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Processing temperature tuned interfacial microstructure and protonic and oxide ionic conductivities of well-sintered $Sm_{0.2}Ce_{0.8}O_{1.9}$- Na_2CO_3 nanocomposite electrolytes for intermediate temperature solid oxide fuel cells

Chuanming Li, Yanwei Zeng*, Zhentao Wang, Zhupeng Ye, Yuan Zhang

State Key Laboratory of Materials-oriented Chemical Engineering, College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, PR China

HIGHLIGHTS

- Well-sintered SDC-NC nanocomposite electrolytes were prepared and studied.
- Interfacial electrical conductivities can be controlled by prefiring temperature.
- Interfacial phase may be identified and quantified by Raman spectroscopy.

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ABSTRACT

Well-sintered SDC-NC ($Sm_{0.2}Ce_{0.8}O_{1.9}$-Na_2CO_3) nanocomposites have been prepared through a rare-earth/sodium complex carbonate precipitation, powder prefirings at the temperatures 400, 500 and 600 °C and sintering at 800 °C. Their sintering performances, phase components and microstructures have been characterized by Archimedean method, XRD and FESEM techniques. In particular, the influence of the interfacial interactions between the phases of SDC and NC on the microstructures and electrical conductivities of SDC-NC nanocomposites have been investigated by AC impedance and Raman spectroscopies. It has been found that on the basis of the fitting analysis of AC impedance data, the oxide ionic and protonic conductivities of interfacial and non-interfacial phases in the SDC-NC nanocomposites are found to be strongly dependent upon their prefiring temperatures with the sample of SN-600 showing the highest values of 73.2/33.7 and 51.1/105.4 μS/cm at 300 °C, respectively. The single cell based on the electrolyte of SN-600 presents an OCV of 0.992 V and peak power density of 421 mW/cm^2 at 550 °C. The interfacial interactions between the phases of SDC and NC inside SDC-NC nanocomposites are considered responsible for their differences in microstructure and electrical conductivity.

1. Introduction

Over the past years, a new category of nanocomposite electrolytes composed of ceria-based oxides and alkaline metal carbonates have been extensively investigated as prospective electrolytes potentially applied to the intermediate temperature SOFCs (IT-SOFCs) [1–7]. Compared with single phase oxide electrolytes, for instance, SDC and YSZ, these nanocomposite electrolytes were found to exhibit great advantages, such as suppressed electronic conductivity in reducing atmospheres and concurrent conduction of protons and oxygen ions with high exploitable electrical conductivities, which allow the thereby developed cells to achieve excellent output performance in the temperatures range from 500 to 600 °C [8–15]. It was ever reported by Ma et al. that a single cell with SDC-Na_2CO_3 nanocomposite electrolyte provided a steady power output of 620 mW/cm^2 over 12 h [16]. X. D. Wang et al. also reported a higher power density of 800 mW/cm^2 at 550 °C by using same materials [17]. In addition, R. Raza et al. announced that using

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* Corresponding author. State Key Laboratory of Materials-oriented Chemical Engineering, School of Materials Science and Engineering, Nanjing Tech University, 5# New Model Road, Nanjing 210009, PR China.
E-mail addresses: stephen_zeng@163.com, stephen_zeng@njtech.edu.cn (Y. Zeng).

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Na_2CO_3 instead of Li/Na-carbonate can greatly improve the ionic transport performance and then boost the cells to output a peak power density of as high as 1150 mW/cm^2 at 500 °C [18]. Recently, A. Rafique et al. reported the research work on the single cells with Sr/Sm co-doped ceria-Na_2CO_3 nanocomposites, which could supply a power density of 900 mW/cm^2 at 550 °C [19].

To understand the high exploitable electrical conductivities of SDC-carbonate nanocomposite electrolytes, considerable research efforts have been committed since the nanocomposite electrolytes of this kind started to receive attention. C. M. Lapa et al. ever used an AC impedance spectroscopy to examine the ionic conductions in SDC-NC nanocomposites and claimed that the conductivities of oxygen ions at 500 °C could reach 0.79 mS/cm on a SDC-30 wt%NC nanocomposite [20]. A. Maheshwari et al. investigated the conducting behavior of oxide ions in CDC-NC nanocomposites by AC impedance spectroscopy and the results showed that the oxide ionic conductivity is about 0.28 mS/cm at 600 °C [21]. In addition, R. Raza et al. studied the conductivities of oxide ions and protons in CSDC-Na_2CO_3 nanocomposites in air and H_2, respectively, by AC impedance spectroscopy and suggested that the co-doping effect that could bring about the increase in oxygen vacancies near the interface between ceria and carbonate facilitates the migrations of oxide ions and protons [22]. More interestingly, X. D. Wang et al. employed a four-probe DC technique to measure the protonic and oxide ionic conductivities of SDC-NC nanocomposites and declared that the oxide ionic conductivity is about 5 mS/cm at 600 °C, while the protonic ones can reach as high as 60 mS/cm thanks to the strong interfacial interactions between the phases of SDC and NC, which is expect to set up a quick path for the migration of protons [23]. In addition, with emphasis on the interface property across the phases of SDC and carbonates, several comprehensive investigations have been reported. J. B. Huang et al. ever studied the SDC-Li/Na-carbonate nanocomposites with various volume fractions of carbonate by means of IR spectroscopy and found that the two bands for the bi-dentate carbonate around 864 cm^{-1} and 1450 cm^{-1} obviously split into two new peaks centered at 883.3 and 860.2 cm^{-1} as well as 1504.4 and 1434.9 cm^{-1}, respectively [24]. S. L. Yin et al. reported the distinctive changes in Raman spectra of SDC-Na_2CO_3 nanocomposites and declared that the interfacial interactions between the phases of SDC and Na_2CO_3 are so strong as to cause the symmetrical vibration mode of carbonate ions to shift by 15 cm^{-1} in the Raman spectrum in comparison with that in crystalline Na_2CO_3 [25]. Also, similar experimental phenomena were observed by A. Uthayakumar [26].

