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Study of Transport and Electrical Properties of PEO: PVP: $NaClO_2$ Based Polymer Electrolyte

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Abstract

The polymer electrolyte PEO: PVP: $NaClO_2$ was prepared by solution cast technique. Polymers PEO, PVP, $NaClO_2$ were taken separately at three different ratio with as (40:50:10), (35:50:15), (30:50:20), (25:50:25), (20:50:30) and (15:50:35). Experimental technique such as electrical conductivity measurement in the temperature range 313K to 343K and transference number measurement were used to characterize this electrolyte. Here 25 wt% of $NaClO_2$ has the highest conductivity. Here the values of transference number, conductivity and activation energy are calculated and evaluated in the Table.

Keywords: Polymer electrolyte, PEO, PVP, $NaClO_2$.

Introduction

The polymer electrolyte (Solutions) serve as electronic insulators between the anode and cathode but it must be a good ionic conductor. Polyethylene oxide (PEO) is used as the polymer matrix because it is chemically inert, able to dissolve in number of inorganic salts and it provides moderate ionic conductivity. Polymer electrolytes based on PEO complexed with $NaClO_3$, $AgNO_3$ and $NaYF_4$ etc. have been reported [1]-[6]. Also the polymer electrolytes based on PVP complexed with $NaClO_3$ have been prepared [7]-[8]. The polymer electrolyte based on PEO, PVP complexed with $NaClO_3$ were prepared [9].Keeping this view in mind, authors prepared polymer electrolyte based on PEO, PVP complexed with $NaClO_2$ and study their transport and electrical properties.

Preparation of polymer electrolyte

The polymers PEO and PVP were taken separately at different ratio with $NaClO_2$ wt% as (40:50:10) (35:50:15), (30:50:20), (25:50:25), (20:50:30) and (15:50:35). Each mixture dissolved in methanol for making polymer-salt mixture into solution. To obtain the perfect solution of this mixture, the solution was stirred well for 24 hours and powered into a polypropylene dishes. The solution was slowly evaporated at room temperature. Thus, thin film of polymer electrolyte was prepared by solution cast technique. Further these films were crushed into powder form. Now, this powder was processed on the pellet machine having pressure of 6 ton at room temperature into circular shapes. Thickness of all samples was measured by using digimatic micrometer (Mitutoyo Make, Japan) with least count 1um.Thickness of the sample vary in the range of 0.110 to 0.910 mm. These pallets (polymer electrolyte) are used for measuring electrical conductivity and transference number.

Result and Discussion

1 Transference Number

The transference number gives quantitative information of the extent of ionic and electronic contribution to the total conductivity. The ionic/electronic transference number can be defined as,

$$t_{ion} = \sigma_{ion}/\sigma_T = I_{ion}/I_T \qquad (1)$$

$$t_e = \sigma_e/\sigma_T = I_e/I_T \qquad (2)$$

Where, σ_{ion}/σ_e and I_{ion}/I_e are the conductivity and current contribution due to ions/ electrons respectively. The ionic/electronic transference number was measured by using dc polarization technique [10], in which a PEO: PVP: $NaClO_2$ polymer electrolytes are sandwiched between blocking (Graphite) and non-blocking (Silver) electrodes. A constant dc voltage (0.5V) is applied across the sample and the resultant current (pA) was recorded as a function of time.

The current versus time plot of the PEO: PVP: $NaClO_2$ polymer electrolytes with different $NaClO_2$ wt% are shown in fig. 1.

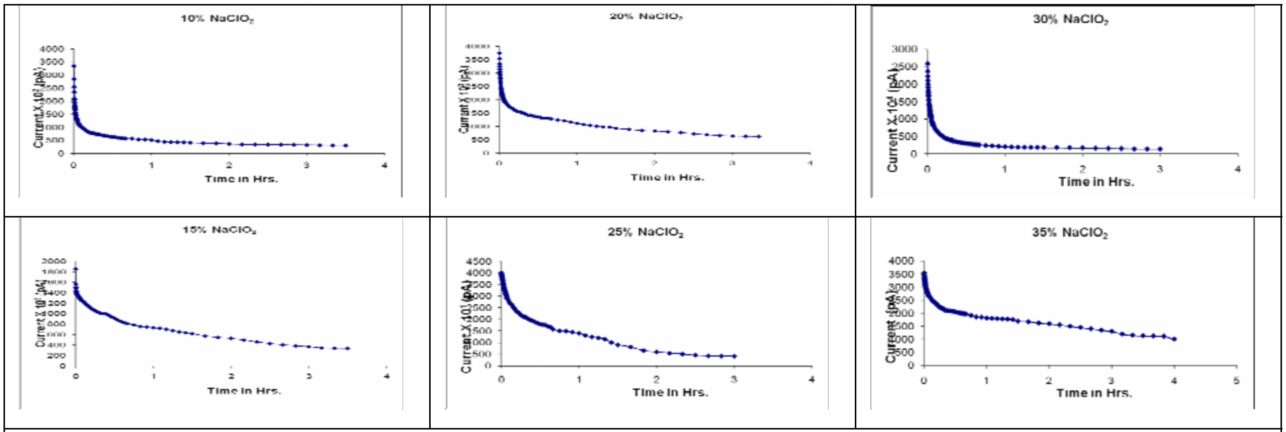

Fig. 1- Current versus time plot for different $NaClO_2$ Concentration 10, 15, 20, 25, 30 and 35 wt%.

