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Influence of Plasticizer on a PEO based K+ ion conducting Polymer electrolyte system for Battery applications

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Abstract : Poly Ethylene Oxide (PEO) based Solid polymer electrolyte films with $KHCO_3$ and $KHCO_3$+ plasticizer (Dimethyl formamide) have been prepared using a solution casting technique. The complexation of the Polymer PEO with $KHCO_3$ and $KHCO_3$+ DMF (Dimethyl formamide) was confirmed by IR and XRD studies. The conductivity-temperature plots showed an increase in conductivity with increasing temperature. The increase in conductivity is about ten times larger in the plasticized (PEO + $KHCO_3$) polymer electrolyte systems compared with pure (PEO + $KHCO_3$) polymer electrolyte system. The transference data indicated that the charge transport in these polymer electrolyte systems is predominantly due to ions. Using this polymer electrolyte system, a polymer battery or an electrochemical cell with configuration K^+ / (PEO + $KHCO_3$ + plasticizer) / (I_2 + C + Electrolyte) was fabricated and its discharge characteristics were studied for a constant load of 100 KΩ. The Open circuit voltage (OCV), Short circuit current (SCC), Discharge time, Current density and Power density were evaluated. A number of other battery parameters associated with the battery were evaluated and compared with the data from earlier reported in this paper.
Keywords: Solid polymer electrolyte, Solution casting technique, Transport number, Discharge characteristics.

1. Introduction

In consistence with the rapid progress in size, thickness reduction of electronic devices and development of multimedia industries in recent years, demand has been increasing to fabricate small sized portable devices. Today it is almost universally accepted that such combination of size and thickness can only be obtained by using non conventional electrodes and electrolyte materials and that the most promising choices are those based on lithium operating systems. With this situation, attempts have been made in poly (ethylene oxide) (PEO) based polymer electrolytes to reach an appreciable electrical conductivity at ambient temperature[1,2]. The liquid electrolytes have high ionic conductivity and offers very good contact with electrodes. But the major problems associated with liquid electrolytes are cell leakage, corrosion, self discharge process, drying out of the cell, loss of electrolyte and severe restrictions on the capability of useful discharge at very low temperatures. Interest in developing solid state batteries was motivated impart by the hope that the above problems would be minimized when the liquid electrolyte is replaced by a solid electrolyte. Hence solid polymer electrolytes have many advantages, viz. high ionic conductivity, high specific energy, wide electrochemical stability windows, light and easy processibility.

The solvent or salt-solution is retained in solid polymeric electrolyte and helps in ionic conduction process, whereas the host polymer acts as a matrix. Solid polymer electrolytes provide applications as separators in rechargeable batteries, super capacitors, fuel cells and other electrochemical devices[3]. Many research groups have reported various polymer electrolytes based on lithium, sodium, magnesium and zinc salts to realize respective battery systems. Particularly, the Li based batteries, which are mostly reported in literature. So, their alternatives in the form of magnesium, zinc and sodium batteries are reported, although these are not extensively studied[4]. The development of potassium rechargeable batteries would be an interesting study because potassium may be considered as an alternative to lithium as a negative electrode (anode) due to its low cost, natural abundance, non-toxic, low atomic mass (39.09) and high electrochemical reduction potential[5]. It is therefore a need to develop high Potassium ion conducting non-aqueous electrolytes suitable for the fabrication of rechargeable potassium batteries. In the field of polymer electrolytes, interest began after the pioneering studies on polyethylene oxide (PEO) based complexes reported by Wright et.al. [6], Armand and Co-workers[7,8].

In the Present Paper, the authors reported solid polymer electrolyte films of PEO, PEO+KHCO$_3$ and PEO+KHCO$_3$ + Plasticizer (DMF) systems. Fixed amount of plasticizer (DMF) is added to all PEO +KHCO$_3$ electrolyte systems to study the effect of the plasticizer. Several experimental techniques such as XRD, IR were employed to characterize this polymer electrolyte system. Few electrical properties such as composition dependence conductivity, temperature dependence conductivity in the temperature range of 308- 368K, transport number measurements and discharge studies were in use to observe the behavior of both unplasticized (PEO+KHCO$_3$) and plasticized (PEO+KHCO$_3$+DMF) solid electrolyte systems. Based on these electrolytes, a solid polymer battery was fabricated with the configuration anode / polymer electrolyte / cathode. The discharge characteristics of the battery have been studied for a constant load of 100 KΩ. The results of these investigations are reported in the present paper.

