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Improved ionic conductivity of calcium doped ceria-salt chloride composites: The eutectic effect

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ABSTRACT

Solid oxide fuel cells (SOFC) are considered as one of the most promising power generation technologies. The current high operating temperature (700-1000 °C) of SOFCs hinders their commercialization. Recently ceria – based composite materials are widely used because it is found to have a high conductivity below 600 °C. This paper analyzes the conductivity of the doped ceria based chloride composite systems, by varying the chloride combination as KCl and eutectic LiCl-KCl. The calcium doped ceria (CDC) has been prepared by the mechanochemical milling. The thermal decomposition process and structure of the samples were characterized by TGA and XRD respectively. The ionic conductivity of CDC/Salt composites was determined by electrochemical impedance spectroscopy (EIS). The CDC/LiCl-KCl samples show significantly enhanced conductivity when compared to that of the CDC/KCl samples. This shows that the use of the eutectic salt in the composite electrolyte can effectively lower the operation temperature of SOFC due to improved ionic conductivity.

KEYWORDS

Solid oxide fuel cells;
Calcium doped ceria;
Composite electrolyte.

INTRODUCTION

Fuel Cells are wonderful devices which converts the chemical energy of the fuels into electrical energy. Solid Oxide Fuel Cells (SOFCs) are gaining more attention now-a-days because of their high efficiencies and low emissions[1,2]. And also natural gases like methane can be used as fuel. But its high operating temperature (around 1000 °C) is the major factor which hinders its commercialization.

Many works have been carried out in an attempt to reduce the operating temperature. There are two ways in which it can be done. One way is to reduce the thickness of the electrolyte and the other is by the usage of new electrolyte materials. A good conductivity at the intermediate temperature (600 °C-800 °C) was achieved by the usage of the new electrolyte materials.

In the beginning, the Yttria stabilized Zirconia (YSZ) was widely used as an electrolyte. But it had low ionic conductivity at intermediate temperature. Calcium doped Ceria (CDC) was found to be a potential electrolyte which was found to have a good ionic conductivity at the intermediate temperature. But pure CDC was found to have some electronic conductivity which significantly reduced the overall performance of the fuel cell[3,4].

Then the usage of the several composite electrolytes was analyzed. Composite electrolytes are a physical mixture of two or more solid phases that possess different ionic conductivity properties. Composite materials usually show enhanced conductivity, mainly due to the high conductivity in the interface regions formed between the components. More the interface regions more will be the ionic conductivity. Various salts like chlorides, carbonates and sulphates have been used for making the composites and the ionic conductivity increased because of that[5-7].

Low melting eutectic salts like $LiCl-SrCl_2$ wer used with the doped ceria and found to have good ionic conductivity[8]. The salts with the low melting points were preferred as the ionic conductivity in the composite began only after the salt melts[9-11]. In the present study, a new eutectic salt (LiCl-KCl) was mixed with the Calcium Doped Ceria (CDC), which was prepared by the mechanochemical milling[12-14]. The composites were characterized by TGA, XRD and SEM and their conductivities was analyzed with Electrochemical Impedance Spectroscopy (EIS) and the results were compared with the CDC-KCl composite.

EXPERIMENTAL

Calcium doped ceria (CDC) was synthesized by the mechanochemical method with the starting material of CeO_2 as well as CaO (weight ratio 4:1). Ethanol was added as a milling medium to prevent excessive abrasion. The mixture was then milled using a planetary ball mill at 250 rpm for 6 and 8 hours under two different milling mediums i.e dry and wet. It was then dried at 60-70 °C to evaporate the ethanol. Then the doped ceria powder milled under various conditions was calcined at 950 °C. Single phase of the calcium doped ceria and doping of calcium oxide in ceria were characterized by X-ray diffraction analysis (XRD) (Philips X'pert pro super Diffractometer with Cu Kα radiation) in 2s range of 10-90° at 2°/minute. The crystal size of the powders was found using the Scherrer formula and the one with the smaller size has been chosen for preparing composites. The six hours dry milled doped ceria powder was found to have a crystal size of around 700nm whereas other powders have crystal size in the range of about 900nm. The powder with the smaller size was chosen because as the size decreases, the grain boundary area will be more, leading to the increased conductivity[8]. The composite was prepared by wet and dry mixing of the components. The LiCl and KCl (molar ratio 1:1) were first dissolved in methanol. Then the CDC powder was added to the mixture followed by thorough grinding. After grinding, the slurry was dried and calcined at 300 °C in air for 1hour to get the composite effect. The weight ratio between CDC powder and chloride (containing crystalline water) was maintained as 12:5[9].

