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Preparation and Characterization of (PEO+$NaClO_3$) Based Polymer Electrolyte System and Its Application as an Electrochemical Cell

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ABSTRACT
Ion conducting polymer electrolyte films of poly (ethylene oxide) (PEO) complexed with $NaClO_3$ salt have been prepared in the weight ratios (90:10), (80:20) and (70:30) by solution-casting technique using methanol and water as solvents. The complexation of poly (ethylene oxide) (PEO) and $NaClO_3$ have been studied by using X-ray diffraction (XRD), IR and differential scanning calorimetry (DSC). Using these polymer electrolyte films, solid-state electrochemical cells are fabricated and their discharge characteristics are examined for a constant load of 100 kΩ. Several cell parameters associated with the cells evaluated and reported.
Keywords – Polymer, poly (ethylene oxide), X-ray diffraction, differential scanning calorimetry, electrochemical cells.

I. INTRODUCTION

A variety of ion-conducting materials, polymer salt complexes are of current significance on account of their possible application as solid electrolytes in solid electrochemical devices such as energy conversion units like batteries, fuel cells, electro chromic display devices, smart windows, photo-electrochemical solar cells, etc. [1-5]. The major advantages of polymeric electrolytes are their mechanical properties, the ease of fabrication of thin films of desirable size, and their ability to form proper electrode-electrolyte contacts. Poly (ethylene oxide) (PEO), in particular, is an exceptional polymer which dissolves high concentrations of a wide variety of salts to form polymeric electrolytes [6]. The complexes of PEO with a number of alkali salts such as $LiBF_4$, $LiPF_6$ and $LiB(C_6H_5)_4$ [7], LiSCN [8], $LiSO_3CF_3$ and $LiClO_4$ [9], NaSCN [10], $NaPF_6$ [11], $NaYF_4$ & KYF_4 [12] and $KBrO_3$ [13] are reported.

In an attempt to investigate the possibility of fabricating electrochemical cells based on other polymer, studies have been conducted on electrochemical cells based on poly (acrylamide) (PA) and poly(vinyl pyrrolidone) (PVP) polymers [14-17]. In this present work (PEO+$NaClO_3$) based polymer electrolyte electrochemical cells have been fabricated and studied its discharge characteristics.

II. EXPERIMENTAL

Ion conducting solid state polymer electrolyte films (thickness ≅ 100 – 150 μm) of PEO [Aldrich, molecular weight ($4X10^5$)] complexed with $NaClO_3$ salt have been prepared in the weight ratios (90:10), (80:20) and (70:30) by solution-casting technique using methanol and water as solvents. The solutions were stirred for 15-20 hr, were cast on polypropylene dishes, and were evaporated slowly at room temperature. Finally, the films were dried thoroughly at 10^{-3} Torr [17]. X-ray diffraction (XRD) analyses of all the samples were carried out by using a SIEMES / D 5000 X-ray diffractometer (Cu K_α radiation λ = 1.5406 Å). The infrared spectrum of polymer electrolyte films was recorded on a PERKIN ELMER FTIR spectrophotometer [Model 1605] in the range of 1000 – 4000 cm^{-1}. DSC (TA 2010 Instrument) was used to study the melting temperatures of the polymer electrolyte films [18]. Solid state electrochemical cells have been fabricated with the configuration Na / (PEO + $NaClO_3$) / (I_2 + C + electrolyte), the details about the fabrication of the electrochemical cells are given elsewhere [19]. The discharge characteristic studies of these cells were monitored for a constant load of 100 kΩ.

III. RESULT AND DISCUSSION

X-ray diffraction:

X-ray diffraction (XRD) patterns of pure PEO and $NaClO_3$ are shown in Fig. 1. A comparison of the diffraction spectra of complexed PEO with that of pure PEO and $NaClO_3$ reveals the following details:

- XRD pattern obtained in the 2θ range of 10^o to 30^o, where the complexed PEO films to be less intense than those for the pure PEO films, which indicates that the addition of $NaClO_3$ to the polymer causes a decrease in the degree of crytallinity of the polymer PEO.

- Peaks corresponding to the uncomplexed PEO are also present, on one those of the $NaClO_3$, in complexed PEO films, showing the simultaneous presence of both crystalline uncomplexed and complexed PEO [20–24].
- For the higher concentration of $NaClO_3$ salt in the polymer, no sharp peaks were observed, which indicates the dominant presence of an amorphous phase.

