

Role of Salt Concentration on Conductivity and Discharge Characteristics of PMMA Based Polymer Electrolyte System

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Abstract- Solid polymer electrolyte films based on PMMA were prepared in different NaClO₄ salt concentrations by solution cast technique. The features of complexion of these electrolytes were studied by X-ray diffraction (XRD). Film morphology was examined by Scanning Electron Microscopy (SEM). The electrical conductivity of pure and NaClO₄ doped polymer electrolyte films was studied in the temperature range 303-393 K. The electrical conductivity increased with increasing dopant concentration and exhibited Arrhenius type dependent with temperature. The increase in conductivity with dopant concentration may be attributed to the formation of charge transfer complexes. Transport number data showed that the charge transport in this electrolyte system is predominately due to ions. Using this polymer electrolyte, solid state electrochemical cell have been fabricated, and their discharge profiles were studied under a constant load of 100 kΩ.

Index Terms- Polymer electrolyte film, XRD, SEM, Electrical conductivity, Transference number and Discharge characteristics

I. INTRODUCTION

Investigations show that ion-conducting polymers exhibit many excellent properties, and they are the most promising electrolytes used in a variety of electrochemical devices [1-3] such as rechargeable batteries, fuel cells, super capacitors, chemical sensors, electro chromic windows, etc. Among the polymer electrolyte systems, solid polymer electrolytes (SPEs) have many advantages such as ionic conductivity, high-energy density, leak proof, solvent-free condition, wide electrochemical stability windows, easy processability, and light weight.

Literature reveals that electrical transport properties in a polymer occur through the amorphous phase rather than crystalline [4]. In view of this notion concluded from nuclear magnetic resonance spectroscopy data, it appears more appropriate to select a polymer host that is predominantly amorphous such as PMMA having ~96% amorphous content at 25°C [5]. In addition, PMMA is a lightweight and transparent polymer having lesser reactivity toward lithium-metal-based anode, thereby providing scope for the improvement of electrode-electrolyte interfacial stability. These expected

advantages provided substantial impetus to modify PMMA, which is predominantly insulating with only electronic transport, into an ionically conducting system. Subsequently, a number of ionically conducting SPE and gel polymer electrolyte based on PMMA with different combinations of salts and solvents, such as PMMA-LiClO₄ [6–8], PMMA-NH₄CF₃SO₃ [9], PMMA-LiBF₄ [10], PMMA-Li₂SO₄ [11], with solvents such as acetonitrile, ethylene carbonate, and propylene carbonate, etc. have been reported in the literature.

Extensive research has been carried out on Li⁺ salts complexed polymer electrolytes. However, only a few attempts have been made on electrolytes based sodium complexed films. Use of sodium in the poly electrolytes has several advantages over their lithium counter parts. Sodium is available in abundance at a cheaper cost than lithium. It is feasible to obtain solid electrolytes of sufficiently high conductivity because sodium does not form any alloy with the electrode materials, such as aluminum and nickel. Furthermore, the softness of these materials makes it easier to achieve and maintain contact with other components in the battery. Investigations have also been made [12–14] on sodium ion-conducting polymer electrolyte based on PEO, polypropylene oxide (PPO), and polybismethoxy ethoxy phosphazene (MEEP) complexed with NaI, NaClO₄, NaSCN, and NACF₃SO₃.

In the present paper, we report the effect of sodium salt concentration on conductivity, transference number and discharge profile of PMMA based polymer electrolyte system.

II. EXPERIMENTAL

Films (thickness, ~150 μm) of pure PMMA+NaClO₄ in the wt.% ratios (95:05), (90:10), (85:15), and (80:20) for conductivity measurements and battery discharge profiles were prepared by the solution-cast technique using tetrahydrofuran (THF) as solvent. The mixture of these solutions was stirred for 10–12 h, cast onto polypropylene dishes, and evaporated slowly at room temperature. The final product was vacuum dried thoroughly at 10–3 mbar.