2. Experimental

Thin Films (thickness $\approx$ 100 - 150μm) of pure PEO (Aldrich Mw $\approx$ 6x10^5) and various compositions of complex films of PEO with KHCO$_3$ salt and PEO with KHCO$_3$ + DMF were prepared with different weight ratios of polymer and salt (90:10), (80:20), (70:30) for constant proportion of plasticizer by a solution-cast technique using methanol (water free) as solvent. The X-ray diffraction studies of these films are carried out with the help of PHILIPS PW 3710 X-ray diffractometer in the range 10°-70°. The infrared (IR) spectrum of these films has been recorded with the help of JASCO FT/IR-5300 spectrophotometer in the range 400-4000 cm^{-1}. The DC conductivity has been measured using the lab made conductivity setup[9,10] in the temperature range 303-368K. 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$_3$+DMF under a DC bias (step potential 1.5V) was used. The resulting current was monitored as a function of time with a Keithley electrometer (Keithley Inc., model 614). The transient ionic current (TIC) measurement technique[14] is used to evaluate the mobility of the ion species.

A Solid Polymer battery was fabricated with the configuration K $^+$ / (PEO + KHCO$_3$ + DMF) / (I$_2$ + C + electrolyte). The details about the fabrication of the electrochemical cells are given elsewhere[15].   The discharge characteristic studies of these electrochemical cells were monitored at a constant load of 100 KΩ.

3. Results and Discussion

The complexation of the polymer PEO, salt KHCO$_3$ and plasticizer DMF were confirmed by using IR spectroscopy. The IR spectra of pure PEO, PEO complexed with KHCO$_3$ were recorded with the help of JASCO FT/IR–5300 spectrophotometer in the range 400-4000 cm^{-1} and are shown in Fig-1. The intensity of aliphatic C-H stretching vibration band observed around 2950 cm^{-1} in PEO is observed to be decreases by increasing the concentration of KHCO$_3$ salt 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 KHCO$_3$ and (PEO +KHCO$_3$) with plasticizer (DMF).

Fig-2 shows the X-ray diffractogram of Pure PEO, PEO + KHCO$_3$ and PEO + KHCO$_3$ + Plasticizer electrolyte systems. Usually well-defined sharp peaks indicate the crystalline nature. A comparison of the diffraction spectra of complexed PEO with that of the pure PEO film reveals the following differences. The diffraction peaks observed for 2θ values at 19.1^o and 23.3^o were found to be less intense in complexed PEO films compared to the pure PEO film. This indicated that the addition of KHCO$_3$ salt caused a decrease in the degree of crystallinity of the polymer PEO. This can be due to the interruption of the semi-crystalline structure

of the film by KHCO3 salt[16], established a correlation between the intensity of the peak and the degree of crystallinity. Peaks corresponding to the polymer PEO were also present in the complexed PEO films. This showed the simultaneous presence of both crystalline complexed and uncomplexed PEO. Thus the result of X-ray diffraction and IR data clearly establishes the complexation with different weight ratios of $KHCO_3$ and plasticizer with the polymer PEO.

Transmittance (A. U.)

