Journal of Engineering and Applied Sciences 12 (13): 3345-3348, 2017
ISSN: 1816-949X

Application of Nanostructured ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$: CeO_2 for Solid Oxidefuel Cell

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Abstract: Synthesis, characterization, electrical and dielectrical properties have been made in nanostructured components of ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$: Al_2O_3, ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$: SiO_2, ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$: CeO_2 solid electrolyte systems. The system ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$ with 1.1, 5.3, 10.8 and 20 mole percentages of Al_2O_3 (1000, 300 and 60 nm), SiO_2 (20 nm) and CeO_2 (10 nm) have been characterized through X-ray diffraction, DSC and SEM. The electrical and dielectrical properties of these materials have shown an increase in conductivity as the temperature rises from room temperature to almost melting point of pure system. The enhancement of ionic conductivity observed to an increase with m/o and reaches to maximum at 10.8 m/o for Al_2O_3 (1000 nm), 10.8 m/o for Al_2O_3 (300 nm), 5.3 m/o for Al_2O_3 (60 nm), 10.8 m/o for SiO_2 (20 nm) and 10.8 m/o for CeO_2 (10 nm) mole percentages followed by a fall of conductivity with further increase of dispersion to the host material. X-ray diffraction patterns of pure mixed system ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$ and 1.1, 5.3, 10.8 and 20 m/o dispersed systems have shown that pure phases of host and dispersoid materials coexist in the dispersed systems indicating that there is no chemical reaction between them. The enhancement of conductivity in these systemsis explained as due to the increased concentration of defects in space charge region formed between the host and nano particles of dispersoid. The optimized nanoceria added to ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$ is considered to give the best performance for application in the solid oxide fuel cells.

Key words: Composite solid electrolyte, ionic conductors, conductivity enhancement, dispersoid, nanostructure, space charge region

INTRODUCTION

Ionic conductors are important in the area of solid-state ionics. Solid-state ionics is the study of solid electrolytes and their uses. Some materials that fall into this category include inorganic crystalline and polycrystalline solids, mixed crystals, ceramics, glasses, polymers, composites, etc. Solidstate ionic devices such as solid oxide fuel cells can be much more reliable and long-lasting. The phenomenon relies on the hopping of ionswhich was first predicted by Lehovec (1953). Our earlier studies on ${}_{x}Ba(NO_3)_2$-${}_{(1-x)}KNO_3$ mixed system have shown that the conductivity is maximum at x = 0.19 (Devi *et al*., 2012). In the present study, we have aimed at enhancing the conductivity in ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$ by dispersing it with different insulating materials of various mole percentages.

MATERIALS AND METHODS

Experimental: The starting materials, $Ba(NO_3)_2$ and KNO_3, taken from Qualigens fine chemicals (SQ) of 99.5% purity are first dissolved in double distilled water and then allowed to grow single crystals. The crystals obtained are then crushed in an agate mortar and sieved. Then, the dispersoids of γ-Al_2O_3 with different particle sizes viz. 1000, 300, 60 nm, SiO_2 with particle size 20 nm and CeO_2 of 10 nm is used as received from Adolf Meller, Co., USA. Then, the mixed crystal powder and the dispersoids individually taken in a particular composition were mixed in the presence of acetone for an hour, manually until the acetone got evaporated completely. Pellets were prepared by using a steel die at a pressure of 0.89 GPa and were sintered at about 180°C of their melting point for 24 h. After cleaning the surfaces an electrode material (silver) was applied for good electrical contact. Pellet was then mounted in a spring loaded sample holder and annealed at about 150°C (1/3rd of respective sample melting point) for 4 h before the data was recorded.

RESULTS AND DISCUSSION

Conductivity versus reciprocal temperature for ${}_{0.19}Ba(NO_3)_2$-${}_{0.81}KNO_3$ and various composite systems, viz. 10.8 m/o-Al_2O_3 (1 μm) (Devi *et al*., 2014) 10.8 m/o-Al_2O_3 (0.3 μm) (Devi *et al*., 2014), 5.3 m/o-Al_2O_3

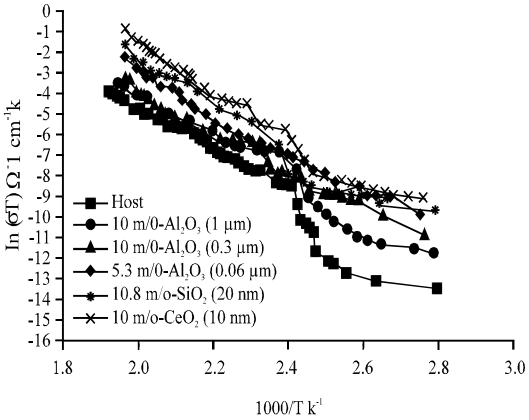

Fig. 1: Conductivity versus reciprocal temperature plots for host ($_{0.19}$Ba(NO $)_{3}$-$_{2\ 0.81}$KNO $)_3$ with various dispersoids