Another composite CDC/KCl was prepared by the dry mixing method. The prepared CDC was mixed with KCl salt maintaining a weight ratio of CDC: KCl as 12:5. The mixture was well ground in an agate mortar, calcined at 650 °C in air for 1h.

The thermal property measurements of the composites were carried out using thermogravimetry analysis (TGA) with a heating rate of 5^0/minute in the synthetic air. SEM (Scanning Electron Microscopy) images were taken to analyze the surface morphology of the composites. Energy dispersive spectroscopy (EDAX) was taken for the confirmation of elemental composition of the composite. Powder X-ray diffraction (XRD) patterns of the samples were collected using Philips X'pert pro super Diffractometer with Cu Kα radiation for phase analysis and crystal size calculation.

The CDC-LiCl/KCl and CDC-LiCl nanocomposite materials were pressed under 300 MPa into pellets, followed by sintering at 175 °C and 387 °C for 1 hour. The electrical conductivity of the composite electrolytes was measured by Solartron 1355 Frequency Response Analyzer in the frequency range from 1 mHz to 1MHz with an applied signal of 20 mV.

RESULTS AND DISCUSSION

The X-ray Diffraction pattern of the 6 hrs dry milled CeO_2 based powders doped with CaO as shown below in Figure 1 was analyzed using the JCPDS file and the doping was confirmed. Figure 2 and 3 show the powder XRD pattern of both the single CDC and the composite electrolyte CDC-LiCl-KCl, CDC-KCl at room temperature. It showed that no peak for crystal-

