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Impression of (PEO+$KBrO_3$+Plasticizer) Polymer Electrolyte as Carbon Monoxide Gas Sensor

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ABSTRACT
Solid state polymer electrolytes have been prepared by with poly (ethylene oxide) (PEO), $KBrO_3$ salt and plasticizer (Dimethyle Formamide [DMF]) by using solution – casting technique. These polymer electrolytes have been prepared in the weight ratios (90:10), (80:20) and (70:30). The complexations of salt and polymer have been examined by using X-ray diffraction (XRD) and Differential Scanning Calorimetry (DSC). Carbon monoxide gas sensors have been fabricated by using (PEO+$KBrO_3$+Plasticizer) polymer electrolytes and premeditated its sensitivities at various temperatures. The sensitivity of the gas sensor has been observed at various concentrations of carbon monoxide gas.
Keywords: Differential Scanning Calorimetry, Gas Sensor, Poly (ethylene oxide), Polymer, X-ray diffraction.

I. INTRODUCTION

Solid state polymer electrolytes have been emerging technology due its various applications in the field of science and technology. As a result, polymer electrolytes have been fabricated like as fuel cells, sensors, electrochemical display devices, smart windows, photochemical cells etc. The polymer electrolytes have technological advantages, for example long self-life, tremendous miniaturization, broad temperature range of operation along with low cost. These solids show significant high ionic conductivities at their operating temperatures [1-5].

Polymer electrolytes can be shaped in the form of thin film, and it was used for gas sensor applications. A few of investigations are materialized on proton conducting polymer electrolytes and their application to gas sensors. No efforts have been observed for the preparation of sensors using ionic conducting polymer electrolytes. Keeping these aspects in view, in this present study (PEO+$KBrO_3$+Plasticizer) polymer electrolytes were fabricated by solution casting technique, where Dimethyle formamide (DMF) is used as plasticizer. Complexation of PEO, $KBrO_3$ and plasticizer has been confined by using X-ray diffraction (XRD) and Differential Scanning Calorimetry (DSC). (PEO+ $KBrO_3$+Plasticizer) based polymer electrolyte carbon monoxide gas sensors have been fabricated and premeditated its characteristics at different temperatures and also at different concentrations of carbon monoxide gas.

II. EXPERIMENTAL

Solid state polymer electrolyte films (thickness ≅ 100 – 150 µm) of PEO [Aldrich, molecular weight ($6X10^5$)] complexed with $KBrO_3$ salt and plasticizer have been prepared in the weight ratios (90:10), (80:20) and (70:30) by using solution-casting technique with methanol and water as solvents. The solutions were stirred for 15-20 hr, and casted on polypropylene dishes, as well as it was evaporated gradually at room temperature. At last, the films were dried carefully at 10^{-3} Torr [6]. X-ray diffraction (XRD) investigation were carried for all the samples by using a SIEMES / D 5000 X-ray diffractometer (Cu K_α radiation λ = 1.5406 Å) [7]. Differential Scanning Calorimetry (DSC) (TA 2010 instrument) was used to find the melting temperatures of these polymer electrolyte films [8].

In addition to that, an electrochemical sensor has been fabricated with (PEO+$KBrO_3$+Plasticizer) polymer electrolyte. An aluminium tube was dipped in the solution of (PEO+$KBrO_3$+Plasticizer) container for 10 minutes and it is removed from that solution. Solution was allowed for evaporation at room temperature. When this process was done several times, after that the aluminium tube substrate holds a coating of (PEO+$KBrO_3$+Plasticizer) polymer electrolyte on its superficial surface. This aluminium tube substrate is provided with two silver electrodes. The resistance of the substance was calculated in the presence and absence of carbon monoxide gas taken in concentration in ppm in dry air. The operating temperature and the concentration of carbon monoxide gas are varied in order to study the sensitivity of carbon monoxide gas sensors.