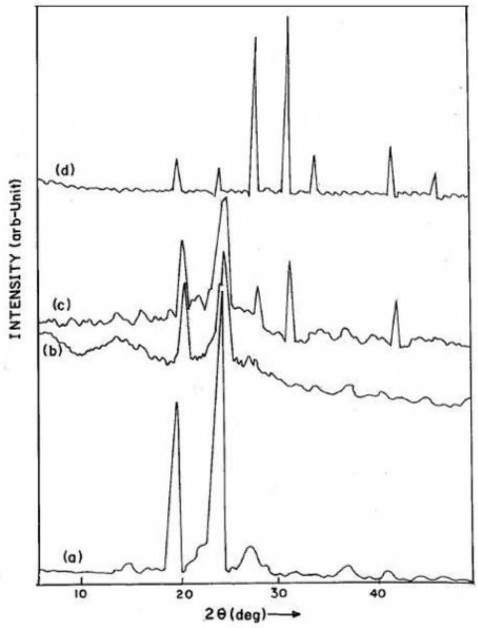

Fig. 1 X – ray diffraction spectra (a) Pure PEO (b) (PEO+$NaClO_3$) [90:10] (c) (PEO+$NaClO_3$) [70:30] (d) $NaClO_3$

Therefore, the XRD pattern clearly indicates a complexation between the $NaClO_3$ salt and the PEO polymer.

IR studies:

The complexation of pure PEO with $NaClO_3$ salt has been extensively studied using vibrational spectroscopic studies [20]. The IR spectra of pure PEO, $NaClO_3$ and PEO complexed with $NaClO_3$ are shown in Fig.2. The following differences in the spectral features have been observed on comparing the spectra of complexed PEO with pure PEO and $NaClO_3$.

- The intensity of the aliphatic C-H stretching vibrational band observed around 2897.1 cm^{-1} in PEO decreases with increasing concentration of $NaClO_3$ salt in the polymer.
- The width of the C-O Stretching band observed around 1095.2 cm^{-1} in PEO also showed an increase with an increase of $NaClO_3$ in the polymer.
- Several new peaks around 4329.6, 4002.0, 2363.4 and 1280.8 cm^{-1} have been observed in complexed PEO.

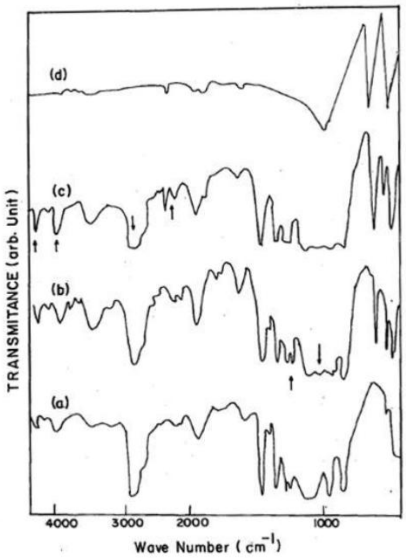

Fig. 2 IR spectra (a) Pure PEO (b) (PEO + $NaClO_3$) [90:10] (c) (PEO + $NaClO_3$) [70:30] (d) $NaClO_3$.

The appearance of new peaks along with changes in existing peaks (and / or their disappearance) in the IR spectra directly indicates the complexation of $NaClO_3$ with PEO. If the cations of $NaClO_3$ get coordinated with the ether oxygen of PEO, the spectral changes are expected to be in the COC stretching and deformation ranges. The decrease in the width of 1095.2 cm^{-1} band, which is assigned to COC symmetrical and asymmetrical stretching [21-22], suggests the coordination / complexation of the salt with the polymer PEO.

Studies of Differential Scanning Calorimetry (DSC):

Figure 3 shows the differential scanning calorimetry (DSC) curves of pure PEO and various compositions of complexed PEO. At 70^oC an endothermic peak corresponding to the melting temperature (T_m) of the pure PEO was observed. With the addition of $NaClO_3$ to pure PEO, the melting temperature (T_m) slightly shifted towards lower temperatures [18 & 23].

