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Preparation and characterization of GDC-Li_2SO_4/Li_2CO_3 nanocomposite electrolytes for applications in intermediate solid oxide fuel cells

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ABSTRACT

$Gd_{0.1}Ce_{0.9}O_{1.95}$/Li_2CO_3-Li_2SO_4 (GDC/LCS) nanocomposite electrolytes were prepared through nano-powders mixing, prefiring and sintering operations. The phase components and microstructures of the as-prepared nanocomposite were characterized by XRD, FESEM, TG-DSC and IR spectroscopy. AC impedance spectroscopy and DC polarization method were utilized to measure their electrical conductivities under different conditions. It has been found that the GDC/LCS nanocomposite have a very homogeneous microstructure, where the LCS is mostly in amorphous state due to the strong interfacial interactions between the GDC and LCS. In addition, their overall electrical conductivity was found to increase with temperature in air, featured with a sharp activation energy change from 1.01 to 0.30 eV around 520 °C, and reach 108.7 mS/cm at 600 °C, while their protonic and oxide ionic conductivities were 16 mS/cm in H_2 and 5 mS/cm in air at the same temperature, respectively. The single cell built up of the GDC/LCS nanocomposite showed an open-circuit voltage of 1.01 V and peak power density of 272 mW/cm^2 at 600 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted considerable attention because of their high conversion efficiency, environmental friendliness and wide fuel flexibility [1]. Traditional SOFCs based on yttrium-stabilized ZrO_2 electrolytes have excellent electrical properties at high temperatures (~ 1000 °C) [2,3]. However, high operating temperature leads to lots of problems, such as high cost, thermal instability of electrode and electrolyte materials, and so on [4,5]. Therefore, to reduce the operating temperature of SOFCs, research efforts have been committed to explore novel electrolyte materials with acceptable electrical performances in the intermediate temperature range (IT, from 600 to 800 °C) and the low temperature range (LT, < 600 °C).

Over the years, the composite electrolytes composed of ceria-based oxides and carbonates or sulfates have been extensively investigated for the potential applications in the IT-SOFCs, thanks to their high protonic conductivity available in the intermediate temperatures range [6,7]. Y.C. Zhao et al. ever used an electrochemical pumping method to study the ionic conductions in the SDC-30 wt%$LiNaCO_3$ composite electrolyte and found that its effective conductivities of protons and oxygen ions at 650 °C could reach 22 mS/cm and 71 mS/cm, respectively [8]. L.D. Fan et al. investigated the conducting behavior of protons and oxide ions in SDC-$LiNaCO_3$ composites using DC polarization technique and found that their protonic conductivity was about 40 mS/cm while the oxide ionic one was 22 mS/cm at 600 °C [9]. To understand the enhancements in protonic/oxide ionic conductivities in SDC-LNC composite electrolytes, many efforts have been focused on exploration of the interfacial microstructure between doped ceria and Li/Na-carbonates. J.B. Huang et al. utilized IR spectroscopy to investigate the interfacial interaction between the SDC and carbonate phases and found that the interfacial interaction may cause the bidentate carbonate IR bands at 864 and 1450 cm^{-1} to split as the carbonate content was increased. This finding revealed the existence of interfacial interaction between the phases of SDC and carbonate. Moreover, they speculated that this interaction could cause the cationic vacancies to aggregate in the space-charge zones between the SDC and carbonate. The resulting electric field would speed up the motion of relevant defects with increased temperature [10]. In addition, L. Zhang et al. discovered the interfacial interaction between the $Ce_{0.8}Gd_{0.05}Y_{0.15}O_{1.9}$ (GYDC) and carbonate in view of the fact that the IR band at 1446 cm^{-1} that belongs to carbonate splits into two bands at 1449 and 1503 cm^{-1} for the GYDC/carbonate composite fired

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at 680 °C, indicating that certain interactions occurred between the GYDC and carbonate [11]. Evidently, the strong interfacial interactions between the phases of doped-ceria and carbonates may strongly enhance the protonic and oxide ionic conductivities of doped ceria/ carbonate composite electrolytes.

As regards the composite electrolytes of metal oxides and sulfates, many researches have also been reported. B. Zhu et al. ever investigated the protonic conductivity of Li_2SO_4 phase by DC polarization method and declared it may reach as high as 0.043 S/cm at 600 °C [12]. N.F. Uvarov ever prepared a Li_2SO_4/Al_2O_3 composite electrolyte and suggested that an ionic conductivity of 0.018 S/cm can be observed for the composite electrolyte with a mole fraction of 50% Li_2SO_4 [13]. Some researches were reported on the single cells with the composite electrolytes of sulfates and metal oxides. B. Heed et al. reported that a single cell with pure Li_2SO_4 as electrolyte could give a peak power density of 130 mW/cm^2 at 600 °C [14]. B. Zhu et al. constructed a single cell with the Li_2SO_4–Al_2O_3 composite electrolyte and achieved a current density of ~ 100 mA/cm^2 at a terminal voltage of 0.4 V [15]. W.M. Lv et al. prepared a single cell with SDC–20 wt%$LiNaSO_4$ composite as the electrolyte and reached an output power density of 390 mW/cm^2 at 600 °C [16].

Up to date, however, most of the research efforts were mainly focused on either oxide/carbonate or oxide/sulfate and few researches were reported on the ternary composite electrolytes of oxide/carbonate/sulfate though significant progresses have been achieved in the both binary composite electrolytes. As a matter of fact, carbonate and sulfate possess different chemical properties and they are expected to show some synergetic contributions to the electrical performance of a composite electrolyte containing both carbonate and sulfate.