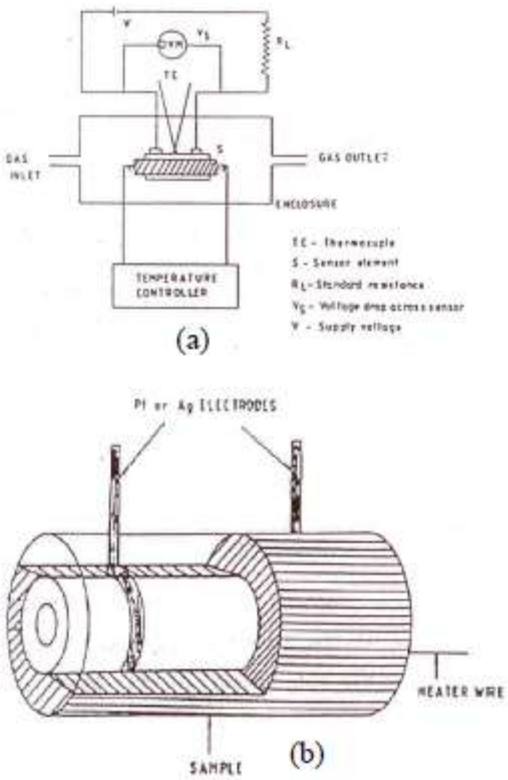

Fig.1. (a) & (b) Schematic of measurement setup used to study the sensitivity of the carbon monoxide gas sensor.

For the resistance measurements the sensor element was placed on temperature – controlled tungsten coil heater inside a glass enclosure. A load resistance R_L was associated in series with the sensor element R_S. The input circuit voltage was applied across R_S and R_L. Carbon monoxide gas was passed into the enclosure through the inlet. The resistance of the sensor was acquiring by measuring the voltage drop (V_S) across the sensor element [9-11]. A chromel – alumel thermocouple (T_c) was placed on the device to indicate the operating temperature. This temperature measurement was within an accuracy of ± 2^{o}C. But it is originate that there is no considerable alteration in the sensitivity. The schematic of the measurement setup is shown in Fig.1. The sensor sensitivity (S) is defined as the ratio of the change in electrical resistance in the presence of gas $R_a - R_g = \Delta R$, to that in air, R_a.

$$S = \frac{[R_a - R_g]}{R_a} = \frac{\Delta R}{R_a}$$

Where

R_a is resistance in the presence of air.

R_g is resistance in the presence of carbon monoxide gas.

To estimate the sensitivity the electrical resistance of the electrolytes was measured in the presence and absence of carbon monoxide gas.

III. RESULT AND DISCUSSIONS

1). X-ray diffraction (XRD) analyses:

The X-ray diffraction (XRD) patterns of pure PEO, $KBrO_3$ and (PEO+$KBrO_3$+Plasticizer) were given in Fig. 2. The evaluation of the diffraction spectra of complexed PEO with that of pure PEO and $KBrO_3$ reveals the subsequent differences. The diffraction peaks observed between $2\theta = 10^0$ and 50^0 are found to be less intense in complexed PEO films compared to pure PEO films.

- This specifies that the addition of [$KBrO_3$+ Plasticizer] to the polymer causes a reduction in the degree of crystallinity of the polymer PEO.
- Peaks corresponding to the uncomplexed PEO are also present jointly with that of [$KBrO_3$+ Plasticizer] in complexed PEO films viewing the simultaneous presence of both crystalline uncomplexed and complexed PEO. Earlier workers [12-15] have been reported similar results on PEO complexed systems.
- Approximately no sharp peaks were observed for higher concentration of the [$KBrO_3$+ Plasticizer] salt in the polymer, representing the dominant presence of an amorphous phase.

Therefore, the XRD details for these films obviously verifying the complexation of the polymer PEO with $KBrO_3$ and Plasticizer.

