The Effect of Nano Filler Al_2O_3 on ($PEO+KClO_4$) Based Polymer Electrolyte Gas Sensors

T. Sreekanth and V. Madhusudhana Reddy

***Abstract*—Growth of solid polymer electrolytes is driven by their tremendous technological applications. Therefore, solid-state polymer electrolyte have been prepared by solution – casting method by using poly (ethylene oxide) (PEO), $KClO_4$ salt and Nano filler Al_2O_3. The complexation of poly (ethylene oxide) (PEO), KClO4and Al2O3 have been studied by using X-ray diffraction (XRD), IR and differential scanning calorimetry (DSC). Solid state electrochemical carbon monoxide gas sensors have been fabricated by using polymer electrolytes (PEO+ KClO4) and (PEO+ $KClO_4$+Nano filler Al_2O_3) and studied their sensitivities at different temperatures, and at different carbon monoxide gas concentrations. From these studies it is concluded that nano filler added polymer electrolytes sensor have more sensitivity when compared to the polymer electrolytes without nano filler.**

***Index Terms*—Polymer, poly (ethylene oxide), x-ray diffraction, gas sensor.**

I. Introduction

Over the last few decades, a considerable amount of research work has been reported on solid polymer electrolytes due to the technological advantages, such as long self-life, extreme miniaturization, wide temperature range of operation and they can be prepared easily with low cost. These solids exhibit appreciable high ionic conductivities at their operating temperatures [1]–[5]. Polymer electrolytes can be shaped in the form of thin film, there by reducing the internal resistance leading to gas sensing material application. A few of reports are materialized on proton conducting polymer electrolytes and their application to gas sensors. No attempts were witnessed for the preparation of sensors using ionic conductors. Keeping these aspects in view, the authors are used (PEO+ $KClO_4$) and (PEO+ $KClO_4$+Nano filler Al_2O_3) based polymer electrolytes which were fabricated by using solution casting technique. Complexation of the PEO and $KClO_4$ was confirmed by using X-ray diffraction (XRD), IR and differential scanning calorimetry (DSC). (PEO+ $KClO_4$) and (PEO+ $KClO_4$+Nano filler Al_2O_3) based polymer electrolyte carbon monoxide gas sensors were fabricated and studied their characteristics at different temperatures and also at different concentrations of carbon monoxide gas.

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II. Experimental

Ion conducting polymer electrolyte films (thickness ≅ 100–150 μm) of PEO [Aldrich, molecular weight (4×10^5)] complexed with $KClO_4$ salt have been prepared in the weight ratios (90:10), (80:20) and (70:30) by solution-casting technique using methanol and water as solvents. Nano alumina (Al_2O_3) having particle size ~10nm, has been used as filler for these polymer electrolytes. The solutions were stirred for 15-20 hr, were cast using polypropylene dishes, and were evaporated slowly at room temperature. Finally, the films were dried thoroughly at 10^{-3} Torr [6]. X-ray diffraction (XRD) analyses of all the samples were carried out by using a SIEMES / D 5000 X-ray diffractometer (Cu K_α radiation $\lambda = 1.5406$ Å). The infrared spectrum of polymer electrolyte films was recorded on a PERKIN ELMER FTIR spectrophotometer [Model 1605] in the range of 1000 – 4000 cm^{-1}. DSC (TA 2010 instrument) was used to study the melting temperatures of the polymer electrolyte films [7]. Carbon monoxide gas sensor was fabricated by using (PEO+ $KClO_4$) and (PEO+ $KClO_4$+Nano filler Al_2O_3) based polymer electrolytes and studied their characteristics at different temperatures and also for different gas concentrations. The sensor sensitivity is found to be better in nano filler added polymer electrolyte complexed sensors.

III. Result and Discussion

A. X-Ray Diffraction (XRD) Analyses

The X-ray diffraction (XRD) pattern of pure PEO, $KClO_4$ complexed PEO and [PEO+$KClO_4$+Nano filler Al_2O_3] are given in Fig. 1. A comparison of the diffraction spectra of complexed PEO with that of pure PEO and $KClO_4$ reveals the following differences. The diffraction peaks observed between $2\theta = 10^0$ and 30^0 are found to be less intense in complexed PEO films compared to pure PEO films.

