June 2009 Volume 5 Issue 3

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 5(3), 2009 [270-273]

Enhancement of d.c. ionic conductivity in KNO_3-Al_2O_3 composite solid electrolyte system

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Received: 3rd March, 2009 ; Accepted: 8th March, 2009

ABSTRACT

The composite solid electrolyte, KNO_3 dispersed with alumina (Al_2O_3), has been investigated through XRD, DSC and D.C. Ionic Conductivity techniques. The composite containing 10 m/o alumina exhibits maximum conductivity, about 2 orders of magnitude higher than that of pure KNO_3. The enhanced conductivity is attributed to the excess cation vacancies generated in the space charge region of the matrix phase surrounding the alumina particles as a consequence of stabilization of cations at the dispersoid surface due to internal adsorption. XRD and DSC studies reveal that there was no new phase formed.

KEYWORDS

Composites;
Solid electrolytes;
Space charge layer;
Ionic conductivity;
Dispersoid.

1. INTRODUCTION

Composite solid electrolytes comprise a new class of ion-conducting materials suitable for practical applications, as their electrical and mechanical properties can be easily controlled by variation of the concentration of the dispersed component. Conductivity of composites is governed mainly by the ionic transport via interface regions of the ionic crystal[1]. Ionic conductors containing dispersed second phase particle (DSPP) are called " composite ionic conductors". The addition of DSPP to normal ionic conductors causes an increase in the conductivity. This phenomenon has attracted a great deal of attention from both chemists and physicists, since the pioneer work by Liang in 1973[2].

Mechanisms for enhancing ionic conductivity are important from the point of view of their applications in the development of fuel cells, sensors and solid state batteries.

Heterogeneous doping has been widely used for the enhancement of ionic conductivity in the recent times. Two-phase composites consist of an ionic conductor and a highly insulating dispersoid, such as Al_2O_3, TiO_2, SiO_2, Fe_2O_3, ZrO_2, MgO etc.[3-7]. The conductivity of some composite solid electrolytes may exceed that of pure components by several orders of magnitude. A number of theoretical models have been proposed to account for the conductivity behavior of these heterogeneously doped solid electrolytes[6-11].

Therefore, it is of considerable scientific and practical interest to find heterogeneous additives capable of increasing the ionic conductivity. Now that the focus has changed from alkali halides or silver halides to predominantly alkali nitrates, sulfates and carbonates, we have considered KNO_3 as the host material as a part of our studies in alkali nitrates. Alumina, frequently used as a chemically inert additive, is understood to give more enhancement in conductivity as compared to other insulating oxides. In this work the electrical, thermal and structural properties of KNO_3-Al_2O_3 composites are presented.

2. EXPERIMENTAL

KNO_3 powder obtained from Analar Grade BDH (British Drug House) chemical of 99.5% purity, is first dissolved in double distilled water and then allowed to grow single crystals. The crystals so obtained are crushed in an agate mortar and then sieved. And the dispersoid (Al_2O_3 of size 60 nm) of 99.8% was used, as received from Adolf Meller Co. U.S.A.. Both the powders taken in a particular composition were mixed in the presence of acetone for about an hour, until the acetone got evaporated completely. Pellets of 10-12mm diameter and 3.4mm thickness were prepared by using a steel die at a pressure of about 0.46GPa. The pellets so obtained were sintered at 250^0C for about 24 hours. After polishing the surfaces, carbon dag was applied for electrical contact. The pellet was mounted in a spring-loaded crystal holder and annealed at 150^0C for 12hours before the start of an actual experiment. A constant rate of heating of about 2^0C per minute was maintained. The temperature recorded was by a Cr-Al thermocouple. A small dc voltage of 1 Volt was applied across the sample and the current was measured by using Keithley 614 electrometer.

3. RESULTS AND DISCUSSION

X-ray diffractograms on potassium nitrate (pure and dispersed with 10 m/o Al_2O_3), at room temperature, are shown in figure 1. On comparing the patterns of pure and dispersed systems in figures 1(a) and 1(b) that there are no new peaks indicate that no solid solution is formed in these systems. Such observations in case of NaCl-Al_2O_3[12], KCl-Al_2O_3[13], CsCl-Al_2O_3[14] and $NaNO_3$-Al_2O_3[15] solid electrolyte systems have also ruled out the formation of solid solutions in them.

