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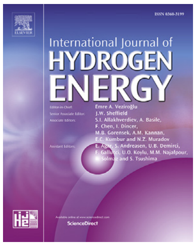

Investigation of layered $Ni_{0.8}Co_{0.15}Al_{0.05}LiO_2$ in electrode for low-temperature solid oxide fuel cells

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ABSTRACT

A symmetrical cell composed of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ electrolyte is constructed with 0.5 mm thickness and $Ni_{0.8}Co_{0.15}Al_{0.05}LiO_2$ (NCAL)-foam Ni composite electrodes. Electrochemical performance of the cell and electrochemical impedance spectra (EIS) are measured using the three-electrode method. The maximum power densities of the cell are 93.6 and 159.7 mW cm^{-2} at 500 and 550 °C, respectively. The polarization resistances of the cathode are 0.393 and 0.729 Ω cm^{-2} at 550 and 500 °C, indicating that NCAL has good ORR activity. HT-XRD results for NCAL do not show phase transitions or any additional new phases at elevated temperatures, indicating that NCAL has a stable phase structure. The surface characteristics of the NCAL powders are studied by XPS and FTIR. The results reveal that Li_2CO_3 and the cation-disordered “NiO-like” phase are formed on the surface of the layered NCAL structure due to prolonged exposure to air and contain a large number of oxygen vacancies. The cation-disordered “NiO-like” phase and Li_2CO_3 composite in the melt and partial melt states in the high temperature region are considered to possess very high ionic conductivity and lower activation energy for oxygen reduction reactions.

Introduction

Large-scale commercialization of solid oxide fuel cells (SOFCs) may be achieved by reducing operating temperatures to the low temperature (LT) range (400–600 °C) [1]. The problems of performance degradation caused by the high operation temperature of SOFC and the high cost of the SOFC system can be solved by reducing the operating temperature [2,3]. However, at low temperatures, the larger polarization resistances associated with the oxygen reduction reaction (ORR) result in a substantial reduction in SOFC performance. It has been reported that the conventional pure electronic conductor LSM cannot meet the needs of low-temperature solid oxide fuel cells (LTSOFC) [4]. Mixed ionic and electronic conducting (MIEC) cathodes, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF), $La_{0.6}Sr_{0.4}CoO_3$ (LSCO), $Sm_{0.5}Sr_{0.5}CoO_3Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), and layered-perovskite oxides $LnBaCo_2O_{5+\delta}$ (LBCO, L = Lanthanide), can extend the oxygen reduction zone from a narrow band along the triple-phase boundary (TPB) to the entire surface of the MIEC due to its higher ionic conductivity [5–13]. It is not easy to use the MIEC electrode to reduce the operating temperature of SOFC below 600 °C. To reduce the

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operating temperature of SOFC to less than 600 °C, considerable effort has been expended to increase the number of active reaction sites located at the TPB [14–16]. Infiltration of fine dispersed particles and connected particles of the cathode lead to an improvement in cell power [17]. It has been reported that the nanoscale composite cathodes can significantly increase the electrode's specific surface area [15,16]. However, at low temperatures, in order to achieve high performance of the cell, a very thin electrolyte film with high fabrication cost is required, indicating that the ORR catalytic activity of the cathode materials used at present is still too poor at low temperature.

Another strategy to improve the cathode performance is to identify a new oxide material with high MIEC performance and good catalytic activity of ORR at low temperature. Lithiated transition-metal oxides are generally used as lithium ion battery materials and usually possess high electronic conductivity; if there is a certain degree of oxygen ion conductivity, it can be used as a potential MIEC cathode material. In recent years, using lithiated transition-metal oxides as cathode materials for SOFC has attracted considerable attention [18–24]. Remarkable electrochemical performance of an SOFC with a lithium-containing oxide cathode has been reported [18–20]. Zhang et al. fabricated a symmetrical SOFC with composition $Li_{0.3}Ni_{0.7}O|Ce_{0.8}Gd_{0.05}Y_{0.15}O_{1.9}|Li_{0.3}Ni_{0.7}O$ by a one-step dry-pressing method, in which peak power density was 503 mW cm^{-2} at 600 °C in H_2 [19]. The Ni-SDC anode-supported SOFC with a $Li_{0.2}Ni_{0.79}Co_{0.2}Zn_{0.01}O_2$/SDC composite cathode shows a peak power density of 0.62 W cm^{-2} in H_2 at 550 °C [18]. Lithium salt-oxide composites have been previously studied as oxygen ion conductors [24]. Lan et al. indicated that the $LiFeO_2$-$LiAlO_2$ composite displays O^{2-}/H^+ mixed conduction under H_2/air fuel cell conditions [25]. Fan et al. studied the $LiNi_{0.8}Co_{0.2}O_2$ (LNCO) cathode on a $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_3$ proton-conducting electrolyte, indicating that LNCO shows good oxygen reduction reaction activity [23].

