Effect of nano-particles of alumina in the composite solid electrolyte system (1-X)Pb(NO₃)₂ – X γ-Al₂O₃

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ABSTRACT

Composite solid electrolytes in the system $(1-x)Pb(NO_3)_2 – x \gamma-Al_2O_3$ were prepared by dispersing the nano particles of alumina (60 nm) by mechanical mixing in the presence of acetone at room temperature. Characterization was done by the X-Ray Diffractometry and ruled out the formation solid solutions of these composite systems with different mole percentages of alumina. Electrical conductivity studies with temperature have shown a substantial enhancement of the order of 1-2 orders of magnitude in the dispersed system for 3.14 mole percent in the extrinsic conduction region with respect to the pure host material. This enhancement of conductivity was observed to vary with m/o alumina and peaking at a particular mole percent was explained on the basis of creation of anion vacancies in the space-charge region formed at the interfaces between the host and dispersoid particles. The fall of enhancement at higher mole percent was attributed due to the blocking effects of alumina particles in these dispersed systems.

Keywords: Enhancement, Dispersoid, Solid Electrolyte

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INTRODUCTION

Until nineteen sixties, a very few devices based on ion conducting materials were available. Out of the known devices, majority of them were based on liquid aqueous electrolytes. These devices were reported to suffer from a number of major shortcomings such as, limited temperature range of operation, less rugged, limited shelf life and difficulty in constructing miniature thin films. In order to eliminate the above shortcomings there was a need to replace the liquid electrolytes with some suitable ion conducting solids. As an early attempt, ion-conducting solids such as alkali halides, silver halides were used. However, these solids were remained unsatisfactory choices as replacement of liquid electrolytes because of their poor conduction. Since then the search for solids having high ionic conductivity was continuously on. This situation was changed when two new kinds of solid systems namely M Ag₄I₅ (where M = Rb, K, NH₄) [1-3] and Na-β-alumina [4] exhibiting high Ag^+ and Na^+ ion conductivity($\sigma =10^{-1}\Omega^{-1}cm^{-1}$) in respective electrolytes at room temperature and at moderately high temperatures were discovered. Later a large number of solid electrolytes with different mobile ion species, namely H^+, Li^+, Na^+, K^+, Ag^+, Cu^+, F^-, O^-, NO_3^- etc.have been reported. Amongst, Li^+ and Na^+ ion conducting solid electrolytes have been developed for high energy density batteries because of their light weight and high electrochemical potential [5,6]. Similarly O^{2-} and F^- ion conducting solid electrolytes were found to be useful materials for solid state gas sensors [7].

Various attempts have been made to realize the high ionic conductivity and low electronic conductivity of solid electrolytes at ambient temperature, they include (a) Stabilization of open channel structure by substituting different