- This indicates that the addition of [$KClO_4$+Nano filler] to the polymer causes a decrease in the degree of crystallinity of the polymer PEO.
- Peaks corresponding to the uncomplexed PEO are also present together with that of [$KClO_4$+Nano filler] in complexed PEO films showing the simultaneous presence of both crystalline uncomplexed and complexed PEO. Earlier workers [7]-[11] have been reported similar results on PEO complexed systems.
- Almost no sharp peaks were observed for higher concentration of the [$KClO_4$+Nano filler Al_2O_3] salt in the polymer, indicating the dominant presence of an amorphous phase.

Thus, the XRD data for these films clearly confirm the complexation of the polymer PEO with $KClO_4$ and Nano filler Al_2O_3.

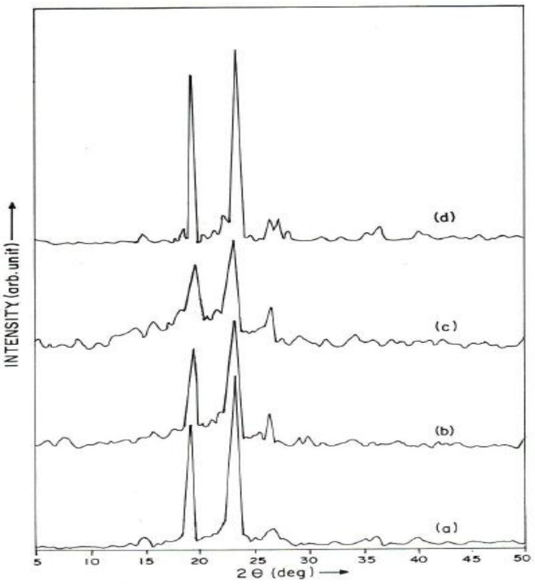

Fig. 1. X-ray diffraction pattern (a) Pure PEO, (b) [PEO + $KClO_4$ + Nano filler Al_2O_3] (80:20) (c) [PEO + $KClO_4$+ Nano filler Al_2O_3] (70:30) and (d) $KClO_4$.

B. IR Studies

The IR spectra of pure PEO, $KClO_4$ and [PEO +$KClO_4$+ Nano composite filler Al_2O_3] complexed with $KClO_4$ are shown in Fig. 2. The following differences in the spectral features have been observed on comparing the spectra of complexed PEO with pure PEO and $KClO_4$.

- The intensity of the aliphatic C-H stretching vibrational band observed around 2872.1 cm^{-1} in PEO decreases with increasing concentration of $KClO_4$ salt in the polymer.
- The width of the C-O Stretching band observed around 1117.7 cm^{-1} in PEO also showed an increase with an increase of $KClO_4$ in the polymer.
- The intensity of the stretching bands observed around 1960.0 and 4003.4 cm^{-1} in PEO showed a decrease with an increase of $KClO_4$ in the polymer
- The peak observed around 1464.9 cm^{-1} in pure PEO is shifted towards higher wave number side with increase of salt in the polymer.
- Several new peaks around 461.8, 532.3 and 673.3 cm^{-1} have been observed in complexed PEO.

The appearance of new peaks along with changes in existing peaks (and / or their disappearance) in the IR spectra directly indicates the complexation of $KClO_4$ with PEO. If the cations of $KClO_4$ get coordinated with the ether oxygen of PEO, the spectral changes are expected to be in the COC stretching and deformation ranges. The decrease in the width of 1117.7 cm^{-1} band, which is assigned to COC symmetrical and asymmetrical stretching [8]-[12], suggests the coordination / complexation of the salt with the polymer PEO.

It has been known for a decade that the addition of inorganic nano fillers to a polymer-salt system decreases the glass transition temperature [13], [14], which helps to soften the polymer backbone and increases its segmental motion such segmental motion provides voids or free volume which enables the easy flow of ions through the material when there is an applied electric field.

