

CONDUCTIVITY STUDIES OF (PEO +KHCO₃) SOLID ELECTROLYTE SYSTEM AND ITS APPLICATION AS AN ELECTROCHEMICAL CELL

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Abstract

Solid polymer electrolyte system, polyethylene oxide (PEO) complexed with potassium bicarbonate (KHCO₃) salt was prepared by solution-cast technique. Several experimental techniques such as infrared radiation (IR), differential scanning calorimeter (DSC), and composition dependence conductivity, temperature dependence conductivity in the temperature range of 308–368 K and transport number measurements were employed to characterize this polymer electrolyte system. The conductivity of the (PEO+KHCO₃) electrolyte was found to be about 3 times larger than that of pure PEO at room temperature. The transference data indicated that the charge transport in these polymer electrolyte systems is predominantly due to K⁺ ions. Using this polymer electrolyte an electrochemical cell with configuration K⁺/(PEO+KHCO₃)/(I₂+C+electrolyte) was fabricated and its discharge characteristics are studied. A number of other cell parameters associated with the cell were evaluated and are reported in this paper.

Keywords: Complex, polymer electrolyte, ionic conductivity, transport number, electrochemical cell.

1. Introduction

The research and development of polymer electrolytes for ambient temperature rechargeable lithium and solid ion batteries have always an identifiable. The ionic conductivity in high molecular weight polyethylene oxide (PEO) doped with sodium and potassium salts were first reported by Wright [1]. The technological implications of these PEO based electrolytes, such as their use in lithium batteries were realized and suggested by Armand [2]. These reports related to these solid electrolytes have been reported in reviews by many researchers [3,4].

Nomenclatures

E_a	Activation energy, eV
I_e	Electronic current, mA
I_i	Ionic current, mA
I_T	Initial total current, mA
R_T	Room temperature, K
T_m	Melting point, °C
t_{ele}	Electronic transport numbers
t_I	Ionic transference number
t_{ion}	Ionic transport numbers

Greek Symbols

σ	Conductivity, Scm ⁻¹
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Abbreviations

DSC	Differential scanning calorimeter
IR	Infrared radiation
OCV	Open circuit voltage
PEO	Polyethylene oxide
PVP	Polyvinylpyrrolidone
SCC	Short circuit current

In general, the polymer component of PEO based composite electrolyte is a mixture of crystalline and amorphous phases, ratio of which depends to a great extent on compositions of the electrolyte, temperature and thermal history. The solid polymer electrolytes, i.e., polymer salt complexes are of technological interest due to their possible application as solid electrolytes in different devices such as energy conversion units (batteries/fuel cells), electro-chromic display devices/smart windows and photo-electrochemical solar cells, etc., [5-8]. Subsequently studies on PEO-based polymer electrolyte complexes using alkali salts [8-10] were developed in this field.

In the present paper, the authors report solid ion conducting polymer electrolyte based on (PEO+KHCO₃) system. Several analytical techniques, such as infrared radiation (IR) and differential scanning calorimeter (DSC) studies, composition dependent conductivity, transport number measurements and temperature dependent conductivity in the temperature range 308-368 K were performed to characterize these polymer electrolytes. Based on these electrolytes, an electrochemical cell was fabricated with the configuration anode/polymer electrolyte/cathode. The discharge characteristics of the cell have been studied at a constant load of 100 kΩ. The results of these investigations are reported in this present paper.

2. Experiment

Pure PEO (Aldrich $\approx 6 \times 10^5$) complexes with a fine powder of potassium bicarbonate salts (KHCO₃) were prepared in the stoichiometric ratios (90:10), (80:20), (70:30) by a solution - cast technique using methanol (water free) as solvent. The IR spectra in these films were recorded with the help of JASCO

FT/IR-5300 spectrophotometer in the range 400-4000 cm^{-1} . The DSC patterns of pure PEO and PEO complexed with KHCO_3 for the ratio 70:30 compositions were studied using DSC (TA 2010).

