

## THERMAL STABILITY AND CELL POTENTIAL DISCHARGE CHARACTERISTIC STUDIES OF A NEW SILVER ION CONDUCTING GLASS POLYMER

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### ABSTRACT

Thermal stability studies of a new hot-press synthesized silver ion conducting glass polymer electrolytes (GPEs):  $(1-x)$  PEO:  $x$   $[0.75\text{AgI}:0.25(\text{Ag}_2\text{O}:\text{WO}_3)]$ , where  $0 \leq x \leq 50$  wt.%, are reported. The composition: 70PEO: 30 $[0.75\text{AgI}:0.25(\text{Ag}_2\text{O}:\text{WO}_3)]$  with ionic conductivity ( $\sigma \sim 6.5 \times 10^{-7}$  S.cm<sup>-1</sup>) have been identified as optimum conducting composition (OCC) from the room temperature dependent conductivity studies. Thermal stability and conductivity enhancement have been explained with the help of thermo-gravimetric analysis (TGA) and temperature dependent ionic conductivity studies of all the samples. Solid state polymer battery has been formed by using the GPE OCC as an electrolyte and cell potential discharge characteristic studies have been done at different load resistances.

Keywords— Glass polymer electrolytes, TGA, ionic conductivity, polymer battery

### INTRODUCTION

Glass polymer electrolytes (GPEs) is one of the important areas of research in the last 30 years and these are potentially used for applications in solid state devices (Gray, 1997; Cho & Liu, 1997; Chandra et al., 1988; Bhatt et al., 2020). Flexible solid polymer electrolytes (SPEs) or glass-polymer electrolytes (GPEs), which are based on poly ethelene oxide (PEO), have a great deal of technological promise for the creation of various energy devices, including polymer batteries, sensors, smart windows, and other electrochemical devices. Recently, glass polymer electrolytes (GPEs) have been created for applications in solid state devices, including batteries, sensors, electrochemical displays, etc. These GPEs have exceptional ionic conductivity because they are kept in the highly conductive amorphous phase. They also improve the stability of the interface between an electrode and an electrolyte, extend shelf life by lowering the rate of PEO

recrystallization, and increase the quantity of ions that can be transferred (Kumar et al., 1994; Zhang et al., 2002).

In general, SPEs/ GPEs are prepared using the traditional solution-cast and sol-gel methods. Recently, a new hot-press method has been developed for casting SPE/GPE films (Appetecchi et al., 2003; Chandra et al., 2022). This method shows the great procedural advantages over the conventional methods. A new Ag<sup>+</sup> ion conducting glass polymer electrolytes (GPEs): (1-x) PEO: x [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)], where 0 ≤ x ≤ 50 wt.% have been synthesized by hot-press method in our previous communication (Sahu et al., 2023).

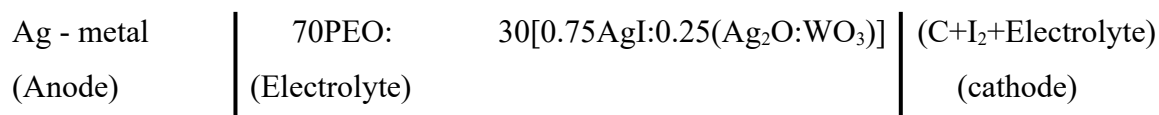
In the present investigation, we report the thermal studies of a newly synthesized hot-pressed. synthesis of a novel glass polymer electrolytes (GPEs): (1-x) PEO: x [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)], where 0 ≤ x ≤ 50 wt.%. Temperature dependent ionic conductivity (σ) and ionic transference number (t<sub>ion</sub>) measurements were also done at room temperature and above. A new solid state polymer battery has been synthesised by using the newly synthesized GPE OCC as an electrolyte and cell potential discharge characteristic studies have been done at different load resistances.

## EXPERIMENTAL

For the synthesis of present GPEs: (1-x) PEO: x [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)], where 0 ≤ x ≤ 50 wt.%, the AR grade chemicals: poly (ethylene oxide) PEO (10<sup>5</sup> Mw, Aldrich, USA), AgI (purity >98%), Ag<sub>2</sub>O (>98%) & WO<sub>3</sub> (>99%) were used. The GPEs were synthesized by hot-press method. The details related to synthesis procedure has been given in our previous communication (Sahu et al., 2023).

