Short communication

Study on calcium and samarium co-doped ceria based nanocomposite electrolytes

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ABSTRACT

Calcium co-doped SDC-based nanocomposite electrolyte ($Ce_{0.8}Sm_{0.2-x}Ca_xO_{2-\delta}-Na_2CO_3$) was synthesized by a co-precipitation method. The microstructure and morphology of the composite electrolytes were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM), and thermal properties were determined with differential scanning calorimetry (DSC). The particle size, as shown by TEM imaging, was 5–20 nm, which is in a good agreement with the SEM and XRD results. The co-doping effect on both interfaces of the composite electrolyte and doped bulk effect inside the ceria was studied. The excellent performance of the fuel cell was about 1000 mW cm^{-2} at 560 °C and at the very low temperature of 350 °C the power density was 200 mW cm^{-2}. This paper may give a new approach to develop functional nanocomposite electrolyte for low-temperature solid oxide fuel cell (LTSOFC).

1. Introduction

Solid oxide fuel cells (SOFCs) have gained attention because of their high energy conversion efficiency and fuel flexibility [1,2]. The current SOFC technology is still so expensive, that many efforts have been undertaken to introduce new materials, which can work more efficiently at low temperatures. Many researchers for better intermediate-temperature SOFC performance [2–5] have successfully studied the doped ceria.

Several authors have investigated co-doping effects and have reported that co-doped ceria is an effective solution for obtaining better performance and good ionic conductivity at low temperatures [3–10]. For example, Maricle et al. have pointed out "singly doped ceria develops electronic as well as ionic conductivity, which contributes to loss of efficiency at low power levels". They introduced the double dopant approach, lowering the electronic conductivity under fuel conditions, enabling ceria to be a useful electrolyte [1]. Following this advance, Ishihara et al. developed an electrolyte using the co-doped ceria technique and achieved notable performance but at high temperature [3].

Therefore, our efforts have been made to develop a new nanocomposite electrolyte, which can work at much lower SOFC operating temperatures based on co-doped ceria, which can give better performance than pure SDC (single doped ceria by samarium) at low temperatures, as previously reported by other authors [1–10]. Co-doping has many advantages [1–5] over single doped ceria, including better low-temperature performance, better electrode compatibility and good conductivity. However, single-ion or co-ion doping could not eliminate the pure ceria phase drawbacks, e.g. electronic conduction and mechanical limitations. In our work, doping has been used not only to improve the ceria phase properties, but more importantly to modify the particle surface properties in order to create interfacial functions between two constituent phases in a composite type material, so-called nanocomposites [12,13].

There are two major challenges for the commercialization of SOFC, one is to lower the temperature and second is to explore new, more cost-effective, and stable compositions. We have selected calcium (Ca^{2+}), the divalent cation, as a co-dopant because of relatively low cost and widely available on the market [13]. Besides, CaO is very attractive due to a distinctive co-doping effect into the ceria host lattice. It has also ionic-radius compatibility with the host cation [14].

The co-doping is a good approach for the structure modification of ceria-based material to improve the oxygen ion conductivity at low-temperature range (300–600 °C). The introduction of the

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co-doped ceria with alkaline earth and rare earth ions can also lead to improve the ionic conductivity [15,16].

This paper presents a new electrolyte $Ce_{0.8}Sm_{0.2-x}Ca_xO_{2-\delta}$–$Na_2CO_3$ (CSDC) for the LTSOFC, co-doped ceria-based composite, which offers better low-temperature performance. We have analyzed this material by XRD, SEM, and TEM and tested it in a SOFC. We have developed a series of nanocomposite electrolytes [12,17,18]. One of these, offering better low-temperature performance, is described in this paper [17,18].