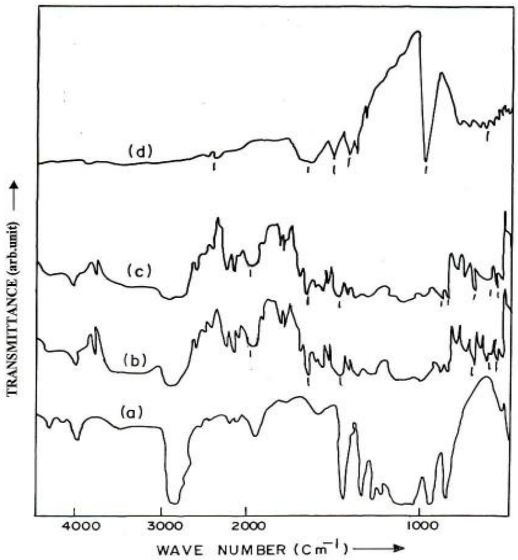

Fig. 2. IR Spectra (a) Pure PEO, (b) [PEO + $KClO_4$ + Nano filler Al_2O_3] (80:20), (c) [PEO + $KClO_4$+ Nano filler Al_2O_3] (70:30) and (d) $KClO_4$.

C. Studies of Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimetry (DSC) curves of pure PEO and PEO complexed with [$KClO_4$+ Nano filler Al_2O_3] for various compositions are shown in Fig. 3. An endothermic peak is observed at 70°C, which corresponding to melting temperature of pure PEO. The slight shift in the melting point T_m, towards lower temperature is due to the addition of [$KClO_4$+ Nano filler Al_2O_3] to the polymer and various compositions of [PEO+ $KClO_4$+ Nano filler Al_2O_3] are presented in the Table I. Similar result on PEO complexed system has also been reported by earlier workers [15]-[17].

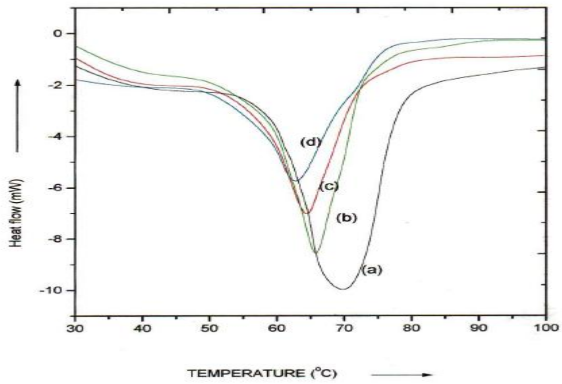

Fig. 3. DSC curves (a) Pure PEO, (b) [PEO + $KClO_4$ + Nano filler Al_2O_3] (90:10), (c) [PEO + $KClO_4$+ Nano filler Al_2O_3] (80:20) and (d) [PEO + $KClO_4$+ Nano filler Al_2O_3] (70:30).

TABLE I: MELTING TEMPERATURE OF PEO AND COMPLEXED POLYMER ELECTROLYTE SYSTEMS OBTAINED FROM DSC STUDIES

Polymer electrolyte	*Melting temperature (T_m) °C*
Pure PEO	70
[PEO+ $KClO_4$+ Nano filler Al_2O_3] (90:10)	66
[PEO+ $KClO_4$+ Nano filler Al_2O_3] (80:20)	64
[PEO+ $KClO_4$+ Nano filler Al_2O_3] (70:30)	63

D. (PEO+K ClO_4) and (PEO + $KClO_4$+ Nano Filler Al_2O_3) Electrolyte Based Carbon Monoxide Gas Senso

Polymer electrolytes have been synthesized by using Poly (ethylene oxide) (PEO) complexed with $KClO_4$ salt for various composition ratios [(90:10), (80:20) and (70:30)]. Using these polymer electrolytes, the gas sensors have been designed and their characteristics were studied for carbon monoxide gas. The sensor resistance changed when carbon monoxide gas was exposed to the polymer electrolyte film. The sensor returns to its original state as soon as the carbon monoxide gas is removed. The output values change to its original value within 8-10 seconds time [18].