← **Wave Number (Cm^{-1})**
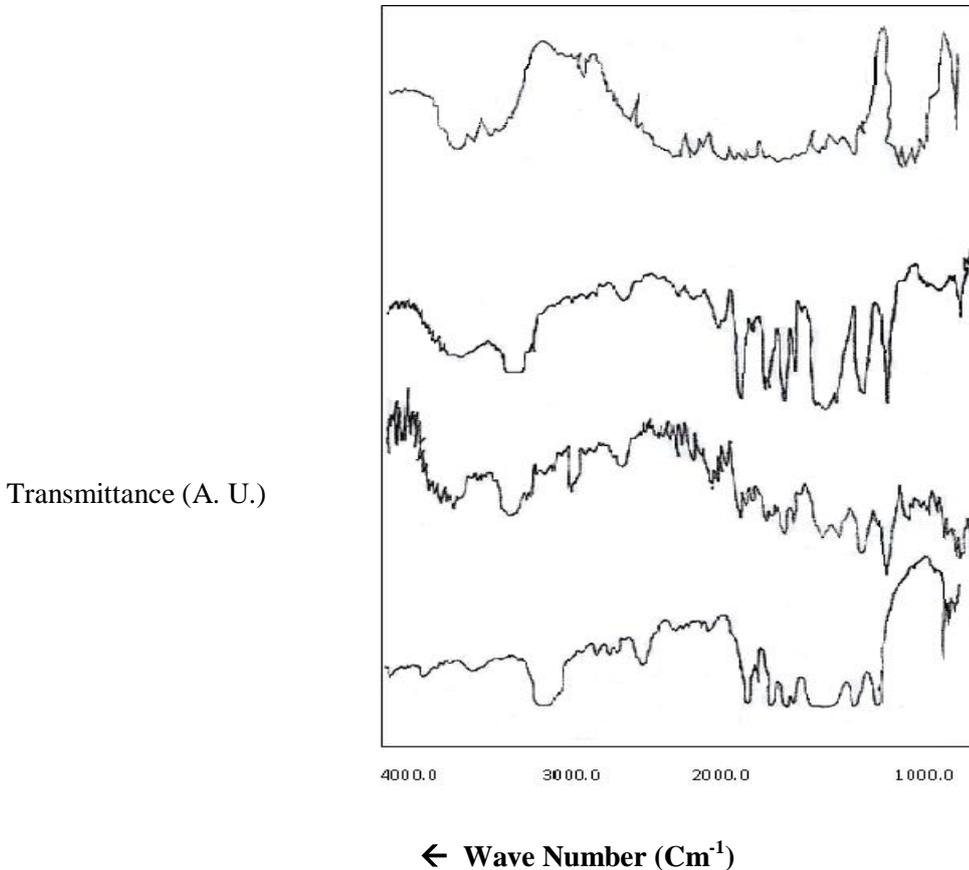
Fig.1: IR-Spectra of (a) PURE PEO   (b) PEO+KHCO$_3$+Plasticizer (80:20)
(c) PEO+KHCO$_3$ + Plasticizer (70:30)   (d) KHCO$_3$

The variation in DC conductivity (Log σ as a function of $KHCO_3$ salt concentration in plasticized polymer PEO at various temperatures is given in Fig –3. The data reveal that the conductivity of pure PEO is about 6.78×10^{-10} S /cm at room temperature (R_T) and increases to 1.58 (10^{-7} S/cm for 30 wt. % of $KHCO_3$ in the absence of plasticizer. This value again increases to 0.57 (10^{-6} S/cm at room temperature due to the addition of plasticizer (DMF). Conductivity increases rapidly from 0 wt.% to 10 wt.% of $KHCO_3$ but 10 wt.% to 30 wt.% it becomes flat. The increase in conductivity at lower dopant concentrations of $KHCO_3$ is attributed to the formation of charge transfer complexes or decrease in the crystallinity[17,18], whereas the slow increase in higher dopant concentrations is due to the formation of ionic aggregates. These ionic aggregates impede the conduction process and decrease the conductivity.

The conductivity data at room temperature is reported in Table-1. From Fig-4 and Table-1 the following conclusions can be drawn.

(a) In the temperature range of study, the conductivity is found to increase with temperature in pure PEO and also in all the compositions of PEO + $KHCO_3$+ plasticizer polymer electrolyte systems.