2. Experimental

2.1. Sample preparation

A co-doped SDC-based electrolyte $(Ce_{0.8}Sm_{0.2-x}Ca_xO_{2-\delta}$–$Na_2CO_3)$ was synthesized by a co-precipitation method [16,17]. Initial ingredients Ce $(NO_3)_3 \cdot 6H_2O$ (Sigma–Aldrich, 99.99%) and Sm $(NO_3)_3 \cdot 6H_2O$ (Sigma–Aldrich, 99.999%) and Ca $(NO_3)_2 \cdot 4H_2O$ (Sigma–Aldrich, 99.99%) were dissolved in de-ionic water with an optimal molar ratio of Ce^{3+}:Sm^{3+}:Ca^{2+} = 4:1:1 to form a 0.1 mol L^{-1} solution.

Then the Na_2CO_3 solution of 0.2 mol L^{-1} was added drop by drop to this solution, which was stirred for 30 min, giving a white precipitate. The precipitate was washed, filtered and dried in the oven for 12 h at 80 °C and sintered at 800 °C for 4 h in the air atmosphere. Then the powder was ground in a mortar before using for the measurements.

A fuel cell was fabricated in a configuration of anode (mixture of NiOCuO and CSDC)/electrolyte (CSDC)/cathode (mixture of lithiated NiO and CSDC) by the dry pressing method at 250 MPa. The size of the fuel cell was fabricated with 13 mm in diameter and 0.80 mm in thickness (which consists of 0.35 mm anode cermet, 0.25 mm electrolyte, 0.20 mm cathode layer) and an active area was 0.64 cm². These cells were sintered at 650 °C for 45 min to form a dense pellet. The SOFC was tested at 400–580 °C, where hydrogen and air were used as fuel and oxidant, respectively. The gas flow rates were in the range of 80–110 ml min⁻¹ at 1 atm pressure.

2.2. Sample characterization

The phase structure of as prepare sample was characterized by a D/Max 3A X-ray diffractometer (XRD, Regaku, Tokyo, Japan) with Cu Kα radiation. Thermal properties of the sample were measured with a differential scanning calorimetry (DSC) 2920 thermal analyzer (TA Instruments, New Castle, DE 19720, USA).

The microstructure and morphology were examined using an XL-30 scanning electron microscope (SEM, Philips, Amsterdam, Netherlands). The composition of the sample was examined using the energy-dispersive X-ray spectroscopy (EDX) unit attached to the SEM.

For the detailed morphology and microstructure including the crystal size and shape, the transmission electron microscope (TEM) was employed using a JEM-2100F transmission electron microscope (TEM, JEOL, Tokyo, Japan) with a carbon-coated copper grid. The performance of the SOFC was obtained by a computerized instrument (L43, Tianjin, China) over the temperature range 400–580 °C.

The ionic conductivity and AC impedance spectra of the Ca co-doped nanocomposite electrolyte were determined by a two probe AC impedance method using a VERASTA2273 impedance analyzer (Princeton Applied Research, Oak Ridge, TN) in the range of 0.1 Hz–1 MHz in the range of 300–600 °C. The curve fitting and resistance calculations were made using ZSimpWin (Princeton Applied Research, Oak Ridge, TN) software.
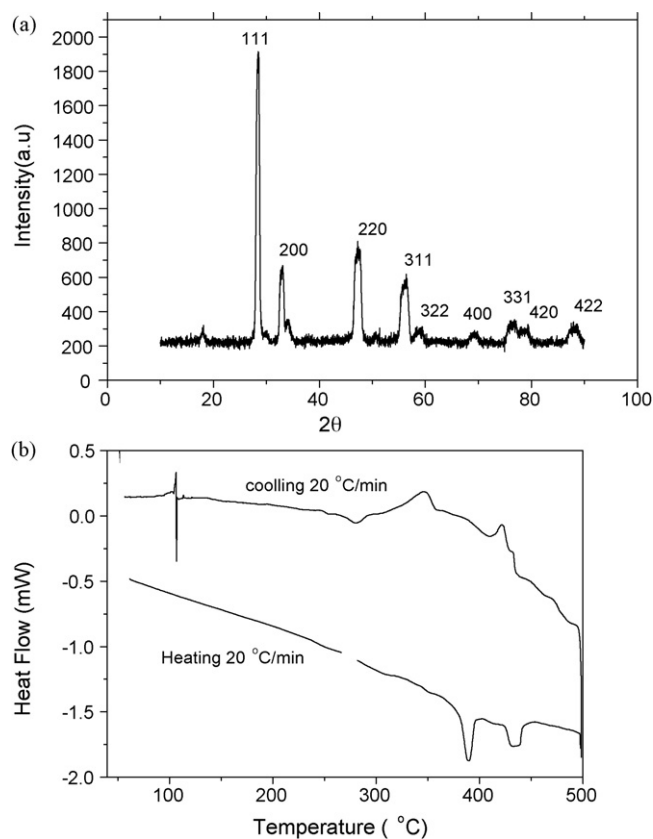

