

ABSTRACT

The power generation from renewable energy resources has widely attracted, due to increase in energy demands and environmental concern. Fuel cells (FCs) are the electrochemical devices for the direct conversion of chemical energy into electrical energy without the emission of green house gas. In Solid oxide fuel cells (SOFC), hydrogen and oxygen are introduced at the anode and the cathode side, respectively. The solid electrolyte is placed in between two electrodes and plays a crucial role in transporting the oxygen ions.

The oxygen anion is moved from cathode to anode side through the oxygen ion vacancy in the electrolyte for initiating the reaction between hydrogen and oxygen to form water with an open cell voltage (OCV) of 1.12V. For commercialization, with this OCV, the minimum current density requirement for the cell is $100\text{mA}/\text{cm}^2$. In order to achieve this current density, the oxygen ion conductivity of the electrolyte should be greater than or equal to $0.1\text{ S}/\text{cm}$.

However, YSZ with monoclinic crystal structure exhibits oxygen ionic conductivity of $0.1\text{S}/\text{cm}$ at 1000°C . If the required ionic conductivity is achieved between 600°C to 800°C (intermediate temperature) then several problems including thermal expansion mismatch between the electrode-electrolyte interfaces and ceramic interconnectors can be avoided. If the ceramic is replaced by stainless steel then the easy and flexible design of interconnector is achieved which subsequently leads to higher efficiency and lower fabrication cost of SOFC.

An alternate electrolyte material, doped ceria with fluorite crystal structure shows promising characteristic with required ionic conductivity at 800°C. The oxygen vacancies are created when Ce^{4+} (1.01Å) is partially replaced by aliovalent cation like Gd^{3+} (1.07Å) and/or Sm^{3+} (1.09Å) ions. However, at lower oxygen partial pressure, ceria undergoes reduction from Ce^{4+} to Ce^{3+} ions results in undesired electronic conductivity which hampers its commercialization. Another class of electrolyte material, doped barium cerate with orthorhombic perovskite structure shows the ionic conductivity of 0.016 S/cm at 800°C. Even though, the conductivity is lesser than the doped ceria, the absence of electronic conductivity of the electrolyte makes them as a potential candidate for SOFC applications. In addition, the perovskite structures are extremely tolerant for the creation of oxygen vacancy by accepting the different mixture of aliovalent cation like Gd^{3+} , Sm^{3+} , into its crystal lattice.

In order to address the limitations of both doped ceria and doped barium cerate, the present investigation is targeted to the preparation and characterization of composite electrolyte with two phase microstructure for SOFC application. In such composite electrolytes, both doped ceria phase and doped barium cerate phase acts as a matrix and reinforcement, respectively, and can be operated at intermediate temperature (IT) without compromising the required ionic conductivity.

Cerium Nitrate, Barium Nitrate and Gadolinium oxide are the precursor used for the preparation of $\text{Ba}_x\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ powder with the composition range from $x=0.1$ to 0.4 mol fraction through co precipitation method. The as prepared powder is calcined at 300°C, 600°C and 900°C to ascertain the temperature of phase formation. From DSC-TG analysis, the phase formation temperature for GDC-BCG is identified as 900°C. XRD

pattern for all the compositions shows the presence of set of diffraction peaks confirms the formation of GDC and BCG phase in the powder calcined at 900°C. The crystallite size of both the phase for all the samples are found to increase with increase in Ba content. HRTEM results reveal that the average particle size distribution range from 10nm- 50nm and the d spacing between planes are in good agreement with XRD results. The density values are found to increase from 87-91% with increase in Ba content and XRD patterns show the absence of BCG phase for conventionally sintered pellets.

The green pellets are sintered at 1400°C, using microwave furnace within the minimum soaking time of 20 minutes. The density of sintered composite is measured and found to be ~90% of theoretical density with reduced porosity. XRD pattern for microwave sintered composite confirms the presence of both GDC and BCG phase at 1400°C. From SEM analysis, it is inferred that rod shaped grains belongs to BCG and micron sized grains belongs to GDC. As the Ba concentration increases, the rod like grains are well placed in the voids of GDC grain and effectively increases the density of the composite. The conductivity measurement is carried out using impedance analyzer and reveals that the composites sintered through microwave have resulted with the high ionic conductivity of 1.19×10^{-3} S/cm at 700°C.

Cerium Nitrate, Barium Nitrate and Samarium Nitrate are the precursor used for the preparation of $\text{Ba}_x\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ powder with the composition range from $x= 0.1$ to 0.4 mol fraction through co precipitation method. The calcination temperature for the as prepared powder is identified from DSC-TGA thermogram. The XRD pattern for the as prepared powder calcined at 900°C confirm the existence of both SDC and BCS phase. The crystallite size for SDC and BCS phase is found to increase with Ba content.

The average particle size distribution is analyzed through TEM and found to vary from 10nm- 30nm and the d spacing between planes is also found to match with XRD results. The ring pattern in selected area electron diffraction (SAED) for all compositions reveals that the as prepared powder is polycrystalline nature.

The density of the SDC-BCS composite shows ~91% of theoretical density and the value is much closer to the density of Gd based composites. The structural analysis for SDC-BCS composite shows the existence of both the phases. The loss of Ba content is reduced in the composite through microwave sintering. The BCS phase is successfully retained at 1400°C using microwave technique. The microstructural analysis reveals that the grains are almost uniform in size. The micron sized grains belongs to SDC and sub micron sized grains belongs to BCS, acts as matrix and reinforcement, respectively. The increase in BCS grains in between micron sized grains increases the density of the composite. From impedance analysis, the total ionic conductivity is 5.28×10^{-3} S/cm measured at 700°C for SDC-BCS composite.

Hence, the gadolinium doped barium cerate (GDC-BCG) and samarium doped barium cerate (SDC-BCS) based composite electrolytes with dual phase microstructure is successfully prepared through co-precipitation and microwave method. By using microwave technique, the percentage of barium loss is effectively reduced in minimum soaking time and the existence of BCG/BCS phase is successfully retained. The encompass of this dual matrix structure in the composite resolved the drawbacks of individual phases and their advantages is retained for better ionic conductivity in composite electrolyte.