



ICONN 2015 [4th -6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Conductivity studies on nano CdO dispersed PVC-PVdF polymer nano composite electrolytes

D.Ravindran^{1*}, P.Vickraman², N.Sankarasubramanian³, T.Sornakumar⁴

^{1,3}Department of Physics, Thiagarajar College of Engineering,
Madurai-625015, India

²Department of Physics, The Gandhigram Rural Institute - Deemed University
Gandhigram - 624302, India.

⁴Department of Mechanical Engineering, Thiagarajar College of Engineering,
Madurai-625015, India

Abstract: Nano-sized CdO particles were synthesized through sol-gel method and dispersed as filler in PVC-PVdF blend matrix with lithium perchlorate (LiClO₄) as dopant salt. Propylene carbonate (PC) was used as plasticizer and tetrahydrofuran (THF) as common solvent. The content (wt %) of CdO particles in the electrolyte was systematically varied to examine its influence on the ionic conductivity of the membranes. The electrolyte films were subjected to AC impedance analysis in the frequency range 10-100 KHz. The analysis shows the dependency of conductivity on the CdO content and the film with 4 wt% filler exhibits a maximum conductivity of 6.214×10^{-5} S/cm.

Introduction

Solid state ionic devices such as Li⁺ ion batteries, electro chromic devices, fuel cells, chemical sensors etc. are drawing much attention in view of our energy needs and environment safety¹⁻². Electrochemical energy production is under serious consideration as an alternate energy sources as it is sustainable, user and environment friendly. More over the miniaturization and portable electronic devices such as laptop computers, cellular phones, digital watches etc. have increased the demand for light weight high energy density rechargeable secondary batteries. Solid polymer electrolytes (SPE) have been studied for more than three decades owing its several advantages such as high ionic conductivity, high specific energy, solvent-free condition, wide electrochemical stability windows and easy process ability³. The functions of polymer electrolytes are i. act as separator between anode and cathode ii. provide good insulation to electrons to avoid internal short-circuits and iii. allow fast and selective transport to the desired ions. The development of SPE has gone through three stages. The dry polymer electrolytes are synthesized by dissolving the polymer and lithium salt in a suitable solvent. The conductivity of these systems is generally too low for practical application. The next stage is plasticized or gel polymer electrolytes where organic aprotic solvent with low viscosity and higher dielectric constant are incorporated⁴. However, they suffer from several drawbacks, such as decomposition, volatilization, reaction toward lithium metal electrode and also deterioration of the mechanical properties. To overcome these difficulties nano ceramic materials are dispersed in the membrane and it enhanced the

conductivity as well as mechanical stability of the film. The addition of fillers provide a significant increase in the conductivity, inhibits re-crystallization of the polymer, lowers the glass transition temperature (T_g) and increase cation transport number⁵. The enhanced cation conduction is believed to be due to the active interface between polymer and filler surface, which is based on the Lewis acid-base interaction. In the present work we have prepared PVC-PVdF blend based polymer electrolyte with lithium perchlorate (LiClO_4) as dopant salt. PVC can act as a mechanical stiffener in the electrolyte due to its immiscibility with the plasticizer. PVC-based polymer electrolyte plasticized with ethylene carbonate and propylene carbonate has been reported to applicable to lithium metal and lithium-ion secondary batteries⁶. LiClO_4 was chosen due to its smaller ionic radius and high solubility in most of the organic solvents. Cadmium Oxide (CdO) is n-type direct band gap semiconductor and widely used in photodiodes, photovoltaic cells, gas sensor etc. The content (wt%) of CdO particles was systematically varied and its effect on the conductivity profile of the electrolyte was studied through XRD and AC impedance analysis.

Experimental

All the reagents used in the synthesis of CdO were analytical grade and used without any purification. $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.5 M) was dissolved in distilled water. Ammonia solution was added to above solution dropwise until pH value of about 8 reached. The white precipitate formed was filtered and washed 4-5 times. Then it was dried in air and the resulting powder was calcinated at 400°C for 2 h⁷. Poly (vinyl chloride) PVC with average molecular weight 60,000 and anhydride lithium perchlorate (LiClO_4) was purchased from Sigma-Aldrich. The LiClO_4 was dried in vacuum at 100°C for 24 h prior to use. Poly ethylene glycol (PEG) (m.wt=200) was procured from CDH, India. The plasticizer propylene carbonate (PC) and the anhydrous tetrahydrofuran (THF) was obtained from Merck. The appropriate wt% of polymer (PVC+PEG) and LiClO_4 was dissolved in the solvent separately. These two solutions were mixed together then plasticizer (PC) was added and the mixed solution was stirred continuously. Then after complete dissolution appropriate amount of CdO filler were added slowly. The solution was again stirred slowly at constant rate for a period of 14-16 h to get a homogeneous gel solution and it was degassed to remove air bubbles. The highly viscous solution thus obtained was cast on cleaned glass plate and the cast films were allowed to stand in air at room temperature to allow slow evaporation of solvent. The residual THF was further removed by drying in vacuum at 60°C for 24 h. The films were visually examined for their dryness and free-standing nature.