Fig. 1. (a) X-ray diffraction pattern for CSDC and (b) DSC curve.

3. Results and discussion

3.1. Phase analysis/crystal structure

Fig. 1(a) shows the as-prepared sample XRD diffraction patterns are same as those of the pure ceria, only the 2θ values slightly shifted towards higher angle. No individual phase of Sm_2O_3 or $CaCO_3$ could be detected. This shows that Sm^{3+} and Ca^{2+} have been co-doped into ceria. As reported before [12] in the above sample preparation, it could form a doped ceria–Na_2CO_3 two-phase composite. Same with that SDC–Na_2CO_3 composite, the Na_2CO_3 is amorphously distributed, since no peaks for them were observed, in contrast to our previous work [12].

The XRD results show that the CSDC crystal structure after sintering at 800 °C is cubic fluorite structure of ceria, giving an electrolyte with high oxide ion mobility [12–14]. Its average crystallite size was calculated to be in the range 15–20 nm using Scherrer formula.

3.2. DSC

Fig. 1(b) displays the DSC curve of the co-doped sample at heating and cooling rates of 20 °C min⁻¹. There are endothermic effects in temperatures between 400 °C and 450 °C. The curves show that the co-doped nanocomposite electrolyte containing Ca^{2+} as co-dopant and Na_2CO_3 as a second phase is different from the SDC (single doped ceria by samarium). Compared to the SDC–Na_2CO_3 composite system the endothermic effect moves from lower to higher temperatures with the calcium co-doping which may cause the changes of the particle surface properties [12,14]. The individual doped ceria, no matter single- or co-doping, and Na_2CO_3 have no any thermal effects in this measured temperature range [12,14]. The endothermic effect was caused by the interfaces or interfacial

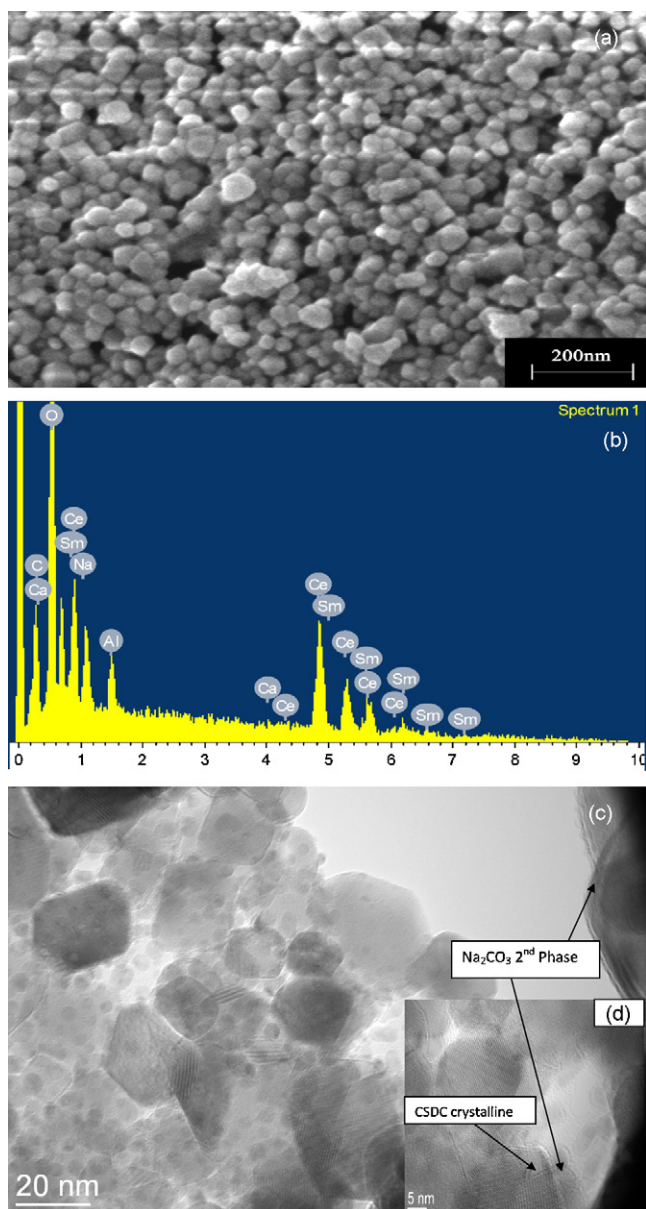Fig. 3. *I–V/I–P* characteristics of a fuel cell at different temperatures.

