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Theoretical description on the interface-enhanced conductivity of SDC/LiNa-carbonate composite electrolytes

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ABSTRACT

SDC ($Ce_{0.8}Sm_{0.2}O_{1.9}$)/LiNa-carbonates composite electrolytes for intermediate temperature SOFCs have been prepared by infiltrating molten $LiNaCO_3$ into the pre-sintered porous SDC pellets with distinctive porosity structures. XRD, SEM and Mercury Porosimetry were employed to structurally characterize the SDC pellets and the composite electrolytes, while AC impedance spectroscopy was used to measure their ionic conductivities. It has been found that the conductivities of SDC-carbonate composites are strongly affected by the porosity structure parameters of SDC pellets including the tortuosity of pore channels and their specific interface area, depending on the dimensions of SDC grains and the built-up pores. According to the ideas of charge transport in tortuous pore channels, a theoretical description on the interface-enhanced conductivities of SDC-carbonates composites has been achieved. It agrees well with the experimental data and reveals that the conductivity of composite electrolytes may be linearly increased with the specific SDC-carbonate interface area, but inversely proportional to the square of tortuosity as well.

1. Introduction

Over the past years, extensive efforts have been committed to the investigations of doped ceria-based electrolytes for their potential application in the intermediate temperature SOFCs [1,2]. The ceria doped with aliovalent cations often shows high oxide ionic conductivities despite the emergence of small electronic conductance sometimes. In particulars, the composite electrolytes of Sm-doped ceria (SDC) and LiNa-carbonates possess a suppressed electronic conduction in reducing atmosphere and a greatly enhanced ionic conductivity (0.01–1 S cm^{-1}), which is one to two orders of the magnitude higher than that of single phase SDC [3,4]. Although researches were also extended to the composites of doped ceria with other inorganic salts, SDC/carbonate composites have been attracting more attention for their excellent single cell performance [5].

However, on the other hand, intensive studies on the conductance enhancements involved in doped-ceria/carbonate composites have witnessed a sluggish progress due to the complicated interface microstructures between the two constituent phases though a simple preparation method is usually adopted to fabricate the materials, which includes the powder mixing of doped-ceria and carbonates, pressing and then sintering at the temperatures from 600 °C to 800 °C for 1–2 h [6,7].

In this paper, we report the latest work on the interface-enhanced conductance of SDC/LiNa-carbonate composite electrolytes with distinctive interface microstructures, which were fabricated by infiltrating the molten carbonate into pre-sintered porous SDC pellets with different porosity structures. The conducting behavior of SDC-carbonate composites have been measured and theoretically related to the porosity structure parameters of SDC pellets with the help of ideas of charge transport in tortuous pore channels.

2. Experimental procedure

Preparation of SDC-carbonate composite electrolytes: Two methods were used to prepare porous SDC pellets with nearly equal porosities [8,9]. Using the complex-gel auto-combustion process [10], ultrafine SDC powder was first synthesized and then turned into porous SDC pellets by sintering at 1250 °C for 4 h. The as-obtained porous SDC pellets, designated as SDC-1, were featured with fine grains and small pore sizes. By the second method, the similar process was used to prepare the mixed powders of SDC and NiO and then have the SDC/NiO composite pellets sintered at 1500 °C for 4 h. After that, the SDC/NiO pellets were subjected to a reduction treatment in hydrogen at 500 °C for 4 h and then immerged in a dilute nitric acid for 30 h to completely remove the nickel phase. The as-obtained porous SDC pellets, designated as SDC-2, show relatively coarse grains and large pore sizes. Subsequently, the SDC-1 and SDC-2 pellets were immersed in a molten

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salt of eutectic $LiNaCO_3$ at 550 °C for 10 h to impregnate them with the molten salt and finally obtain the SDC/LiNa-carbonate composites, designated as SDC/LN-1 and SDC/LN-2, respectively.

Analysis and characterization: X-ray Diffractometer (XRD, ARL X′TRA), with CuKa radiation ($\lambda = 1.5406$ Å) and a tube power of 40 kV/35 mA, and Scanning Electron Microscope (SEM, JSM-5900, Hitachi S-3600N) were used for the phase identification and microstructural characterization of the samples. The porosities and pore size distributions of the porous SDC pellets were measured by Mercury Porosimeter (Poremaster GT-60). The ionic conductivities of the composite electrolytes were measured at the temperatures from 500 to 650 °C on AC impedance spectroscopy (Solartron 1260 and 1286) with an alternating signal of 10 mV in the frequency range from 0.1 Hz to 1 MHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of samples SDC/LN-1 and SDC/LN-2. It can be seen that both samples demonstrate the same diffraction patterns, which can be indexed to the cubic fluorite-type structure of CeO2 (JCPDS 34-0394), and no reflections by LiNa-carbonate and other impurity phases can be observed. It is the same as usually observed [11], suggesting that the carbonates in SDC-carbonate composites may exist in an amorphous state.

