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EFFECT OF SURFACTANT ON SYNTHESIS AND CHARACTERIZATION OF CeO_2 BASED P(S-MMA) GEL POLYMER ELECTROLYTE FOR LITHUM POLYMER BATTERY

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Abstract - In this work, Cerium oxide (CeO_2) nano particles were nucleated by mixing an aqueous solution of cerium nitrate ($Ce(NO_3)_3$. $6H_2O$ and sodium hydroxide (NaOH) using Poly vinyl pyrrolidone (PVP) as surfactant and the absence of surfactant respectively by Modified co-precipitation method at room temperature. The as prepared optimized wt.% of surfactant assisted and surfactant free CeO_2 nano particles (6 wt.%) were dispersed through the optimized P(S-MMA) (27)-$LiClO_4$(8) –EC+PC(65) system by solution casting technique. For comparison, the CeO_2 free polymer system was also prepared. The as prepared polymer films were characterized by XRD, FTIR and Impedance studies. In the XRD, all the peaks pertaining to salt and polymer were disappeared except CeO_2 phase. The complexation of the polymer matrix was confirmed through FTIR analyses. Surfactant assisted CeO_2 samples show the maximum conductivity was 8.15×10^{-3} S cm^{-1}. It seemed to obey the temperature dependent ionic conductivity relation. The incorporation of CeO_2 in the polymer electrolyte will enhance the other electrochemical property.

***Key Words*:** **Cerium oxide, Poly vinyl pyrrolidone, Ionic conductivity, Surfactant, XRD.**

1.INTRODUCTION

Due to ever-increasing energy demands and consumption, along with the resulting global environment problems and air pollution, the development of energy storage systems, especially, high-performance, low-cost and environmental-friendly electrochemical energy storage devices, has attracted great attention around the world during past several years [1,2]. A conventional Lithium ion battery is contained two electrodes and an electrolyte. Electrolyte is one of the key components, which act as the ion transport pathways. The cell capacity, working temperature range, safely issues and cyclability of the lithium ion batteries are influenced significantly by the selected electrolyte. According to the physical state, the electrolytes can be categorized into liquid electrolyte and solid electrolyte. Liquid electrolyte is broadly used in the Lithium polymer battery because of their high ionic conductivity. However, safety problems associated with Lithium metal anodes and reaction of volatile and flammable organic solvents and leakage of electrolyte. Safety risks can be substantially lowered if the organic liquid electrolytes are replaced by nonvolatile and non-flammable solid electrolytes [3-5]. A major issues with solid polymer electrolytes, however is the low ionic conductivity at ambient temperature. This is due to the low segmental mobility of the polymer chain incorporated with lithium salt. In this respect, most of the research has focused on the preparation and characterization of gel polymer electrolytes (GPEs) which exhibit high ionic conductivity at ambient temperature comparable to the liquid electrolytes; other properties such as mechanical strength, solvent retention ability and sub-ambient temperature conductivity should further be improved for practical applications.

One possible strategy to improve the conductivity is to form the composite polymer gel to add the inorganic filler in to the polymer to form the composite polymer electrolyte (CPE). The inorganic filler served as the solid plasticizers, can kinetically impede the reorganization of the polymer chains, and in turn the facilitate the dissociation lithium salts and the motion of Li^+ ions, due to the Lewis acid-base interaction between the polymer and filler or filler and ionic species.

Hitherto, the systematic study of CeO_2 nano particle based P(S-MMA) polymer electrolyte is scarce in the literatures. Due to tune the particle size of the CeO_2 nano particle, ceria nano particle using PVP as surfactant in aqueous media was successfully synthesized by co-precipitation method and surfactant free CeO_2 was also prepared for comparison. The as prepared CeO_2 nano particle was dispersed to the optimized P(S-MMA) gel polymer matrix using the solution casting technique. Then, as prepared polymer film was characterized using XRD, FTIR and Impedance analyses.