(b) The conductivity – temperature plots follow the Arrhenius behavior throughout, but with two regions (region-I and region-II), with two activation energies above and below melting point (T_m) of the polymer. In region-I (i.e. below T_m) the conductivity slowly increases with temperature up to 65^0C. At 65^0C there is a sudden increase in conductivity. In the region-II (i.e above T_m) the conductivity again rapidly increases with temperature. Similar behavior has been discovered in all the compositions of PEO + KHCO3 and PEO + KHCO3 + plasticizer polymer electrolyte systems.
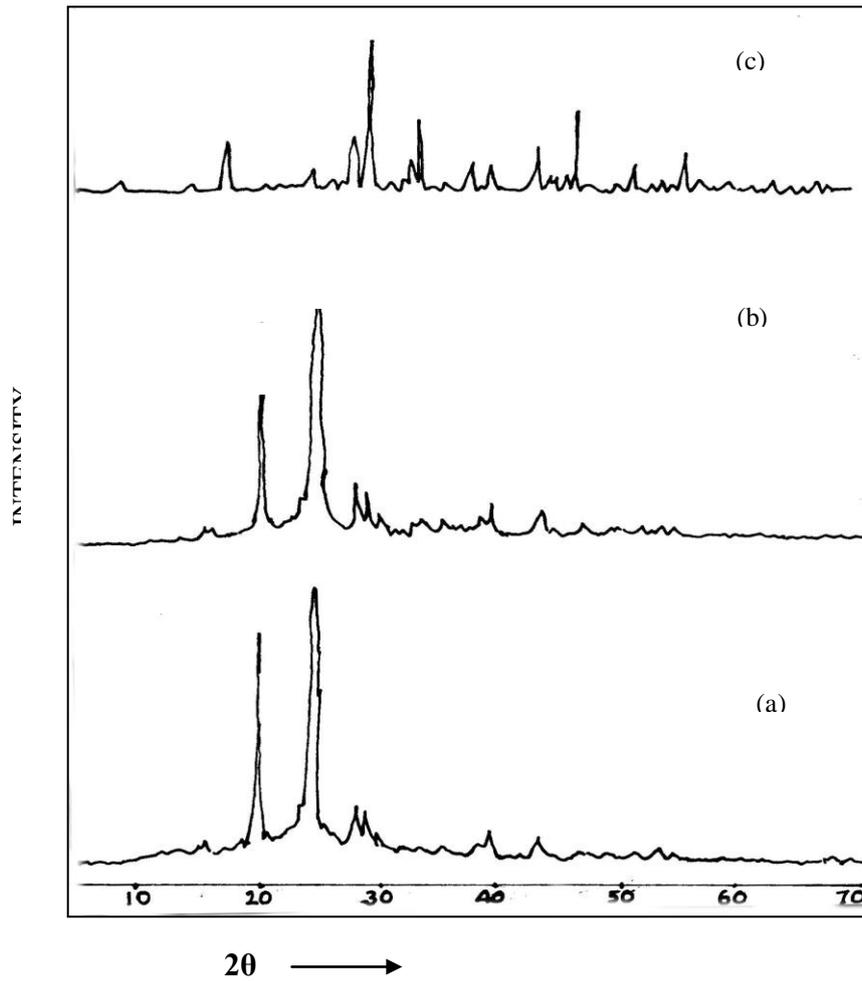
Fig.2 XRD – Spectra of (a) Pure PEO (b) PEO + KHCO$_3$ + Plasticizer (90:10) (c) PEO + KHCO$_3$
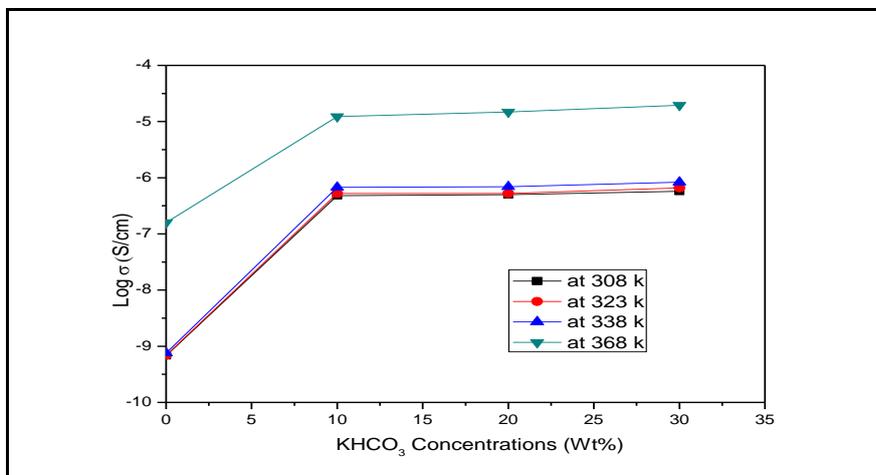
Fig.3 Composition dependence of conductivity in (PEO + KHCO$_3$ + plasticizer) Polymer Electrolyte system at different temperatures
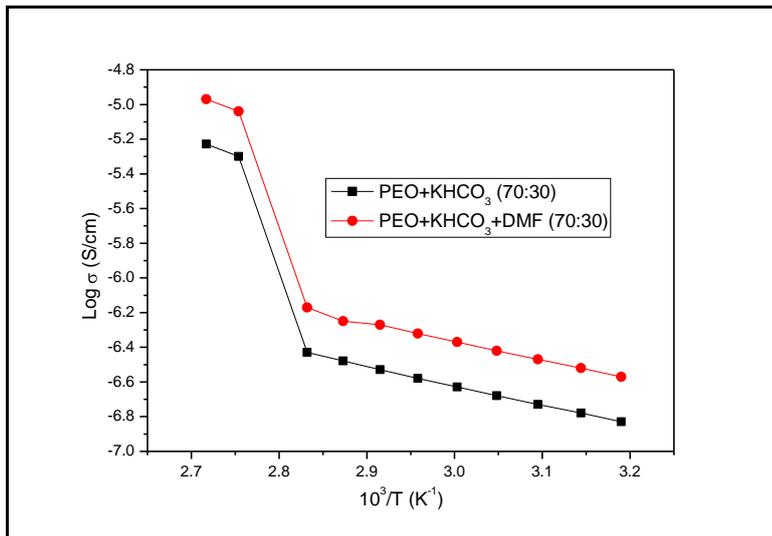
Fig: 4: The temperature verses D.C. conductivity of PEO + KHCO$_3$ (70:30) and PEO + KHCO$_3$ +DMF (70:30).