Recently, $Ni_{0.8}Co_{0.15}Al_{0.05}LiO_2$ (NCAL) and foam Ni composite was used as an electrode to construct several symmetrical SOFCs with different electrolytes, which have achieved good performance at low temperatures [26–29]. However, the ORR mechanism of NCAL has not been thoroughly studied. In this study, we fabricated a $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC) electrolyte-supported symmetrical SOFC with foam Ni-NCAL as an electrode. The high temperature stability and ORR mechanism of NCAL were investigated.

Experimental

GDC powder was synthesized by a sol-gel method. Stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$ (A.R. Xiya Reagent Ltd., Shandong, China) and Gd_2O_3 (A.R. Xiya Reagent Ltd., Shandong, China) were dissolved in diluted HNO_3(A.R. Xiya Reagent Ltd., Shandong, China) and citric acid (A.R. Xiya Reagent Ltd., Shandong, China) was added as the complexant. The molar ratio of metal cations to citric acid was 1:1.5. The solution was evaporated and dried to form dry gel. The GDC powder was obtained by firing the dry gel at 800 °C for 2 h. As-prepared GDC powder was subsequently pressed into pellets by an isostatic pressing method under 200 MPa and sintered at 1550 °C for 5 h in air. The thickness and diameter of the GDC electrolyte were 0.5 mm and 14 mm, respectively. NCAL was purchased from Tianjin Bamo Sci. & Tech. Joint Stock Ltd., China. The NCAL powder and terpineol was mixed into slurry with weight ratio of about 3:1 and coated onto Ni-foam, and then baked in an oven at 80 °C for 20 min. The Ni-foam is reticulated and plays a supporting role and a current collector. The Ni-foam coated with NCAL was then cut into a wafer with a diameter of 13 mm. The as-prepared GDC electrolyte was sandwiched into two pieces of NCAL-coated Ni-foam and assembled into a cell. Pt line was wrapped around the GDC electrolyte as a reference electrode. The symmetrical cell was then fixed in the performance-testing device. H_2 and air were passed into the two sides of the cell as fuel and oxidant, respectively. The effective area of the cell during the performance test was 0.64 cm^2. The flow rate of H_2 and air were both 100 ml min^{-1}. The electrochemical performance of the cell was measured at 550 and 500 °C using a VersaSTAT3 electrochemical system (Princeton Applied Research). The electrochemical impedance spectra (EIS) of the full cell and half-cell were measured between 0.1 Hz and 1 MHz with ac voltage of 10 mV amplitude under an open-circuit condition. The phase structure of the NCAL powder and NCAL-coated Ni-foam were characterized using an X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.154056$ nm; Ultima IV, Rigaku). The temperature-dependent structure evolution of the NCAL powder was also evaluated by a high temperature in situ powder X-ray diffractometer with Cu-Kα radiation (SMART LAB 9 kW, Rigaku). The surface characteristics of the NCAL powder were analysed using X-ray photoelectron spectroscopy (XPS). The XPS spectra were recorded on a Thermo Scientific Escalab 250Xi XPS system with a monochromatic twin anode Al/Mg X-ray source. The binding energies and oxidation states were obtained from high-resolution scans. Micro-structures of the cells were characterized with FE-SEM (FEI Quanta FEG 250). Fourier Transform infrared spectroscopy (FTIR) was used to determine the characteristic peak position of Li_2CO_3 on the surface of NCAL powder.

Results and discussion

Fig. 1 shows the microstructure of the raw NCAL powder and the cross-section SEM images of the cell. As seen from Fig. 1(a), the raw NCAL powder has a spherical shape, and the average particle size is approximately 15 μm. The SEM sample of the cell was prepared by inlaying the single cell using an epoxy resin inlay. The cross-section of the cell sample was polished by diamond solution before SEM characterization. Fig. 1(b) shows the cross section image of the cell. The thickness of the GDC electrolyte is approximately 0.5 mm. As seen from Fig. 1(c), the dark-grey circular particles are NCAL and the silvery white metal is nickel foam. The Ni foam-NCAL electrode shows a porous structure with areas where the Ni-foam and GDC electrolyte are in direct contact. Fig. 1(d) shows a magnified view of the GDC electrolyte, from which one can see that the GDC electrolyte is very dense and has no obvious pores.

Fig. 2(a) shows the schematic diagram of the as-prepared cell performance test. The electrochemical performance of

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