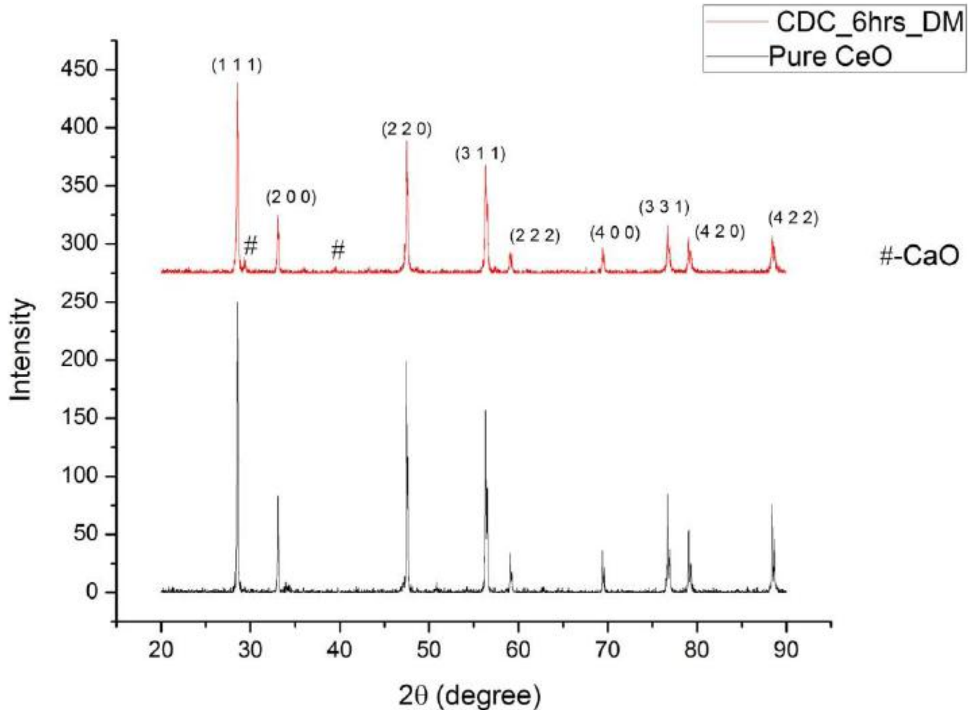

Figure 1 : XRD patterns of calcined CDC powder and pure ceria

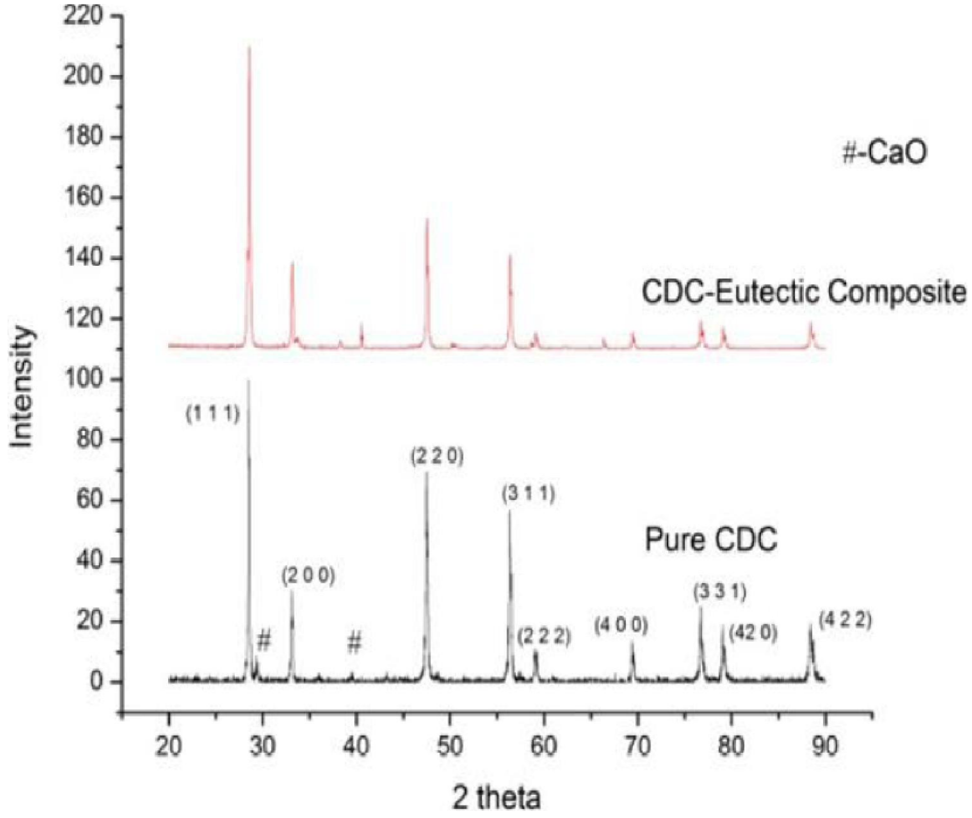

Figure 2 : XRD patterns of sintered powder of pure CDC and CDC-LiCl/KCl composite

line salt appeaed in the pattern. The eutectic salt/KCl became amorphous after thorough grinding followed by heat treatment. The well dispersed salt in the composite electrolyte is expected to provide a good ionic transport path.

