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Research Article

INFLUENCE OF SALT CONCENTRATION ON PMMA+DMF+TiO₂ POLYMER ELECTROLYTE SYSTEM FOR ELECTROCHEMICAL CELL APPLICATIONS

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ABSTRACT

Polymer electrolyte films of (PMMA +DMF+TiO₂) with NaClO₄ have been prepared by solution cast technique. The features of complexation of the electrolytes were studied by X-ray diffraction (XRD). DC conductivity of the films was measured in the temperature range 303-393 K. In the temperature range studied, three regions with different activation energies were observed. Transference number data showed that the charge transport in this system is predominantly due to ions only. Electrochemical cells of configuration Na/(PMMA +DMF+TiO₂+ NaClO₄)/(I₂+C+ electrolyte) were fabricated and the discharge characteristics of these cells were studied under a constant load of 100KΩ. The open circuit voltage, short circuit current and discharge time for plateau region were measured. Several other cell parameters evaluated and are reported.

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INTRODUCTION

In the context of present day market trends in electronic and microelectronic devices that call for miniaturization and suitable form factors for efficient use of device space, the properties of solid polymer electrolytes such as their high compliance, good adherence to electrodes and the possibility of fabricating the polymers into thin films are attractive. The study of these materials has attracted considerable attention in view of their potential applications in various electrochemical devices such as solid state batteries, fuel cells, sensors, timers, capacitors, memory devices etc.(A.L. Laskar *et al* 1989, BVR Chowdari *et al* 1992, S. Ramesh *et al* 2010, K. Rama mohan *et al* 2015, J. Ramesh babu *et al* 2018)

PMMA is an amorphous polymer and it's far a drab, obvious, plastic with an excellent life period and properly mechanical homes. Further, only a few attempts are made on electrolytes based on sodium complexed films. Other than the scientific hobby, using sodium has several benefits over their lithium counterparts. Sodium is to be had in abundance at a less expensive value than lithium. It can be possible to gain strong electrolytes of sufficiently excessive conductivity due to the fact sodium does not shape alloy with aluminium, making it possible to use this steel as a modern collector as opposed to the dearer and heavier nickel. Moreover, the softness of these

materials makes it less complicated to attain and preserve touch with other additives in the battery. Investigations have also been made (D. Fautex *et al* 1987, S.G.Greenbaum *et al* 1988) on sodium ion conducting polymer electrolyte system primarily based on PEO, PPO and MEEP.

In the present investigation we report the influence of NaClO₄ salt concentration on conductivity, transference number and discharge profile of PMMA+DMF+TiO₂ based polymer electrolyte system.

Experimental Detail

Preparation of polymer electrolyte films

In the present study films of PMMA+DMF+TiO₂ (Dimethyl form amide (2ml) and TiO₂ nanoparticles 10 wt% were added to PMMA) and NaClO₄ complexed films were prepared in the weight ratio (95:05), (90:10), (85:15) and (80:20) by solution cast technique using tetrahydrofuran as solvent. The solutions had been thoroughly stirred for 10-12 hours to get a homogeneous solution. The stirred solution become forged onto polypropylene dishes and allowed to evaporate slowly at room temperature. After one or two days stable polymer layers shaped as thin films with nearly 150 μm thickness at the bottom of dishes. Those films had been dried in a vacuum (10⁻³ torr) to

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get rid of the residual lines of water, then carefully separated from the dishes and stored in evacuated desiccators.

Characterization techniques

X-ray diffraction (XRD) studies had been carried out the usage of SEIFERT X-ray diffractometer. The DC conductivity of pure PMMA+DMF+TiO₂ and NaClO₄ doped polymer electrolytes became studied as a characteristic of temperature starting from 303 K to 393 K and the activation energies had been evaluated. The total ionic transference number (t_{ion}) became evaluated with the aid of wagner's polarization method (J.B. Wagner *et al* 1957). On this method, freshly prepared polymer electrolyte films were polarized within the configuration Na/polymer electrolyte/C below a dc bias (step ability of 1.5 V). The resulting current was monitored as a function of time. After polarizing the electrolyte, the transference number t_{ion} became 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+DMF+TiO₂+NaClO₄ polymer electrolytes, electrochemical cells with configuration Na/PMMA+DMF+TiO₂+NaClO₄ / (I₂+C+electrolyte) were fabricated. The discharge characteristics of the cells were studied under a constant load 100 kΩ.