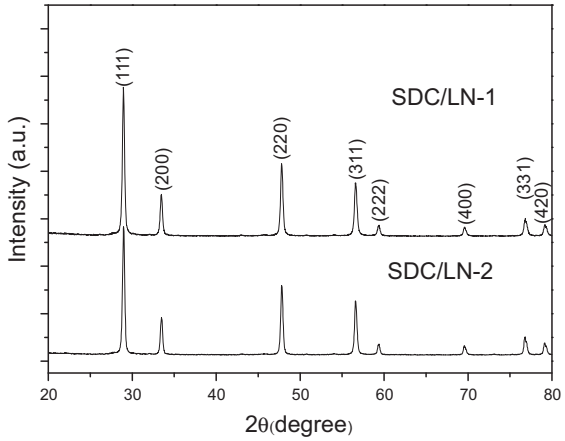

Fig. 1. XRD patterns of SDC-carbonate composites SDC/LN-1 and SDC/LN-2.

In Fig. 2, the SEM images for the samples SDC-1 and SDC-2 clearly show their distinctive microstructures, characterized with the uniform crystal grains around 0.50 μm in size for SDC-1 and around 1.28 μm for SDC-2. Fig. 2c and d gives the cross-section distributions of pores for the two samples, which were derived by image analysis with the help of Photoshop 8.0 from their SEM images, and the cross-section porosity of SDC-1 and SDC-2 are thereby estimated at 11.13% and 30.75%, respectively.

Fig. 3 shows the pore size distributions for the samples SDC-1 and SDC-2. It can be seen that the two porous SDC pellets possess similar mono-modal pore size distributions, close values in volume porosity, but quite different average pore sizes. For the SDC-1, the average pore size and volume porosity are 198 nm and 35.24%, while they are 400 nm and 36.72% for the SDC-2, respectively.

In Fig. 4 are shown the typical AC impedance spectra for the composite samples SDC/LN-1 and SDC/LN-2 at 550 °C and 650 °C in air. Their ionic conductivities at the temperatures from 550 °C to 650 °C are given in Fig. 5, which were obtained by fitting the impedance data with the equivalent circuit inserted in Fig. 4 and the calculations according to the sample's geometry [12].

It is interesting to note that the composite electrolyte SDC/LN-2, which possesses coarse SDC grains and relatively thick pore channels filled with carbonate, shows higher ionic conductivity than the SDC/LN-1 composed of fine grains and thin channels over the whole temperature range under study, though they both have nearly the same volumetric porosity around 36%. Moreover, their conductivity ratio σ_c/σ_f appears to not change with the temperature, $\sigma_c/\sigma_f \approx 2.9804$, suggesting that it is solely determined by the composite microstructures.

To reach a good understanding of these results, we think that the total conductivity should include the contribution from the interface between SDC and carbonate phase in this 2-phased composite electrolyte in addition to the mixed conductivity by

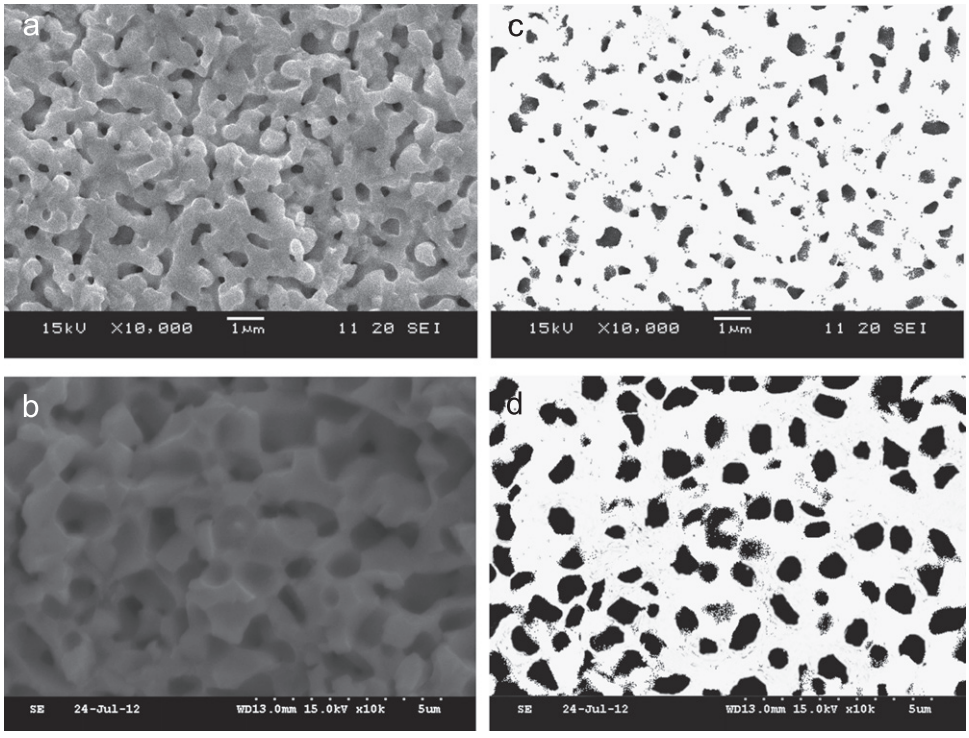

Fig. 2. SEM images of porous SDC samples: SDC-1 (a) and SDC-2 (b), and their cross-section distributions of pores (c) and (d) in sequence.