(0.06 µm) (Devi *et al.*, 2014), 10.8 m/o-SiO_2 (10 nm) (Devi *et al.*, 2015a, b), 10.8 m/o-CeO_2 (10 nm) (Devi *et al.*, 2015a, b; Maier, 1985; Stoneham *et al.*, 1979; Ashutosh and Sergiy, 2014; Jow and Wagner, 1979; Shahi and Wagner, 1981; Nakamura and Goodenough, 1982; Fujitsu *et al.*, 1985; Fujitsu *et al.*, 1986; Tahmassebpour, 2016; Reddy, 2013; Esfahani *et al.*, 2013; Huang *et al.*, 2014; Shukla *et al.*, 1986; Hariharan and Maier, 1995; Elahinia *et al.*, 2015; Kunchur *et al.*, 2013) is shown in Fig. 1. It is concluded from the plot that among the various dispersoids CeO_2 is giving rise to maximum enhancement of three orders. The incorporation of nano dispersoid particles not only reduces the interfacial resistance but also provides better enhancement in conductivity.

The reason for the enhancement in conductivity is explained as the size of CeO_2 is minimum with respect to other dispersoids and it is a general trend that the conductivity increases as the size of the particle decreases. According to theoretical models proposed by Maier (1985), Stoneham *et al.* (1979), Jow and Wagner (1979) the enhancement is inversely proportional to the radius of the dispersoid particle. According to them when the submicron-size particles of dispersoid material (CeO_2) are dispersed into the host matrix salt ($_{0.19}Ba(NO_3)_2$-$_{0.81}KNO_3$) a space charge region of thickness (λ) is created around the dispersoid particles embedded in the host salt as shown in Fig. 2a. An excess of defect concentration gets accumulated at the space charge boundary as shown in Fig. 2b which ultimately contributes to the increase in the conductivity.

Such a behavior was noticed in many systems such as CuCl-Al_2O_3 (Jow and Wagner, 1979), AgI-Al_2O_3 (Shahi and Wagner, 1981) LiBr.H_2O-Al_2O_3 (Nakamura and Goodenough, 1982), CaF_2-Al_2O_3 (Fujitsu *et al.*, 1985) and $SrCl_2$-Al_2O_3 (Fujitsu *et al.*, 1986) Cu-SiO_2 (Tahmassebpour, 2016). $NaNO_3$-SiO_2 (Reddy, 2013), CeO_2-CaF_2 (Esfahani *et al.*, 2013), etc. Hence, nano dimension dispersoid particles are expected to exhibit larger enhancements in the conductivity. As well the ceria particles can be associated with different hydroxyl groups called nucleophillicgroups on their surfaces if present, these can attract cations. By characterization of Flourier Transform Infrared (FTIR) spectra as shown in Fig. 3 an infrared band at 3420 cm^{-1} corresponding to hydroxyl groups from H_2O was observed for CeO_2. More over, the structure of CeO_{20} (fluorite) also supports for better enhancement in conductivity comparing to λ-Al_2O_3

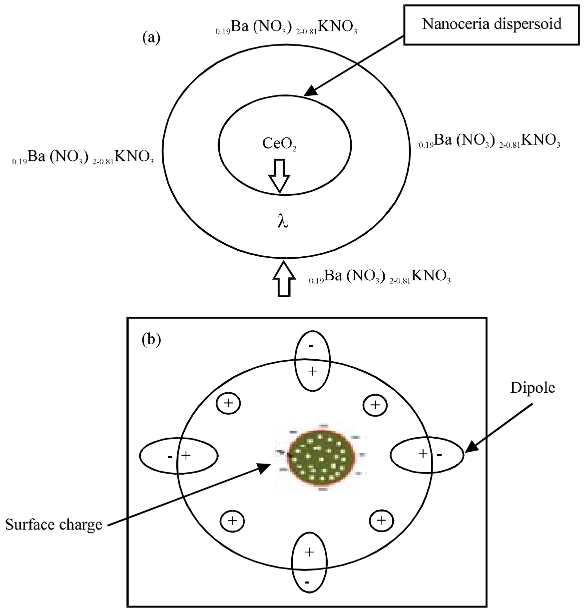

Fig. 2: Maier's space charge model for $_{0.19}Ba(NO_3)_2$-$_{0.81}KNO_3$: CeO_2 composite electrolyte system: a) A dispersoid particle (CeO_2) embedded in host salt ($_{0.19}Ba(NO_3)_2$-$_{0.81}KNO_3$) and bearing a space charge layer of thickness λ; b) Schematic presentation of the space charge effect