RESULTS AND DISCUSSION

XRD Analysis

Fig 1 (a-f) shows the X-ray diffraction (XRD) patterns of pure PMMA+DMF+TiO₂, NaClO₄ complexed PMMA+DMF+TiO₂ and NaClO₄ salt. Comparison of the XRD patterns of complexed PMMA+DMF+TiO₂ films with those of pure PMMA+DMF+TiO₂ and NaClO₄ reveals the following differences. The broad hump observed for 2θ values around 14° is less intense in complexed PMMA+DMF+TiO₂ films compared with those in pure film. This indicates that the addition of NaClO₄ salt causes a decrease in the degree of crystallinity and simultaneous increase in the amorphocity of the PMMA+DMF+TiO₂ complexed films. This change in intensity and broadening of the hump with increase of salt concentration suggests the increasing amorphous nature of the complexed polymer electrolytes. The crystalline peaks for 2θ values at 14, 23, 46 and 52° corresponding to NaClO₄ were found absent in complexed PMMA+DMF+TiO₂. This indicates the absence of any excess (uncomplexed) salt in the complexed polymer electrolyte films. Decrease in the intensity of the broad hump at higher concentration of NaClO₄ salt indicates the dominant presence of amorphous phase. This amorphous nature is responsible for greater ionic diffusivity resulting in high ionic conductivity (S. Rajendran *et al* 2003).

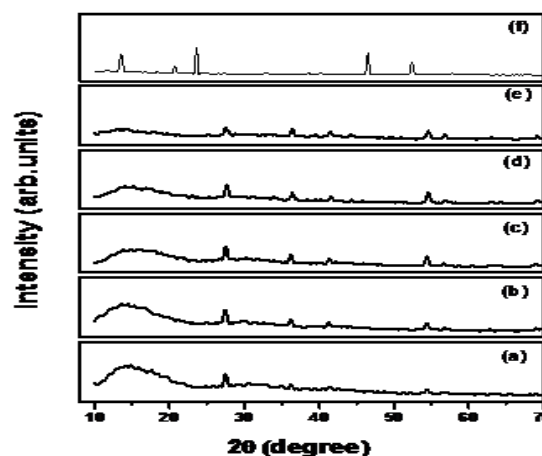


Fig 1 XRD plots of (a) PMMA+DMF+TiO₂ (b) PMMA +DMF+TiO₂+NaClO₄ (95:05) (c) PMMA +DMF+TiO₂+NaClO₄ (90:10) (d) PMMA+DMF+TiO₂+NaClO₄ (85:15) (e) PMMA+DMF+TiO₂+NaClO₄ (80:20) and (f) NaClO₄ salt

DC Conductivity

The variation of room temperature (303 K) dc conductivity (σ) as a function of composition of NaClO₄ in PMMA+DMF+TiO₂ for different weight percent ratios of NaClO₄ is shown in Fig 2. The conductivity of pure PMMA+DMF+TiO₂ was $2.82 \times 10^{-8} \text{ Scm}^{-1}$ at room temperature and its value increased by increasing salt concentration upto 20 wt% of NaClO₄. But when the dopant concentration was increased beyond 20 wt%, the conductivity started decreasing. The increase in conductivity at lower dopant concentrations of NaClO₄ may be attributed to the increase of charge carriers and decrease in the crystallinity of the polymer electrolyte (Ch V. Subba Reddy *et al* 2006)

Figure. 3 shows that 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+DMF+TiO₂ 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 (S.D. Druger *et al* 1983 & 1985) 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 (T. Miyamoto *et al* 1973). 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 the proportionality constant, E_a , the activation energy, and k , the Boltzmann constant.

The activation energies, for all the three regions, were calculated from the slopes of $\log \sigma$ vs $1000/T$ plots and the values are shown in Table 1. The activation energy is a combination of energy of charge carrier creation (defect formation) and the energy of ion migration that can be evaluated by linear fitting of the Arrhenius plots (M.J. Reddy *et al* 1999). Therefore, it can be suggested that the activation energy is the energy required to provide a conductive condition

for the migration of ions. From the table it was found the activation energies decreased with increasing salt concentration. This may be due to the fact that the addition of small amounts of dopant forms charge transfer complexes in the host lattice and increases the conductivity by providing additional charges in the lattice resulting in a decrease of activation energy.