Fig. 4 shows the variation of the sensitivity with carbon monoxide gas concentration for different operating temperatures. From the figure, it is observed that the gas sensitivity increases with increase in gas concentration and with increase in operating temperature. The sensitivity (S) have been measured as a function of composition (Wt%) of (PEO+$KClO_4$) polymer electrolyte with carbon monoxide gas concentration for various temperatures is shown in Fig. 5. From the figure, it is clear that the gas sensitivity also increase with increase in the composition of the polymer electrolyte.

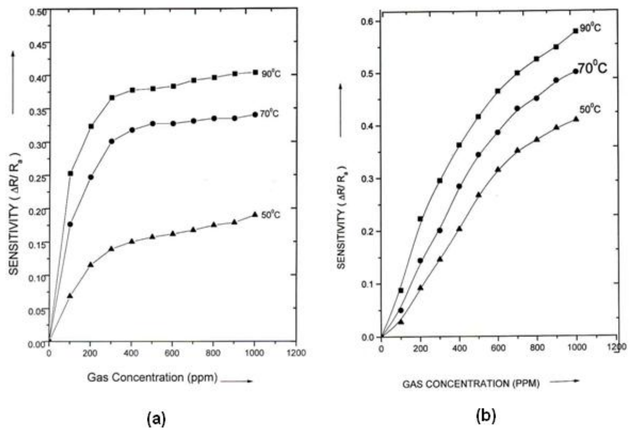

Fig. 4. (a) (PEO+$KClO_4$) (70:30) and (b) (PEO+$KClO_4$+nano filler Al_2O_3) (70:30) based gas sensor sensitivity as a function of temperature for different gas concentrations (ppm).

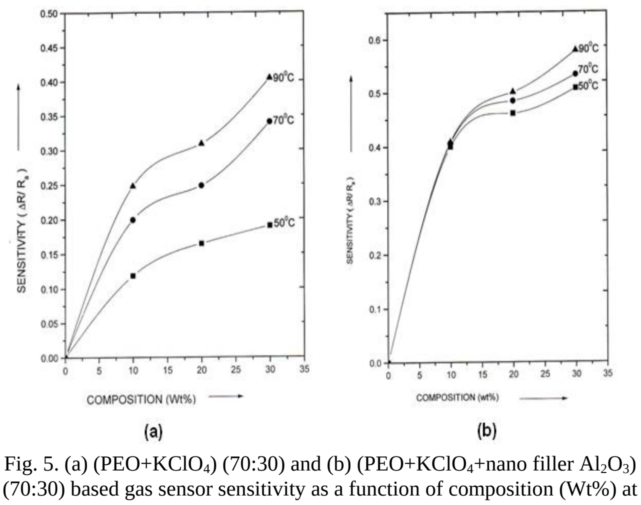

Fig. 5. (a) (PEO+$KClO_4$) (70:30) and (b) (PEO+$KClO_4$+nano filler Al_2O_3) (70:30) based gas sensor sensitivity as a function of composition (Wt%) at different temperatures.

The variation of the sensitivity of carbon monoxide gas sensor with temperature for various gas concentrations is shown in Fig. 6. From the above figures, it is clear that the gas sensitivity also increases with increase in the composition of polymer electrolyte.

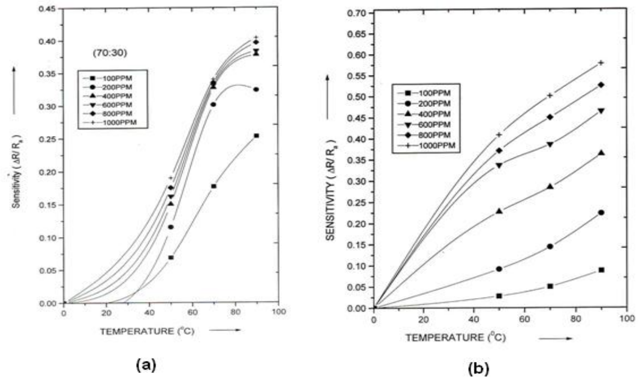

Fig. 6. (a) (PEO+$KClO_4$) (70:30) and (b) (PEO+$KClO_4$+nano filler Al_2O_3) (70:30) based gas sensor sensitivity as a function of gas concentration at different temperatures.