However, most of the SDC-carbonate nanocomposites reported in literature [27,28] should have fairly low relative densities because they were often prepared by using a light-sintering technology, regardless of their good performance measured on the test cells. It has become a great concern since such a less-densified electrolyte would gradually deteriorate in electrical performance due to possible changes in phase components and microstructures during a long term operation of fuel cells. Up to date, nevertheless, some research work, although not much, in this regard has been reported. Y. F. Jing et al. ever prepared SDC-Li/Na-carbonate nanocomposites with a density higher than 95% of the theoretical value by spark plasma sintering (SPS) method and claimed that the ionic conductivity of SDC-Li/Na carbonate nanocomposites treated with SPS was remarkably enhanced due to the improvement of microstructures [29]. Additionally, through optimizing the synthesis of SDC-carbonate nanocomposite powder and prolonging the sintering time, S. A. Muhammed et al. successfully prepared the SDC-Li/Na-carbonate nanocomposites with a relative density of 97% and suggested that the single cell based on such highly densified SDC-Li/Na-carbonate nanocomposites demonstrated an enhancement of 279% in power density, in contrary to the sample with a relative density of ~85%, and of 4% in open circuit voltage at 650 °C, respectively [30]. Evidently, such an increase in relative density of SDC-carbonate nanocomposites may be favorable for the improvement in their electrical performance. However, as a matter of fact, the enhanced thermal treatments of SDC-carbonate nanocomposites for higher relative density would inevitably lead to remarkable changes in microstructures and then significantly affect their electrical properties. Thus, more efforts are expected to be committed to the densification study of SDC-NC nanocomposites with emphasis on the changes in their microstructures and properties, which are taking place during the preparation process at elevated temperatures.

In this paper, we report our latest work on the SDC-NC nanocomposites with high density and well-controlled microstructure. On the basis of the phase identification, microstructural characterization and, especially, the analysis of AC impedance spectra, as a useful probe into the interface between the phases of crystalline SDC and amorphous NC, the relationships between the prefiring treatments of SDC-NC nanocomposites and their microstructures and electrical conductive behaviors have been systematically investigated. It is believed to be helpful for deeper exploration and further improvement of high performance SDC-NC nanocomposites.

2. Experimental procedure

2.1. Synthesis and preparation of samples

At first, SDC-NC nanocomposite powders were synthesized and prepared by a rare earth nitrate/sodium complex carbonate precipitation method and subsequent prefiring treatment. Stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ were dissolved in deionized water to form a 0.5 M metal ion aqueous solution. Then, according to the CO_3^{2-}/metal ion molar ratio of 2:1, 0.5 M Na_2CO_3 aqueous solution was added into the solution at a rate of 10 mL/min under vigorous stirring. Afterwards, the white precipitate of complex carbonate $Na[Ce,Sm](CO_3)_2$ [25] was separated through a vacuum filtration and washed three times with deionized water, followed by drying in an oven at 80 °C. It was then prefired at 400, 500 and 600 °C for 2 h to obtain the raw SDC-NC nanocomposite powders, which were subsequently ground in an agate mortar for 2, 4, 6 and 8 h with alcohol as a medium to determine their appropriate grinding times for achieving well-dispersed SDC-NC nanocomposite powders.

To prepare the SDC-NC nanocomposite samples, the well-dispersed SDC-NC nanocomposite powders were pressed at 300 MPa for 2min into discs with dimensions $\phi 12 \times 1$ mm. After sintered at 800 °C for 5 h, the SDC-NC nanocomposite samples were denoted as SN-400, SN-500 and SN-600 according to their prefiring temperatures, respectively.

To fabricate the anode supported single cells for performance test, 0.3 g anode material and 0.1 g well-dispersed SDC-NC nanocomposite powders were carefully fed into the die cavity in sequence and then pressed at 300 MPa for 2 min into $\phi 12$ mm pellets. The anode material was a powder mixture of 40 wt% NiO and 60 wt% SDC-NC nanocomposite, which was prefired at 600 °C and well dispersed by grinding. After sintered at 800 °C for 5 h, the pellets were painted with a cathode slurry, composed of 40 wt% $LiNiO_2$ and 60 wt% SDC-NC nanocomposite (the same as above), dispersed in terpineol with ethyl cellulose as organic medium, on the side of electrolyte to form cathode layer before they were subject to another thermal treatment at 700 °C for 1 h. Finally, the anode and cathode sides were coated with Ag-paste as current collectors to form the single cells with an active area of 0.52 cm^2.