DSC traces of potassium nitrate pure and dispersed with 5 and 10 mole percent of alumina are shown in figure 2. The known[16-17] transition at 138^0C and its melting at 337^0C appear in the form of two endotherms in this figure 2(a). The figures 2(b) and 2(c) imply that transition temperature is slightly changed and melting point is practically unaffected in the dispersed systems. A small and very broad hump is observed in the range 250^0C- 275^0C. This hump could be due to the formation of an amorphous phase within the space charge layer that is expected to form between the host material and the dispersoid particles[18-20].

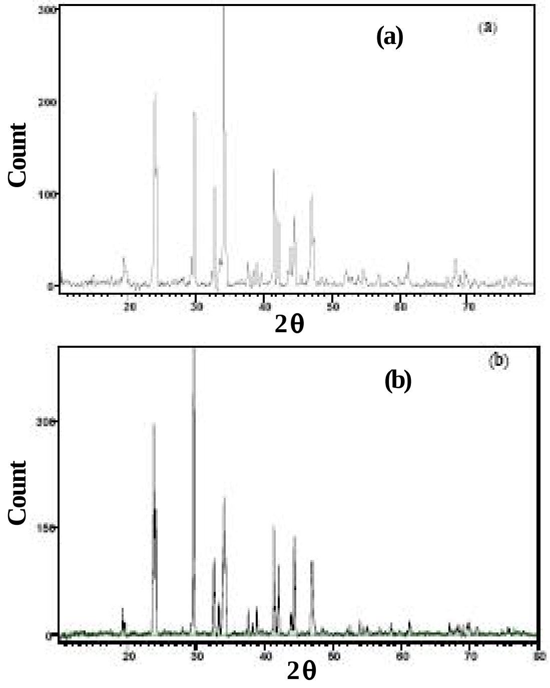

Figure 1 : X-ray powder diffraction for (a) KNO_3 Pure and (b) KNO_3-Al_2O_3 (10 m/o) solid electrolyte systems

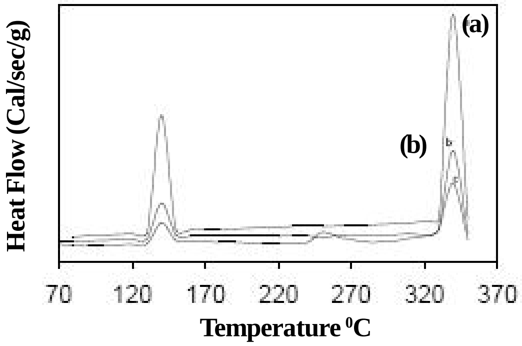

Figure 2 : DSC curves for (a) KNO_3 pure (b) KNO_3-Al_2O_3 (5 m/o) (c) KNO_3-Al_2O_3 (10m/o)

The temperature dependence of dc ionic conductivity with reciprocal temperature from room temperature to nearly the melting point of host material for pure and dispersed with 1, 5, 10 and 20 mole percent alumina is shown in figure 3. Conductivity in pure KNO_3 can be seen to increase linearly with temperature up to its transition temperature (137^0C) followed by a bend

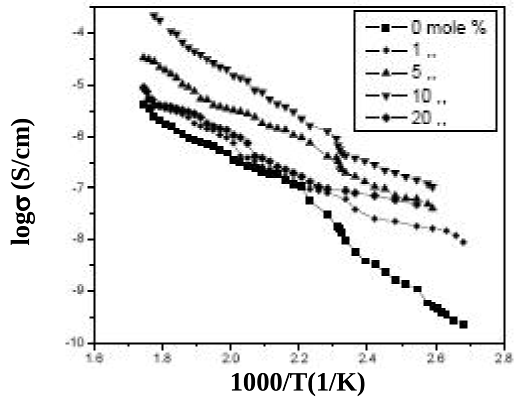

Figure 3 : Log(s) versus 1000/T for KNO_3 and KNO_3:Al_2O_3 at different mole percentages

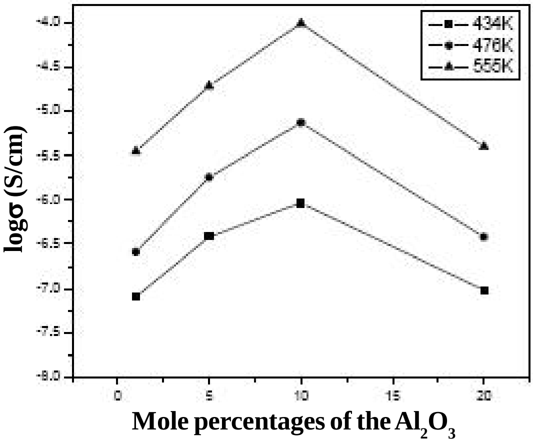

Figure 4 : Conductivity (s) versus m/o of the dispersoid at different temperatures