Thermal stability has been done with the help of thermos-gravimetric analysis (TGA) [model:SDT Universal]. Temperature dependent ionic conductivity measurements have been carried out with the help of an LCR bridge [model: HIOKI 3520, Japan] at a fixed frequency 5 kHz. Ionic transference number (t<sub>ion</sub>) measurements were also determined by using the dc polarization method at different temperatures (Chandra et al., 1988; Chandra, 2013).

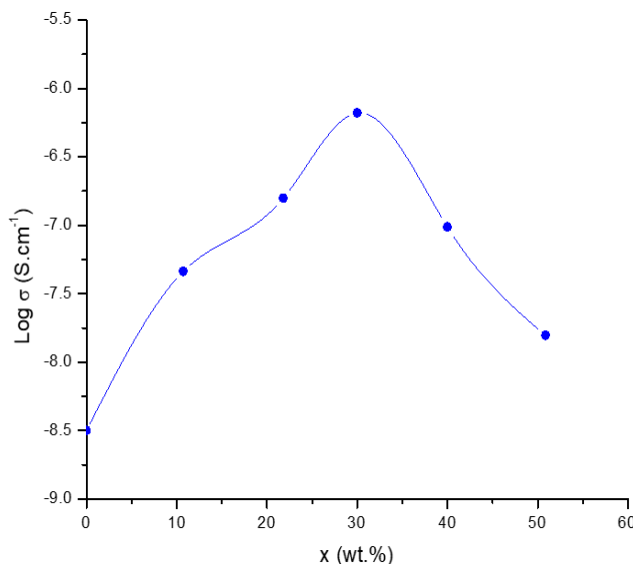
Solid-state polymer batteries were fabricated in the following cell configuration:



The cathode in the film form has been prepared by hot-pressing the slurry of the physical mixture of elemental iodine ( $I_2$ ), the conducting graphite (C) and NCPE in 1:1:1 weight ratio at  $\sim 70^\circ C$ . The cell performances were studied under 100 and 50 k $\Omega$  load condition at room temperature. The cell potential discharge profiles were drawn as a function of time and some important cell parameters were calculated from the discharge curves.

## RESULTS AND DISCUSSION

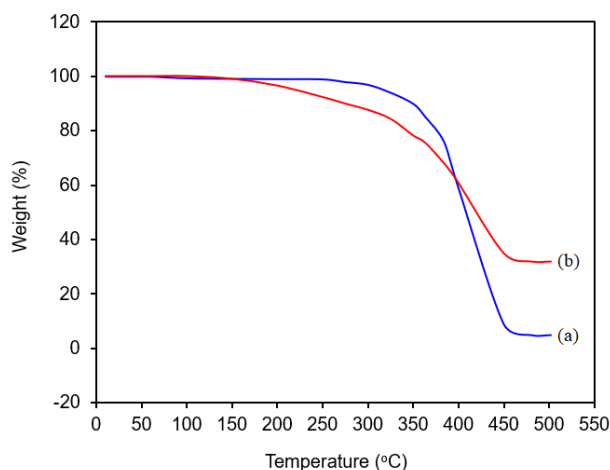
Figure 1 shows the ‘Log  $\sigma - x$ ’ plot for hot-press synthesized GPEs: (1-x) PEO: x [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)], where  $0 \leq x \leq 50$  wt.%(Sahu et al., 2023). The maximum conductivity at room temperature was obtained at  $x = 30$  wt.% of doping salt with conductivity  $\sim 6.5 \times 10^{-7}$  S.cm<sup>-1</sup>, referred to as optimum conducting composition (OCC). Two orders of conductivity enhancement in GPE OCC obtained and this is due to the increase in degree of amorphicity, as reported in our previous communication.



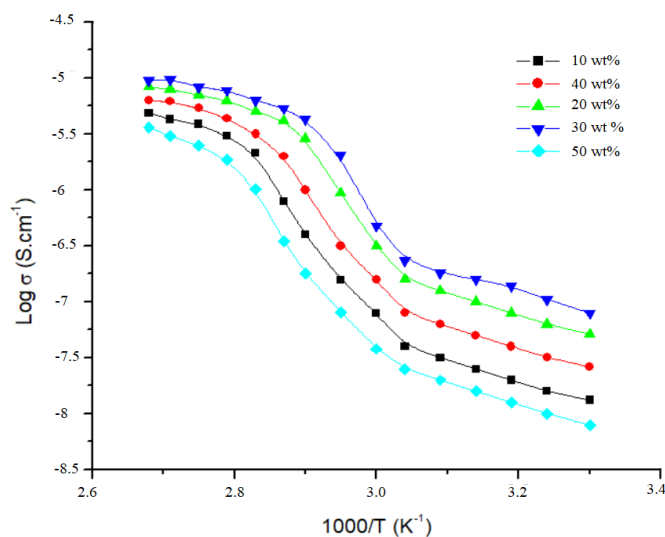
**Fig. 1. ‘Log  $\sigma - x$ ’ plot for GPEs: (1-x) PEO: x [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)], where  $0 \leq x \leq 50$  wt.%(Sahu et al., 2023).**

