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Development of melt infiltrated gadolinium doped ceria-carbonate composite electrolytes for intermediate temperature solid oxide fuel cells

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ABSTRACT

Composite electrolyte of gadolinium doped ceria and lithium sodium carbonate ($(LiNa)_2CO_3$-GDC) showing enhanced stability and mechanical strength has been fabricated using melt infiltration technique and tested as solid oxide fuel cell (SOFC) electrolytes. Porous matrix of GDC is fabricated by sintering at 1450 °C and subsequently the prefabricated matrix is melt infiltrated with mixture of $(LiNa)_2CO_3$ (1:1 wt ratio). Ionic conductivities of the electrolytes, current-voltage characteristics and impedance spectra of the electrolyte supported bilayers with hydrogen as fuel and air as oxidant are measured. Physical characteristics of the composite electrolytes analysed using X-ray diffraction, scanning electron microscope (SEM), energy dispersive spectroscope, fourier transform infrared spectroscope and thermal gravimetric analysis show spatial distribution of active interphases, where in pore filled with $(LiNa)_2CO_3$ melt into prefabricated GDC matrix. As carbonate phase completely fills the GDC matrix, the ionic conductivity of melt infiltrated 30 wt% $(LiNa)_2CO_3$-GDC composite electrolyte is comparable to that of the solid state synthesised electrolyte at 600 °C. The performance of melt infiltrated 30 wt% $(LiNa)_2CO_3$-GDC composite electrolyte (~2 mm) is much better (223 $mW\,cm^{-2}$ at 579 $mA\,cm^{-2}$) than that prepared by solid state method at 750 °C. The morphology, thermal analysis and electrochemical studies of melt infiltrated composite electrolytes reveal better cell performance due to well sintered stable structure.

1. Introduction

Low temperature SOFCs (LT-SOFCs) have several advantages over high temperature HT-SOFC (>700 °C) such as low cost, ease of fabrication and early start up [1–5]. However, state of the art yttria-stabilized zirconia has very negligible oxide ion conductivity at low temperature. In recent years, multiphase composite materials like alkali carbonate-GDC/SDC (M_2CO_3-GDC/SDC) have received increasing attention and find their applicability for electrolytes in LT-SOFC, CO_2 separation membranes and electrochemical synthesis of ammonia [6–16]. Among them lithium sodium carbonate-GDC/SDC ($(NaLi)_2CO_3$-GDC/SDC) composite seems to be one of the prominent electrolyte materials as it has high ionic conductivity (>0.05 $S\,cm^{-1}$) with property to facilitate oxide and carbonate transport at intermediate temperature [17–21].

Melting of carbonate eutectic mixture necessitates the lower sintering temperature in conventional solid-state mixing route for the fabrication of $(NaLi)_2CO_3$-GDC/SDC-composite electrolyte. It compromises the proper sintering, mechanical strength and grain growth. Sintering and stability issues of these composite electrolytes have been tried to mitigate using pre-sintered porous GDC/SDC matrix and thereafter melt infiltrated with $(LiNa)_2CO_3$ mixture (weight ratio 1:1). The investigation on melt infiltration technique in the context of GDC/SDC-$(NaLi)_2CO_3$ composite electrolytes for LT-SOFC is scanty although some research groups reported their application as CO_2 separation membranes and SOFC composite electrolyte [22–26]. Zhang et al. [22] reported 0.35–0.55 $S\,cm^{-1}$ conductivity in dry air at 650 °C for 40 wt% $(NaLi)_2CO_3$ infiltrated SDC composite electrolyte. In their study the amount of porosity has been taken as the amount of infiltration. The research group of Marques et al. [14,25,26] achieved high conductivities (1.9×10^{-1} to 2.2×10^{-2}) and permeation rates (0.6 $cm^{-3}min^{-1}$ cm^{-2}) in melt infiltrated ceramic oxide matrix for CO_2 separation membrane by impregnated eutectic mixture of $(NaLi)_2CO_3$ into pellets fabricated

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using coarsened $Ce_{0.9}Gd_{0.1}O_{1.95}$ powder. Usually, it is not possible to achieve 100% pore filling because of complex nature of pore connectivity, tortuosity and higher viscosity of carbonates. Initially, an attempt has been made by our group to infiltrate porous GDC structure with $(LiNa)_2CO_3$ solution following the work of Tiwari and Basu [27]. Repeated infiltration of $(LiNa)_2CO_3$ solution yields only 2–3 wt% loading in porous GDC pellet leading to insufficient $(LiNa)_2CO_3$ loading in GDC composite electrolyte. Although melt infiltration of porous GDC structure by carbonates has certain advantage with respect to stability and durability of electrolyte, it is very difficult to control the loadings and ensure complete coverage of the void space of the porous GDC structure.