Thermogravimetric analysis (TGA) of the compos-

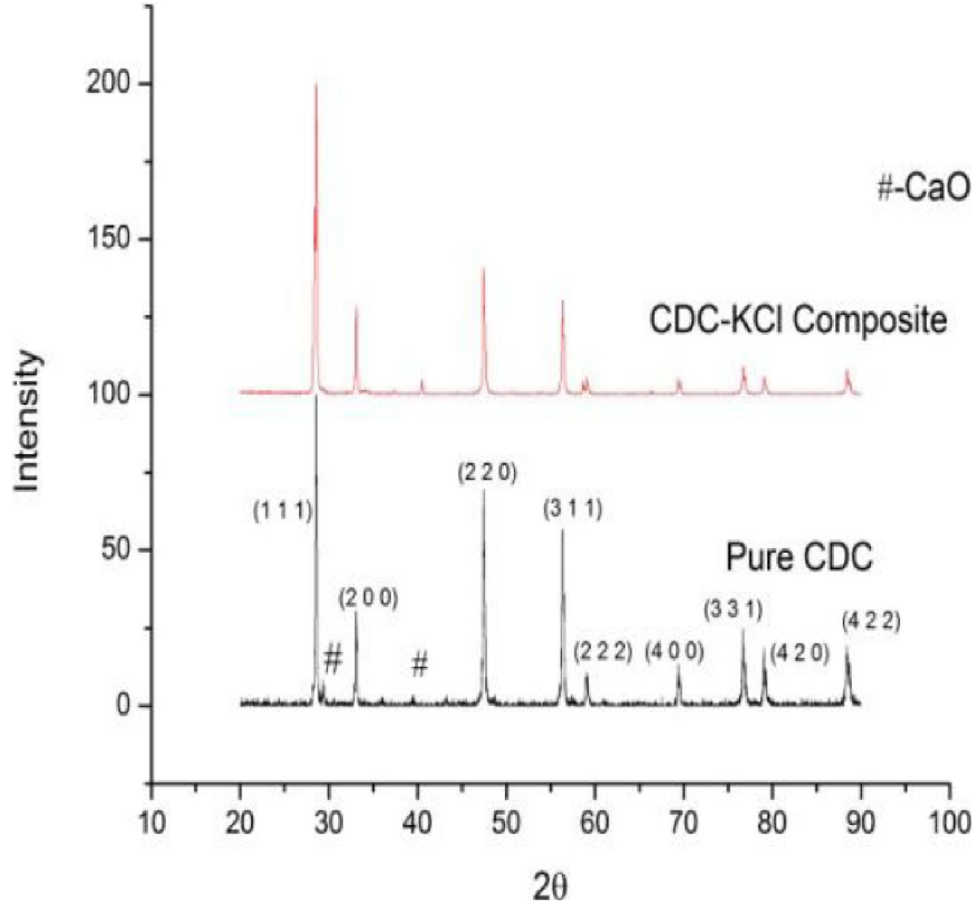

Figure 3 : XRD patterns of sintered powder of pure CDC and CDC-KCl composite

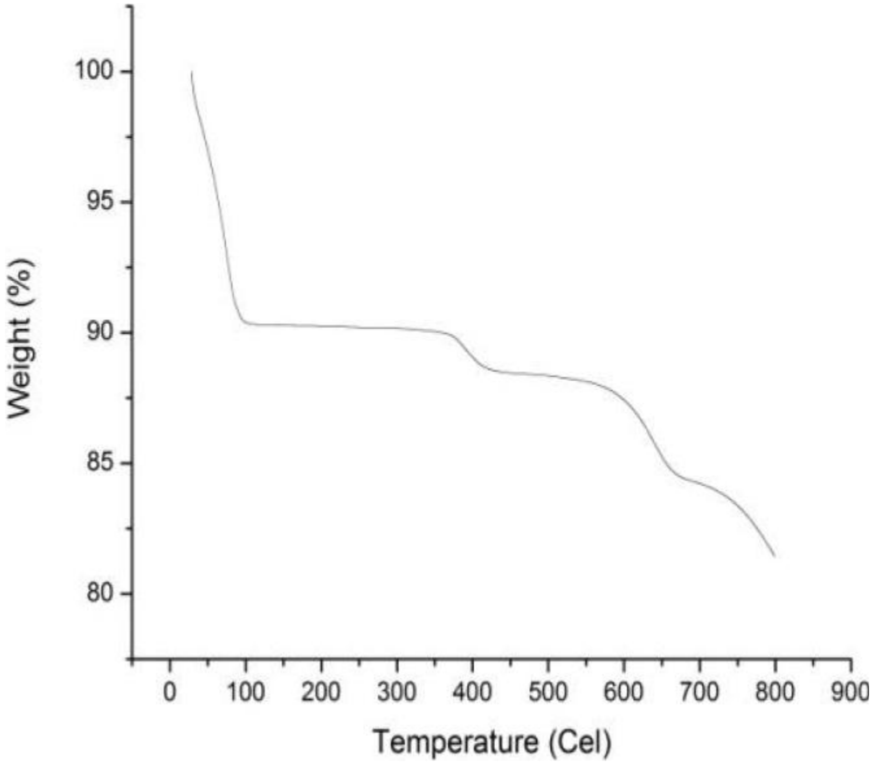

Figure 4 : TGA graph of as prepared CDC/LiCl-KCl composite

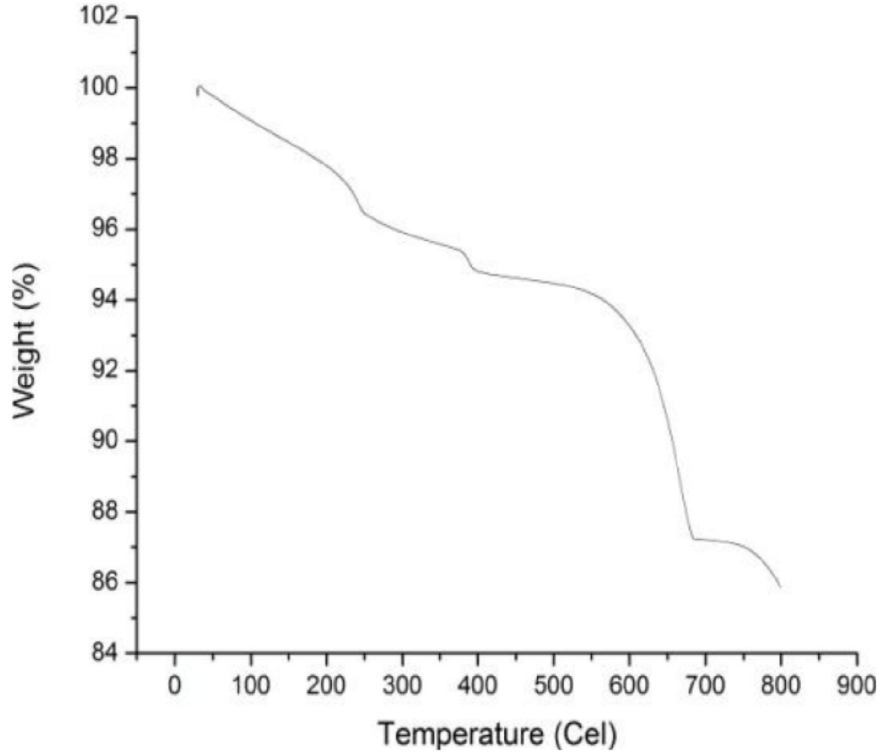

Figure 5 : TGA graph of as prepared CDC/KCl composite

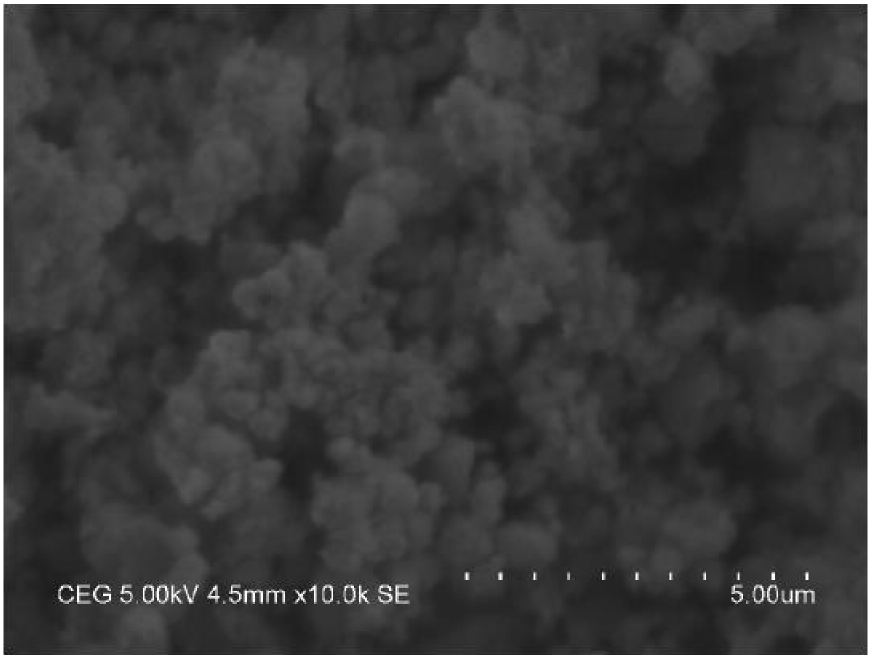

Figure 6 : SEM image of as prepared CDC/LiCl-KCl composite

ites was carried out and the results are shown in Figure 4 and Figure 5. It can be clearly seen from the curve in Figure 4 that two main weight loss processes took place in the temperature range of (i) room temperature to 150 °C (ii) around 400°C. The graph also indicated that the composite was stable in the temperature range of 150 °C-400°C.

The initial mass loss was due to the loss of water in the temperature range of room temperature to 150°C. The second loss was due to the melting of the salt in the temperature range around 400°C, in the case of LiCl-KCl eutectic composite. From the Figure 5, it can be

