

Effect of plasticizer on conductivity and cell parameters of (PMMA+NaClO₄) polymer electrolyte system

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Abstract: The effect of a plasticizer dimethyl formamide (DMF) on the properties of a sodium ion conducting electrolyte based on poly(methyl-methacrylate) (PMMA) complexed with sodium perchlorate (NaClO₄) prepared using solution cast technique was investigated. The features of complexation of the electrolytes were studied by X-ray diffraction. Film morphology was examined by Scanning Electron Microscopy (SEM). Various experimental techniques, such as electrical conductivity (temperature dependence) and transference number measurements were used to characterize these polymer electrolyte films. Transference number data show that the charge transference in this polymer electrolyte system is predominantly due to ions. Electrochemical cells of configuration Na/PMMA+NaClO₄/(I₂+C+electrolyte) and Na/PMMA+NaClO₄+plasticizer/(I₂+C+electrolyte) were fabricated. The discharge characteristics of the cells were studied under a constant load of 100 kΩ. The open-circuit voltage, short-circuit current and discharge time for the plateau region were measured. The PMMA+NaClO₄ polymer electrolyte system with added plasticizer showed an increased discharge time with respect to pure PMMA+NaClO₄ electrolyte system.

Keywords: Polymer electrolyte, XRD, SEM, Electrical conductivity, Transference number and Discharge profile

I. Introduction

In recent years, polymer electrolytes have been widely studied due to their applicability for a variety of solid state and electrochemical device applications including batteries, fuel cells, supercapacitors, electrochromic devices and chemical sensors [1-2]. Solid polymer electrolytes have many advantages, such as no leakage, volumetric stability, ease of fabrication of thin films of desired size, and wide electrochemical stability windows [3]. Various approaches such as blending [4, 5], copolymerization [6], plasticization [7], addition of ceramic fillers [8] etc. have been made to enhance the ionic conductivity of polymer electrolytes [9]. The most important advances in increasing the ionic conductivity of polymer electrolytes were brought into effect by the incorporation of suitable amounts of plasticizers [10]. Because plasticizers are low in molecular weight, nonvolatile substances (mostly liquids) that, when added to a polymer, improve its flexibility, processability, and, hence utility. Generally, low molecular weight, high dielectric constant polar organic solvents such as ethylene carbonate (EC) [11], propylene carbonate (PC) [12], polyethylene glycol (PEG) [13], dimethylformamide (DMF) [6], dimethylsulfoxide (DMSO) [14], dioctyl phthalate (DOP) [15] and dibutyl phthalate (DBP) [16] have been used in polymer electrolytes to enhance their room temperature ionic conductivities. The conductivities of these electrolytes critically depend on the physical properties of the plasticizer such as its viscosity and dielectric constant. A plasticizer improves the electrical conductivity of polymer electrolyte by (i) increasing the amorphous content of polymer electrolytes; (ii) dissociating ion aggregates present in polymer electrolytes and (iii) lowering the glass transition temperature, T_g [17].

Poly(methyl-methacrylate) (PMMA) is an amorphous polymer and it is a colorless, transparent, plastic with an excellent life period and good mechanical properties. PMMA based electrolyte is less reactive towards the sodium electrode or it induces a more favorable passivation film on the electrode surface. So it is of great significance to realize the manipulation of conductivity and electrochemical properties of plasticized PMMA system. This paper reports the results of our investigation on the ionic conductivity, transference and electrochemical nature of pure and sodium perchlorate (NaClO₄)-doped PMMA plasticized by DMF.

II. Experimental

2.1 Polymer electrolyte films preparation

Films (thickness, 150 μm) of pure PMMA, PMMA+ NaClO₄ and PMMA+ NaClO₄+plasticizer were prepared in weight percent ratio of 80:20 with tetrahydrofuran as solvent using solution cast technique. DMF was used in small quantities (2 ml) as a plasticizer in these films. The solutions were thoroughly stirred for 10–12 h and, then, cast onto polypropylene dishes and evaporated slowly at room temperature. The final product was vacuum dried thoroughly at 10⁻³ m bar.