In our study, the porous pellets are prepared by an easy one step technique where both sintering and introduction of porosity is carried out simultaneously in contrast to the previous attempt made by the investigators [22–24]. In the present work, the variation of $(LiNa)_2CO_3$ loading from 7 to 30 wt% and subsequent measurement of the conductivity in air environment has been carried out and the distinguishing feature of our work is the fuel cell performance study of melt infiltrated electrolyte and its comparison with that of solid state method. So far, to the best of our knowledge no one has reported the cell testing of melt infiltrated $(LiNa)_2CO_3$-GDC composite electrolyte in full cell (anode/electrolyte/cathode). The microstructure of electrode-electrolyte system has direct effect on the performance of SOFC and thus well sintered GDC electrolyte matrix is used for infiltration purpose. Electrochemical impedance spectra along with the detailed microstructural analysis of the $(LiNa)_2CO_3$-GDC composite electrolyte has been discussed to understand the process of melt infiltration as a novel technique for the development of $(LiNa)_2CO_3$-GDC composite electrolyte. The performance of bilayers (($(LiNa)_2CO_3$-GDC) electrolyte/NiO composite anode (50 wt% NiO + 50 wt% $(LiNa)_2CO_3$-GDC)) fabricated through melt infiltration method has been measured and compared with the bilayer prepared through solid state method. The SEM results show that the carbonate phase is closely connected and well spread on the GDC surface, which provide sufficient percolation of conducting medium throughout the electrolyte matrix leading to better ionic transport in case of melt infiltrated route of composite electrolyte fabrication. The morphological changes after carbonate infiltration into GDC matrix and post cell testing characterisation is done using field emission scanning electron microscope (FESEM). The transmission electron microscope (TEM), selected area electron diffraction (SAED) and fourier transform infrared spectra (FTIR) have been carried out for physical characterisation of $(LiNa)_2CO_3$-GDC electrolyte. The different phase such as ceria and carbonate and their thermal stability are studied using x-ray diffraction (XRD) and thermogravimetric analyses (TGA), respectively.

2. Experimental

The $(LiNa)_2CO_3$-GDC composite electrolyte was fabricated by two methods i) melt infiltration (MI) and ii) solid state method (SS).

2.1. Melt infiltration method

At first, performer was induced into the powder of GDC ($Ce_{0.8}Gd_{0.2}O_{2-\delta}$, Fuel Cell Materials, USA) by adding 25–40 wt% starch (Merck) and homogenised in a mechanical mortar and pestle. 5% poly vinyl alcohol (PVA) binder was added to the mix and was used to fabricate the pellets of 20 mm diameter and 1–3 mm thickness. For pelletizing, the powder was loaded into a die and pressed at 300 kg cm^2 in an isostatic press for 5 min. These pellets were sintered at 1450 °C in a furnace with heating rate of 2°/min, resulting in the formation of porous GDC matrix. Porosity of the sintered GDC pellets was found to be 30–40% using Archimedes method. Equal weight ratio of Li_2CO_3 and Na_2CO_3 (Alfa Aesar Puratronic 99.998%) was taken separately and homogenised in a mechanical mortar and pestle. Well homogenised mixture of $(LiNa)_2CO_3$ was placed in a crucible and melted in a muffle furnace. Dry, porous GDC pellets were weighed and placed in $(LiNa)_2CO_3$ melt inside the furnace. The $(LiNa)_2CO_3$ melt infiltration into the porous matrix of GDC was carried out at 580 °C for 1 h. The excess carbonate on the surface of the porous GDC pellet was scrapped off until the surface of GDC electrolyte was visible and the pellets were cleaned and again weighed. The weight difference was taken as the wt.% carbonate infiltrated into the porous matrix. The amount of the carbonate infiltrated into prefabricated porous GDC matrix is difficult to control and it does not always depend on how much pore former is added. The density of the $(LiNa)_2CO_3$ is 2.30 g cm^{-3} at room temperature and 1.96 g cm^{-3} at melting temperature. On melting of carbonate, it expands and this expansion ensures that the open pores if any in the porous matrix of GDC are filled with the molten carbonate at the operating temperature. Silver wire current collector was attached using silver paste to the both sides of the pellet and left to dry at 200 °C. The bilayer cells were prepared by painting NiO composite anode (50 wt% NiO + 50 wt% $(LiNa)_2CO_3$-GDC) on $(LiNa)_2CO_3$-GDC electrolyte. The cells prepared through melt infiltration method were electrolyte supported. The fuel cell configuration used was Ag (paste) as cathode, $(LiNa)_2CO_3$-GDC) (melt infiltrated) or $(LiNa)_2CO_3$-GDC) (solid method) as electrolyte and NiO composite (50 wt% NiO + 50 wt% $(LiNa)_2CO_3$-GDC) as anode.

2.2. Solid state method

The required amount of $(LiNa)_2CO_3$ was added to GDC powder and homogenised in a mortar and pestle. The powder mix was die pressed and sintered at 680 °C as mentioned by Chokalingum and Basu [11,12,20]. The silver wire and silver paste was used as current collector for the electrolyte to measure ionic conductivity in air atmosphere. The cells prepared through solid state method were electrolyte supported with same thickness (~2 mm) as that of the melt infiltrated fuel cells. It must be noted that same NiO composite anode (50 wt% NiO + 50 wt% $(LiNa)_2CO_3$-GDC) and cathode material (Ag paste) was used for both the solid state and melt infiltrated cells for comparison purpose. For clear understanding schematic representation of fabrication process (melt infiltration and solid state) and SEM micrographs of $(LiNa)_2CO_3$-GDC composite electrolytes is presented in Fig. 1(a–c).

2.3. Physical and electrochemical characterisation

The microstructure analysis before and after infiltration of $(LiNa)_2CO_3$ into GDC porous matrix was carried out with a field emission scanning electron microscope (FESEM) (model FEI Quanta 200F SEM). Energy dispersive spectroscopy (EDS) was done using JEOL-JSM-6010 PLUS/LA. A Rigaku MiniFlex X-ray diffractometer with source Cu kα radiation ($\lambda = 1.54$ Å) and 40 kV was used for phase identification. The measurement was carried over 2θ range of 15-75° with a step size of 4°/min and the data obtained was matched with joint committee on powder diffraction standards (JCPDS). The sample porosity was measured by Archimedes principle using water displacement method, where the pre-weighed dried sample pellets were immersed in acetone/ethanol/isopropyl alcohol and kept for about an hour till the sample pellet was saturated. The porosity was calculated using formula, $\Phi =$ pore volume/bulk volume, where the bulk volume is the sum of the solid volume and the pore volume. The specific surface area of porous and melt infiltrated GDC electrolyte was measured by the