Short Communication

Sintering and electrical properties of $Ce_{0.75}Sm_{0.2}Li_{0.05}O_{1.95}$

Santanu Basu[*], Subhasis Khamrui, N.R. Bandyopadhyay

School of Material Science & Engineering, IIEST(formerly BESU), Shibpur, India

ABSTRACT

Ceria-based electrolytes have been widely investigated in intermediate-temperature solid oxide fuel cell (SOFC), which might be operated at 500—600 °C. Samarium doped (20 mol%) ceria (20SDC) one of the most promising material in this class of compounds. In this work we report effect of lattice substitution of 5 mol % Li on Sm in (20SDC). It was prepared by citrate—nitrate auto combustion synthesis having a powder of average particle size ~50 nm. The sintered density of more than 98% of the theoretical density at 950 °C has been achieved. Increased ionic conductivity (lattice) at 500 °C has also been achieved in $Ce_{0.75}Sm_{0.2}Li_{0.05}O_{1.95}$ compare to that of $Ce_{0.8}Sm_{0.2}O_{1.95}$. Corresponding activation energy of conduction ~0.7 eV has been calculated in the temperature range of 200—600 °C. In reducing atmosphere the electrical conductivity has not been altered much. Thus $Ce_{0.75}Sm_{0.2}Li_{0.05}O_{1.95}$ has been found to be quite promising in terms of reducing the processing temperature as well as operating temperature of SOFC.

Introduction

CeO_2-based oxides are well known for their high ionic conductivity, which is reflected in their application as electrolyte for low temperature solid oxide fuel cell (LT-SOFC) operating at 500—600 °C [1—3]. Choices of rare earth cation substitutions are numerous due to relatively large host lattice size of cerium oxide [4]. 20 mol% samarium doped cerium oxide (20SDC) is one of the highest ionic conducting material among the doped compositions [5]. CeO_2 substituted with samarium are claimed to have low redox stability than the conventional yttria stabilized zirconia (YSZ) because of the variable oxidation states of Ce at higher temperature in reducing atmosphere, significant electronic conductivity is observed as the electronic conductivity in CeO_2 increases by hopping of polaron between Ce^{3+} and Ce^{4+} charge states in the reducing environment [6,7]. Again densifications of ceria based materials are difficult to obtain below 1500 °C [8].

Li_2O was evaluated as a promising sintering aid for $Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC) [9]. Conductivity of GDC was found to be increased by addition of Li or Co [10]. The enhancement of conductivity was recognized to the electronic conduction due to segregation or dissolution of heavy metal oxides on the grain boundaries [11,12]. It has also been proposed that $LiNO_3$

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* *Corresponding author.* School of Material Science and Engineering (SMSE), IIEST (Formerly BESU), Shibpur, Howrah — 711103, West Bengal, India. Tel.: +91 33 2555 3402.
  E-mail address: santanubasu72@hotmail.com (S. Basu).

melted and evaporated in large part during sintering, and thus, enhanced the ionic conductivity especially at the grain boundaries [13]. Li et al. [14] reported that bulk (lattice) conductivity of the 20SDC remained unaffected with addition of Li^{+}, however electrical conductivity at grain boundaries of low-temperature sintered SDC was increased.

Considering scarcity of information in literature on the lattice substitution of Li^{+1} in SDC we employ Li^{+1} as a lattice substitute to 20SDC. The aim of the present work is to investigate whether minute (5 mol%) concentration of Li^{+1} can enter the lattice of 20SDC and its effect on sintering, conductivity and redox stability of 20SDC.

Experimental procedure

Ce$_{0.75}$Sm$_{0.2}$Li$_{0.05}$O$_{1.95}$ powder was prepared by citrate—nitrate route of auto combustion technique [15]. Calculated proportions of ceric ammonium nitrate, samarium nitrate hexahydrate and lithium nitrate were mixed in deionised water with citric acid maintaining citrate to nitrate ratio of 0.3. The as-synthesized powder was calcined at 400 °C for 6 h to remove carbonaceous residues. X-ray diffractograms of the powders were recorded by Philips X'pert X-ray diffractometer (Cu-Ka radiation, 40 kV, 40 mA). The structural parameters were refined employing a least-square fitting program FullProf. The powder morphology and grain microstructures were examined by SEM (Hitachi High-TechScienceSystemCorporation,Model S—3400N).

The calcined powders were pressed uniaxially with a specific pressure of 170 MPa to prepare green pellets (dia.~10 mm) and subsequently sintered at 950 °C for 2 h in air. The densities of the pellets were determined by standard Archimedes principle. Two probe alternating current (ac) impedance measurements were conducted on sintered, electroded samples in the frequency range 0.1 Hz—10 MHz with an applied voltage of 0.1 V using a Solartron frequency response analyzer (FRA 1260) in the temperature range 200—600 °C. The impedance data were analyzed using Z-VIEW software. For the electrical and electrochemical measurement platinum paste (metalor) was used as electrode on both sides of the sintered disk and the contacts were cured at 900 °C for 2 h. AC impedance of the samples were performed in the heating cycles and sufficient time was allowed for equilibration of both oxygen partial pressure (atmosphere) and temperature. Few low temperature impedance data were discarded due high presence of stray error.