The dc conductivity has been measured using the lab made conductivity set up in the temperature range 303-368 K [10]. The ionic and electronic transport numbers (t_{ion} and t_{ele}) were evaluated by means of Wagner's polarization technique [11, 12]. In this technique, a freshly prepared film of PEO+ KHCO_3 under a dc bias (step potential 1.5 V) was used. The resulting current was monitored as a function of time with a Keithley electrometer (Keithley Inc., model 614).

An electrochemical cell was fabricated with the configuration $\text{K}^+ / (\text{PEO} + \text{KHCO}_3) / (\text{I}_2 + \text{C} + \text{electrolyte})$. The details about the fabrication of electrochemical cells are given elsewhere [13, 14]. The discharge characteristic studies of these electrochemical cells were monitored at a constant load of 100 k Ω .

3. Results and Discussion

The variation in dc conductivity (σ) as a function of KHCO_3 composition in PEO at room temperature (R_T) and 368 K is given in Fig. 1. Conductivity data at R_T and 368 K are reported in Table 1. The following conclusions can be drawn:

- The conductivity of pure PEO is approximately $10^{-10} \text{ Scm}^{-1}$ at room temperature and its value increases sharply to 10^{-7} Scm^{-1} on complexing with 10 wt % KHCO_3 . The increase in conductivity becomes slower on further addition of KHCO_3 to the polymer. This behavior has been explained by various researchers, who have studied PVP and PEO based polymer electrolyte in terms of ion association and the formation of charge multipliers [15-19].
- The ionic conductivity in the polymer complexes may be interpreted on the basis of a hopping mechanism between coordinating sites, local structural relaxations and segmented motions of the polymer chains. These are essential to assure high conductivity of the electrolyte [20,21].

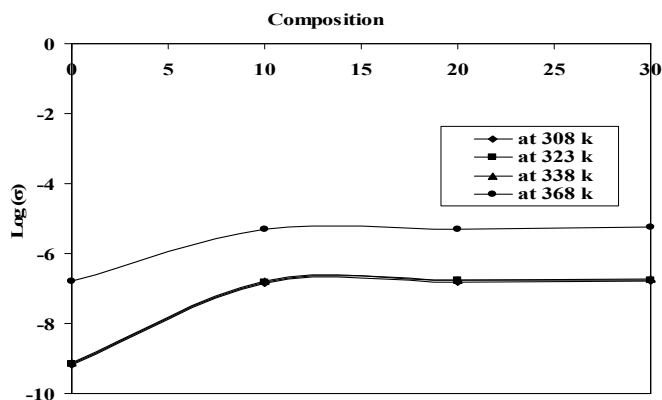
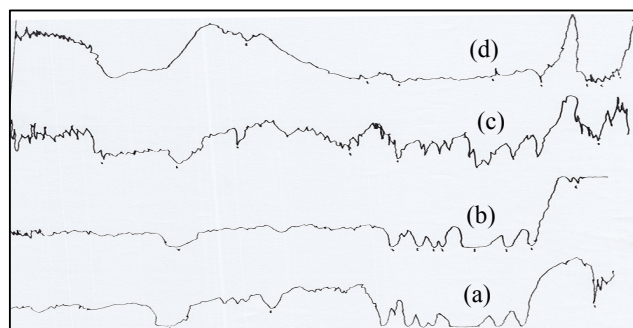


Fig. 1. Composition Dependence of (PEO + KHCO_3) Polymer Electrolyte System at Different Temperatures.

Table 1. Conductivity, Activation Energies and Transference Numbers of (PEO+KHCO₃) Electrolyte System.

