

**DEVELOPMENT OF ORGANIC/INORGANIC COMPOSITE  
ELECTROLYTE MATERIALS BASED ON POLY (ETHYLENE  
OXIDE) AND MONTMORILLONITE (PEO/MMT) FOR  
APPLICATIONS IN ELECTROCHEMICAL DEVICES**

A THESIS PRESENTED BY

CHINTHAN HEMAPA MANORATNE ✓

to the Board of Study in Chemical Sciences of the  
**POSTGRADUATE INSTITUTE OF SCIENCE**

in partial fulfillment of the requirement  
for the award of the degree of

**MASTER OF PHILOSOPHY IN CHEMISTRY**

of the

**UNIVERSITY OF PERADENIYA**

**SRI LANKA**

**2005**

**591012**

# DEVELOPMENT OF ORGANIC/INORGANIC COMPOSITE ELECTROLYTE MATERIALS BASED ON POLY (ETHYLENE OXIDE) AND MONTMORILLONITE (PEO/MMT) FOR APPLICATIONS IN ELECTROCHEMICAL DEVICES.

C. H. Manoratne

Department of Chemistry

University of Peradeniya

Peradeniya

Sri Lanka

The widespread research activities and the understanding of some apparently inert and electrically insulating materials which, can promote the ionic conductivity of polymer electrolytes have opened up a new page in the development of conducting materials. Montmorillonite (MMT) is an inert and electrically insulating material in its pure state, and one of the clay minerals of smectite group, which shows unique features of marked cation exchange properties, film formation from fine dispersions in water or other organic solvents, expandability, taking up water or organic molecules between their interlayer spacing. Organic/inorganic composite polymer electrolytes formed by incorporating MMT as a plasticizer into PEO based electrolytes show enhanced ionic conductivities compared to the MMT free electrolytes.

In this research work, an attempt was made to improve the ionic conductivity of the systems of MMT/poly(ethylene oxide) (PEO)/cations ( $\text{Li}^+$ ) and the polymer electrolyte system of  $(\text{PEO})_6\text{LiCF}_3\text{SO}_3$  by incorporating montmorillonite (MMT) as the plasticizer. The ionic conductivity, thermal properties, crystallinity, and the bonding were systematically characterized by ac-impedance spectroscopy, differential scanning calorimetry (DSC), X-ray diffraction spectroscopy (XRD), and fourier transformed infrared spectroscopy (FTIR), respectively.

The XRD data reveal that the MMT has a d-spacing of 15.49 Å, which is attributed to the presence of  $\text{Na}^+$  and two water layers within interlayers at room temperature. The removal of water brings the d-spacing to 9.97 Å. The  $\text{Li}^+$  exchange gives a d-spacing of 15.57 Å which on dehydration gives d-spacing of 9.97 Å. Solution intercalation of PEO into MMT and MMTLi results in the enhancement of d-spacing up to ~ 18.73 Å which readily takes up water enhancing the d-spacing to ~ 23.33 Å. These results show clearly that PEO is readily intercalated in MMT at a composition of 6% PEO. The enhancement of d-spacing at 6% PEO composition has not been observed previously.

FTIR spectroscopy is a powerful tool in the characterization of microscopic properties in electrolytic systems [1, 4]. Ordinary montmorillonite (MMTNa) shows typical vibrational modes at  $916\text{ cm}^{-1}$   $\nu(\text{Al-O-H})$ ,  $1040\text{ cm}^{-1}$   $\nu(\text{Si-O})$  and a band in the region  $3300\text{ cm}^{-1}$ - $3700\text{ cm}^{-1}$  due to  $\nu(\text{OH})$  stretching modes. Clearly two types of  $\nu(\text{O-H})$  are seen: isolated OH groups and those involved in hydrogen bonding. The  $\text{Li}^+$  exchange decreases the extent of isolated hydroxyl groups, but the extent of H-bonding increases. This suggests that  $\text{Li}^+$  is coordinated by the octahedral unit of the MMT, through the O atoms (ions) of free Al-O-H groups. The enhancement of ionic conductivity measured using ac impedance analyzer supports this arrangement. The intercalation of PEO in MMTLi reverses the above process by forming H-bonds with  $\text{Li}^+$ . The amount of free O-H then increases and the extent of hydrogen bonded O-H decreases.

The comparison of FTIR spectra of MMT, PEO,  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ , and  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3 + 5\text{ wt.}\%$  MMT clearly shows that the interactions take place between these constituents, as the intensities of typical stretching vibrational modes of  $916\text{ cm}^{-1}$   $\nu(\text{Al-O-H})$ ,  $1040\text{ cm}^{-1}$   $\nu(\text{Si-O})$  and  $3300$ - $3700\text{ cm}^{-1}$   $\nu(\text{OH})$  in MMT, and the vibrational modes of  $\text{CH}_2$  rocking at  $948$  and  $840\text{ cm}^{-1}$  and C-O stretching at  $1149$  and  $1090\text{ cm}^{-1}$  in PEO are changed. The change of symmetric bending mode of  $\text{CF}_3$  [ $\delta_s(\text{CF}_3)$ ] at  $752\text{ cm}^{-1}$  in lithium triflate has altogether supported the conformation of the electrolyte system and the corresponding conductivity enhancements. The specific, balanced interactions with the corresponding properties can only be found in the system of  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3 + 5\text{ wt.}\%$  MMT.

The ac impedance data reveal that the ionic conductivity of  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  system is changed with the concentration of MMT. Maximum conductivity of  $4.15 \times 10^{-7}\text{ S cm}^{-1}$  at room temperature was observed for the system of  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3 + 5\text{ wt.}\%$  MMT. The DSC and XRD data clearly show that the crystalline nature of PEO is reduced when MMT is added and the glass transition temperature and the melting temperature are also reduced. The resulting amorphous environment evidently contributes to the enhancement of ionic conductivity.