1.1 Materials and methods:

P (S-MMA) (Mol.wt 100.000-150.000), $LiClO_4$, Ethylene carbonate (EC) and Propylene carbonate (PC) were from Sigma Aldrich Limited, U.S.A. Tetra hydro furan (THF) (E-Merck, Germany) were used in the experiment. All the electrolytes were prepared by the conventional solution casting technique. The appropriate weights of P(S-MMA) and $LiClO_4$ were dried at 100°C at vacuum oven and dissolved in distilled tetrahydrofuran (THF) followed by the addition of plasticizers. The solution was then stirred continuously until the mixture took a homogenous viscous liquid appearance. The as prepared CeO_2 (6) wt. % were dispersed through the polymer electrolyte. The resulting solution was poured onto a glass Petri plate and the THF was allowed to evaporate in air at room temperature. This procedure provided mechanically stable, free standing and flexible films with thickness between 300 and 400 μm. The films further dried for 24h in vacuum at 60°C to remove any trace of THF. X- Diffraction measurements were carried out on the CeO_2 powder/Polymer electrolyte system at room temperature using an XPERT-PRO with CuKα radiation. FTIR study was made using Thermo Nicolet 380 Instrument Corporation and kBr in the 4000-400 cm^{-1} region. The surface and particle morphology of the samples were observed using a scanning Electron microscope (SEM).

Impedance spectroscopy was used to determine the ionic conductivity of the polymer composite films. Measurements were performed over the frequency range 1MHz to 10Hz, by means of frequency analyzer AUTOLAB/PGSTAT 30 (potentiostat/galvanostat) the polymer electrolyte films were sandwiched between two stainless steel electrodes which acted as blocking electrode for the ions.

2 RESULTS AND DISCUSSION

The XRD pattern provides information related to the complexation, composite formation, crystalline-amorphous phase contents for composite polymer electrolyte. Fig.1 depicts the XRD pattern of P(S-MMA)(a), $LiClO_4$(b), CeO_2 (c)and P(S-MMA)(27)-LiClO4(8)-EC+PC(65)-bare(d)-Surfactant free 6wt.% CeO_2(e)and PVP assisted 6wt.%CeO_2 (f). XRD pattern of CeO_2 shows several characteristic peaks at 2θ= 28.41,33.05, 47.49 and 56.31° corresponds to (110), (200), (220) and (311) reflections respectively. These reflections are also present e and f samples respectively. It is observed that no additional XRD reflections corresponding to $LiClO_4$ are found in CPEs, which is confirming proper complexation of P(S-MMA) and $LiClO_4$.

FTIR is an efficient tool to study the local structural changes in polymers. The IR spectra of these materials vary according to the content of the film and may be able to display the existence of the complexation. The Fourier Transform Infrared spectrum of the prepared complexes (d-f) is depicted in Fig. 2. The O-H stretching has been obtained in the region 3600 - 3100 cm^{-1}. The CH_2 scissoring mode of MMA appears at 1484, which is shifted in the complexes. These $\gamma_{C=O}$ skeletal breathing of EC appears at 1810 cm^{-1} is shifted to the lower wave numbers in the complexes which confirms the EC has been complexed into the polymer matrices [6]. The Ce-O stretching vibration was observed at 504 cm^{-1} is shifted in to the 598 cm^{-1} in the polymer matrix. The shifting of peaks in the disappearance of some peaks in the complexes with respective pure designates the complex formation.