2.2 characterization techniques

X-ray diffraction (XRD) studies were performed using SEIFERT X-ray diffractometer. 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 transference number (t_{ion}) was evaluated by means of Wagner's polarization technique [18]. 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 transference 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 and PMMA+NaClO₄+plasticizer polymer electrolytes, electrochemical cells with configuration Na/PMMA+NaClO₄/(I₂+C+electrolyte) and Na/PMMA+NaClO₄+plasticizer/(I₂+C+electrolyte) were fabricated. The discharge characteristics of the cells were studied under a constant load 100 kΩ. The initial current in the battery when constant load of 100 kΩ was connected to the battery was taken as short-circuit current. Details regarding the circuit and the electrochemical cell design are given in Ref. [19].

III. Result And Discussion

3.1 XRD analysis

To investigate the influence of sodium salt on PMMA structure, XRD studies were performed. Fig.1 (a-d) shows the XRD patterns of pure PMMA, PMMA complexed with NaClO₄, plasticized (PMMA+NaClO₄) and NaClO₄ salt. Comparison of the XRD patterns of complexed PMMA films with those of pure PMMA and NaClO₄ reveals the following differences. Peak observed for 2θ values around 14° is 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. 1d) 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 is responsible for greater ionic diffusivity resulting high ionic conductivity [20].

3.2 Scanning electron microscopy

The morphology of pure PMMA, NaClO₄ complexed PMMA and plasticized (PMMA+NaClO₄) polymer electrolyte systems were studied using SEM technique, was uniform type, but with different degrees of roughness as shown in Fig. 2 (a-c). The increase of the degree of roughness for PMMA+NaClO₄ system (Fig. 2(b)) indicates segregation of the dopant in the host matrix. Fig. 2(c) showed a marked change in the surface properties and texture of the composite polymer film. Such changes may be attributed to the fact that plasticization causes a reduction in crystallinity of the host polymer and subsequent in the overall amorphous fraction in the material.

The higher conductivity observed in plasticized polymer electrolyte is believed to result from the lower degree of crystallinity and uniform morphology, which is confirmed from XRD studies.

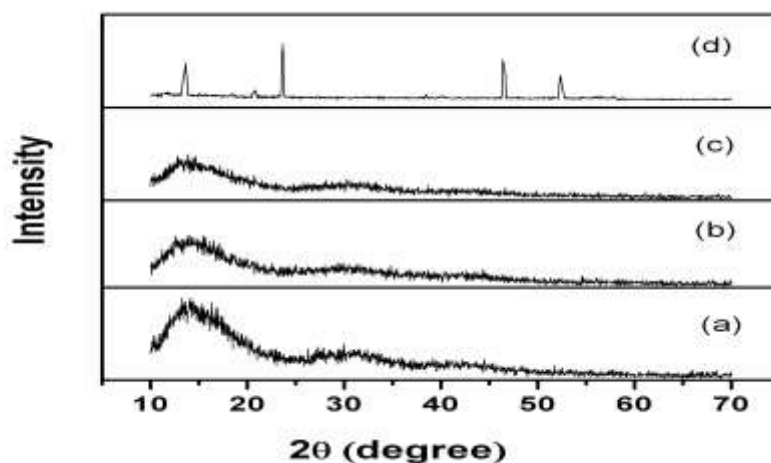


Fig. 1. XRD plots of (a) Pure PMMA (b) PMMA+NaClO₄ (80:20) (c) PMMA+NaClO₄ (80:20)+ plasticizer (d) NaClO₄ salt.

