

LI-ION TRANSPORT IN $\text{Li}_2\text{SO}_4 - \text{Fe}_2\text{O}_3$ NANOCOMPOSITES BELOW ITS SUPERIONIC TRANSITION

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Abstract

New nanocomposite ceramic electrolytes with enhanced conductivity at low temperatures have been mechanically prepared based on $\text{Li}_2\text{SO}_4\text{-Fe}_2\text{O}_3$ system. Nanocomposites with filler concentrations of $x = 0.1\text{-}0.5$ have been studied by impedance spectroscopy and thermal analysis in the temperature range of $200\text{-}500^\circ\text{C}$. Unusual dependence of the conductivity on increasing Fe_2O_3 content has been noted: both the ionic conductivity (σ) below a transition temperature at about $T_t = 350^\circ\text{C}$, as well as this temperature, increase. A step change to lower values is observed in the dc-conductivity data at T_t which also increases with the Fe_2O_3 content. However, above T_t the temperature dependence of σ is almost independent of the oxide concentration. This thermal behavior of Li-ion transport is attributed to lattice defects generation in Li_2SO_4 with increasing the content of dispersed Fe_2O_3 nanoparticles below T_t . However, above T_t , the results indicate that the nanoparticles no longer affect Li-ion transport.

Keywords: *Nanocomposite, Electrolyte, Ion conductivity, nanoparticles*

Resumen

Nuevos electrolitos cerámicos nanoestructurados que resultan con conductividades más altas a bajas temperaturas han sido mecánicamente preparados con base en el sistema $\text{Li}_2\text{SO}_4\text{-Fe}_2\text{O}_3$. Las compositas con concentración del dispersor de $x = 0.1\text{-}0.5$ han sido estudiadas por espectroscopia de impedancias y análisis térmico en el rango de temperatura $200\text{-}500^\circ\text{C}$. Se nota una inusual dependencia de la conductividad con el incremento del contenido de Fe_2O_3 : se incrementan la conductividad iónica (σ) por debajo de una temperatura de transición a $T_t = 350^\circ\text{C}$, así como también esta temperatura. Se observó un cambio escalonado a valores más bajos en los datos de conductividad-dc a T_t la cual se incrementa con el contenido de Fe_2O_3 . No obstante, por encima de T_t la dependencia de la temperatura con σ es casi independiente de la concentración del óxido. Este comportamiento térmico del transporte del ión Li se atribuye a la generación de defectos de red en Li_2SO_4 con el incremento del contenido de nanopartículas dispersas de Fe_2O_3 por debajo de T_t . No obstante, por encima de T_t , los resultados indican que las nanopartículas no afectan mayormente el transporte del ión Li.

Palabras Claves: *Nanocomposita, Electrolito, Conductividad iónica, Nanoparticulas*

1. INTRODUCTION

There is a special interest on developing composite solid electrolytes with high chemical and thermal stability and low fabrication cost for application in intermediate temperature ($400\text{-}700^\circ\text{C}$) fuel cell systems. The main focus of the most research initiatives has been directed at lowering the transition temperature to superionic state and increasing the conductivity of solid electrolytes.

Enhancing the conductivity of solid electrolytes involves the dispersal of fine inert particles of insulator like Al_2O_3 , Fe_2O_3 , SiO_2 , etc, in the host

matrix forming a two phase composite system. The ionic conductivity of several solid electrolytes has been increased significantly, from 1 to 3 orders of magnitude, by dispersing fine, insulating particle of inert additive [1-4]. This type of conductivity enhancement is called composite effect, and there are some theoretical models for explanation it: the interface mechanism, which involves space charge layer formation between the conducting and the insulating phase, enhanced conduction at the core of the interface, or an interfacial phase formation and effects of adsorbed surface moisture and impurities;

the matrix mechanism, involves enhanced charge transportation along grain boundaries and dislocations, the stabilization of highly conducting metastable phases due to a homogeneous doping of the matrix [4,5].

There is a special interest, on the ion-conducting ceramic composites membranes due to their mechanical and transport properties and low fabrication cost as electrolytes in fuel cells [6-8]. Some studies reported conductivity enhancement through composite formation by using Al_2O_3 . Jain *et al* [9] reported a moderate increase in the conductivity of $\text{Na}_2\text{SO}_4\text{-Al}_2\text{O}_3$ for composites with 5.5 and 35% Al_2O_3 and the conductivity increased by 1 order of magnitude at 400°C and 2 orders of magnitude at 200°C for 35% Al_2O_3 . Gopalan [3] reported a conductivity increased by a factor of 60 at 400°C and almost 200 times at 200°C for 5% Al_2O_3 .