(c) The temperature, T_m which corresponds to the melting point ($\approx 65^oC$) of the polymer, there is a change from the semi crystalline to amorphous phase transition. Due to phase change, the conductivity shows a sudden increase at T_m. The existence of two regions in the conductivity – temperature plots has been observed in a number of PEO based polymer electrolytes[23-25].

(d) The conductivity data plots of log (σ_T) versus (10^3 /T) for (PEO + KHCO$_3$), (PEO +KHCO$_3$ +DMF) are shown in Fig-4. From the graph it can be observed that the plots can be divided into two regions.   On increasing the doping concentration, the conductivity is found to vary in a non-linear manner. In the polymer electrolyte systems [PEO+KHCO$_3$], [PEO+KHCO$_3$+DMF], DC conductivity is found to be in the order of ~ 10^{-7} S cm^{-1}and 10^{-6} S cm^{-1} respectively.   The conductivity values at room temperature (R$_T$) and at 368K the activation energies are given in Table-2, for pure and complexed PEO with KHCO$_3$ and PEO with KHCO$_3$ + plasticizer (DMF) in different weight ratios.

Table 1. Conductivity and Activation Energies for Pure PEO, (PEO + KHCO$_3$) and PEO + KHCO$_3$ + plasticizer (DMF) electrolyte systems.

Solid Electrolyte	Conductivity at 308 K Room temperature (R$_T$) (S cm^{-1})	Conductivity 3at 368 K (S cm^{-1})	Activation Energies in (eV)	
			Region I	Region II
Pure PEO	6.78×10^{-10}	1.58×10^{-7}	0.34	0.59
PEO + KHCO$_3$(90:10)	1.40×10^{-7}	4.82×10^{-6}	0.29	0.37
PEO + KHCO$_3$(80:20)	1.51×10^{-7}	5.07×10^{-6}	0.24	0.34
PEO + KHCO$_3$ (70:30)	1.58×10^{-7}	5.86×10^{-6}	0.21	0.3
PEO+KHCO$_3$+DMF (90:10)	0.48×10^{-6}	1.22×10^{-5}	0.31	0.35
PEO+KHCO$_3$+DMF (80:20)	0.50×10^{-6}	1.47×10^{-5}	0.29	0.32
PEO+KHCO$_3$+DMF (70:30)	0.57×10^{-6}	1.93×10^{-5}	0.18	0.29

The ionic transference number has been measured from the polarization current versus time plot, using the equation.

$t_{ion} = (i_i - i_f) / i_i$

Where i_i is the initial current and i_f is the final residual current.