The ionic conductivity of the composite polymer electrolytes was determined by employing AC impedance analysis by maintenance signal voltage as 10 mV in the temperature range 303-343 K. The d.c conductivity values were calculated from the complex impedance plot is shown in Fig.3 Using the relation $\sigma=l/R_bA$ where l-the thickness; A-Area of the electrolyte film; R_b is the bulk resistance which is obtained from the intercept of the resistance in complex-impedance plot. The maximum conductivity value 8.13×10^{-3} S cm^{-1} is obtained for 6 wt. % of surfactant assisted CeO_2 based CPE (b). P(S-MMA) gel based free filler film exhibits a conductivity value of about 4.42×10^{-5} S cm^{-1}. After incorporating plasticizer with the proper concentration of CeO_2, the conductivity is improved by two orders of magnitude. The ionic conductivity value of about 2.35×10^{-4} Scm^{-1} is obtained for 6wt.% surfactant free CeO_2 based CPE (c). Theoretically, for symmetric cell consisting stainless electrode, the impedance of the specimen appears as two portions; one is at the higher frequencies semi-circular corresponding to the bulk electrolyte impedance and the other at low frequencies straight line parallel to the imaginary axis related to the interfacial impedance. The surfactant based CeO_2 itself facilitates higher ionic conduction and mechanical strength for the electrolyte, the plasticizer EC provides more flexibility with greater conducting pathways for mobile species because of its high dielectric constant such as 89.6 at 40°C. The inclusion of ceramic fillers enhances free volume, which leads to higher salt dissociation, and also the defects introduced while dispersing the composite particles. A new transport mechanism develops because of an interaction of the polymer and ceramic phases. This transport mechanism provides a path for the conduction of lithium ions [7,8]. Therefore an appreciable enhancement in the conductivity has been obtained for the heterogeneous electrolyte. The improvement in conductivity can also be attributed to the ceramic particles, acting as a nucleation centre for the formation of minute crystallites and the ceramic particles aiding in the formation of amorphous phases in the polymer electrolyte [9].

Fig.4 shows the variation of ln conductivity with inverse absolute temperature for various compositions of CeO_2 based ratio of P(S-MMA) (27)-$LiClO_4$ (8) - EC+PC (65) complexes. Temperature-dependent ionic conductivity plots seem to obey the Arrhenius relation [10] which described the transport properties in a viscous matrix via a simple hopping mechanism decoupled from polymer-chain breathing. In addition, the change of conductivity with temperature can be explained by increase in the free volume of the system that facilitates the migration of ions.

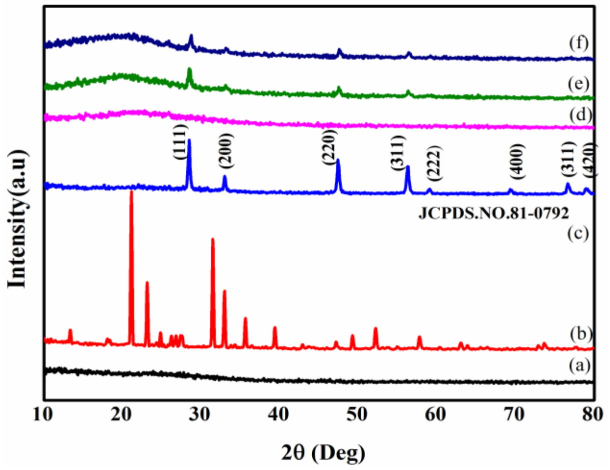

Fig.1 XRD pattern of a)P(S-MMA) b)LiClO4 c) CeO2d) P(S-MMA)(27)-LiClO4(8)-EC+PC(65)-6 wt.% CeO2(e)--6 wt% surfactant assisted CeO2 (f)

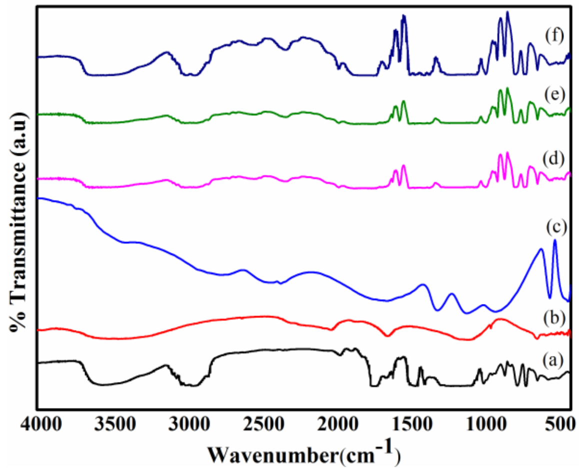

Fig.2 FTIR spectra of a)P(S-MMA) b)LiClO4 c) CeO2d) P(S-MMA)(27)-LiClO4(8)-EC+PC(65)-6 wt.% CeO2(e)--6 wt% surfactant assisted CeO2 (f)

