filler with polymer matrix. The highest ionic conductivity at an ambient temperature has been found to be $7.17 \times 10^{-3} \text{ S cm}^{-1}$ for 12% of TiO₂ polymer electrolyte.

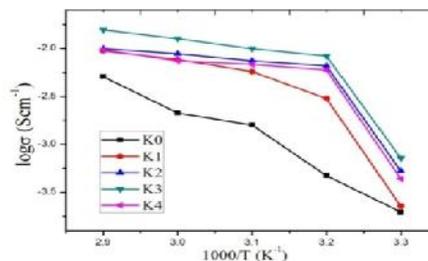


Figure 3- Temperature dependent ionic plots of the prepared samples

3. TEMPERATURE DEPENDENCE OF IONIC CONDUCTIVITY

The temperature dependence of ionic conductivity of the prepared polymer electrolyte films were subjected to conductivity measurements at five different temperatures viz 303K, 313K, 323K, 333K, 343K. Temperature dependence ionic conductivity plots of the samples are shown in figure 3. From the table 1 it is observed that as temperature increases the ionic conductivity values also increase over the temperature

range and polymer could observe a volumetric change in it. Increase in ionic conductivity with the increase of temperature can be related to the increase in the number of mobile charge carriers contributing to the transport of ions. The higher the number of charge carriers, the higher is the mobility and hence the higher in the conductivity. This can be explained on the basis of free volume model and hopping of charge carriers between localized states [7].

Film	TiO ₂ ratio	Ionic conductivity values at different temperatures X10 ⁻³ S cm ⁻¹				
		303K	313K	323K	333K	343K
K0	0	0.967	2.718	3.923	6.231	8.955
K1	4	2.264	3.013	5.746	7.713	9.426
K2	8	5.253	6.570	7.462	8.793	9.954
K3	12	7.165	8.331	9.946	12.694	15.624
K4	16	4.370	5.991	6.818	7.462	9.695

Table 1- Ionic conductivity values for PEO (72%) - PVP (8%) - LiClO₄ (8%) - PC (12%) - TiO₂ (0% , 4% , 8% , 12% , 16%) polymer electrolyte systems

The ions, solvated molecules or polymer segments can move into the free volume. The resulting conductivity represented by the overall mobility of ion and polymer is determined by the free volume around the polymer chain. This leads to an increase in ion mobility and segmental mobility that assist ion transport and virtually compensate for the retarding effect of ion clouds. It has been found that temperature dependent ionic conductivity of the sample with different concentrations seems to obey VTF relation [8]. Free volume around the polymer chain causes the mobility of ions and polymer segments and hence conductivity increases. Thus the increment of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobility.

4. SEM ANALYSIS

The SEM images of the polymer electrolyte film for best conductivity sample K3 is studied. It has been observed that the TiO₂ nanoparticles are uniformly dispersed in the composite. It is noted that the TiO₂ nanoparticles were embedded in polymer matrix, and this could be expected the pore formation in the range of 1µm which may induce the conductivity of the electrolyte. The content of TiO₂ blends with polymer matrix the film surfaces become smooth. Also, it's grain size decreases, with a reduction in the number of grain aggregates that tend to enhance the ionic movement. Consequently, the conductivity increases. It is evident from the image of the surface of the film that the ceramic had not undergone any chemical reaction with the polymer. The 12 wt% TiO₂ based complex shows that the ceramic particles present in the samples are more dispersed.

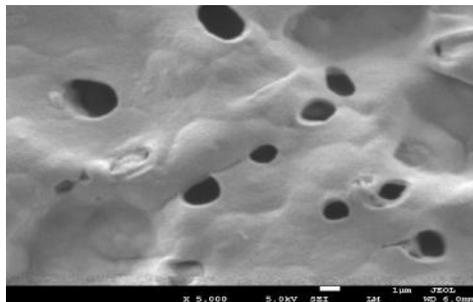


Figure 4- The morphology image of the sample K3

5. TG/DTA ANALYSIS

The graph shows the TG/DTA performance of the sample K3 (thermal stability about 250°C) at exhibiting higher ionic conductivity with the concentration of 12 wt% of TiO₂ nanofiller. The major weight loss is observed in the range of 260°C may be due to the degradation of propylene carbonate (PC) with the polymer matrix because of the boiling point of the PC is 242°C and it may also be due to the blended polymer degradation. DTA curve of the sample shows exothermic peaks initially at 140°C and major

peak at around 260°C which are well correlated with the weight loss of the sample observed in TG curve. It is also found that the complete decomposition of the sample takes place between 280°C and 300°C with the corresponding weight loss of about 60–70 wt%. After 280°C, no appreciable weight loss is observed. In DTA curve the exothermic curve occurs in the range of 260°C-310°C. This indicates the decomposition of the polymer film is in agreement with the observed TG results.

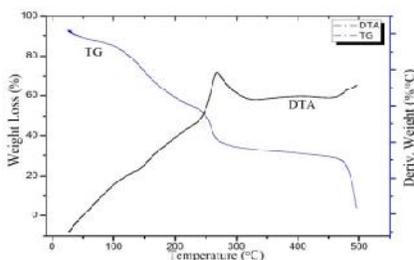


Figure 5- The Thermal analysis of the sample K3

CONCLUSION

Nano composite polymer electrolytes based on PEO/PVP with constant salt ratio of LiClO_4 and the plasticizer propylene carbonate (PC) were prepared for varies concentration of TiO_2 . The dissociation of the lithium salt and the interaction between the inert filler and the polymer salt complex were confirmed by X-ray diffraction analysis. It was found that 12wt% of the filler added PEO(72) - PVP(8) - LiClO_4 (8) - PC(12) complex showed higher ionic conductivity has been found to be $7.17 \times 10^{-3} \text{ S cm}^{-1}$ for 12% of TiO_2 polymer electrolyte than the other concentration systems. High resolution of the sample surface was characterized by scanning electron microscopy (SEM). The TG - DTA thermal analysis study of the membrane having maximum ionic conductivity was performed and identified that the polymer composite electrolyte is stable up to 250 °C. Hence this system can be performed as electrolyte for lithium battery fabrication.

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