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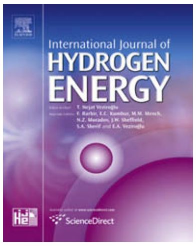

Characterization and evaluation of $La_{0.8}Sr_{0.2}Co_{0.8}Ni_{0.2}O_{3-\delta}$ prepared by a polymer-assisted combustion synthesis as a cathode material for intermediate temperature solid oxide fuel cells

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ABSTRACT

A modified polymer-assisted combustion synthesis method is developed for preparation of $La_{0.8}Sr_{0.2}Co_{0.8}Ni_{0.2}O_{3-\delta}$ (LSCN) nano-sized cathode particles by using organic additives (glucose and acrylamide) and metal nitrates. The effect of the organic additives, pH value of starting solution and calcination temperature on the formation of the LSCN perovskite phase and microstructure of the powders is investigated. Chemical compatibility between the LSCN and Y_2O_3 stabilized ZrO_2 (YSZ) and Gd_2O_3 doped CeO_2 (GDC) is evaluated and electrochemical activity of LSCN cathode is evaluated. The prepared LSCN is chemically compatible with the YSZ only at temperatures below 850 °C. The electrode area specific resistance (ASR) is 0.30 and 0.10 Ω cm^2 at 700 and 750 °C, respectively. These results suggest that such prepared LSCN is a promising alternative cathode material for intermediate temperature SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) are considered as one of the most promising energy conversion devices that exhibit advantages of high efficiency, fuel flexibility and low environmental pollution. Recently, significant progress has been achieved in reducing the operation temperature of SOFCs from traditional 1000 °C to intermediate temperature range between 600 and 800 °C [1,2]. However, several major issues associated with the reduced operating temperature are the increase in electrolyte and electrode resistivities and the polarization losses of electrode reactions, particularly the oxygen reduction reaction in the cathode. In order to compensate for the ohmic losses at lower temperatures, electrolytes with higher ionic conductivities and thin film electrolyte/electrode assemblies have been developed [3,4]; and alternative cathode materials with a high mixed ionic-electronic conductivity (MIEC) have been employed. Compared to traditional $La_{1-x}Sr_xMnO_3$ (LSM)

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perovskite cathode material, the MIECs can effectively decrease the cathode polarization at reduced temperatures by extending the reactive zones from the electrode–electrolyte interface region to the whole body of the electrode [5,6]. Cathode material performance is very dependent on temperature, grain size, microstructure and the formation or deposition process [7], and the microstructure which is closely related to the morphological characteristics of the starting powder materials and the firing temperatures to fix the electrode material on the electrolyte. The morphology of the powder is affected by the synthesis techniques.

Perovskite cathode materials were prepared previously by numerous methods, including EDTA-citric complex method [8], sol–gel method [9], glycine–nitrate method [10,11], Pechini method [12,13] and freeze–drying method [14]. In the present study, a modified polymer-assisted combustion method is introduced for the preparation of $La_{0.8}Sr_{0.2}Co_{0.8}Ni_{0.2}O_{3-\delta}$ (LSCN). The thermal decomposition behavior of the gelled precursor, the phase formation of the oxide and the morphology of the powder were examined. The chemical compatibility and electrocatalytic activity for the oxygen reduction reaction were evaluated.

2. Experimental

2.1. *Materials synthesis*

The LSCN perovskite oxide powder was synthesized using a modified polymer-assisted combustion synthesis method with glucose and acrylamide as the fuel and dispersing agent, respectively. In this method, stoichiometric amounts of $La(NO_3)_3\cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $C_6H_{12}O_6\cdot H_2O$ and acrylamide (99.9%, Sinopharm Chemical Reagent Co. Ltd) in 2:3 molar ratio were first dissolved in distilled water under magnetic agitation. The water content in the nitrates was confirmed by thermogravimetric analysis (TG/DTA, PerkinElmer Instruments Co. Ltd.) at a heating rate of 5 °C/min in flowing air. For most of the experiments (unless otherwise stated), 5:1 molar ratio of the organic additives (glucose and acrylamide) to the metal nitrates was used. In order to study the effect of the organic additives on the phase formation of the LSCN, the molar ratio was varied from 2:1 to 7:1. Ammonia solution (25 wt%) was added into the solution dropwise under stirring. The pH value of the solution was controlled within the range of 6 to 10. Such prepared solution was heated to 180 °C in an oven for 10 h, forming a viscous gel and then changing quickly to a porous and black-colored xerogel. Finally, the xerogel was calcined at various temperatures between 450 °C and 800 °C for 2 h in air to form the oxide powders.