Results and discussion

The X-ray patterns of as-synthesized and 400 °C calcined Ce$_{0.75}$Sm$_{0.2}$Li$_{0.05}$O$_{1.95}$ powders are shown in Fig. 1. The formation of completely phase-pure CeO$_2$ with cubic fluorite structure is observed in both cases which indicate that Ce$_{0.75}$Sm$_{0.2}$Li$_{0.05}$O$_{1.95}$ does not show any additional peak for lithium oxide or other complexes. The crystallite size, calculated from Scherrer's formula, is found to be ~40 and 45 nm for as-synthesized and calcined Ce$_{0.75}$Sm$_{0.2}$Li$_{0.05}$O$_{1.95}$ powders, respectively. The powder morphology of as-synthesized
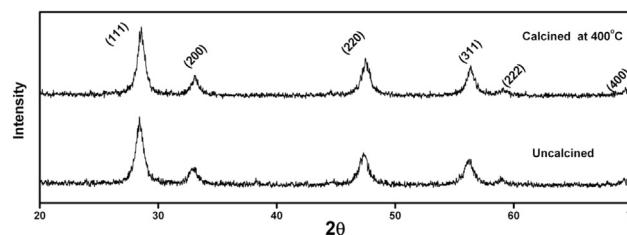

Fig. 1 — X-ray patterns of as-synthesized and 400 °C calcined Ce$_{0.75}$Sm$_{0.2}$Li$_{0.05}$O$_{1.95}$.

powder indicates particle agglomeration with estimated size of ~50 nm (inset Fig. 2). It has been found that lattice parameter decreases minutely (5.4092 Å) for Ce$_{0.75}$Sm$_{0.2}$Li$_{0.05}$O$_{1.95}$ compare to 20SDC (Ce$_{0.8}$Sm$_{0.2}$O$_{1.95}$) (5.4132 Å) which is evitable from the fact that r$_{Li}^{+1}$(viii) (0.92 Å) is slightly lower than that of r$_{Ce}^{+4}$(Viii) (0.97Å). This strongly supports lattice substitution of Li^{+1}. Samples sintered at 950 °C for 2hr reaches >98% relative density which can be achieved by 20SDC only at around 1250 °C. The corresponding dense microstructure having average grain size in the range 200—500 nm is shown in Fig. 2. No secondary phase accumulation at grain boundary is evident which is further manifested from the XRD of 950 °C sintered sample (inset Fig. 2). In order to confirm that there is no secondary phase present in the sintered samples, slow scanned XRD patterns were recorded. Fig. 2 inset shows a slow scanned XRD patterns of Ce$_{0.75}$Sm$_{0.2}$Li$_{0.05}$O$_{1.95}$ sintered at 950 °C for a selected 2θ region (32—34°) corresponding to the most intense diffraction peak which does not show any presence of secondary phases like Li$_2$O or LiOH (reported to show intense at 33° peak and small bulge near 32° for Li$_2$O and LiOH respectively) [16]. In fact formation of LiOH or Li carbonates are very negligible as in this work combustion synthesis have been used in this work which being a highly exothermic process restrict formation of such compounds. Even if such compound formed it will definitely decompose during calcinations and initial stage of sintering. Densification of 20SDC is enhanced by addition of Li^{+1} by means of lattice diffusion of host atoms [17] which is contradictory with the decrease of lattice parameter hence the free cell volume. Zhu et al. [8] has explained similar enhancement of sintering of 20GDC (Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$) with addition of Li^{+1} might be due to very high vapor pressure of Li$_2$O (at 1000 °C, the vapor pressure reaches1.09 E^{-8} bar for Li$_2$O). They have also postulated that Li diffusion into the GDC lattice and Li$_2$O vaporization from the GDC lattice may take place consecutively at elevated temperature.

In this work we differ with their view and postulate that substitution of Ce^{+4} by Li^{+1} can increase the oxygen vacancy by following Kroger — Vink equation.

$$\text{Li}_2\text{O} \xrightarrow{2\text{CeO}_2} 2\text{Li}_{Ce}^{///} + 3\text{V}_O^{\bullet\bullet} + \text{O}_O^x \qquad (1)$$
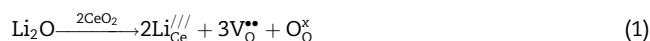
Thus incorporation of each Li^{+1} is compensated by three oxygen vacancy. Increase of V$_O^{\bullet\bullet}$ number enhance the vacancy diffusion. Enhanced vacancy diffusion results in quicker mass transport to the opposite direction results in densification in spite of small decrease of lattice parameters.

Impedance spectra at 300 °C for Ce$_{0.75}$Sm$_{0.2}$Li$_{0.05}$O$_{1.95}$ sample, sintered at 950 °C in air and hydrogen atmosphere is