TABLE 1: Activation energies for KNO_3-Al_2O_3 composites

Mole percentages	logσ (140^0C)	logσ (200^0C)	Temperature range(^{0}C)	Activation energy(E)(eV)
0	-8.493	-6.726	110-250	0.89
1	-7.590	-6.648	110-250	0.59
5	-7.017	-5.801	110-250	0.67
10	-6.622	-3.702	110-250	0.52
20	-7.025	-7.148	110-250	0.57

in the conductivity plot. From about 300^0C and then after it appears to be entering into the formation region, where conductivity is largely due to intrinsic defects. In the dispersed systems the enhancement in conductivity is observed to increase with m/o with a threshold at 10 mole percent where from enhancement starts falling with further increase in mole percent i.e. for 20 mole percent. The maximum enhancement at 10 mole percent is observed to be about 2 orders of magnitude with respect to pure KNO_3 in the extrinsic conduction region. It may be noticed from the plot that conductivity values for pure at about 140^0C and 200^0C are 10^{-8} and 10^{-6} S/cm whereas these are 10^{-6} and 10^{-3} S/cm respectively for KNO_3-10 m/o Al_2O_3. Variation of logσ with mole percent of alumina, at different temperatures, is shown in figure 4. It can be seen from this figure that the maximum enhancement occurs at 10 mole percent of alumina in this system.

The observed enhancement in the conductivity of the KNO_3-Al_2O_3 system is discussed in terms of the formation of space charge layer at the interface between the host matrix and the dispersoid. The mechanism of formation of space charge layer in a Frenkel type defect solid is understood as follows. The defect species, which is involved in ionic conduction of the matrix, may be repelled from or attracted to the interface resulting in the formation of a space charge region[3,5,7,8]. Thus, in a Frenkel solid, if the cations are attracted to the interface, the vacancy concentration in the space charge region will be increased relative to the bulk value. Repulsion of cations by the inert phase will increase the concentration of interstitials in the space charge region. The space charge region is thus associated with an increased concentration of defects. Thus additional contribution to the total conductivity from the space charge region accounts for the enhancement in ionic conductivity. KNO_3 being a Frenkel disordered material[21] the stabilization of K^+ ions at the Al_2O_3 surface, thereby creating excess cation vacancies at the interface is more probable[5-10].

The activation energies for KNO_3-Al_2O_3 composites derived from logσ versus 1000/T plots vary between 0.89 to 0.52 eV where 0.89 correspond to pure nitrate and 0.59 to 0.57 for dispersed systems. These are shown in TABLE 1. It may be noticed from the table that the activation energy for the dispersed composites in general is lesser than that of pure KNO_3. However, it is independent of the alumina content, and is fairly constant These results lead to the conclusion that the enhanced conductivity in KNO_3-Al_2O_3 composites is due to the increased concentration of cation (K^+) vacancies[22-23].

When the concentration of Al_2O_3 is low, all the particles are completely surrounded by the host matrix. Conductivity of the system increases with increasing concentration of Al_2O_3 because it amounts to the increase in the highly conducting bonds between dispersoid particle and host matrix. Subsequently, when the total volume of the interface layers is most effectively linked together, the total number of highly conducting bonds become maximum, consequently sample would show maximum conductivity.

As the concentration of Al_2O_3 further increase, Al_2O_3 particles cannot be completely covered by the interface layers simply because the available host cannot envelop all the Al_2O_3 particles, number of non-conducting bonds increase and therefore conductivity decreases[7-10,24].

4. CONCLUSIONS

The composite solid electrolytes KNO_3 dispersed with alumina has been investigated through XRD, DSC and two probe dc ionic conductivity techniques. The composite containing 10 m/o alumina has the maximum conductivity, about 2 orders of magnitude higher than that of pure KNO_3. The enhancement of conductivity is interpreted in terms of the formation of space charge region between the host matrix and dispersoid. The formations of cation vacancies are more probable than the interstitials in the interfacial region.

ACKNOWLEDGMENTS

The authors thank the Head, Department of Physics, Osmania University, for the experimental facility.

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