2.2. *Materials characterization*

The behavior of the xerogel during temperature increase was analyzed by thermogravimetric analysis and differential thermal analysis (TG/DTA, PerkinElmer Instruments Co. Ltd.). The formed phase in calcined powders was identified by X-ray diffraction (XRD) using a Phillips X'Pert Pro diffractometer with Cu Kα radiation. The diffraction patterns were registered over a 2θ range between 20 and 80° and the lattice parameters were calculated using the Jade-5 software (Material Data, Inc.). The specific surface area of the powder calcined at 800 °C was determined as 16.12 $m^2\ g^{-1}$ by the BET method (Micromeritics Instrument Co. Ltd.). The chemical compatibility between the prepared LSCN powder and Y_2O_3 stabilized ZrO_2 (TZ8Y, Tosoh, Japan) and in-house $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) electrolytes was studied by firing LSCN/YSZ and LSCN/GDC mixed powders at 1:1 weight ratio at temperatures 800, 850, 900, 1000 and 1100 °C in air for 10 h, followed by XRD phase analysis. A Sirion 200 scanning electron microscope (SEM) and a Tecnai G2 20 transmission electron microscopy (TEM) were employed to examine the morphology of the LSCN powders.

Using a specimen sintered at 1450 °C for 2 h with a dimension of 5 × 5 × 20 mm, the coefficient of thermal expansion (CTE) of the prepared LSCN was measured in air in the temperature range of 30–1000 °C by a DIL402C thermal mechanical analyzer (NETZSCH Ltd.); and the electrical conductivity of the prepared LSCN was measured by a DC four-point method at temperatures ranging from 50 °C to 1000 °C in flowing air.

2.3. *Electrocatalytic activity evaluation*

Electrolyte substrates were prepared by die pressing 8% mol Y_2O_3–ZrO_2 powder (YSZ, Tosoh, Japan), followed by sintering at 1500 °C for 4hrs in air. The substrate disks were 21 mm in diameter and 1.2 mm in thickness. For preparing LSCN electrodes onto YSZ electrolyte disks with a thin GDC buffer layer of approximately 8 μm in between, the GDC buffer layer was firstly applied to the YSZ electrolyte disk by paste screen printing, followed by sintering at 1250 °C for 2 h in air. The LSCN paste was then screen printed on the buffer layer and sintered at 1000 °C for 2 h in air to form the cathode with a thickness of 8 to 10 μm and an active area of 0.5 cm^2. 5 wt% cellulose binder was used for preparing the pastes. For electrochemical impedance measurement of the cathode, Pt paste was painted on top of the cathode and was fired at 850 °C for 2 h as the current collector and on the opposite side of the electrolyte disk as the counter and reference electrodes. The counter electrode was positioned symmetrically opposite to the working electrode and the reference electrode was a ring at the edge of the electrolyte substrate. Electrochemical impedance spectra of the above prepared cells were obtained in a frequency range of 0.1 Hz to 100 kHz with signal amplitude of 10 mV at temperatures between 600 and 750 °C using an impedance/gain phase analyzer (Solartron 1260) and an electrochemical interface analyzer (Solartron 1287) at open circuit. The electrode interface (polarization) resistance (R_E) was derived from the difference between the low- and high-frequency intercepts at the real impedance axis. The cross-sectioned morphology of the specimen assembly was observed by the SEM mentioned above.

3. Results and discussion

3.1. *Thermal analysis of precursor powders*

Fig. 1 is the TG and DTA results of the xerogel, represented by the LSCN with 5:1 molar ratio of the organic additives to