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cations and anions in AgI and CuI (b) formation of polymer metal salt complexes (c) Glassy electrolytes and (d) dispersion of insoluble, insulating, fine particles of oxides like Al_2O_3, SiO_2 into ionic matrices such as AgI, LiI etc. The focus of research in the field of solid state ionics, which was once dominated by crystalline solid electrolytes has now been mostly directed towards the development and characterization of polymer, glassy and dispersed composite solid electrolyte systems. In the present study we have synthesized and characterized a new solid electrolyte system by dispersing the nano-particles of γ-Alumina into a rare earth lead nitrate. dc ionic conductivity with temperature has been measured by using two probe dc technique with varying mole percentage of alumina.
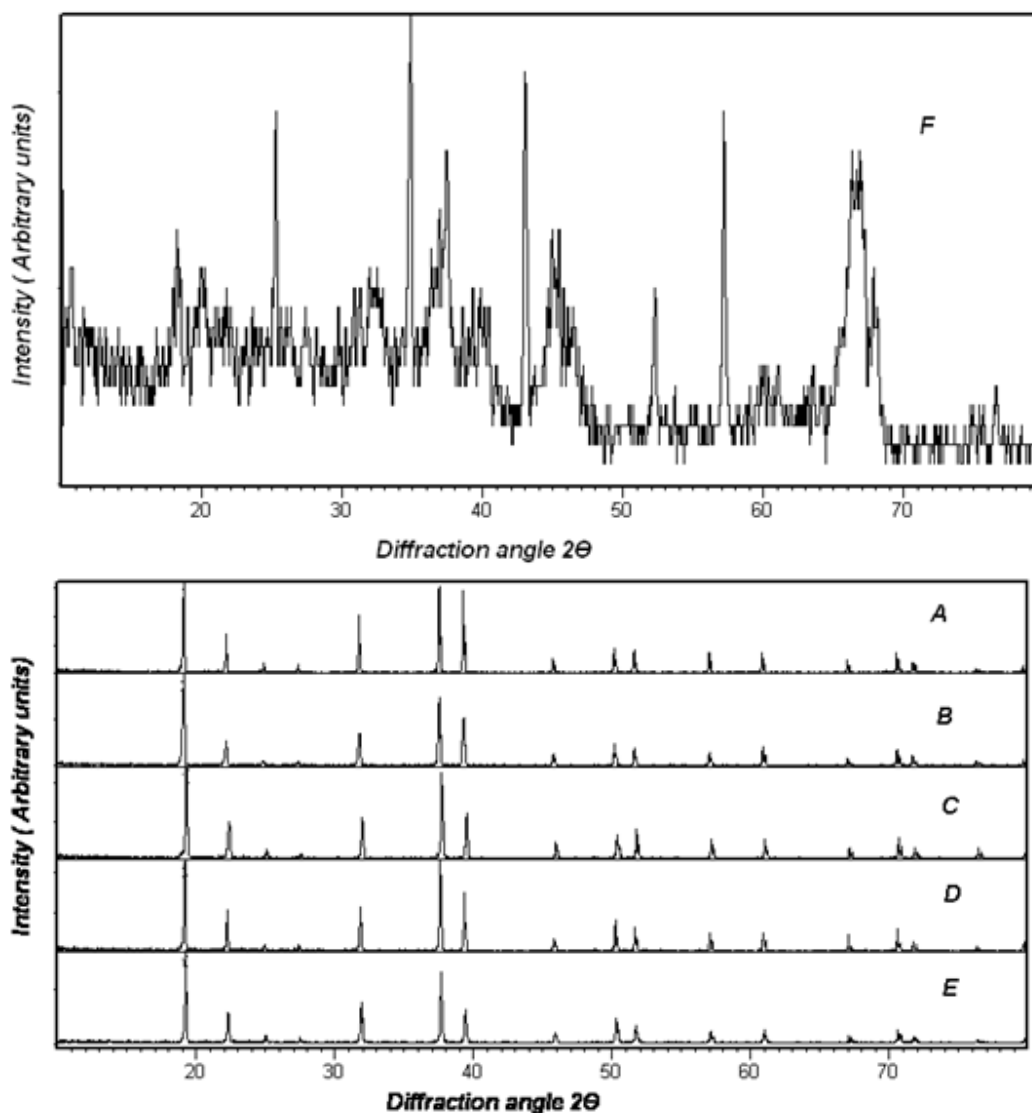

Fig.1: XRD patterns of Pure $Pb(NO_3)_2$ (A), dispersed with 0.80 m/o of Al_2O_3 (B), 3.14 m/o of Al_2O_3 (C), 4.94 m/o of Al_2O_3 (D), 6.10 m/o of Al_2O_3 (E) and Pure Al_2O_3 (F)

MATERIALS AND METHODS

The fine powder of host material, $Pb(NO_3)_2$ was obtained by crushing and sieving the single crystals grown by solution growth method. The starting salt of 99⁒ purity was supplied by Fine Chemicals (Mumbai), India. The dispersoid, insulating alumina powder of 99.8⁒ purity, was used as received from Adolf Miller Company (U.S.A.) of average particle size 60 nanometers. The powders of the samples were prepared by mixing the γ-Al_2O_3 of 0.80, 3.14, 6.10 and 11.52 mole percentages in $Pb(NO_3)_2$ in the presence of acetone and ground in an agate mortar for about an

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hour and dried at 100°C. Powder X-ray diffractograms on these systems were recorded at room temperature using Xpert (Phillips) machine. The radiation used in this was filtered CuK_{α} ($\lambda = 1.542A°$) and the scanning speed was 3° per minute. These are shown as Fig1. The pellets of 12mm diameter and 3-4mm thickness were prepared at a pressure of 0.19Gpa. in a steel dye and were sintered at 300°C for 24 hours for attaining uniform density throughout the sample. These pellets were applied with silver paint on either flat sides to act as the blocking electrodes and mounted on the sample holder for conductivity measurements. And then the entire sample holder was kept inside the muffle of the furnace and allowed the sample to anneal at 100°C for about three hours to attain good electrical contacts. Applying one-volt dc potential across the sample and carried out the conductivity studies using Agilent digital multimeter. The temperature range covered was from about 100°C to up to the melting point of the host material.