Fig. 2. (a) SEM images of CSDC, (b) EDX, (c) high-resolution TEM images of CSDC composite electrolyte components and (d) CSDC crystalline fringes and amorphous state Na$_2$CO$_3$.

structure transition between the co-doped ceria and Na$_2$CO$_3$. The same situation occurs in this work.

3.3. Microstructure/morphology

Fig. 2(a) shows the microstructure of the co-doped ceria–Na$_2$CO$_3$ composites, obtained by SEM. The morphology of the sample is largely homogeneous, signifying a rather dense.

In the co-doped powder, homogeneity and chemical composition were determined by EDX as shown in Fig. 2(b). The results are in good agreement with the experimental stoichiometric indexes and the nominal composition of CSDC.

Fig. 2(c) shows a TEM image of an as-prepared sample. It is evident that its particles are smaller than the 50 nm value for SDC from the high-resolution TEM image. This observation is a confirmation of the SEM and XRD results for particle size calculations. We observed some particles have core–shell from TEM which are also agreement of the previous reported results [12]. The CSDC (core)
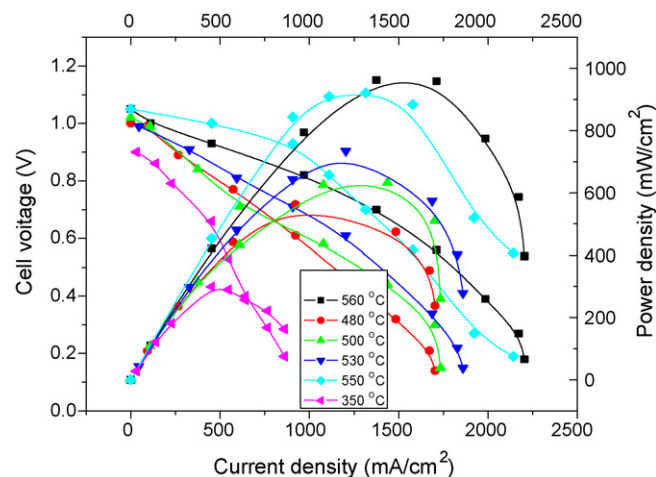
have crystalline fringes and Na$_2$CO$_3$ (shell) have no lattice fringe is to be considered as an amorphous state, can be seen in the images (Fig. 2(c) and (d)). It can also be considered that the dark field in the TEM image is related to Na$_2$CO$_3$, due to the different contrast between Na$_2$CO$_3$ and the other particles and carbon film substrate present.