X-ray diffraction (XRD) studies were performed using SEIFERT X-ray diffractometer in the range 10-70°. The

morphology of the samples was studied using JOEL JSM 840A Scanning electron microscope (SEM). The DC conductivity of pure and NaClO₄ doped polymer electrolytes was studied as a function of temperature ranging from 303 K to 393 K, and the activation energies were evaluated. The total ionic transport number (t_{ion}) was evaluated by means of Wagner's polarization technique [15]. In this technique, freshly prepared polymer electrolyte films were polarized in the configuration Na/polymer electrolyte/C under a dc bias (step potential of 1.5 V). The resulting current was monitored as a function of time. After polarizing the electrolyte, the transport number (t_{ion}) was calculated from the initial current I_i and the final residual current I_f , i.e.,

$$t_{ion} = (I_i - I_f) / I_i$$

$$t_{ele} = 1 - t_{ion}$$

Using (PMMA+NaClO₄) as the electrolyte, electrochemical cells with configuration Na/(PMMA+NaClO₄)/(I₂+C+electrolyte) were fabricated. The discharge characteristics of the cells were studied under a constant load of 100 kΩ.

III. RESULTS AND DISCUSSION

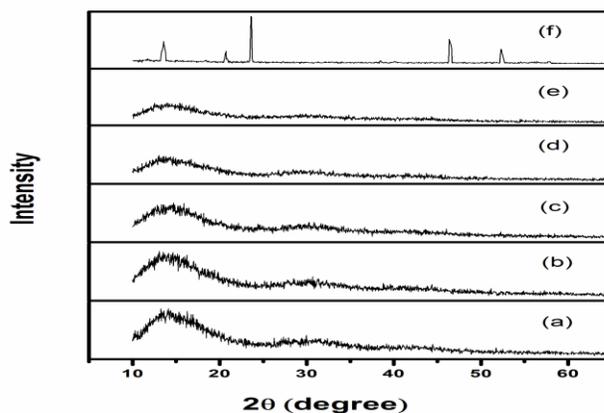
A. X-ray diffraction studies

In order to investigate the influence of sodium salt on PMMA structure, XRD studies were performed. Figure 1 (a–f) shows the XRD patterns of pure PMMA, NaClO₄ salt, and PMMA complexed with NaClO₄ salt. Comparison of the XRD patterns of complexed PMMA films with those of pure PMMA and NaClO₄ reveals the following differences. Peaks observed for 2θ values around 14° are less intense in complexed PMMA films compared to those in pure PMMA film. This indicates that the addition of NaClO₄ salt causes a decrease in the degree of crystallinity of the PMMA complex. The crystalline peaks for 2θ values at 14, 23, 46 and 52° corresponding to NaClO₄ (Fig. 1f) are absent in complexed PMMA. This indicates the absence of any excess (uncomplexed) salt in the complexed polymer electrolyte films. Therefore, it may be confirmed that complexation has taken place in the amorphous phase. This amorphous nature resulted in greater ionic diffusivity with high ionic conductivity, as amorphous polymers have flexible backbone [16].

B. SEM analysis

The morphology of pure PMMA and NaClO₄ complexed PMMA based composite polymer electrolytes with weight percent ratios (95:05), (90:10), (85:15) and (80:20) studied using the SEM technique, was of uniform type, but with different degree of roughness as shown in Fig2 (a-f). This suggests that the PMMA molecules disperse in the soft-

Fig. 1 XRD patterns of (a) Pure PMMA (b) PMMA+NaClO₄ (95:05) (c) PMMA+NaClO₄ (90:10) (d) PMMA+NaClO₄ (85:15) (e) PMMA+NaClO₄ (80:20) and (f) NaClO₄ salt.



segment phase with little influence on the micro phase separation and mixing of the hard and soft segments. The increase of the degree of roughness with increased NaClO₄ salt concentration indicates segregation of the dopant in the host matrix. The difference in morphology of the NaClO₄ doped films is consistent with the significant differences in the ionic conductivity of these films. The higher conductivity observed in the polymer electrolyte is believed to result from the lower degree of crystallinity and uniform morphology, which is confirmed from XRD studies.