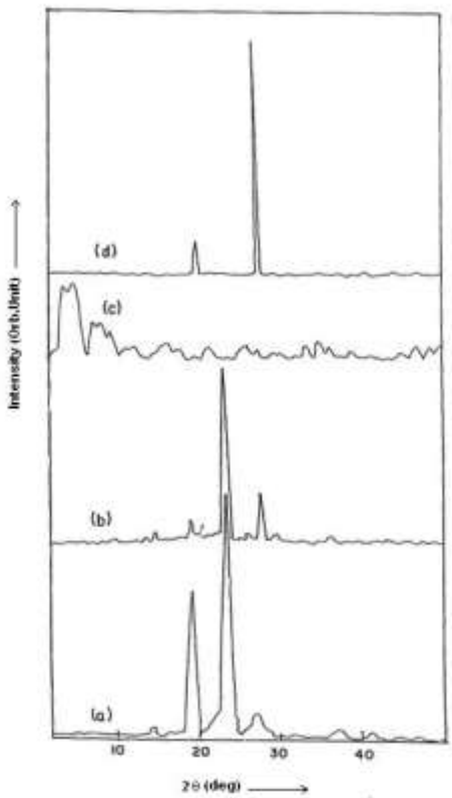

Fig. 2. X-ray diffraction spectra (a) Pure PEO (b) [PEO+$KBrO_3$+Plasticizer] (90:10) (c) [PEO+$KBrO_3$+Plasticizer] (70:30) (d) $KBrO_3$

2). Studies of Differential Scanning Calorimetry (DSC):

The Differential Scanning Calorimetry (DSC) curves of pure PEO and PEO complexed with [$KBro_3$+Plasticizer] for various compositions are shown in Fig.3. An endothermic peak is observed at 70^{o}C, which subsequent to melting temperature of pure PEO. The slight shift in the melting point T_m, towards lesser temperature is due to the addition of [$KBrO_3$+Plasticizer] to the polymer and various compositions of (PEO+$KBrO_3$+Plasticizer) are presented in the Table – 1. Similar result on PEO complexed system has also been obtained by earlier workers [16-18].

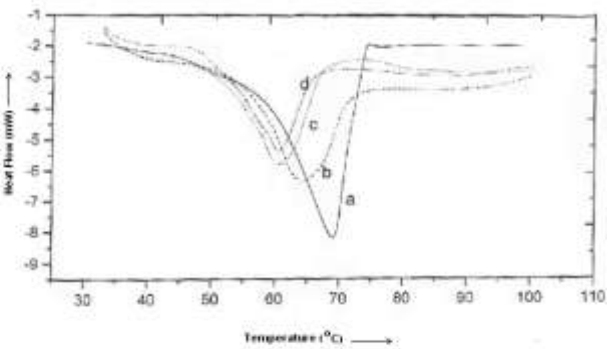

Fig. 3. DSC curves (a) Pure PEO
(b) [PEO+$KBrO_3$+Plasticizer] (90:10)
(c) [PEO+$KBrO_3$+Plasticizer] (80:20)
(d) [PEO+$KBrO_3$+Plasticizer] (70:30)

Table – 1. Melting temperature of PEO and various ratios of [PEO+$KBrO_3$+Plasticizer] polymer electrolyte system obtained from DSC studies.

Polymer Electrolytes	Melting Temperature (T_m)^{o}C
Pure PEO	70
[PEO+$KBrO_3$+Plasticizer] (90:10)	65
[PEO+$KBrO_3$+Plasticizer] (80:20)	61
[PEO+$KBrO_3$+Plasticizer] (70:30)	60

3). (PEO+ $KBrO_3$ + Plasticizer) polymer electrolyte Carbon Monoxide Gas Sensor:

Polymer electrolytes have been prepared by means of Poly (ethylene oxide) (PEO) complexed with $KBrO_3$ salt and plasticizer for various composition proportions [(90:10), (80:20) and (70:30)]. Using these polymer electrolytes, the gas sensors have been fabricated and their characteristics were finding in the presence of carbon monoxide gas. The sensor resistance altered when carbon monoxide gas was exposed to the polymer electrolyte film. The sensor proceeds to its unique state as soon as the carbon monoxide gas is separated. The output values alter to its unique value within 8-10 seconds time [19].