On the other hand, lithium sulphate is known to be a good superionic conductor in α -phase at temperatures higher than 575°C with conductivity of about 1 S/cm, after undergoing a first order transition. But, at lower temperatures, Li_2SO_4 is a poor conductor [1,10]. Moreover, the membranes made of pure lithium sulfate have not good mechanical properties [6]. Some studies reported that an addition of Al_2O_3 leads to formation of $\text{Li}_2\text{SO}_4\text{-Al}_2\text{O}_3$ composites with enhancing of conductivity in three orders of magnitude and good mechanical properties [1,11-13]. B. Zhu *et al* reported [13] the ionic conductivity of the low temperature phase of Li_2SO_4 increased by 3 orders of magnitude for 47% Al_2O_3 , and Uvarov *et al* [11] reported highest conductivity for 50% Al_2O_3 and later they reported [1] that the phase transition temperature of Li_2SO_4 in composites is 100 degrees lower than in pure salt.

Some studies revealed that the effects of various preparative parameters, such as size and form of alumina and also the time of sintering, play an important role on the electrical conductivity of the $\text{Li}_2\text{SO}_4\text{-Al}_2\text{O}_3$ composite system [6,14]. For example, the highest conductivity in this system was found when the grain size of alumina was small enough (nano-sized).

Although there are several reports of sal-ceramic composites based on Al_2O_3 , Na_2SO_4 , etc, no recent reviews on the electrical properties of $\text{Li}_2\text{SO}_4\text{-Fe}_2\text{O}_3$ are available.

We report the study of new nanocomposite ceramic electrolytes with enhanced conductivity at low temperatures which have been mechanically prepared based on the $\text{Li}_2\text{SO}_4\text{-Fe}_2\text{O}_3$ system. The nanocomposites with relative concentration $x = 0.1\text{-}0.5$ have been studied by impedance spectroscopy and thermal analysis in the temperature range of $200\text{-}500^\circ\text{C}$.

2. EXPERIMENTAL

Composites with molar composition in the range $x = 0.1\text{-}0.5$ have been prepared by using conventional mixing of high purity powder of Li_2SO_4 (Merck, 99.99% pure) and nanoparticles of Fe_2O_3 (Merck, average particle size 5-25 nm) in an agate mortar during half hour [1]. The mixtures were thermally treated at 500°C for 2 hours to obtain highly dispersed nanoparticles in the solid matrix. The thermal characterization was carried out using a differential scanning calorimetric Mettler-Toledo DSC-30 in the temperature range $100\text{-}500^\circ\text{C}$, at scanning rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. For conductivity measurements, the powders were pressed into disk-shaped pellets ($5\text{ tons}/\text{cm}^2$) of 10 mm diameter and 1 mm thickness. Afterwards all the pellets were thermally treated again at 500°C for 2 hours. The data were recorded in the frequency range between 5 Hz - 13 MHz with an applied signal of 100 mV, using a computer controlled Hewlett-Packard 4192A LCR Meter. The temperature was measured using a type K, alumel-cromel thermocouple situated as close as possible to the cell.

3. RESULTS AND DISCUSSIONS

Most of salt-ceramic composites reported before show a recognizable, uniform type of conductivity dependence on composition. Similar to others composites as $\text{LiI-Al}_2\text{O}_3$, $\text{Na}_2\text{SO}_4\text{-Al}_2\text{O}_3$, the conductivity in $\text{Li}_2\text{SO}_4\text{-Al}_2\text{O}_3$ also increases with increasing Al_2O_3 content going through the maximum at 50% Al_2O_3 . Such a conductivity maximum can be due to either an intermediate phase with a high ionic conductivity or a high ionic conductivity region in the interface of the grains as described by B. Zhu [13].

Contrary to what it was previously reported, we found unusual concentration dependence of the conductivity on increasing Fe_2O_3 content in $\text{Li}_2\text{SO}_4\text{-Fe}_2\text{O}_3$ composite system.

Figure 1 shows in an Arrhenius type plot, the

temperature dependence of dc-conductivity of $(1-x)\text{Li}_2\text{SO}_4 - x\text{Fe}_2\text{O}_3$ ($x = 0.0-0.5$) in the heating cycle. As it has been previously reported, the Li_2SO_4 has a low conductivity phase at temperature below 575°C . However, we found that the ionic conductivity has a kink at about $T_t = 350^\circ\text{C}$, whose step change to lower values increases with Fe_2O_3 content. Moreover, the transition temperature, T_t , is shifted to high values on increasing x . Above T_t , temperature variation of $\sigma(T)$ is almost independent on the concentration, x .