The crystalline nature of the synthesized CdO was investigated using JEOL, JDX 8030 X-ray diffractometer. The AC conductivity studies were performed using a computer controlled micro Autolab type III Potentiostat/Galvanostat impedance analyzer at ambient temperature. Polymer films were sandwiched between two stainless steel (SS) electrodes under an oscillation potential of 10 mV from 10-100 KHz. The SEM imaging was performed by Philips XL30, EDAX connected to SEM to investigate the elemental analyses of the nanostructure materials.

Results and Discussions

XRD analysis

Fig1. shows the diffraction pattern of synthesized CdO nanoparticles. The diffraction peaks corresponding to $2\theta = 33, 38.5, 55.4, 65.9$ and 69.3° are related to the crystal planes (111), (200), (220), (311), and (222) of face centered cubic phase. All the peaks matching well with standard JCPDS data (05-0640). No other peaks are found indicating the purity of the sample. The sharp intense peaks confirm the crystalline nature of the particles. The size of the particles was determined using Debye Scherre's formula; $D = k\lambda/2\beta \cos\theta$ where k is a constant equal to 0.89, λ the X-ray wavelength (0.154095 nm), β the full wavelength at half maximum (FWHM) and θ the half diffraction angle. The average particle size calculated using the above formula is 36 nm. Fig.2 shows the SEM image of the CdO particles. The image reveals there is no agglomeration of the particles. Fig. 3 shows the EDAX spectrum and confirms the presence of CdO component.

Fig. 4 shows the diffraction spectra of pure PVC, PVdF, PEG, LiClO_4 , CdO filler and the composite electrolyte film without filler and with 4 wt% filler. The broad peak corresponding to PVC shows the amorphous nature of the polymer. The diffraction peak at $2\theta = 20^\circ$ was based on the crystalline structure of PVdF. The two prominent peaks of PEG ($2\theta = 19.2^\circ$ and 23.4°) show the crystalline nature of the polymer. None of the peaks corresponding to lithium salt is found in the membrane indicating the absence of excess salt

in the complexed polymer films. There is a slight decrease in the height of the broad hump of the diffraction pattern of the composite film.