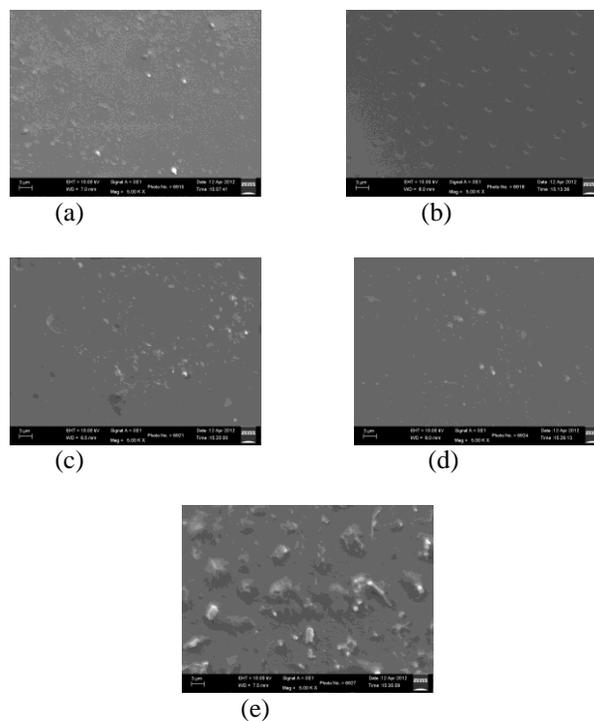


Fig. 2 SEM images of (a) Pure PMMA (b) PMMA+NaClO₄ (95:05) (c) PMMA+NaClO₄ (90:10) (d) PMMA+NaClO₄ (85:15) and (e) PMMA+NaClO₄ (80:20).

C. DC conductivity studies

The variation of conductivity (σ), as a function of composition of NaClO₄ in PMMA for different weight percent of NaClO₄ is shown in Fig. 3. The conductivity of pure PMMA was found to be about 2.95×10^{-9} S/cm at room temperature. It

increased with increasing dopant concentration; however the increase was slow at higher concentration. The increase in conductivity at lower dopant concentrations of NaClO₄ is attributed to the formation of charge carriers or decrease in the crystallinity of the polymer electrolyte. The slow increase at higher concentrations is due to the formation of ionic aggregates. These aggregates impede the conduction process.

Figure. 4 show conductivity vs temperature plots, which follow an Arrhenius nature throughout, with three different activation energies in three regions (region I, II and region III). In region-I, the conductivity of pure PMMA increased slowly with increase in temperature up to 60 °C. Around a particular temperature range (60–90 °C), there was a sudden increase in the variation of σ leading to region-III. This may be due to a transition from a semicrystalline phase to an amorphous phase. According to Druger et al. [17, 18], in polymer electrolytes, the change of conductivity with temperature is due to segmental motion, which results in an increase in the free volume of the system. This increase in free volume would also facilitate the motion of ionic charge [19]. The linear variation of σ vs 1000/T plots can be expressed by the relation,

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where σ_0 is a preexponential factor, E_a is the activation energy, and k is the Boltzmann constant.

The activation energies in the three regions evaluated from the above plots are tabulated in Table 1. From the table, it is clear that the activation energies in all regions decrease with increasing dopant concentration. Increase in the conductivity and decrease in activation energy values for polymer electrolytes can be explained on the basis that the polymer films are known to be mixture of amorphous and crystalline regions and the conductivity of such films may be dominated by the properties of the amorphous region. This may be due to the fact that the addition of small amounts of dopant forms charge complexes in the host lattice [20]. These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice. This results in a decrease of activation energy.