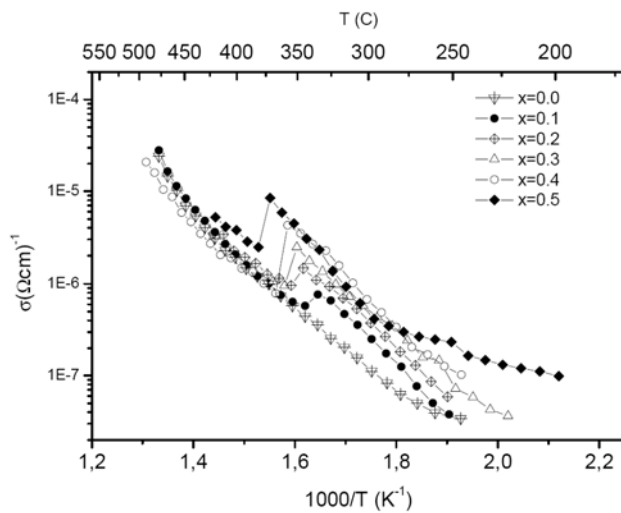


Figure 1. Temperature dependence of the dc-conductivity of $(1-x)\text{Li}_2\text{SO}_4 - x\text{Fe}_2\text{O}_3$ ($x = 0.0-0.5$) in the heating cycle.

Figures 2 and 3 show the concentration variation of T_t and the dc-conductivity $\sigma(T_t)$.

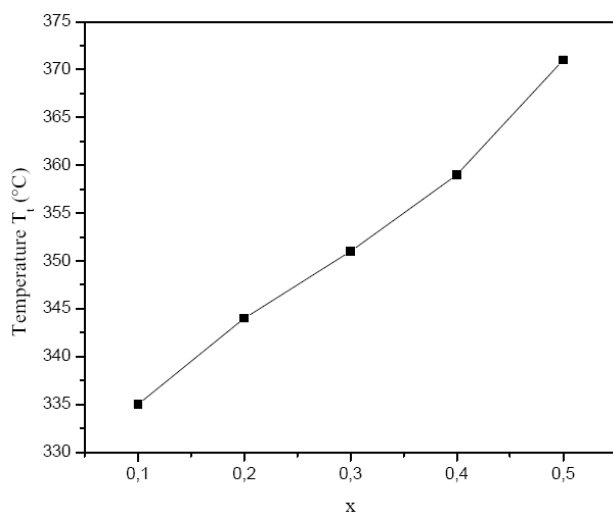


Figure 2. Transition temperature T_t vs x for $(1-x)\text{Li}_2\text{SO}_4 - x\text{Fe}_2\text{O}_3$ ($x = 0.0-0.5$).

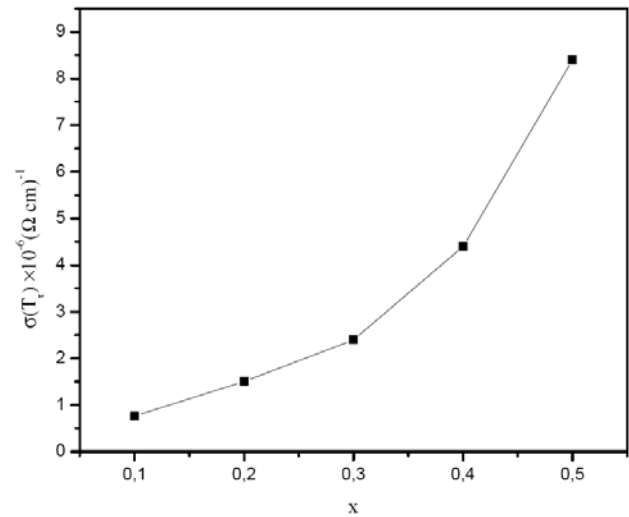


Figure 3. dc-conductivity $\sigma(T_t)$ vs concentration for $(1-x)\text{Li}_2\text{SO}_4 - x\text{Fe}_2\text{O}_3$ ($x = 0.0-0.5$).

The observed behavior in $\sigma(T)$ indicates that the charge carrier density which are generated as a consequence of thermal activated process of lattice defects, is increased below T_t by increasing the concentration of the ceramic filler due to an approximation effects as those proposed in the literature [1-6,9,11,14]. However, above T_t , the results indicate a homogenous amorphous Li_2SO_4 matrix, in which the nanoparticles no longer affect Li-ion transport. Thus, the results may open new routes to increase the ionic conductivity of Li_2SO_4 by properly forming composites, such that it were possible to reach high values at temperatures much lower than its superionic transition at 575°C .

4. CONCLUSIONS

Influence of Fe_2O_3 on the conductivity of $\text{Li}_2\text{SO}_4 - \text{Fe}_2\text{O}_3$ was investigated. The composite conductivity was increased by the ceramic content below a characteristic temperature $T_t = 350^\circ\text{C}$. This temperature also increases with the ceramic concentration. This is probably caused by a change of the volume properties of the ionic salt (amorphization) in small pores of the inert matrix below T_t . However, above T_t the amorphization is completed independently of the ceramic concentration.

Thus, the properties of the composite electrolyte may depend not only of the specific surface of inert dopant, but depend on its porous structure which

will be the subject of a future investigation to increase conductivity in Li₂SO₄-based composites.

5. ACKNOWLEDGEMENTS

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