Fig. 2 shows the TGA curves of pure PEO and GPE OCC: 70PEO: 30[0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)]. It can be clearly shown from the figure that the total weight loss for pure PEO is larger as compared to the newly synthesized GPE. The total weight loss for GPE

OCC is ~ 68 % but for pure PEO is ~ 95 %. The thermal stability of pure polymer has been improved with formation of GPE and it is indicative of complexation of polymer with salts.



**Fig. 2. TGA curves: (a) pure PEO and (b) GPE OCC: 70 PEO: 30 [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)].**



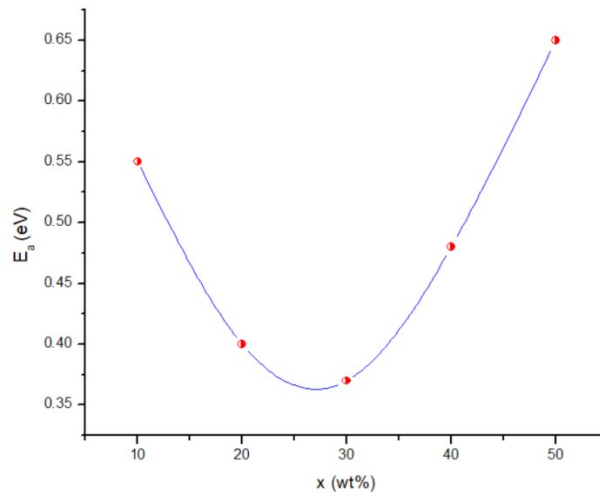
**Fig. 3. 'Log  $\sigma$  -1/T' plot for GPEs: (1-x) PEO: x [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)], where  $0 \leq x \leq 50$  wt.%.**

The ionic conductivity measurement of the present GPEs: (1-x) PEO: x [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)], where  $0 \leq x \leq 50$  wt.%., have been carried out at different temperatures. Figure 3 shows 'Log  $\sigma$ -1/T' plots of the hot-pressed GPEs. It can be clearly seen from the figure that as the temperature increases conductivity is also increases for all the

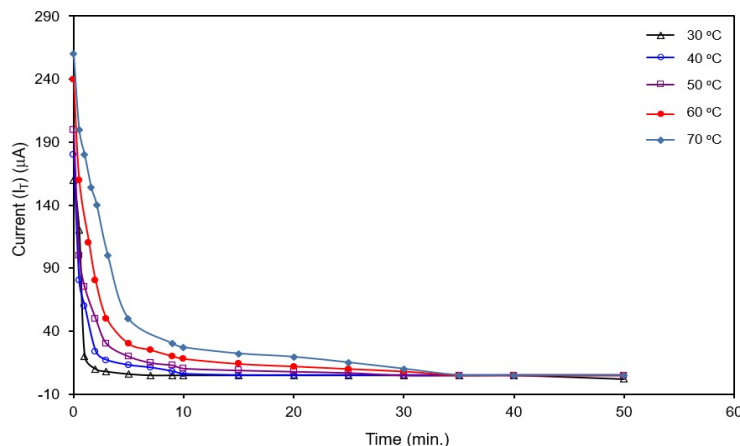
compositions. The increase in conductivity with temperature can also be related to the increase in the number of mobile charge carriers and available of a greater number of conduction paths/ free volumes to the transport of ions. The higher the number of charge carriers, higher the mobility and hence higher the conductivity. This can be explained on the basis of free volume model and hopping of charge carriers (Cohen & Turnbull, 1959; Agrawal & Pandey, 2008). The conductivity increased linearly with temperature, except for an upward change in the slope at ~ 70 °C which corresponds to semi-crystalline to amorphous phase transition temperature of PEO. The linear portion of GPEs (below this transition temperature) exhibited Arrhenius type behavior and can be expressed as:

$$\sigma(T) = \sigma_0 \exp(-E_a/kT) \quad [\text{S.cm}^{-1}]$$

where  $\sigma_0$  is the pre-exponential factor and  $E_a$  is activation energy in (eV),  $k$  is the Boltzmann's constant and  $T$  is the temperature in (°K). Figure 4 shows the ' $E_a$  vs  $x$ ' plot for GPEs. It can be clearly noticed that the activation energy for present GPE OCC is very low as compared to the other samples. It is indicative of high amorphous nature of the polymeric electrolytes, an easy ion transport and hence it can be potentially used for the fabrication of solid-state devices.