3.4. Performance

The significant improvement in fuel cell performance results from the use of co-doped electrolytes. The cell power density P_{max}, with H$_2$ as a fuel, reached a maximum of 980 mW cm^{-2} at 560 °C and at the very low temperature of 350 °C the power density was 200 mW cm^{-2} as shown in Fig. 3. The open-circuit voltage (OCV) was 1.05 V at 560 °C and 0.99 V at 350 °C and indicates that the electrolyte membrane is sufficiently dense. The performance is very encouraging at very low temperatures with the two-phase co-doped nanocomposite electrolyte. This may be attributed from improved chemical surface properties of particles prepared using the co-doping technique, which appears to be useful effective fuel cell performance at lower temperatures.

The obtained performance at lower temperature with co-doped ceria electrolyte is comparatively better with conventional electrolytes YSZ and SDC based on the previous reported results by the researchers particularly, Huang et al. obtained maximum power density 131 mW cm^{-2} at very low temperature 350 °C using YSZ electrolytes [19]; Hibino et al. obtained 101 mW cm^{-2} at 350 °C using ceria-based electrolytes [20]; Shao and Haile have succeeded 1010 mW cm^{-2} and 402 mW cm^{-2} at 600 °C and 500 °C using single-phase SDC electrolyte [21]; and Suzuki et al. demonstrated 1000 mW cm^{-2} at 600 °C using zirconia based electrolytes [22].

There is no electrode polarization process from Fig. 3, because the *I–V* characteristics are linear. The less IR drop from electrolyte ohmic behavior may be the reason for the higher performance at such low temperature. Due to the calcium co-doped two-phase electrolyte, it has a higher conductivity and which also make the excellent performance. By viewing high performance SOFCs in literature [20–22], it is a common fact that the high performance corresponds to linear *I–V* characteristics. In our work, we used CSDC for the anode and cathode, the reaction at electrodes would be enhanced because of the high ionic conductivity of CSDC. Then, electrode polarization resistance may be decreased for this development. More detailed electrochemical characterizations on this phenomenon will be done in the future.
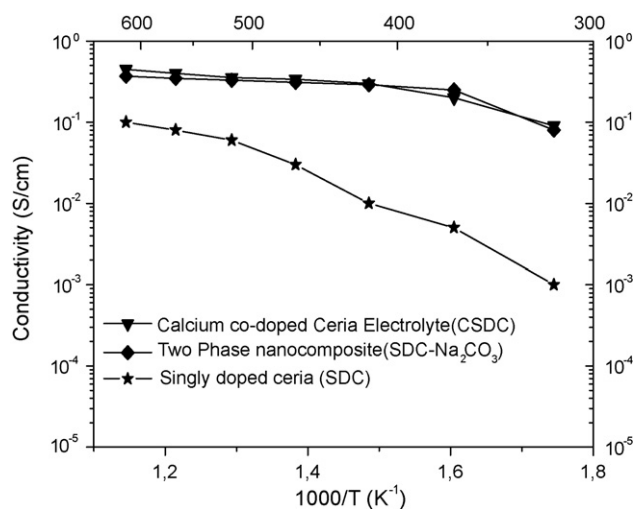
Fig. 4. Conductivity comparisons of different electrolytes with co-doped ceria (CSDC).

Fig. 5. Nyquist plot of the CSDC nanocomposite electrolyte SOFC in air at 550 °C.

3.5. Ionic conductivity

The ionic conductivity of the sintered samples was measured by a two probe AC method. Fig. 4 shows the higher ionic conductivity of 0.1 at 300 °C of the CSDC as compared to the conventional different electrolytes SDC and SDC–Na_2CO_3, respectively. The oxide ion conductivity of ceria is depends on the oxygen vacancies and dopant amount of the materials. To get the optimum conductivity, 20% dopant concentration is necessary [8].

Besides, CaO is very attractive due to a distinctive co-doping effect into the ceria host lattice. It has also ionic-radius compatibility with the host cation. Therefore, the introduction of the co-doped ceria with alkaline earth and rare earth ions can also lead to improve the ionic conductivity and performance in the low-temperature region for SOFC applications. It could also help to overcome the electronic conduction of CeO_2 at in anodic environment and also to enhance the density of solid electrolyte. Furthermore, obtained results highlight the concept of co-doping as an effective tool in designing newer compositions with improved properties.