RESULTS AND DISCUSSION

Fig.1 shows the powder X-ray diffractogram patterns of pure $Pb(NO_3)_2$, pure γ-Al_2O_3 and dispersed with 0.80, 3.14, 6.10, and 11.52 mole percentages of γ-Al_2O_3 composite systems. A general observation from the figure is that there are no new peaks or there is any shift in the position of the peaks. This rule out the possibility of any solid-state reaction taking place or formation of any solid solution in the system. It is also observed that as the m/o of Al_2O_3 increased the disturbance in the baseline increases.
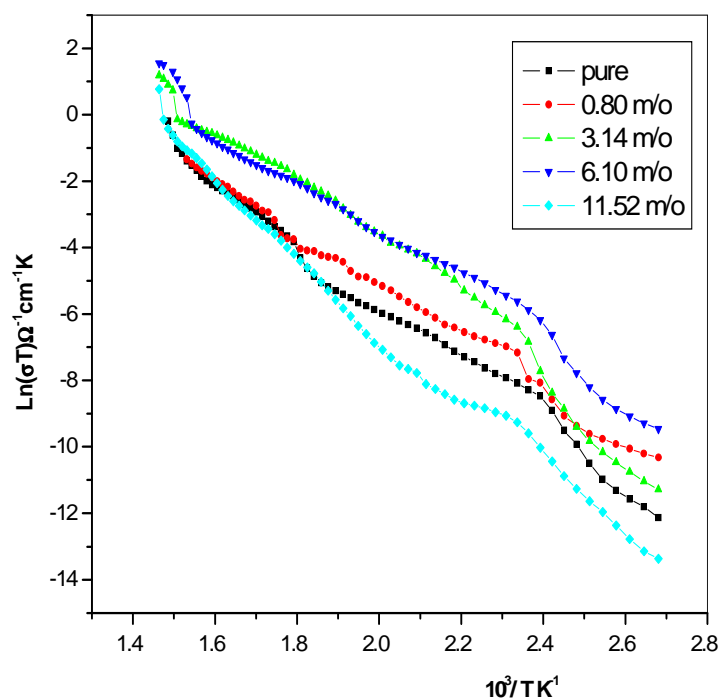
Fig.2: Variation of conductivity with temperature for pure $Pb(NO_3)_2$ and dispersed systems of 0.80, 3.14, 6.10 and 11.52 m/o of Al_2O_3.

Fig.2 shows the variation of conductivity as a function of reciprocal temperature from about 100°C to up to the melting point for the systems dispersed with different m/o of alumina. The filled squares indicate the data for pure $Pb(NO_3)_2$. The plot can be divided into four regions of conductivity and are named as extrinsic precipitated, extrinsic associated, extrinsic motion (unassociated) and intrinsic formation regions respectively from the low temperature end [8]. The enhancement of conductivity is observed for the dispersed systems with m/o 0.80, 3.14 and 6.10 where as for the systems with m/o 11.52 the plot almost coincide with the pure system. The maximum enhancement of 2-3 orders of magnitude was observed for system dispersed with 3.14 m/o with respect to the pure in the extrinsic regions of conductivity shown by triangles in the figure. This enhancement was started decreasing with 11.52 m/o dispersed system which was nearly equal to that of pure system as shown in the figure by triangles. The plots for all

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the mole percentages were found to be merged at very high temperature, which is the intrinsic formation region of conductivity of the host material where the effect of dispersion appears to be negligible.
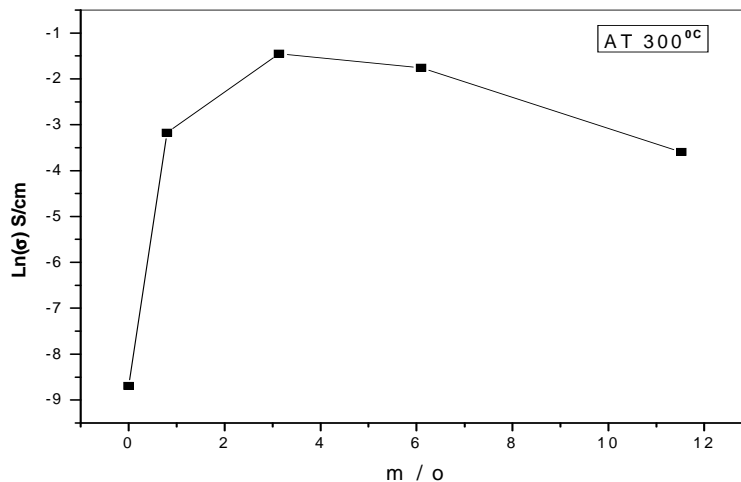