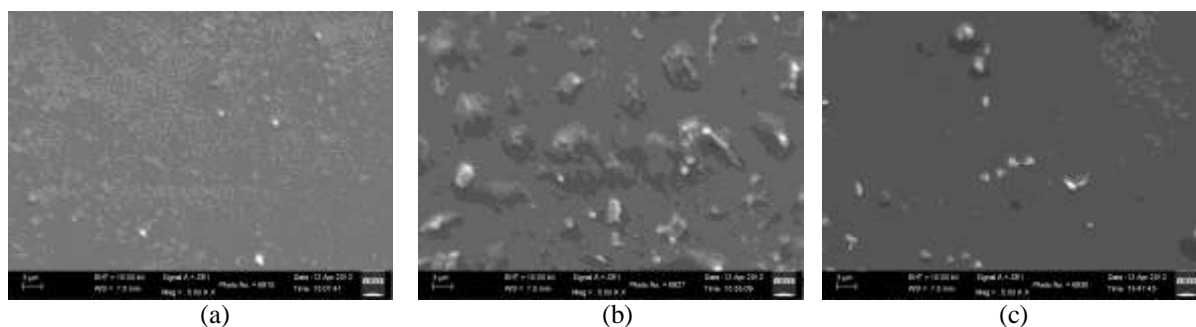


Fig. 2. SEM photographs of (a) Pure PMMA (b) PMMA+NaClO₄ (80:20) (c) PMMA+NaClO₄ (80:20)+plasticizer.

3.3 Conductivity studies

Fig. 3(a-c) shows the variation of log conductivity with inverse absolute temperature for pure PMMA, NaClO₄ doped PMMA and plasticized (PMMA+NaClO₄) solid polymer electrolytes. The conductivity increases with increasing temperature in both pure and NaClO₄ doped PMMA polymer electrolyte system. The increase in conductivity with NaClO₄ may be attributed to the decrease in the degree of crystallinity of polymer matrix [21, 22], or to the formation of charge transfer complexes of NaClO₄ with host lattice. The room temperature conductivities of the samples were 2.95×10^{-9} , 6.45×10^{-7} and 1.94×10^{-6} .

With the addition of plasticizer, the conductivity was found to increase when compared to NaClO₄-doped PMMA polymers. Plasticizer molecules being relatively small in size compared to polymer molecules penetrate the polymer matrix and establish attractive forces/reduce the cohesive forces between the polymer chains and increase the segmental mobility, which enhances the conductivity of polymer electrolyte. To understand the mechanism of conduction, the electrical conductivity was studied as a function of temperature from 303 K to 393 K. The log σ vs $1000/T$ plots exhibited three activation regions (regions I, region II and region III) with different activation energies (Fig. 3). The regression values are close to unity suggesting that the temperature dependent ionic conductivity for the plasticized complexes obeys the Arrhenius rule. Similar results were observed for plasticized polymer electrolytes based on acrylonitrile–methyl methacrylate copolymer [23]. The increasing conductivity with temperature can be linked to the decrease in viscosity and, hence, increased chain flexibility [24]. As the conductivity vs temperature data obeys Arrhenius relationship, the nature of cation transference is quite similar to that occurring in ionic crystals, where ions jump into neighboring vacant sites and, hence, increase the ionic conductivity [25]. Similar behavior has been observed in a number of other polymer electrolytes [26, 27]. The conductivity follows the relation,

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

where σ_0 is the proportionality constant, E_a , the activation energy, T , the absolute temperature, and k is the Boltzmann constant.

At around 60-90°C there was a sharp increase in conductivity. This increase may be explained in terms of the transition of the polymer from crystalline phase to amorphous phase. In the amorphous phase, the polymer chains acquire faster internal modes in which bond rotations produce segmental motion that results in increased conductivity.

