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Development of novel low-temperature SOFCs with co-ionic conducting SDC-carbonate composite electrolytes

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Abstract

A series of ceria-based composite materials consisting of samaria doped ceria (SDC) and binary carbonates(Li_2CO_3–Na_2CO_3) were examined as functional electrolytes for low-temperature solid oxide fuel cells (SOFCs). DTA and SEM techniques were applied to characterize the phase- and micro-structural properties of the composite materials. Conductivity measurements were carried on the composite electrolytes with a.c. impedance in air. A transition of ionic conductivity with temperature was occurred among all samples with different carbonate content, which related to the interface phase. Single cells based on the composite electrolytes, NiO as anode and lithiated NiO as cathode, were fabricated by a simple dry-pressing process and tested at 400–600 °C. The maximum output power at 600 °C increased with the carbonate content in the composite electrolytes, and reached the maximum at 25 wt.%, then decreased. Similar trend has also shown at 500 °C, but the maximum was obtained at 20wt.%. The best performances of 1085 mW cm^{-2} at 600 °C and 690 mW cm^{-2} at 500 °C were achieved for the composite electrolytes containing 25 and 20 wt.% carbonates, respectively. During fuel cell operation, it found that the SDC-carbonate composites are co-ionic (O^{2-}/H^+) conductors. At lower carbonate contents, both oxide–ion and proton conductions were significant, when the content increased to 20–35 wt.%, proton conduction dominated. The detailed conduction mechanism in these composites needs further investigation.

Keywords: Samaria doped ceria (SDC); Carbonate; Composite electrolyte; Co-ionic; Solid oxide fuel cells (SOFCs)

1. Introduction

Solid oxide fuel cells (SOFCs) are considered as one of the most promising power-generation technologies due to their high energy conversion efficiency, fuel flexibility and reduced pollution [1]. However, the current state-of-the-art SOFCs suffer from a variety of challenges for commercialization because of their high operating temperature (about 1000 °C). To develop market competitive SOFCs, considerable research efforts are continuing to decrease cell operating temperature below 600 °C [2]. At such low temperatures, it is possible to use stainless steels for the interconnects and balance-of-plant, resulting in a drastic reduction of manufacturing cost. Low-temperature operation also implies reduced operating cost, increased durability, and quick startup, offering the potential for mobile application.

A key issue to develop low-temperature SOFCs is the use of a highly ionic conducting electrolyte. Recently, extensive progress has been made in the study of low-temperature SOFCs based on a thin-film electrolyte of ceria-based oxide, notably Gd^{3+} or Sm^{3+}-doped CeO_2 (GDC or SDC) [3–7]. However, ceria-based oxides in anodic environment show a mixed ionic-electronic conducting behavior, resulting from the reduction of Ce^{4+} to Ce^{3+}. The electronic conduction poses a significant decrease of the cell voltage, power output and efficiency, as well as poor mechanical property, which has become a barrier to scale up and construct practical devices.

To overcome the disadvantages caused by electronic conduction, functional composite materials based on

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doped ceria and various salts have been developed as electrolytes for SOFCs [8–12]. Among them, ceria-carbonate composite is the most typical composite electrolyte with which the cells have been reported to achieve the best performances. These materials are found to be co-ionic (O^{2-}/H^+) conductors with an ionic conductivity of 0.1 Scm^{-1} below 600 °C. Therefore, they are very promising in low-temperature SOFCs application. Most researches are focused on the special composition of ceria-carbonate composite, e.g. SDC-20 wt.% ($2Li_2CO_3$: $1Na_2CO_3$), but the effects of composition on the material properties and fuel cell performances are seldom studied. This study thus aims to explore new composite electrolytes by examining the effects of carbonate content on the composite conductivities and corresponding fuel cell performances.

2. Experimental

Samaria doped ceria (SDC, $Ce_{0.8}Sm_{0.2}O_{1.9}$) powders were firstly synthesized by oxalate co-precipitation method as reported previously [9]. Then the SDC powders were mixed with various contents (10–35 wt.%) of binary carbonates (53 mol.% Li_2CO_3:47 mol.% Na_2CO_3). The mixtures was ground thoroughly, and then heat-treated at 680 °C in air for 40 min. The resultants were ground again for use.

The phase transition behaviors of the composites were investigated by DTA (STA 409) with a heating rate of 10 °C/min over 200–800 °C temperature range under air atmosphere. The morphology of the composite powders was characterized by SEM (JSM-6301F).