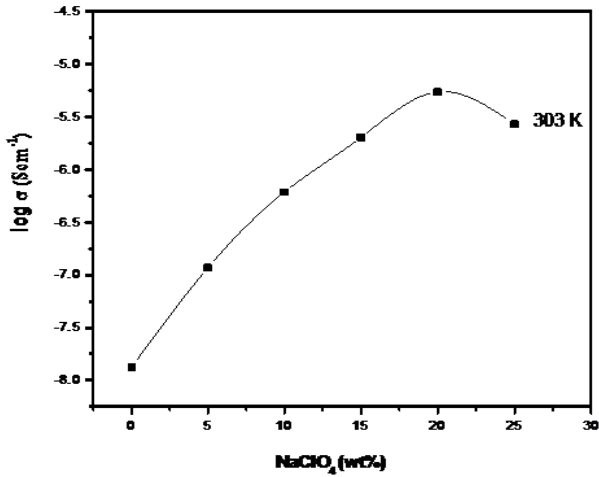


Fig 2 Composition vs conductivity plots of PMMA+NaClO₄+DMF+TiO₂ polymer electrolyte system at room temperature

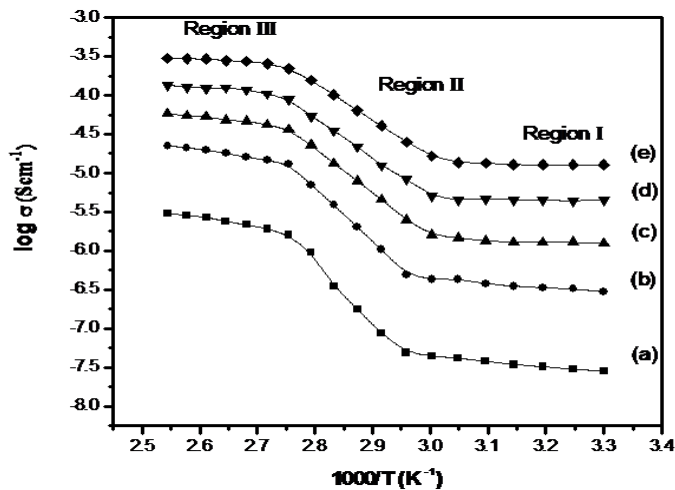


Fig 3 log σ vs $1000/T$ plots of (a) PMMA+DMF+TiO₂ (b) PMMA+DMF+TiO₂(95:05) (c) PMMA+NaClO₄+DMF+TiO₂ (90:10) (d) PMMA+NaClO₄+DMF+TiO₂ (85:15) (e) PMMA+NaClO₄+DMF+TiO₂ (80:20)

Table 1 Activation energies and Transference numbers of PMMA+NaClO₄+DMF+TiO₂ polymer electrolyte films

Polymer electrolyte system (wt%)	Activation energy (eV)			Transference numbers	
	Region I	Region II	Region III	t _{ion}	t _{lec}
PMMA+DMF+TiO ₂	0.25	1.47	0.19	--	--
PMMA+DMF+TiO ₂ +NaClO ₄ (95:05)	0.21	1.30	0.16	0.94	0.06
PMMA+DMF+TiO ₂ +NaClO ₄ (90:10)	0.18	1.21	0.15	0.96	0.04
PMMA+DMF+TiO ₂ +NaClO ₄ (85:15)	0.14	1.12	0.13	0.97	0.03
PMMA+DMF+TiO ₂ +NaClO ₄ (80:20)	0.12	1.06	0.10	0.99	0.01

Transference number

Electronic and ionic transference number measurements play an important role in explaining the conductivity of polymer electrolyte films. Transference numbers of (PMMA+DMF+TiO₂+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. 4). The transference numbers were calculated from the polarization current vs time plot. The resulting data are given in Table 1. For all the compositions of the (PMMA+DMF+TiO₂ +NaClO₄) electrolyte system, the t_{ion} values are found to be in the range 0.94 - 0.99 and t_{lec} values in the range 0.04 - 0.01. This suggests that the charge transport in these electrolytes is predominantly ionic with a negligible contribution from electrons (V.M. Mohan *et al* 2007).

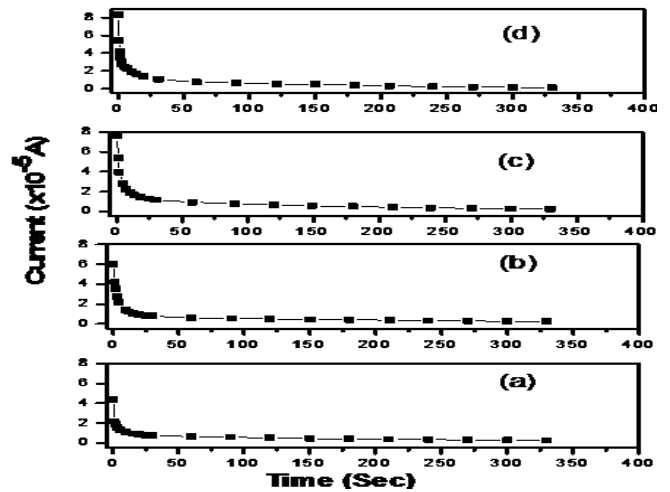


Fig 4 Current vs time plots of (a) PMMA+NaClO₄+DMF+TiO₂ (95:05) (b) PMMA+NaClO₄+DMF+TiO₂ (90:10) (c) PMMA+NaClO₄+DMF+TiO₂ (85:15) (d) PMMA+NaClO₄+DMF+TiO₂ (80:20)