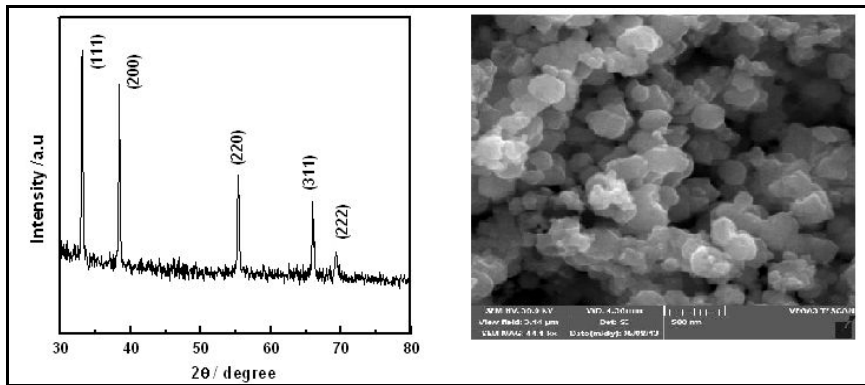


Fig. 1 XRD pattern of synthesized CdO Fig. 2 SEM image of CdO nano particles

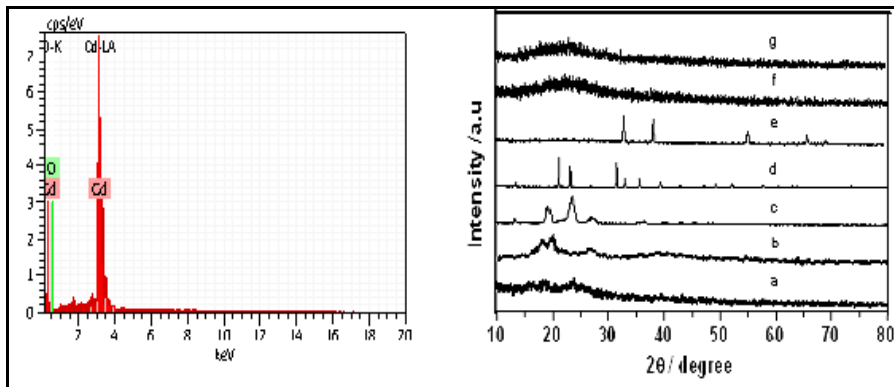


Fig. 3 EDAX spectrum of CdO

Fig. 4 XRD. Film pattern a. PVC b. PVdF c. PEG d. LiClO4 e. CdO f. Film C1 g. Film C5

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy is an excellent tool for characterizing the many of the electrical properties of materials⁸. Fig.5 and Fig.6 shows the complex impedance plot of polymer electrolyte film C2 (with 0.5 wt % filler) and C5 (with 4.0 wt % filler). The conductivity of the polymer electrolyte can be calculated from the relation; $\sigma = l / R_b(\pi r^2)$ where l is the thickness of the electrolyte and r is the radius of the circular disc. The bulk resistance R_b is obtained from the Nyquist plot of real impedance (Z_r) vs imaginary impedance (Z_i) whose numerical value is just the length from the origin to the intersection point of x-axis. The impedance plot of film C1 shows a depressed semicircle at high frequency region and a 45° inclined spike at low frequency region. But the high frequency semicircle is absent for film C5 indicating only resistive component present in the electrolyte. As the filler content increases a local effective pathway is created in the plasticizer rich domain for ionic conduction. The free ions can quickly migrate in this plasticizer rich region as the electric potential alternates between the positive and negative electrodes in an AC field⁹.

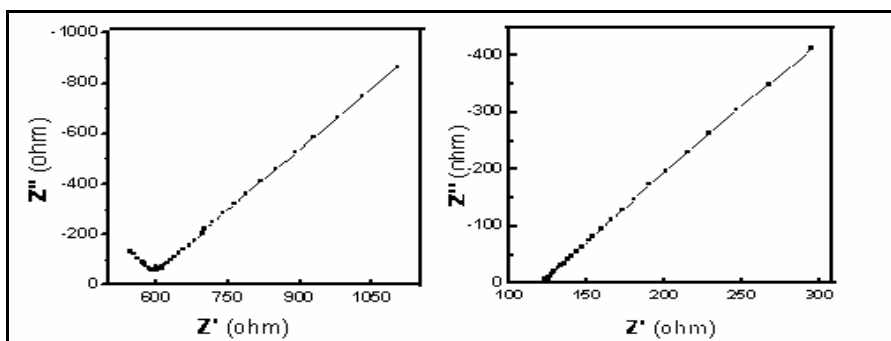


Fig.5 Impedance spectra of film C1

Fig.6 Impedance spectra of film C5

Ionic conductivity studies

The composition and the conductivity values of the electrolyte films are tabulated in Table 1. The film with composition (PVC-PVdF-PEG-PC-LiClO₄-CdO) = (16-5-15-50-10-4) exhibits higher conductivity of 6.214X10⁻⁵ S/cm at room temperature. The conductivity of a polymer electrolyte can be described by the relation, $\sigma = \sum \mu_i n_i q_i$; where μ represent the mobility, n concentration and q the charge of the conducting species. The variation of ionic conductivity at room temperature with respect to the content of nano CdO filler is shown in Fig. 7. The conductivity is not a linear function of filler concentration, as filler concentration increases conductivity increases, reaches a maximum value and decreases. Similar behavior is observed in BaTiO₃ dispersed PVC-PEG polymer electrolytes where the conductivity reaches a maximum value with 5 wt% doped filler and then show a decreasing trend with increasing filler concentration¹⁰.