Fig.3: Varation of dc conductivity with mole percent at 300^{0}C

Fig.3 illustrates the variation of conductivity with mole percent at 300°C indicating the peak enhancement at 3.14 m/o after which a slow fall can be observed. The enhancement of ionic conductivity was reported in many dispersed solid electrolyte systems such as LiI- Al$_2$O$_3$ by Liang [9],CuCl- Al$_2$O$_3$ by Jow and Wagner[10], AgI-Al$_2$O$_3$,AgI-SiO$_2$, AgI-Flyash by Shahi and Wagner[11,12], Sr(NO$_3$)$_2$- Al$_2$O$_3$, Ba(NO$_3$)$_2$- Al$_2$O$_3$ by Reddy et al[13,14], alkali nitrates dispersed with alumina by Madhav Rao et al [15-18] etc. The enhancement of conductivity in these systems could not be explained by the classical doping mechanisms. There is no relevance of classical doping mechanisms in explaining the enhancement of conductivity in these systems. Several theories based on different models have been proposed to explain the experimentally observed large enhancements. However, no single theory or model could explain the features observed in all these systems completely. Some of the theories that partially succeeded in explaining this phenomenon are the following. The formation of space charge region at the interface of the biphasic semiconductors was introduced by Wagner [19], later this was modified by Jow and Wagner [20] in order to explain this enhancement in CuCl$_2$ - Al$_2$O$_3$ dispersed system. Maier [21] has proposed a semi quantitative model, which could overcome some of the inadequacies of Jow and Wagner's model and was able to explain the defect chemistry involved in dispersed solid electrolyte systems.

The formation of defects in these systems can be understood in the following way. The interaction between the mobile ions of host matrix MX and the dispersoid D leads to the formation of vacancies of the mobile ion species in the space-charge region near the MX/D interface. In Frankel defect solids, this can happen either when the mobile ions are attracted to the phase D leaving the vacancies at the interface or repelled into the host ionic matrix MX to form the interstitials. Of these the formation of vacancies was thought to be more appropriate than the formation of interstitials in the systems namely CaF$_2$ – Al$_2$O$_3$ [22], AgCl – Al$_2$O$_3$, [23,24], Sr(NO$_3$)$_2$ - Al$_2$O$_3$ [25], CsNO$_3$ - Al$_2$O$_3$ [26], which are known to be Frankel type defect solids. The increase in the concentration of vacancies at the interface could be due to the presence of hydroxyl groups also known as nucleophilic groups on the surface of the alumina particles which can attract either cation or anion depending on the P^H value of the alumina particles. This increase in the concentration of defects in the space charge region contributes to the enhancement of conductivity in these systems. The rise and fall of enhancement of conductivity with a peak in between, with m/o of alumina can be understood as follows: Initially, for low mole percent of the dispersoid the total surface area of contact between the host material and the dispersoid particles, which is responsible for formation of space-charge region, is small. As mole percent increased, a stage is reached where there is not enough host material to surround the dispersoid particles which tends to the fall of total effective surface area of contact. This is attributed to the fall of enhancement after reaching to a maximum value [25]. In the present system this maximum enhancement occurs for 3.14 m/o and 6.10 m/o and the fall began at 11.52m/o. Roman et al[27] gave the explanation for the enhancement of conductivity macroscopically by proposing random register model using the percolation theory. According to which, the sample

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can be thought of as a three-component system consisting of non-conducting (insulator) bonds, normally conducting bonds and highly conducting bonds of which the last one is considered responsible for the enhancement. Dudney [28] correlated the enhanced conduction in AgCl - Al_2O_3 system with the presence of grain boundaries or dislocations formed by the plastic deformation and primary recrystallization of AgCl. The role of Al_2O_3 particles was thought to limit the grain size of AgCl and stabilize more conductive polycrystalline microstructure. Jow and Wagner on the other hand interpreted the increased number of grains produced with m/o, increase the space charge layers, thereby increasing the conductivity. This increase in number of grains, as per Roman et al[27], is interpreted in terms of the increase in the formation of highly conducting bonds. The enhancement of conductivity in the present system $Pb(NO_3)_2$ - γ-Al_2O_3 in which host is to be a Frankel type defect solid [29] can be explained by assuming alumina to act as a macro-dopant, which increases the concentration of mobile point defects in the interfacial region between the host and dispersoid. Once the threshold m/o is crossed in which enhancement was maximum, the amount of alumina present is large so that the particles of alumina come closer to one another and blocking effect of alumina predominates. Hence the decrease in conductivity is observed. The defect mechanism involved in the present system is thought to be due to the adsorption of nitrate ion on to the surface of alumina leaving the anion vacancies at the interface. The increase in m/o of Al_2O_3 creates more and more such vacancies contributing to the enhancement of conductivity.

CONCLUSION

The Composite solid electrolyte system (1-x)$Pb(NO_3)_2$ – x γ-Al_2O_3 is a new system in which the dispersion of nano-particles of alumina has shown a strong enhancement of conductivity in the extrinsic region of conductivity. These enhancements were observed to increase with mole percent reaching to a peak for a threshold mole percent and subsequently fall of enhancement for higher percentages. This phenomenon was explained on the basis of formation of space charge region at the interface between the host and dispersoid particles.

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