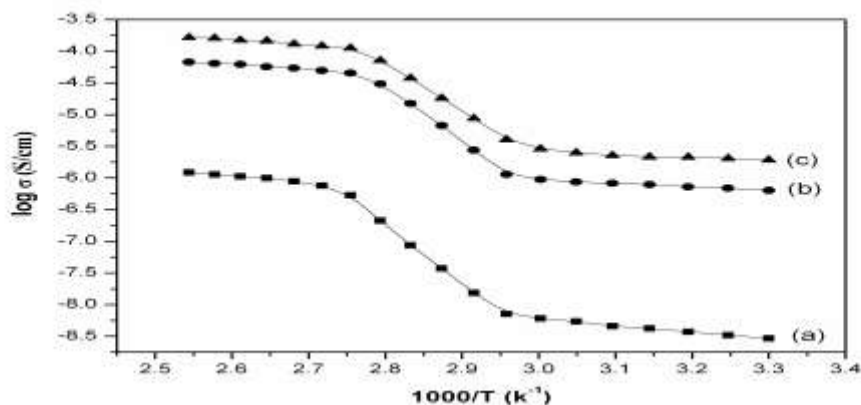


Fig. 3. Plots of log σ vs $1000/T$ for (a) Pure PMMA (b) PMMA+NaClO₄ (80:20) (c) PMMA+NaClO₄ (80:20)+plasticizer.

3.4 Transference number

Transference number measurements of the PMMA+NaClO₄ and PMMA+NaClO₄+plasticizer electrolyte systems were made by means of Wagner’s polarization technique [20]. In this technique, the dc current is monitored as a function of the time on application of a fixed dc voltage across the cell: Na/polymer electrolyte/C. After polarization of the cell with 1.5 V dc, the current vs time plot was obtained, which is shown in Fig. 4(a) for the PMMA+NaClO₄ and in Fig. 4(b) for PMMA+NaClO₄+plasticizer electrolyte system. The calculated transference numbers, t_{ion} and t_{ele} are given in Table 1. From the table we suggest that the charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from the electrons.

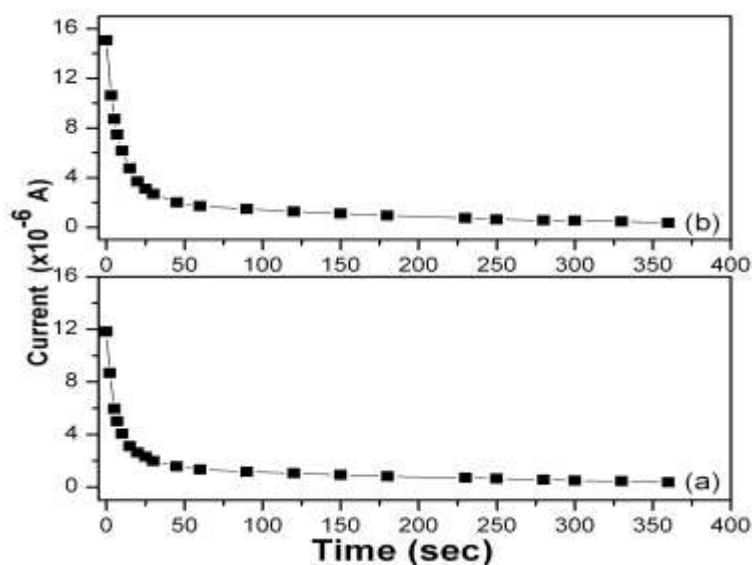


Fig. 4. Current vs time plots of (a) PMMA+NaClO₄ (80:20) (b) PMMA+NaClO₄ (80:20)+ plasticizer.

TABLE 1. Activation energies and transference numbers of pure and plasticized polymer electrolyte system

Polymer electrolyte system	Activation energy			Transference numbers	
	RegionI	RegionII	RegionIII	t_{ion}	t_{ele}
Pure PMMA	0.34	1.90	0.20	--	--
PMMA+NaClO ₄ (80:20)	0.16	1.50	0.15	0.97	0.03
PMMA+NaClO ₄ (80:20)+plasticizer	0.14	1.42	0.12	0.98	0.02