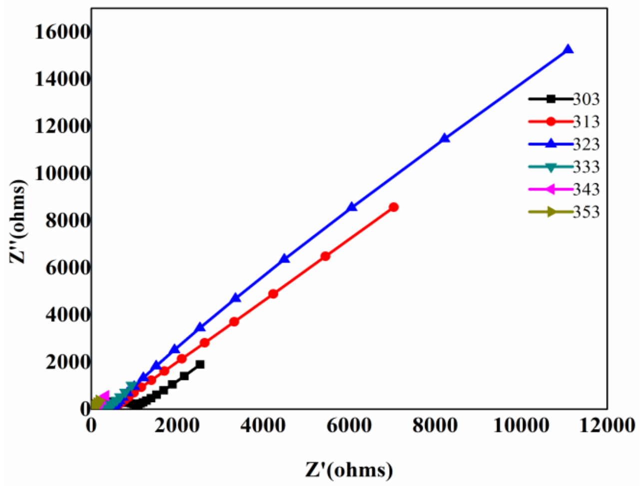

Fig.3 Nyquist plot of P(S-MMA) (27)-LiClO4(8)-EC+PC(65)-6 wt.% surfactant assisted CeO_2 polymer electrolyte in the temperature range 303-353K.

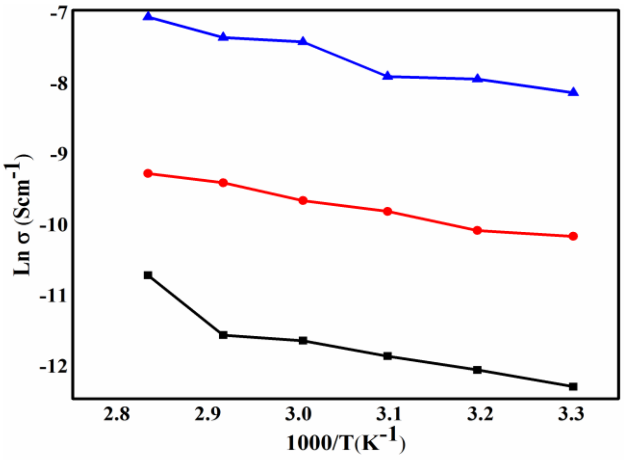

Fig.4 Arrhenius plots of P(S-MMA) (27)-LiClO4 (8)-EC+PC (65)- Bare, 6 wt.% (Surfactant free, Surfactant assisted) CeO_2.

3. CONCLUSIONS

The Ceria (CeO_2) nano particles were successfully synthesized using PVP as surfactant by modified co-precipitation method and surfactant free CeO_2 was also prepared. The as prepared CeO_2 nano particles (6wt.%) such as bare, surfactant free and surfactant assisted CeO_2 nano particles dispersed through optimized P(S-MMA)(27)-$LiClO_4$(8)-EC+PC(65) system by the conventional solution casting method. The as prepared films were analyzed through XRD, FTIR and Impedance analyses. XRD results revealed the amorphous nature of the electrolyte and the shift, absence of peaks and the appearance of new peaks in the FTIR spectra ascertained the complexation of the constituents. The surfactant assisted CeO_2 – P(S-MMA)(27)-$LiClO_4$(8)-EC+PC(65) showed the maximum ionic conductivity of the order of 8.13×10^{-3} Scm^{-1} . It was concluded that the polymer electrolyte suitable for the battery application.

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