Fig-5. Shows the polarization current versus time plot of PEO + KHCO$_3$ and PEO+KHCO$_3$ + (DMF) electrolyte systems respectively. The transference number values for all the samples are found to be close to

unity indicating that the charge transport is predominantly due to potassium ions, whereas the electronic contribution to the charge transport is very small. Mobility of the ionic species (K^+) is measured using transient ionic current method[13,14]. The mobility is determined using the equation

$$U = d^2 / TV$$

Where d is the thickness of the sample, T is the time of flight, and **V** is the applied voltage (1.5V). The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) have been evaluated in ($PEO+KHCO_3$) and ($PEO+KHCO_3+DMF$) systems using Wagner's polarization method[18]. The calculated values of mobility and transference numbers are given in Table-2.
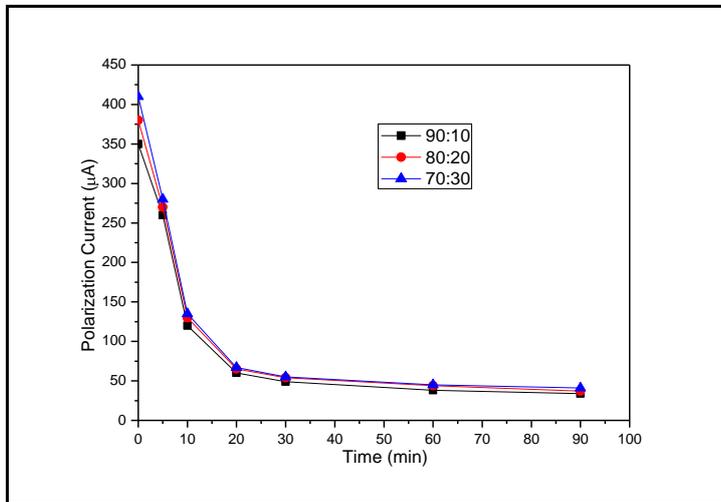
Fig.5. Polarization current versus time of a) PEO + KHCO₃+ plasticizer (DMF) (80:20)
 b) PEO + KHCO₃+ plasticizer (DMF) (70:30)   c) PEO + KHCO₃+ plasticizer (DMF) (60:40)

Table 2: The Values of Mobility and Transference numbers for Pure PEO, (PEO+NaHCO₃) and PEO + NaHCO₃ + Plasticizer (DMF) electrolyte systems

Electrolyte	Transference number (t_{ion})	Mobility (μ) in (cm²/VS)
Pure PEO	-	0.92×10^{-4} cm²/VS
PEO + KHCO₃ (90:10)	0.90	1.51×10^{-4} cm²/VS
PEO + KHCO₃ (80:20)	0.91	1.82×10^{-4} cm²/VS
PEO + KHCO₃ (70:30)	0.92	
PEO+KHCO₃+DMF(90:10)	0.92	2.34×10^{-4} cm²/VS
PEO+KHCO₃+DMF(80:20)	0.93	2.38×10^{-4} cm²/VS
PEO+KHCO₃+ MF (70:30)	0.94	

The variation of ionic conductivity of ($PEO+KHCO_3$) and ($PEO+KHCO_3+DMF$) electrolyte systems is found to follow the Arrhenius relation.

$$\sigma = \sigma_0 / T \exp(-E_a / KT)$$

Where σ_0 is the pre exponential factor, T is absolute temperature, K is the Boltzmann Constant and E_a is the activation energy for the migration of K^+ ions. The thickness of the electrode layer is about 1mm. The surface area and the thickness of the electrolyte are respectively 1.31 cm² and 150 µm. The discharge characteristics are studied for all the cells at room temperature by connecting a load of 100 KΩ.

Fig. 6 shows the discharge characteristic studies of the developed Polymer battery. The initial sharp decrease in the voltage and Current may be due to the polarization effects and / 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 the polymer battery (80:20) are found to be 2.81V and 1.32 mA, respectively. The other cell parameters of this cell were evaluated and summarized below:

Cell weight	= 1.60 gm
Effective area of the cell	= 1.31 cm^2
Thickness of the cell	= 150 μm
Discharge time	= 69 hr
Current density	= 0.98 mA/ cm^2
Power density	= 2.10 Watt/ Kg
Energy density	= 145.2 watt-hour/ kg

The battery parameters calculated for (PEO+KHCO$_3$) and (PEO+KHCO$_3$+DMF) batteries are given in Table 3 along with the parameters reported in other cells[15,17,19].