Discharge Characteristics

Electrochemical cells were fabricated in the configuration (anode) Na/(PMMA+NaClO₄+DMF+TiO₂)/(I₂+C+electrolyte) (cathode) respectively. Fig 5 shows the discharge profiles of the electrochemical cells of the above configuration for a constant load of 100 k Ω . The initial sharp decrease in the voltage and current for all the cells may be because of the polarization and/or formation of a thin layer of sodium salt at the electrode-electrolyte interface (A.A. Mohammad *et al* 2003). The evaluated cell parameters from the discharge characteristic such as OCV, SCC, current density, power density, energy density etc are given in Table 2.

It was observed that all parameters showed an increase with increasing percentage of NaClO₄ in the PMMA+DMF+TiO₂ polymer electrolyte. The maximum values were obtained for the electrolyte with the composition (PMMA+DMF+TiO₂+NaClO₄) (80:20). This may be due to the high ionic conductivity and higher degree of amorphosity of this system when compared to other systems.

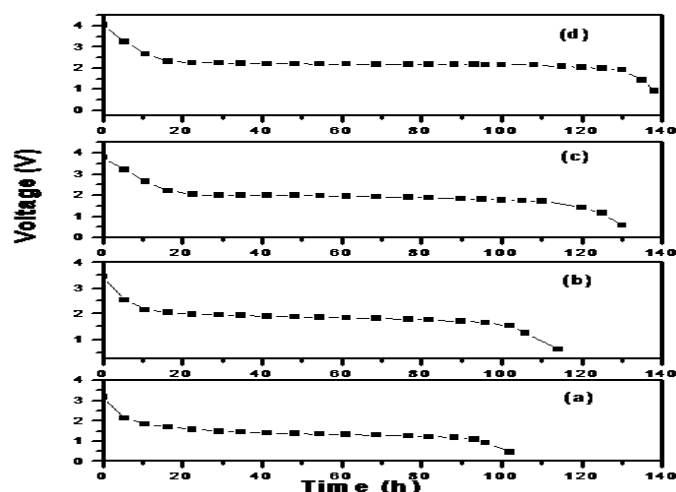


Fig 5 Voltage vs time plots of (a) PMMA+NaClO₄+DMF+TiO₂ (95:05) (b) PMMA+NaClO₄+DMF+TiO₂ (90:10) (c) PMMA+NaClO₄+DMF+TiO₂ (85:15) (d) PMMA+NaClO₄+DMF+TiO₂ (80:20)

Table 2 Cell parameters of (PMMA+NaClO₄+DMF+TiO₂) polymer electrolyte system

Cell parameters	Na/PMMA+DMF+TiO ₂ +NaClO ₄ /I ₂ +C+electrolyte (95:05)	Na/PMMA+DMF+TiO ₂ +NaClO ₄ /I ₂ +C+electrolyte (90:10)	Na/PMMA+DMF+TiO ₂ +NaClO ₄ /I ₂ +C+electrolyte (85:15)	Na/PMMA+DMF+TiO ₂ +NaClO ₄ /I ₂ +C+electrolyte (80:20)
Open circuit voltage (V)	3.18	3.44	3.79	4.04
Short circuit current (mA)	1.24	1.32	1.38	1.41
Effective area of the cell (cm ²)	1.33	1.33	1.33	1.33
Cell weight (gm)	1.41	1.42	1.42	1.43
Discharge time for plateau region (h)	93	102	119	130
Power density (W/kg)	2.81	3.20	3.69	3.98
Energy density (Wh/kg)	261	326	439	517
Current density (mA/cm ²)	0.938	0.995	1.039	1.060
Load (kΩ)	100	100	100	100

CONCLUSIONS

In summary, it could be concluded that the structure, conductivity and discharge properties of PMMA+DMF+TiO₂ 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 and NaClO₄ complexed PMMA+DMF+TiO₂ 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+DMF+TiO₂+ 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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