Films	Conductivity at R_T (Scm ⁻¹)	Conductivity at 368 K (Scm ⁻¹)	Activation energies (eV)		Transference numbers	
			Region I	Region II	t_{ion}	t_{ele}
Pure PEO	6.78×10^{-10}	1.58×10^{-7}	0.34	0.38	-	-
PEO+KHCO ₃ (90:10)	0.14×10^{-7}	4.17×10^{-6}	0.36	0.27	0.90	0.1
PEO+KHCO ₃ (80:20)	0.68×10^{-7}	5.14×10^{-6}	0.24	0.31	0.91	0.09
PEO+KHCO ₃ (70:30)	1.4×10^{-7}	5.90×10^{-6}	0.21	0.35	0.92	0.08

The complexed of the polymer PEO and salt KHCO₃ were confirmed by using IR spectroscopy. The IR spectra of pure PEO, PEO complexed with KHCO₃ were recorded with the help of JASCO FT/IR – 5300 spectrophotometer in the range 400-4000 cm⁻¹ and are shown in Fig. 2. The intensity of the aliphatic C-H stretching vibrations band observed around 2950 cm⁻¹ in PEO was found to decrease with the increase in the concentration of KHCO₃ salt in the polymer. The width of the C-O stretching band observed at around 1100 cm⁻¹ in PEO also showed an increase in the salt concentration in the polymer. Also the appearance of new peaks along with changes in existing peaks (and/or their disappearance) in the IR-spectra directly indicates the complexation of PEO with KHCO₃. This IR data clearly establishes the complexation of KHCO₃ with different weight ratios of the polymer PEO.

**Fig. 2. IR Spectra of**

- a) Pure PEO b) PEO + KHCO₃ (80:20)**
c) PEO + KHCO₃ (70:30) d) KHCO₃.

DSC curves of pure PEO and PEO complexed with KHCO₃ of 70:30 compositions are shown in Fig. 3. An endothermic peak was observed at 650°C, which corresponding to melting temperature (T_m) of pure PEO. The slight shift in the melting point (T_m) towards higher temperature has been observed due to the

addition of KHCO_3 salt to the polymer. Earlier workers [22] have also reported similar result on PEO complexed system.

The variation in conductivity as a function of temperature for pure PEO with different compositions of $(\text{PEO}+\text{KHCO}_3)$ polymer electrolytes over the temperature range of 303-368 K is shown in Fig. 4. The conductivity increases with temperature in pure PEO and also in all the compositions of polymer electrolyte systems. The conductivity versus temperature ($\log \sigma T$ versus $10^3/T$) plots follows the Arrhenius nature throughout, but with two different activation energies above and below melting point (T_m) of the polymer. In region – I, i.e., below T_m , the conductivity of pure PEO increases slowly with temperature up to 65°C . At 65°C there is a sudden increase in conductivity. In region – II, i.e., above T_m , the conductivity again increases with temperature. The calculated conductivity (σ) at room temperature, at 368 K and activation energies (E_a) for pure PEO and $(\text{PEO}+\text{KHCO}_3)$ electrolyte systems are given in Table 1. The conductivity of pure PEO is $\cong 6.78 \times 10^{-10} \text{ Scm}^{-1}$ on complexing with 10 wt % KHCO_3 . Further addition of KHCO_3 to the polymer, the increase in conductivity becomes slow. This behavior has been explained by various researchers, who have studied PEO and PEO based electrolytes, in terms of ion association and the formation of charge multipliers [22-27].

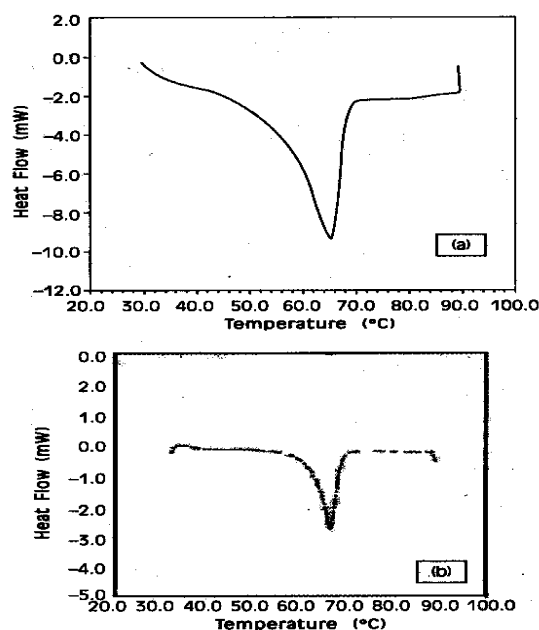


Fig. 3. DSC Curves for a) Pure PEO; b) $\text{PEO}+\text{KHCO}_3$ (70:30).