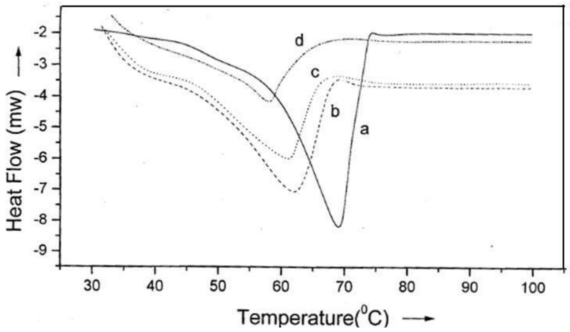

Fig. 3 DSC curves (a) Pure PEO (b) (PEO + $NaClO_3$) [90:10] (c) (PEO + $NaClO_3$) [80:20] (d) (PEO + $NaClO_3$) [70:30].

Electrochemical cells:

Using (PEO+$NaClO_3$) polymer electrolyte films, solid state electrochemical cells have been fabricated with the configuration Na (anode) / (PEO + $NaClO_3$) / (I_2 + C + electrolyte) (cathode). Sodium metal was used as the negative-material, and a mix of iodine (I_2), graphite (C) and electrolyte in the ratio 5:5:1 as the positive. The discharge characteristics of various ratios of (PEO + $NaClO_3$) (90:10), (PEO + $NaClO_3$) (80:20) and (PEO + $NaClO_3$) (70:30) of (PEO + $NaClO_3$) at ambient temperature for a constant load of 100 kΩ are presented in Figure 4.

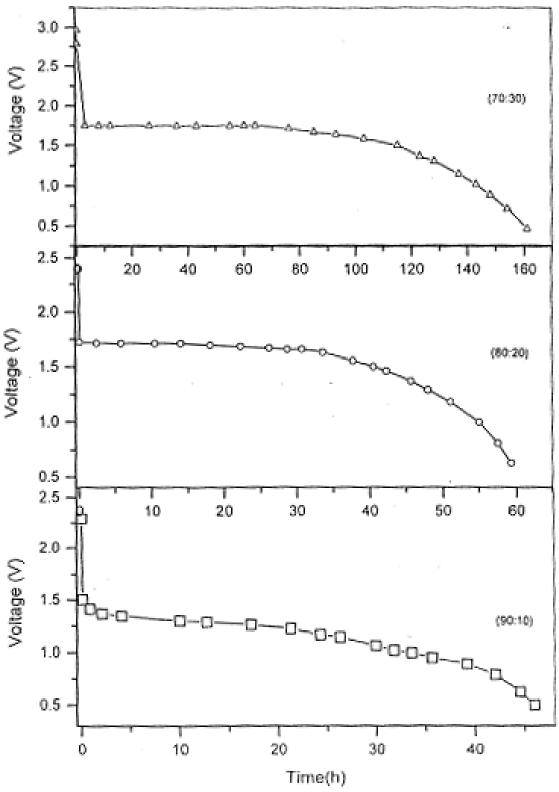

Fig.4 Discharge characteristics of (a) (PEO + $NaClO_3$) [90:10] (b) (PEO + $NaClO_3$) [80:20] and (c) (PEO + $NaClO_3$) [70:30] of Electrochemical cell for a constant load of 100kΩ.

The initial sharp decrease in voltage of these cells may be due to polarization and / or formation of a thin layer of sodium salt at the electrode / electrolyte interface [13, 17 & 19]. The Open-Circuit Voltage (OCV) and Short-Circuit Current (SCC) and other cell parameters for these cells are evaluated and are given in Table 1.

Table 1. Electrochemical cells parameters of various (PEO+$NaClO_3$) polymer electrolyte system.

Cell parameters	(PEO+$NaClO_3$) (90:10)	(PEO+$NaClO_3$) (80:20)	(PEO+$NaClO_3$) (70:30)
Open Circuit Voltage (OCV) (V)	2.29	2.40	2.97
Short Circuit Current (SCC) (μA)	22.01	42.3	346
Area (cm^2)	1.34	1.34	1.34
Weight (gm)	1.23	1.10	1.21
Discharge Time (h)	42	55	142
Current Density ($\mu A/cm^2$)	16.42	31.56	258.20
Power Density (mw/kg)	12.70	20.30	25.30
Energy Density (mw-h/kg)	533.53	1116.87	3592.60

IV. CONCLUSION

($PEO + NaClO_3$) based polymer electrolytes have been prepared by using solution-casting technique with the weight ratios (90:10), (80:20) and (70:30). The complexation of poly (ethylene oxide) (PEO), $NaClO_3$ have been conform by using X-ray diffraction (XRD), IR and differential scanning calorimetry (DSC). Solid-state electrochemical cells have been fabricated and studied its discharge characteristics and other cell parameters.

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