The role of the Na_2CO_3 in the composite electrolyte is to create a second phase as a core–shell as reported before in our work [10,11]. This may form a large interface region for ion conduction paths between the SDC and carbonate at elevated temperatures so that to enhance greatly the material conductivity, e.g. from doped ceria, 10^{-2} S cm^{-1} to 0.1 S cm^{-1} in the composite with Na_2CO_3 at 600 °C [10,11]. This interface has, in principle, no bulk structural limit for the creation of high concentration of mobile ions, and can thus be greatly disordered. This implies that the interfaces have the capacity to contain higher mobile ion concentration than that of the bulk. The electric field distribution in the interfaces between two phases is a key to realize the interfacial superionic conduction, allowing ions to move on particle's surfaces or interfaces by high conductivity pathways.

The higher conductivity of the prepared composite materials is also due to an amorphous Na_2CO_3 shell at lower temperature. It can protect the active surface of SDC and interfaces in nanoscale to enhance the nano-material stability as well as further promote the oxygen ion transportation through the interfacial mechanism [7–11].

3.6. AC impedance

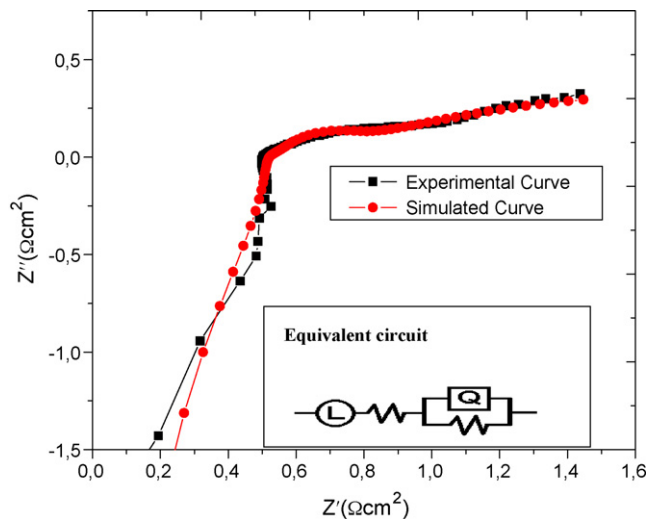The Nyquist plot of the CSDC cell was measured in air at 550 °C under open-circuit conditions. It was observed a typical spectrum with two arcs [23,24]. In Fig. 5 the red line is simulated impedance, while the black line gives experimental values and the inset is the equivalent circuit. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.) The semi-circle observed at high frequencies (1 MHz) is that for ionically conducting material [23,24]. It has been modeled with an equivalent LRQ circuit (L: inductance, R: resistance and Q: the constant phase element, is an ideal capacitance) in series. The inductance L may be as a result of the stainless tube of the measurement device. In nanoscale materials, the difference between bulk and grain boundaries is likely to be smaller and the resultant impedance spectrum may be modeled using a single semi-circle [23,24].

4. Conclusion

Co-doped ceria CSDC electrolyte with Na_2CO_3 as a second phase to form the composite is suitable for preparing a dense electrolyte with controlled composition and modified properties, especially on the particle surface properties. This gives a promising electrolyte for a LTSOFC that will highly improve the SOFC performances at low temperatures. Co-doping can improve the ceria particle properties and create useful functionality on particle surfaces in the composites. The performance of the cell was obtained at lower temperature of 350 °C was 200 mW cm^{-2}, which is the time so high performance has been reported at such temperatures. This performance may result from co-doping and modification of the particle surfaces to give high interfacial functionality at low temperatures. There is good agreement between the XRD, SEM and TEM results to indicate a nanoparticle size range of 5–20 nm. Therefore, the co-doped approach may be a good solution for improving the conductivity and performance of these electrolyte materials for LTSOFCs.

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