For conductivity measurement, the composite powders were cold pressed at 300 MPa into cylindrical pellets (13 mm in diameter and ~1 mm in thickness) using a uniaxial die-press. The green pellets were then sintered at 600 °C for 1 h. It has found that when the carbonate content amounted to or exceeded 40 wt.%, the composite pellets were distorted or unshaped after sintered, so the carbonate content should be less than 40 wt.% in order to keep the composite electrolytes at solid state during fuel cell operation. Silver electrodes were prepared by painting silver paste onto both sides of the pellets, and heated at 600 °C for 40 min. Electrical conductivity of the pellet samples was then measured in air by a.c. impedance spectroscopy at 400–625 °C. The measurements were conducted using a PerkinElmer 5210 frequency response analyzer combined with EG&G PAR potentiostat/galvanostat 263A.

The single cells were fabricated using a dry-pressing process. The composite anode was the mixture of NiO (50 vol.%) and electrolyte (50 vol.%). The cathode powder was composed of lithiated NiO (50 vol.%) mixed with electrolyte (50 vol.%). The anode, electrolyte and cathode were uniaxially pressed into a pellet at a pressure of 300 MPa and then sintered at 600 °C for 30 min in air. The size of the pellets had diameter of 13 mm and thickness of 1.2 mm, including 0.3 mm thick electrolyte. The effective working area of the pellet was 0.785 cm^2. Silver paste was coated afterwards on each electrode surface to improve the electrical contact.

In the measuring procedure, stainless steel was employed as testing holder (see Fig. 1). Before measurement, two pieces of nickel foams were placed on both sides of the holder as current collectors. Then silver glue was applied as the sealant. The single cells were tested between 400 and 600 °C. Hydrogen and air were used as the fuel and the oxidant, respectively. Both gas flow rates were controlled between 40–100 mL/min under 1 atm pressures.

3. Results and discussion

Fig. 1 shows the DTA curves for SDC-(53 mol.% Li_2CO_3:47 mol.% Na_2CO_3) composites of four different compositions, viz. 10, 20, 30, and 35 wt.% binary carbonates. There is only one thermal event in each case, but the position of peak for the composite sample with 10 wt.% binary carbonates (about 613 °C) is differ from those for the other three samples (about 497 °C). The weakly endothermic peak at 613 °C for the sample with 10 wt.% binary carbonates can be attributed to the melting transition of Li_2CO_3, although it slightly deviates from the melting point of the pure Li_2CO_3 (618 °C). While for the other three samples, an intensively endothermic peak at about 497 °C in the DTA curves is related to the melt of the 53 mol.%Li_2CO_3: 47 mol.%Na_2CO_3 eutectic. It can conclude that at lower carbonate content, the binary carbonates were dispersed among the SDC particles and no eutectic was formed after heat-treated, but at higher carbonate content, the binary carbonates trended to aggregate and form eutectic composition. The identity of DTA curves indicates that there is neither a chemical reaction nor any intermediate compound between SDC and Li_2CO_3–Na_2CO_3 binary carbonates.

The scanning electron micrographs for SDC-(53 mol.% Li_2CO_3:47 mol.% Na_2CO_3) composites with carbonate

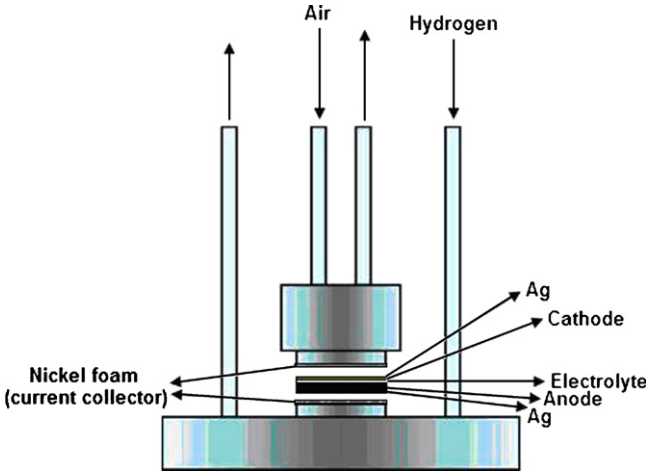

Fig. 1. Schematic of testing holder for fuel cell measurement.