The senses or characteristics of the polymeric film were finding without and with exposed to carbon monoxide gas. The operating voltage for sensor was 10V. The sensitivity (S) of sensor is illustrated as the ratio of change in electrical resistance in the presence of carbon monoxide gas to that in the presence of air.

$$\text{Sensitivity (S)} = \frac{[R_a - R_g]}{R_a} = \frac{\Delta R}{R_a}$$

Using (PEO+$KBrO_3$+Plasticizer) based polymer electrolyte gas sensors have been fabricated and obtained its characteristics at various circumstances. The sensitivity (S) has been measured as a function of composition (Wt %) of $KBrO_3$ in the polymer electrolytes at different temperatures are shown in Fig. 4. From Fig. 4, it is clear that the gas sensitivity augmented with increase in the composition (Wt %) of $KBrO_3$ salt in the polymer electrolyte.

The sensitivity of the (PEO+$KBrO_3$+Plasticizer) based polymer electrolyte gas sensor confirmed an increase with increase in carbon monoxide gas concentration and as will as with enhance of operating temperatures and it was shown in Fig. 5.

Sensitivity of the gas sensor increase with the increase of temperature and it is shown in Fig. 6. At the melting point of the polymer, there is an altered from a semi-crystalline to an amorphous phase. As a result of this phase change, the conductivity shows an abrupt boost at the melting point. The increase in conductivity with temperature is interpreted as a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of polymer [20]. As the amorphous region gradually increases and the sensitivity of the gas sensor augmented with temperature. The values of sensitivity studied for a range of temperatures at constant gas concentration (ppm) are given in Table – 2.

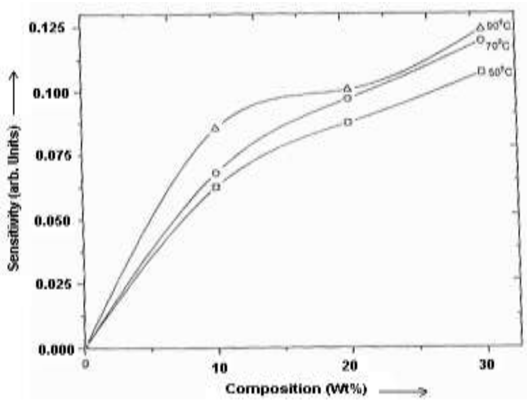

Fig. 4. [PEO+$KBrO_3$+Plasticizer] based gas sensor sensitivity as a function of composition (Wt%) of the electrolyte for different temperatures.

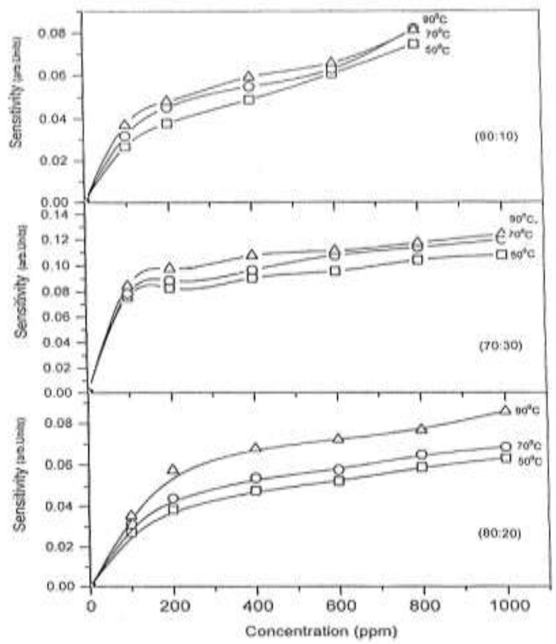

Fig. 5. [PEO+$KBrO_3$+Plasticizer] based gas sensor sensitivity as a function of gas concentration (ppm) for different temperatures.