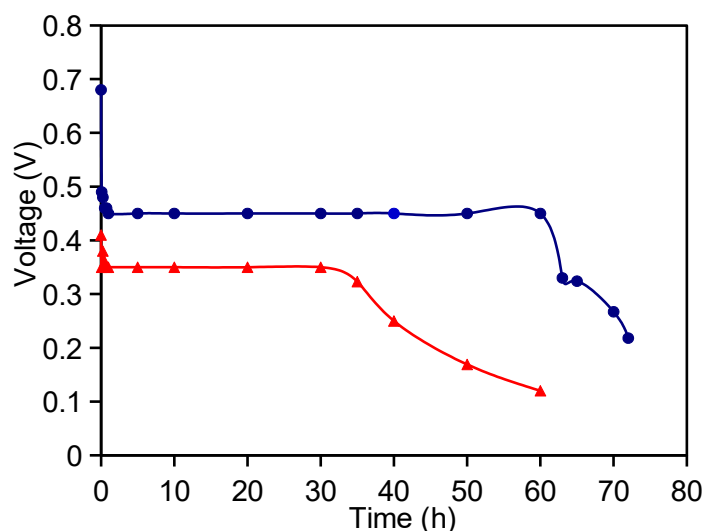


**Fig.4. ' $E_a$ - $x$ ' plot for GPEs: (1-x) PEO: x [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)], where 0 ≤ x ≤ 50 wt.%.**



**Fig. 5. 'Current vs time' plot for GPE OCC: 70 PEO: 30 [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)] at various temperatures.**

Fig. 5 shows the 'current vs time' plot for GPE OCC: 70 PEO: 30 [0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)] at room temperature and above. One can clearly note that  $t_{ion}$  is 0.98 at all the temperatures and hence the charge transport in the present system is predominantly ionic with a negligible contribution ( $\sim 0.2$ ) of electrons.



**Fig. 6. Cell potential discharge profiles for the solid-state polymer battery under 100 kΩ (●) and 50 kΩ (Δ) loads at room temperature.**

Figure 6 shows the cell potential discharge curve for the Ag<sup>+</sup> ion conducting solid-state polymer batteries, when discharged through 100 & 50 kΩ load resistances. An Open Circuit Voltage (OCV)  $\sim 0.68$  V, obtained for all the batteries, decreased sharply in the beginning due to the initial cell polarization effect, then remained almost stable at:  $\sim 0.45$  V for  $\sim 55$  hrs (100 kΩ);  $\sim$

0.35 V for ~ 30 hrs (50 kΩ). One can clearly note that the performances of the batteries have been relatively superior during low current drain states. Table 1 lists some important cell parameters calculated in the plateau region of the discharge profiles. OCV ~ 0.68 V is almost same as compared to the theoretical OCV ~ 0.687 V obtained usually for Ag/ I<sub>2</sub> electrode couple (Minami, 2005; Chandra, 2009).

Table1. Some important cell parameters of the solid-state polymeric cell at room temperature.

Cell Parameters	Loads	
	100 KΩ	50 KΩ
Working voltage (V)	0.45	0.35
Current Density (μA.cm <sup>-2</sup> )	0.35	0.29
Discharge Capacity (μA.h)	23	12.25
Power Density (mW.kg <sup>-1</sup> )	0.388	0.285
Energy Density (mWh.kg <sup>-1</sup> )	20.36	8.52

## CONCLUSIONS

Thermal stability of a newly synthesized silver ion conducting hot-pressed GPE: 70PEO:30[0.75AgI:0.25(Ag<sub>2</sub>O:WO<sub>3</sub>)] has been explained with the help of TGA and temperature dependent ionic conductivity which shows the present GPE is more stable as compared to the pure PEO. Activation energy analysis indicated that this can be potentially used for the solid-state device fabrications. A new polymeric battery has been fabricated and their discharge characteristics were studied under varying load conditions. The cell performed quit satisfactorily under low current drains.

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