Table.1 Composition and conductivity values of polymer electrolytes at RT

| code | PVC wt% | PVdF wt% | PEG wt% | PC wt% | LiClO ₄ wt% | CdO wt% | $\sigma \times 10^{-5}$ S/cm |
|------|---------|----------|---------|--------|------------------------|---------|------------------------------|
| C1 | 20.0 | 5 | 15 | 50 | 10 | 0 | 1.748 |
| C2 | 19.5 | 5 | 15 | 50 | 10 | 0.5 | 1.981 |
| C3 | 19.0 | 5 | 15 | 50 | 10 | 1.0 | 2.035 |
| C4 | 18.0 | 5 | 15 | 50 | 10 | 2.0 | 3.485 |
| C5 | 16.0 | 5 | 15 | 50 | 10 | 4.0 | 6.214 |
| C6 | 14.0 | 5 | 15 | 50 | 10 | 6.0 | 4.235 |

The initial increase in the conductivity due to the addition of CdO could be attributed to the creation of free ions. The ion transport basically occurs due to the movement of Li⁺ ions through the amorphous phase¹¹. The addition of filler increases the ionic conductivity by inhibiting re-crystallization and providing Li⁺ conducting pathways at the filler surface. The decrease in conductivity for 6 wt% filler doped electrolyte can be attributed to the fact that aggregation of CdO nanoparticles favoring inter particle interaction which in turn block the transport of charge carriers¹².

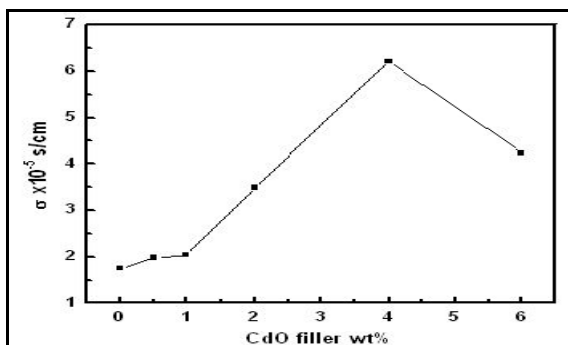


Fig.7 Filler (wt%) vs. Ionic conductivity

Conclusion

Polymer electrolytes with PVC-PVdF blend as matrix and LiClO₄ as salt has been prepared through conventional solution casting method. CdO nanoparticles are synthesized by sol gel method and incorporated as filler to study its influence on the conductivity profile of the electrolyte. The AC impedance analysis reveals strong dependency of conductivity on the CdO concentration. The 4 wt% filler doped exhibits significant enhancement in the conductivity value. Beyond this concentration the conductivity decreases due to blocking effect on the transport of ions resulting from aggregation of nanoparticles.

References

1. Dias FB, Plomp L, Veldhuis JBJ. Trends in polymer electrolytes for secondary lithium batteries. *J Power Sources.*, 2000, 88; 169-191

2. Scrosati B, Croce F, Panero S. Progress in lithium polymer battery R&D. *J Power Sources.*, 2001, 100; 93-100
3. Heitner KL. The search for the better polymer electrolyte. *J Power Sources.*, 2000, 89; 128-131
4. Kim YT, Smotkin ES. The effect of plasticizers on transport and electrochemical properties of PEO-based electrolyte for lithium rechargeable batteries. *Solid State Ionics.*, 2002, 149; 29-37
5. Bhattacharya S, Ghosh A. Effect of ZnO nanoparticles on the structure and ionic relaxation of poly(ethylene oxide) – LiI polymer electrolyte nanocomposites. *J Nanosci Nanotech.*, 2008, 8; 1922-1926
6. Alamgir M, Abraham K. M. Li ion conductive electrolytes based on Poly (vinyl Chloride). *J. Electrochem. Soc.* 1993, 140(6); L96-L97
7. Amrut S Lanje, Raghmani S Ningthoujam, Satish J Sharma, Ramchandra B Pode. Luminescence and electrical resistivity properties of cadmium oxide nanoparticles. *Indian J. of Pure & Applied Physics.*, 2011, 49; 234-238
8. Scrosati B, Croce F, Persi L. Impedance spectroscopy study of PEO-based nanocomposite polymer electrolytes. *J. Electrochem Soc.*, 2000, 147; 1718-1721
9. Subba Reddy Ch.V, Quan-Yao Zhou, Li-Qiang Mai, Wen Chen. Electrochemical studies on PVC/PVdF blend based polymer electrolytes. *J. Solid State Electrochem.* 2007, 11; 543-548
10. Vickraman P, Ravindran D. Investigation on compositional effect of PEG: BaTiO₃ in plasticized PVC-LiBETi polymer composite electrolytes. *Ionics.*, 2011, 17; 565-571
11. Xi J, Tang X. Nanocomposite polymer electrolyte based on poly(ethylene oxide) and solid super acid for lithium polymer battery. *Chem Phys Lett.*, 2004, 393; 271-276
12. Kumar B, Scanlon LG, Spry RJ. On the origin of conductivity enhancement in polymer-ceramic composite electrolytes. *J. Power Sources.*, 2001, 96; 337-342