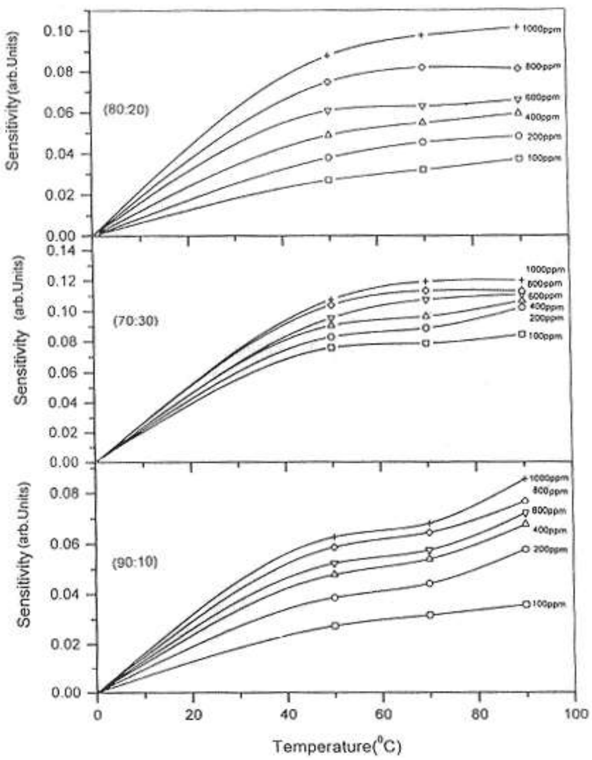

Fig. 6. [PEO+$KBrO_3$+Plasticizer] based gas sensor sensitivity as a function of temperature for different gas concentrations (ppm).

Table – 2. (PEO+ $KBrO_3$+ Plasticizer) based polymer electrolytes gas sensor sensitivity at different temperatures.

Different ratios of (PEO+ $KBrO_3$+Plasticizer) Polymer electrolytes	**Sensitivity at 1000 (ppm)**		
	50°C	***70°C***	***100°C***
(90:10)	0.0626	0.0681	0.0853
(80: 20)	0.0876	0.0972	0.1009
(70: 30)	0.1075	0.1195	0.1238

The following interpretation has been made by examining above three figures (4, 5 & 6) and Table - 2,

- The sensitivity of the gas sensor is found to increase with an increase in the composition of the salt in the polymer PEO.
- The sensitivity of the gas sensor illustrates an increase within increase in carbon monoxide gas concentration.
- The sensitivity of the gas sensor increases with an increase in the temperature.

IV. CONCLUSION

Solid state polymer electrolytes have been prepared by using Poly (ethylene oxide) (PEO) complexed with ($KBrO_3$+ Plasticizer) and equipped with various composition ratios [(90:10), (80:20) and (70:30)]. The complexation of the polymer, $KBrO_3$ and plasticizer were investigated by using XRD study. At 70°C, an endothermic peak was observed in DSC study corresponding to the melting temperature (T_m) of pure PEO. With the addition of $KBrO_3$ to pure PEO, the melting temperature (T_m) was slightly changed towards lower temperature. Using (PEO+$KBrO_3$+Plasticizer) polymer electrolytes, the gas sensors have been fabricated and studied its characteristics in presence of carbon monoxide gas. The sensitivity of the sensor was increase with an increase in the composition of salt in PEO. Carbon monoxide gas sensor sensitivity augmented with an increase in the carbon monoxide gas concentration (ppm) in air. The sensitivity of gas sensor showed an increase with increase of temperature.

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