D. Transference number

Electronic and ionic transference number measurements play an important role in explaining the conductivity of polymer electrolyte films. Transference numbers of (PMMA+NaClO₄) electrolyte system were evaluated using Wagner's polarization technique. In this method, the DC current is monitored as a function of time on application of a fixed DC voltage of 1.5 V across the cell in the configuration Na/(polymer electrolyte)/C. After polarization, the current versus time plot was drawn (Fig. 5). The transference numbers were calculated from the polarization

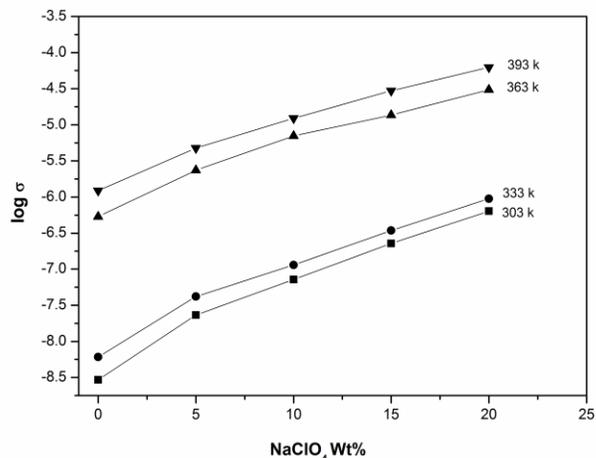


Fig. 3 Composition vs conductivity plots of (PMMA+NaClO₄) polymer electrolyte system at different temperatures.

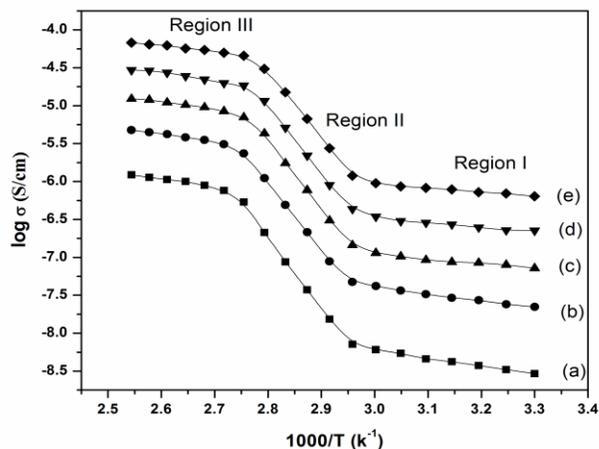


Fig. 4 Temperature dependent conductivity of (a) Pure PMMA (b) PMMA+NaClO₄ (95:05) (c) PMMA+NaClO₄ (90:10) (d) PMMA+NaClO₄ (85:15) and (e) PMMA+NaClO₄ (80:20)

current vs time plot. The resulting data are given in Table 1. For all the compositions of the (PMMA+NaClO₄) electrolyte system, the values of ionic transference numbers are in the range 0.91–0.97. This suggests that the charge transport in these electrolytes is predominantly ionic with a negligible contribution from electrons [21].

E. Discharge profiles of solid state battery

Using the (PMMA+NaClO₄) polymer electrolyte, electrochemical cells were fabricated in the configuration Na(anode)/ (PMMA+NaClO₄)/(I₂+C+electrolyte; cathode). The discharge characteristics of the electrochemical cell for a constant load of 100 k Ω are shown in Fig. 6. The initial sharp decrease in the

Table 1: Activation energies and transference numbers of pure and (PMMA+NaClO₄) polymer electrolyte system

Polymer electrolyte system	Activation energy			Transference numbers	
	Region I	Region I	Region II	t _{ion}	t _{ele}
Pure PMMA	0.34	1.90	0.21	---	---
PMMA+NaClO ₄ (95:05)	0.28	1.74	0.19	0.91	0.09
PMMA+NaClO ₄ (90:10)	0.23	1.68	0.17	0.93	0.07
PMMA+NaClO ₄ (85:15)	0.18	1.60	0.16	0.95	0.05
PMMA+NaClO ₄ (80:20)	0.16	1.50	0.15	0.97	0.03