3.5 Discharge Profile

Using the polymer electrolytes, the electrochemical cells were fabricated in the configurations Na(anode)/(PMMA+NaClO₄)/(I₂+C+electrolyte) and Na(anode)/(PMMA+NaClO₄+plasticizer)/(I₂+C+electrolyte). The discharge characteristics of the electrochemical cells for a constant load of 100 kΩ were evaluated at room temperature and are shown in Fig. 5. The initial sharp decrease in the voltage in these cells may be due to polarization and the formation of thin layer of sodium salt at the electrode–electrolyte interface. The open-circuit voltage and short-circuit current of the PMMA+NaClO₄ (80:20) cell are 3.25 V and 1321 μA, and for the PMMA+NaClO₄(80:20)+plasticizer are 3.40 V and 1372 μA, respectively. Some other parameters for these cells were evaluated and are listed in Table 2. The data indicate that the cell parameters are better in the cell with the plasticizer. This suggests that plasticized polymer electrolyte cells exhibit improved performance and better stability than the pure polymer counterparts. Plasticized polymer electrolytes thus offer an interesting alternative to other reported electrolyte systems for room temperature solid-state batteries.

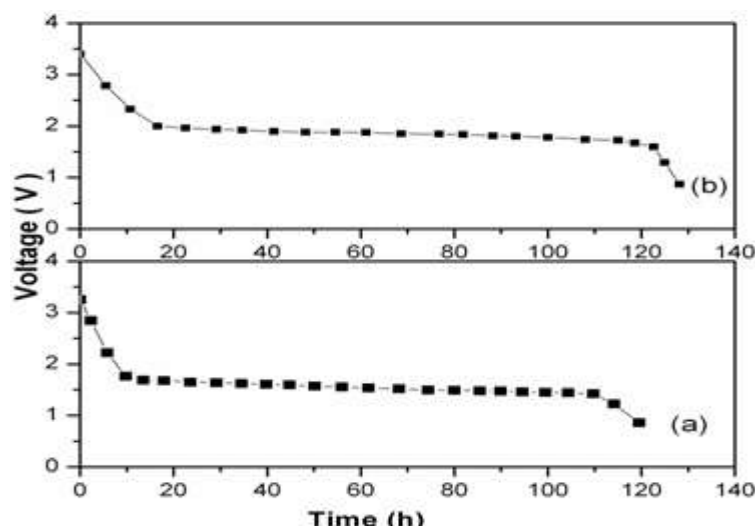


Fig. 5. Discharge characteristics of solid electrochemical cells of the polymer electrolyte system in the figure (a) Na/PMMA+NaClO₄/(I₂+C+electrolyte) (b) Na/PMMA+NaClO₄+plasticizer/(I₂+C+electrolyte)

TABLE 2. Various cell parameters of PMMA+NaClO₄ and Plasticized PMMA+NaClO₄ System

Cell parameters	Na/(PMMA+NaClO ₄)/ (I ₂ +C+electrolyte)	Na/(PMMA+NaClO ₄)+plasticizer / (I ₂ +C+electrolyte)
Open circuit voltage (V)	3.25	3.40
Short circuit current (μA)	1321	1372
Effective area of the cell (cm ²)	1.33	1.33
Cell weight (gm)	1.41	1.42
Discharge time for plateau region (h)	110	122
Power density (W/kg)	3.04	3.28
Energy density (Wh/kg)	334	400
Current density (μA/cm ²)	993	1031
Load (kΩ)	100	100

IV. Conclusions

The XRD study reveals the amorphous nature of the polymer electrolytes. The introduction of salts and plasticizers has proved to be a convenient method to increase the ionic conductivity at ambient temperatures. The value of activation energy decreases with salt concentration and plasticization. The plasticized electrolyte films exhibit better performance, which indicates that such electrolytes are more suitable for fabricating solid-state batteries.

V. Acknowledgements

I would like to thank the authorities of Sri Venkateswara University, Tirupati for providing the necessary facility to carry out my research work and UGC for providing financial assistance.

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