In this paper, we report our latest work on the preparation of nanocomposite electrolytes composed of GDC nanoparticles and binary eutectic salt Li_2CO_3/Li_2SO_4 (LCS). The phase components and microstructures of the composite electrolytes were characterized by XRD, FESEM, TG-DSC and FTIR spectroscopy. With the help of AC impedance spectroscopy and DC polarization method, their total electrical conductivities in air and, especially, the protonic and oxide ionic conductivities in H_2 and air were measured, respectively, at different temperatures, with the results being discussed in details to show their characteristics in electrical conducting behavior. In addition, a single cell based on the as-prepared GDC/LCS nanocomposite electrolyte was constructed and evaluated.

2. Experimental

2.1. Synthesis and preparation of samples

GDC nanocrystallites were prepared via a co-precipitation method. In a typical process, a 0.2 M aqueous solution was formed by dissolving $Gd(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_4 \cdot 6H_2O$ in deionized water at a Gd:Ce molar ratio of 1:9. Then, ammonia solution, as a precipitant, was added into the solution under vigorous stirring until a pH level of 9.5 was reached. After 4 h of steady stirring, a brown precipitate was obtained by separating via vacuum filtration and washing thrice with deionized water and alcohol. Then, the precipitate was dried at 80 °C for 12 h and calcined at 600 °C for 2 h to obtain GDC nanoparticles.

To obtain LCS powders, Li_2CO_3 and Li_2SO_4 were weighed based on the eutectic molar ratio of 61.1:38.9 [17,18]. After grinding together for 2 h in an agate mortar with alcohol as a medium, the mixture was heated at 650 °C for 0.5 h and subsequently cooled to room temperature to achieve a homogenous LCS phase.

The as-prepared GDC powder and LCS were ground together at a volume fraction of 50 vol% in an agate mortar for 3 h. The ground and mixed powders were then prefired at 650 °C for 0.5 h. After regrinding, the homogenous GDC/LCS nanocomposite powders were pressed at 300 MPa into pellets with dimensions of ϕ 12 mm×1 mm. Then, the pellets were sintered at 650 °C for 0.5 h to achieve the GDC/LCS nanocomposite electrolyte. For comparison, the pure GDC nanocomposite particles were also pressed at 300 MPa and then sintering at 1500 °C for 5 h to obtain GDC electrolyte.

To fabricate single cells for output performance measurements, 0.3, 0.1, and 0.1 g anode, GDC/LCS nanocomposite powders, and cathode materials, respectively, were successively added into a stainless steel mold and then pressed at 300 MPa into pellets with dimensions of ϕ 12 mm×0.8 mm. After sintering at 650 °C for 30 min, both the anode and cathode sides of the pellets were coated with Ag paste as current collectors to form single cells with an active area of 0.52 cm^2. The anodic and cathodic materials were prepared by mixing $NiO/LiNiO_2$ and GDC/LCS nanocomposite powders at weight ratios of 2:3, respectively [19,20]. For the sake of comparison, the anode supported single cell based on pure GDC were prepared [21]. The anode and GDC nanopowders weighting about 0.3 and 0.13 g were successively added into a stainless steel mold and then pressed at 300 MPa into pellets. After sintering at 1500 °C for 5 h, appropriate amount of cathode slurry was coated and then heated at 1100 °C for 2 h to obtain single cell sample with similar thickness of anode, electrolyte and cathode layer with those of single cell based on GDC/LCS nanocomposite electrolyte. The Ag paste was used as current collector. The cathode slurry was fabricated by dispersing the cathode materials composed of 40 wt% $La_{0.8}Sr_{0.2}MnO_3$ (LSM) and 60 wt% GDC powders in the solution of terpineol and ethyl cellulose.

2.2. Characterization and electrical measurements

XRD patterns were obtained via X-ray diffractometry (*D*max/RB) with Cu K_α radiation (λ=1.5418 Å) at a 2θ scan range from 10° to 80° and a rate of 5° min^{-1}. The IR spectra of LCS and the GDC/LCS composite were recorded on an FTIR spectrometer (Nexus 670) over the wavelength range of 700–2400 cm^{-1}. The morphology and microstructural features of the GDC/LCS nanocomposite electrolyte were observed by FESEM (Hitachi S-4800). To investigate the thermal stability and identify possible phase changes within the GDC/LCS nanocomposite, thermal analyses were performed on a TG–DSC apparatus (STA 449 C, Netzsch, Germany) in the temperature range of 30–600 °C at a heating rate of 10 °C/min under air flow.

For the measurement of electrical conductivities, pellet samples were coated on both sides with silver as current collector. Total conductivities were measured by AC impedance spectroscopy by using an electrochemical workstation (Solartron SI-1260) with an alternating signal of 5 mV in a frequency range of 0.1–1 MHz and in the temperature range of 400–600 °C. Protonic and oxygen ionic conductivities were measured with the DC polarization method in hydrogen and air atmospheres, respectively, at a gas flow of 20 mL/min. Current–time curves were recorded under a constant DC voltage of 20 mV. As to the output performance tests of single cells, the measurements were carried out at 600 °C in the atmospheres of air on the side of cathode and H_2 with a flow rate of 50 mL/min on the side of anode. The I-V curves were recorded on the electrochemical station (Solartron SI-1260).

3. Results and discussion

3.1. Phase composition and microstructures

Fig. 1 shows the XRD pattern of the GDC/LCS nanocomposite electrolyte, together with those of single phase GDC and LCS for comparison. It can be seen that no alien diffraction peaks can be identified other than those from GDC and LCS phase. However, the intensity of two diffraction peaks belonged to crystalline LCS phase at approximately 36.8° and 42.9° are so weak that it is believed that the LCS phase in GDC/LCS nanocomposites is mostly in amorphous state. This result suggests that the LCS phase in GDC/LCS nanocomposites is strongly prohibited from crystallization due to the strong interfacial