Table 2. Various cell parameters of (PMMA+NaClO₄) polymer electrolyte system

Cell parameters	PMMA+NaClO ₄ (90:10)	PMMA+NaClO ₄ (80:20)
Open circuit voltage (V)	3.09	3.25
Short circuit current (μA)	1231	1321
Effective area of the cell (cm ²)	1.33	1.33
Cell weight (gm)	1.40	1.41
Discharge time for plateau region (h)	92	110
Power density (W/kg)		
Energy density (Wh/kg)	2.71	3.04
Current density (μA/cm ²)	249	334
Load (kΩ)	925	993
	100	100

voltage in these cells may be due to polarization and/or the formation of a thin layer of sodium salt at the electrode–electrolyte interface. The open circuit voltage and short-circuit current and other parameters for these cells were evaluated and are listed in Table 2. The data indicate that cell parameters are better in cells with composition (80:20). The cell parameters of the present study are superior to these of Na⁺-based [22– 25] and Ag⁺-based [26] cells reported in literature. Hence, these cells offer interesting alternatives for room temperature solid state batteries.

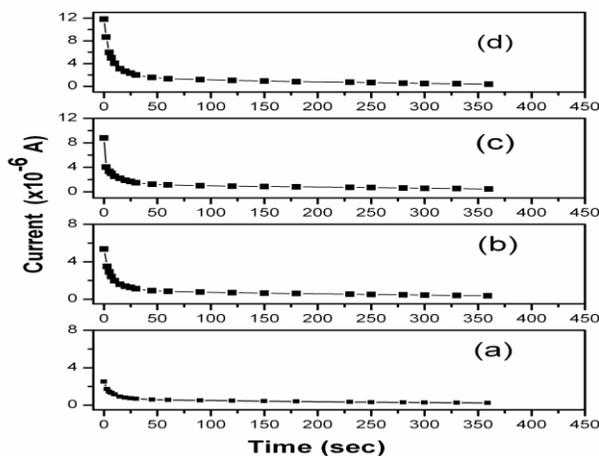


Fig. 5 Current vs time plots of (a) PMMA+NaClO₄ (95:05) (b) PMMA+NaClO₄ (90:10) (c) PMMA+NaClO₄ (85:15) and (d) PMMA+NaClO₄ (80:20).

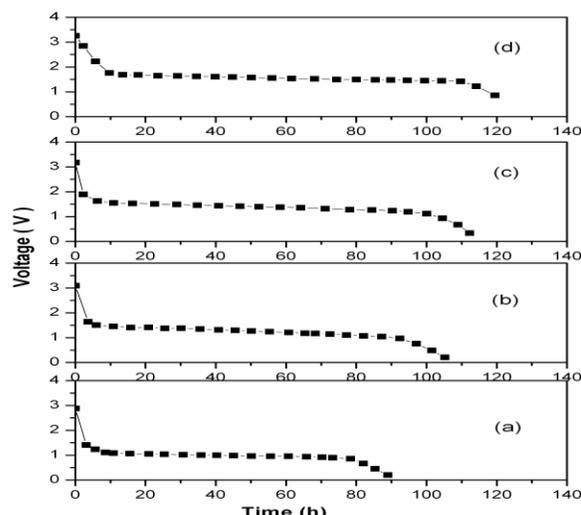


Fig.6 Voltage vs time plots of (a) PMMA+NaClO₄ (95:05) (b) PMMA+NaClO₄ (90:10) (c) PMMA+NaClO₄ (85:15) and (d) PMMA+NaClO₄ (80:20).

IV. CONCLUSION

In summary, it could be concluded that the structure, morphology, conductivity and discharge properties of PMMA polymer electrolyte films can be influenced by complexing it with NaClO₄ salt. The XRD study reveals the amorphous nature of the polymer electrolytes. These studies indicate that the dc conductivity of pure PMMA and (PMMA+NaClO₄) films increased with increasing temperature and dopant concentration. Transference number data showed that the conductivity is mainly due to ions rather than electrons. Parameters were evaluated for (PMMA+ NaClO₄) polymer electrolyte cells. These cells exhibit better performance, which indicates that these cells are suitable for fabricating solid-state batteries.

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