From Table-3 it is clear that the battery parameters are found to be better in plasticizer added (PEO + KHCO$_3$) electrolyte systems, indicating that plasticizer added polymer electrolyte batteries exhibit improved battery/cell performance and are more stable than pure polymer electrolyte batteries. Plasticizer added polymer electrolyte systems, thus offer an interesting alternative to other reported electrolytic systems for room temperature solid state polymer batteries/ electrochemical cells.
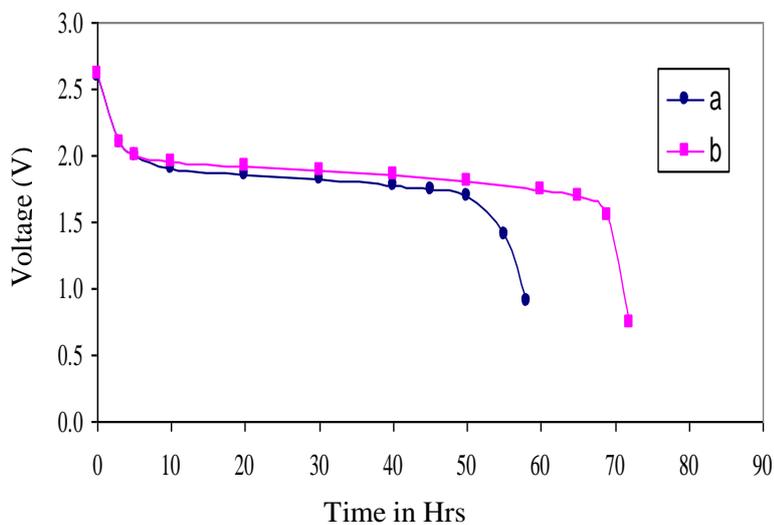
Fig.6: Discharge Characteristics of (a) K/(PEO+KHCO$_3$) /(I$_2$+C+ electrolyte) (70:30) and (b) K/(PEO+KHCO3+Plasticizer) /(I2+C + electrolyte) (70:30) Electrochemical cell for a constant load of 100 K Ω

Table 3: Comparison of Present cell / Battery Parameters with data for other Batteries reported earlier.

Electrochemical cell configuration	Open circuit voltage (V)	Discharge time (hours)	Reference
Ag/(PEO+AgNO$_3$)/(I$_2$+ C+Electrolyte)	0.61	48	[15]
Na/(PVP+NaNO$_3$)/(I$_2$+C+Electrolyte)	2.44	51	[17]
K/(PVP+KYF$_4$)/(I$_2$+ C+Electrolyte)	2.4	51	[19]
K/(PEO + KHCO$_3$ +plasticizer)/ (I$_2$+C+electrolyte)(80:20)	2.9	69	**Present Work**

Conclusions:

Plasticizers are of low molecular weight and non-volatile substances (mostly liquids). When a plasticizer is added to a polymer, it improves its flexibility, processability. Thus the utility of plasticizers substantially reduces the brittleness of many polymers, because the addition of even small quantities markedly reduces the melting point (T_m) of the polymer. This effect is due to a reduction in the cohesive change.

The effect of plasticizer DMF on a polymer electrolyte leads to an increase in conductivity by more than a factor of 10 in plasticizer added polymer electrolyte systems when compared with PEO + $KHCO_3$ polymer electrolyte systems. Also the plasticizer electrolyte systems show an improved mobility value as compared with the PEO + $KHCO_3$ electrolyte systems. From the conductivity data and from Table-2, it is clear that the addition of plasticizer has a remarkable effect on the transport properties of the electrolyte.

The solid polymer battery parameters evaluated for plasticizer added PEO+$KHCO_3$ complexed electrolyte systems exhibit better results when compared with those for PEO+$KHCO_3$ complexed systems, indicating that plasticizer added polymer electrolyte batteries exhibit improved battery performance and higher stability than pure polymer electrolyte systems.

Acknowledgements:

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