Total ionic transference number of polymer electrolyte has been measured by Wagner's Polarization technique [11, 15], which is used to determine the ionic contribution to the total charge transport by measuring the residual electronic current passing through the electrolytes. Three Wagner polarization cells Ag/electrolyte/Ag were prepared by coating silver (Ag) paste as blocking electrode on to the faces of $\text{PEO}+\text{KHCO}_3$ based composition polymer electrolyte systems.

A fixed small dc potential (1.5 V) has been applied across the blocking electrodes and the current passing through the cells is measured as a function of time for one hour to allow the samples to become fully polarized are shown in Fig. 5.

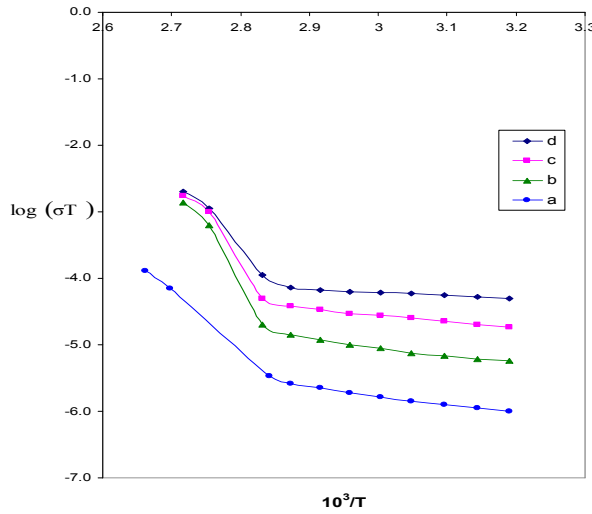


Fig. 4. The Temperature Dependence of dc Conductivity of
 a) Pure PEO b) PEO + KHCO₃ (90:10)
 c) PEO + KHCO₃ (80:20) d) PEO + KHCO₃ (70:30).

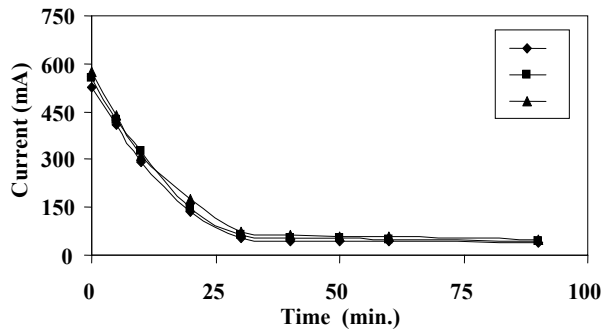


Fig. 5. Current versus Time Plot of
 a) PEO+KHCO₃ (90:10) b) PEO+KHCO₃ (80:20)
 c) PEO+KHCO₃ (70:30).

Initial total current (I_T) which is the sum of ionic (I_i) and electronic (I_e) currents ($I_T = I_i + I_e$) and final current after polarization which is only the electronic current (I_e) are measured. The ionic transference number (t_i) is calculated using the relation

$$t_i = I_i / I_T = (I_T - I_e) / I_T$$

The ionic transference number for all the compositions of the (PEO + KHCO₃) electrolyte system were shown in Table 1. The values of the ionic transference numbers (t_i) are in the range 0.90–0.92 suggest that the charge transport in these polymer electrolyte systems is predominantly ionic accompanied by mass transport and electronic contribution to the total current is negligible.

The area and thickness of the electrolyte are respectively 1.33 cm² and 150 μm. The discharge characteristics are studied for all the cells at room temperature with a constant load of 100 kΩ and are shown in Fig. 6. The initial sharp decrease in the voltage may be due to the polarization effects or the formation of a thin layer of potassium salt at the electrode – electrolyte interface. The open circuit voltage (OCV) and short circuit current (SCC) for these cells are found to be 2.52 V and 0.95 mA respectively. The other cell parameters for these cells are evaluated and summarized in Table 2.