The high current has been observed at initial time period and it starts decreasing with time and then the total current becomes nearly constant at some non zero value. All the samples show the same trend. The final residual current is mainly due to electrons/ holes. The ionic transference number is calculated separately for the polarization current versus time plots using equation (1). The calculated transference numbers for different $NaClO_2$ wt % is shown in Table 1. The variation of transference number with concentration of $NaClO_2$ is shown in fig. 2.

Table 1- Ionic transference number for different $NaClO_2$ wt%

Sr. No.	**$NaClO_2$ (wt%)**	**Ionic transference number (t_{ion})**
1	10	0.91
2	15	0.82
3	20	0.83
4	25	0.98
5	30	0.95
6	35	0.72

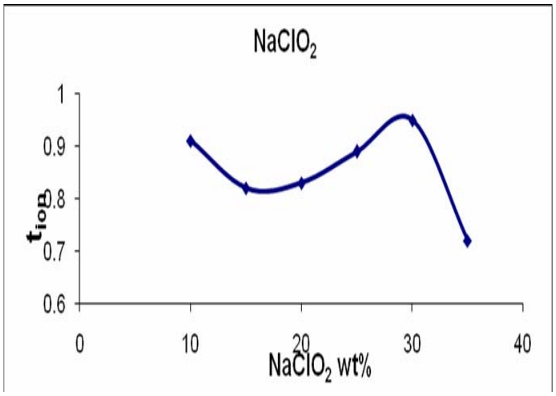

Fig 2 Variation of ionic transference number with $NaCl_2$ wt%

From fig. 2, we see that as concentration increases transference number decreases then it increases and again it will decrease. The ionic transference number is found to be nearly equal to one. So, the conduction is due the movement of ions through the electrolyte.

DC Conductivity

DC conductivity of the samples of different $NaClO_2$ wt% was measured in the temperature range 313 to 343K by measuring the resistance of the samples. It is observed that the value of resistance depends on temperature.

The variation of dc conductivity with wt% of $NaClO_2$, for $NaClO_2$ doped PEO-PVP composite films at 323K is shown in fig. 3. From fig. 3, we see that as concentration increases conductivity increases then it decreases then again increases then it decreases and again it will increases. When the concentration of $NaClO_2$ is 25 wt% the conductivity has the maximum value and reaches to 6.86 x 10^{-7} S/cm.

The temperature dependence of conductivity for different $NaClO_2$ wt % is shown in fig. 4.

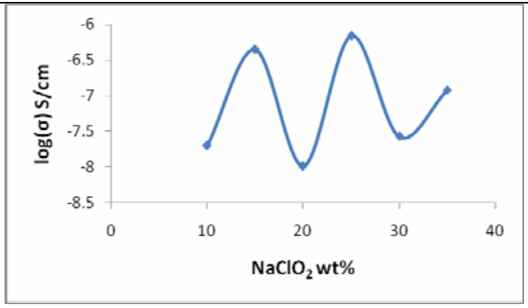

Fig. 3- Variation of conductivity with $NaClO_2$ wt% at 323 K

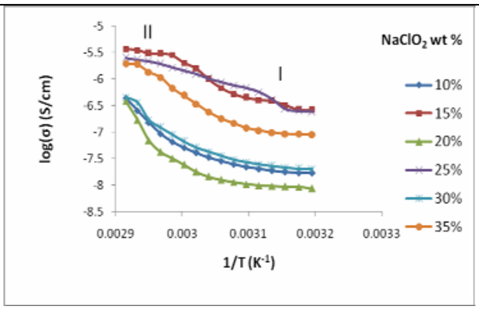

Fig. 4 – Temperature dependence of conductivity for different $NaClO_2$ wt %

The conductivity versus temperature curves of the samples shows increase in conductivity and plot follows the Arrhenius behavior throughout, but with the two activation regions (I and II) with two different activation energies above and below melting point (T_m) of the polymer. Initially the rate of increase in conductivity is slow and after a certain temperature the rise is fast. The increase in conductivity may be due to the transition from the semi crystalline to amorphous phase. Due to this two activation regions are observed in above plot. Similar result was observed for other electrolytes [11-14]

As per Arrhenius relation the dependence of conductivity has the form

$$\sigma = \sigma_0 \exp(-E_a/kT) \qquad (3)$$

Where, σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann constant. Activation energies were calculated from the slop of the plots. The values of Conductivity, Activation Energies for $NaClO_2$ wt% doped with PEO-PVP composite films at 323K shown in the following Table no.2.

Table No. 2: Conductivity, Activation Energies for $NaClO_2$ wt% doped with PEO-PVP composite films at 323K.

Sr.No.	$NaClO_2$ wt %	Conductivity at 323 K (S/cm)	Activation Energy Ea (eV) (Region I)	Activation Energy Ea (eV) (Region II)
1	10	2.19×10^{-8}	0.14	0.77
2	15	4.44×10^{-7}	0.4	0.15
3	20	1.04×10^{-8}	0.13	0.11
4	25	6.86×10^{-7}	0.44	0.28
5	30	2.69×10^{-8}	0.2	0.86
6	35	1.20×10^{-7}	0.22	0.65

Conclusion

From transference number measurement, it is concluded that charge transfer is mainly due the ions. From electrical conductivity measurements, it is observed that conductivity increases with temperature and plot follows the Arrhenius behavior throughout, but with the two activation regions (I and II) with two different activation energies above and below melting point (T_m) of the polymer.

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