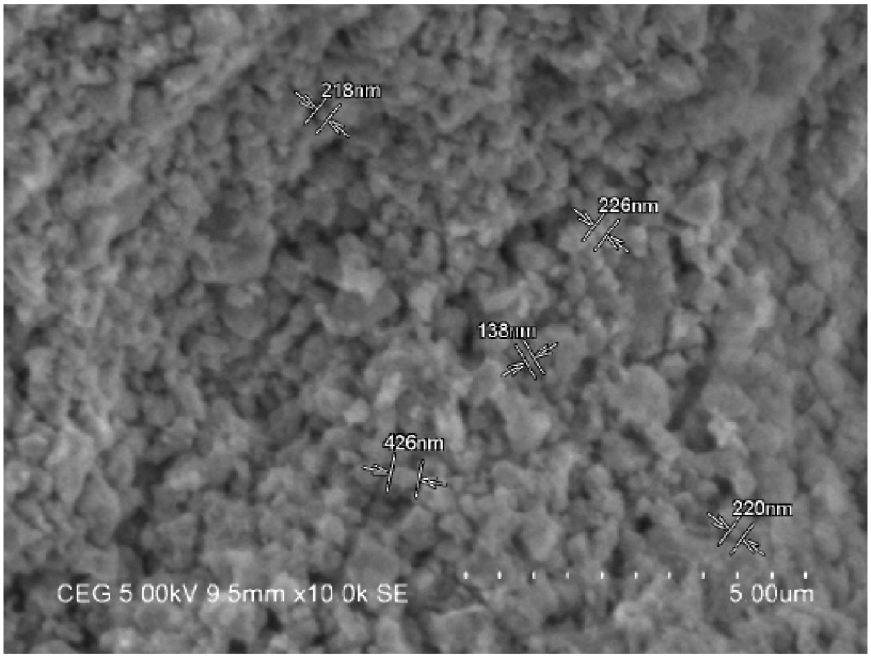

Figure 7 : SEM image of the CDC/LiCl-KCl sintered pellet

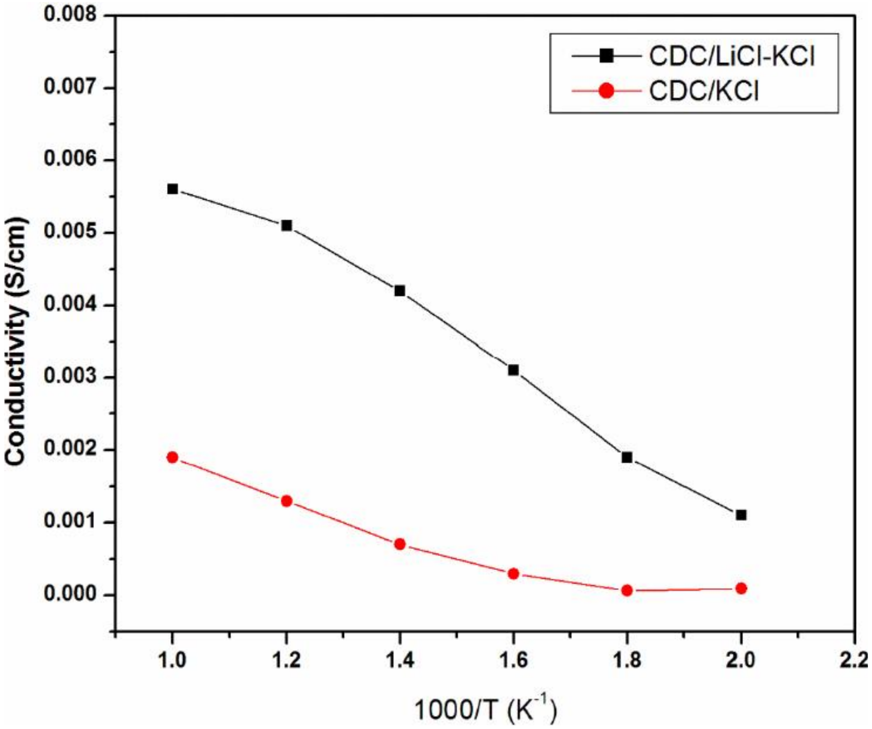

Figure 8 : Temperature dependence of conductivity of CDC/KCl and CDC/LiCl-KCl composites

seen that the major mass loss was in the temperature range of 450 °C-700 °C. It was due to the melting of the KCl in the composite.

Figure 6 shows the SEM image of the as prepared CDC/LiCl-KCl composite. It indicated the uniform distribution of powder particles and the powder particles were distinct i.e., agglomeration of powder particles has not happened. The particles were found to be in a spherical shape.

As the particles were distributed uniformly, it will help in an effective sintering of the powder leading to the reduced porosity. Figure 7 shows the SEM image of the sintered pellet of CDC/LiCl-KCl composite. The image confirmed the effect of the sintering i.e., less porosity. The particle size was also found to be in the range of 200-400 nm which could be an added advantage for conductivity to happen.

The conductivity of CDC/KCl composite and CDC/LiCl-KCl composite were recorded at different temperatures. It was found that, the CDC/KCl composite showed very low conductivity at lower temperatures and increased to 1.9 x 10^{-3} S/cm at 700 °C. On the other hand, for the CDC/LiCl-KCl eutectic composite, the conductivity was appreciable (at lower temperatures) when compared to CDC/KCl composite and increased to a value of 3.1 x 10^{-3} S/cm at around 400^{o} C itself and thereafter increased further up to 5.6 x 10^{-3} S/cm at 700^{o}C.

Thus, the eutectic based composite showed higher conductivity at lower temperature itself (400 °C) than the KCl based composite at 700 °C. Figure 8 displays the temperature dependence of conductivity of CDC/KCl and CDC/LiCl-KCl composite electrolytes. The conductivity of the eutectic based composite was much higher than the conductivity of KCl based composite. Therefore, from the above results, it may be concluded that the CDC based eutectic composites can be used as an alternative potential electrolyte for SOFC operation at intermediate temperatures (below 600 °C).

CONCLUSION

Calcium doped Ceria was prepared using mechanochemical milling and optimized for the smaller crystal size. The optimized powder was then made into composites by wet and dry mixing with LiCl-KCl and KCl respectively. XRD analysis confirmed the doping of calcium in ceria and also confirmed the amorphous nature of the salt in the composite. SEM characterization confirmed the small grain size of the composite which increased the conductivity. The CDC/LiCl-KCl composite showed enhanced conductivity than the CDC/KCl at lower temperature (around 400^{o}C) itself. Thus the doped ceria based eutectic composite system CDC/LiCl-KCl can be used as a promising electrolyte for the low temperature solid oxide fuel cells.

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