The values of sensitivity obtained for various compositions are given in Table II. From these figures and table, the following observations have been made.

TABLE II: THE VALUES OF SENSITIVITY OBTAINED FOR (PEO+$KClO_4$) AND (PEO+$KClO_4$+ NANO FILLER Al_2O_3) POLYMER ELECTROLYTES FOR DIFFERENT GAS CONCENTRATIONS

Polymer Electrolyte Gas Sensor	*Sensitivity at 50 °C*				
	200 ppm	**400 ppm**	**600 ppm**	**800 ppm**	**1000 ppm**
[PEO+$KClO_4$] (90:10)	0.057	0.077	0.085	0.099	0.119
[PEO+$KClO_4$] (80:20)	0.144	0.174	0.187	0.192	0.194
[PEO+$KClO_4$] (70:30)	0.115	0.150	0.161	0.175	0.190
[PEO+ $KClO_4$ + nano filler Al_2O_3] (90:10)	0.116	0.196	0.272	0.335	0.399
[PEO+ $KClO_4$ + nano filler Al_2O_3] (80:20)	0.184	0.184	0.273	0.364	0.406
[PEO+ $KClO_4$ + nano filler Al_2O_3] (70:30)	0.191	0.203	0.315	0.370	0.408

- 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 increases with an increase in the temperature.
- The sensitivity of the gas sensor showed an increase with in increase in carbon monoxide gas concentration.

The sensor sensitivity is found to be better in nano filler added polymer electrolyte complexed sensors. The nano filler added polymer electrolyte sensors have shown better sensor performance than pure polymer electrolyte sensors. It may be occurring because of the nano filler is a inorganic, ceramic, non-volatile substance, which when added to a polymer, improves its flexibility, possibility and hence utility. The nano filler substantially reduces the brittleness of many polymers because its addition even in small quantity markedly reduces the T_g of the polymer. The effect is due to a reduction in the cohesive chains. Nano filler molecule penetrates into the polymer matrix and establishes attractive force between nano filler molecules and the change segments.

These attractive forces reduce the cohesive force between the polymer chains and increase the segmental mobility, this enhances the sensitivity. The sensitivity of the polymer electrolyte gas sensor therefore increases due to the addition of the nano filler to the polymer electrolyte.

IV. Conclusions

Polymer electrolytes have been synthesized by using Poly (ethylene oxide) (PEO) complexed with ($KClO_4$), ($KClO_4$+ Nano filler Al_2O_3) for various composition ratios [(90:10), (80:20) and (70:30)]. The complexation of the polymer, salt and nano filler $Al_2O_3$was confirmed by using XRD and IR studies. At 70^{o}C, an endothermic peak was observed in DSC study corresponding to the melting temperature (T_m) of pure PEO. With the addition of $KClO_4$ to pure PEO, the melting temperature (T_m) was slightly shifted towards lower temperature. Using [PEO+$KClO_4$] and [PEO+ $KClO_4$+ Nano filler Al_2O_3] polymer electrolytes, the gas sensors have been designed and their characteristics were studied for carbon monoxide gas. The sensitivity of the sensor is found to increase with an increase in the composition of salt in PEO. Carbon monoxide gas sensor sensitivity increases with an increase in the Carbon monoxide gas concentration (PPM) in air. The sensitivity of gas sensor showed an increase with increase of operating temperature. The sensor sensitivity is found to be better in nano filler added polymer electrolyte complexed sensors. Thus nano filler added polymer electrolyte sensors have shown better performance than pure polymer electrolyte sensors. The polymer electrolyte films studied are found to be very good sensing elements for carbon monoxide gas in air.

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