The cell parameters calculated for K⁺/(PEO+KHCO₃)/(I₂+C+electrolyte) cell is given in Table 3 along with the parameters reported for other cells [28,29].

It is clear from Table 3 that the cell parameters are found to be better in (PEO+KHCO₃) electrolyte system as compared with the other cells, indicating that (PEO+KHCO₃) electrolyte cells exhibit improved cell performance and are more stable than pure polymer electrolyte cells.

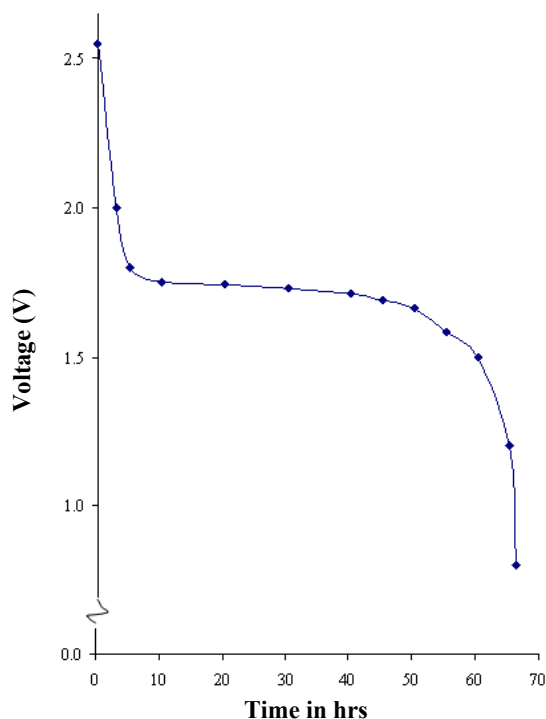


Fig. 6. Discharge Characteristics of K⁺/(PEO+KHCO₃) / (I₂+C+electrolyte) Electrochemical Cell for a Constant Load of 100 kΩ.

On the basis of present study, an electrochemical cell with (PEO+KHCO₃) as electrolyte with improved efficiency is promising. Further work aimed at obtaining higher cell capacities and specific energy is in progress.

Table 2. Electrochemical Cell Parameters of K⁺/(PEO+KHCO₃)/(I₂+C+electrolyte) System.

Cell Parameters	K ⁺ /(PEO+KHCO ₃)/(I ₂ +C+Electrolyte) system
Open circuit voltage (OCV)	2.52 V
Short circuit current (SCC)	0.95 mA
Effective area of the cell	1.33 cm ²
Cell weight	1.49 gm
Load	100 kΩ
Time for plateau region	65 hrs
Power density	1.60 Wkg ⁻¹
Current density	0.714 mA/cm ²
Energy density	104 W-h kg ⁻¹

Table 3. Comparison of Present Cell Parameters with Data for Other Cells Reported Earlier.

Electrochemical cell configuration	Open circuit voltage (OCV) in (V)	Discharge time (hr)	Reference
Ag / (PEO+AgNO ₃)/(I ₂ +C+electrolyte)	0.61	48	[18]
Na/(PEO+ glass)/(I ₂ +C+electrolyte)	2.1	51	[19]
K / (PEO+KYF ₄) / (I ₂ +C+electrolyte)	2.4	51	[20]
K ⁺ /(PEO+KHCO ₃)/(I ₂ +C+electrolyte)	2.52	65	This work

4. Conclusions

The conductivity of (PEO + KHCO₃) (70:30) at R_T was determined to be $1.4 \times 10^{-7} \text{ Scm}^{-1}$ and at 368 K was $9 \times 10^{-6} \text{ Scm}^{-1}$. The charge transport in this polymer electrolyte (PEO+KHCO₃) was predominantly due to ions. The open circuit voltage and short-circuit current for a cell with the configuration K⁺/(PEO+KHCO₃) / (I₂+C+electrolyte) were 2.52 V and 0.95 mA, respectively.

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