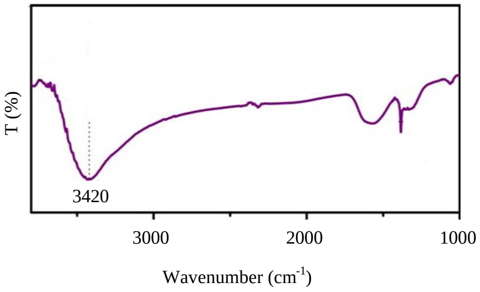

Fig. 3: FTIR spectra of CeO_2

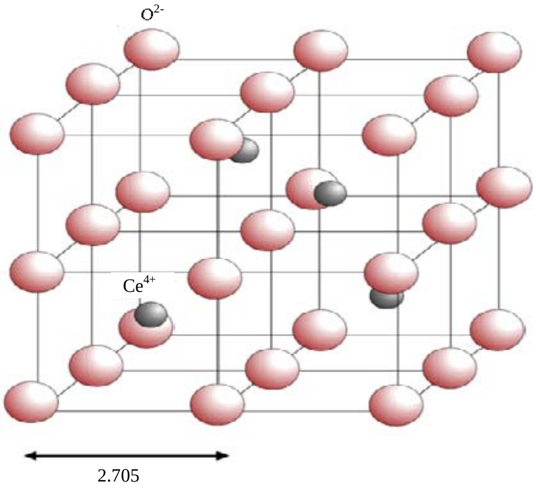

Fig. 4: Structure of CeO_2 unit cell

(cubic)and SiO_2 (amorphous). The fluorite structure of $CeO_2$is shown in Fig. 4. It is found that due to its fluorite structure the oxygen atoms in a ceria crystal are all in plane with one another, allowing for rapid diffusion. As mentioned earlier the mobile K^+ ions contributing to the conductivity the adsorbed O^{2-} ions facilitated by the hydroxyl groups also contributes to the total conductivity. These adsorbed O^{2-} ions to diffuse along the surface of CeO_2 (Huang *et al*., 2014; Shukla *et al*., 1986; Hariharan and Maier, 1995; Elahinia *et al*., 2015; Kunchur *et al*., 2015). The increased diffusion rate of oxygen on the surface of CeO_2 causes increased catalytic activity as well as an increase in ionic conductivity, making ceria interesting as a fuel cell electrolyte in solid-oxide fuel cells (Devi *et al*., 2015a, b). As the number of vacancies increases the ease at which oxygens can move on the surface also increases which in turn enhances the conductivity. Our observation also strenghted with Hariharan and Maier (1995) who reported more enhancement in CeO_2 dispersed system as compared to γ-Al_2O_3 dispersed system in the host CaF_2 (Lehovec, 1953).

The observed enhancement in the conductivity of present system $_{0.19}Ba(NO_3)_2$-$_{0.81}KNO_3$: CeO_2 is discussed in terms of space charge layer formation at the interface due to stabilization of positively charged species (K^+) at the CeO_2 surface thereby creating excess cation vacancies at the surface (Elahinia *et al*., 2015). Therefore, the enhancement of conductivity in dispersed systems is explained as the present system being a cationic defect solid if the cations are attracted to the interface, cation vacancy concentration in the space charge region will be increased relative to the bulk value. Thus, space charge region is associated with an increased concentration of defects. Thus, additional contribution to the total conductivity from the space charge region accounts forthe enhancement in ionic conductivity. As the concentration of dispersoid increases there are more particles of dispersoid and hence more the number of interfaces, resulting in conductivity enhancement.

As well the magnitude of enhancement was noticed to depend on the radius (r) of the dispersoid. The smaller the particle size, the larger the surface area will be and higher the σ-enhancements. Hence, nano-dimension dispersoid particles are expected to exhibit larger enhancements in the conductiivity. For a given mole percent of the dispersoid used, the surface area in contact between the host material and the dispersoid would increase as the particle size of the dispersoid decreases. This in turn would contribute towards higher enhancement of the measured conductivity. As long as the mole percent of the dispersoid has not reached the stage where clustering of particles takes place the enhancement is expected to be directly proportional to the total surface area.

CONCLUSION

DC and AC ionic conductivity studies on solid electrolyte system $_{0.19}Ba(NO_3)_2$-$_{0.81}KNO_3$ and various composite systems, viz. 10.8 m/o-Al_2O_3 (1 μm), 10.8 m/o-Al_2O_3 (0.3 μm), 5.3 m/o-Al_2O_3 (0.06 μm), 10.8 m/o-SiO_2 (10 nm), 10.8 m/o-CeO_2 (10 nm) reveals that the enhancement in 10.8 m/o-CeO_2(10 nm) is maximum of three orders. By the characterization on ceria reveals that an infrared band at 3420 cm^{-1} corresponding to hydroxyl groups from H_2O was observed for CeO_2. When the submicron-size particles of dispersoid material (CeO_2) are dispersed into the host matrix salt ($_{0.19}Ba(NO_3)_2$-$_{0.81}KNO_3$), a space charge region of thickness (λ) is created around the dispersoid particles embedded in the host salt. The adsorbed O^{2-} ions to diffuse along the surface of CeO_2. The increased diffusion rate of oxygen on the surface of CeO_2 causes increased catalytic activity as well as an increase in ionic conductivity, making ceria interesting as a fuel cell electrolyte in solid-oxide fuel cells.

ACKNOWLEDGEMENT

Researchers thank the Head, Department of physics, Osmania University for the experimental facility and Vardhaman College of Engineering for providing Complex Impedance Spectrometer.

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