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$Ca_3Co_2O_6$–$Ce_{0.8}Sm_{0.2}O_{1.9}$ composite cathode material for solid oxide fuel cells

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ABSTRACT

Oxygen-ion transport property greatly affects the electro-catalytic activity of a cathode material in the solid oxide fuel cells. In this work, to enhance the electrochemical activity of hexagonal $Ca_3Co_2O_6$ cathode, fast ion-conductor $Ce_{0.8}Sm_{0.2}O_{1.9}$ is introduced as the second phase, and thus a binary composite is developed, expressed as $(1\text{-}x)Ca_3Co_2O_6/xCe_{0.8}Sm_{0.2}O_{1.9}$ in nominal form. The composites are prepared by one-pot method and X-ray diffraction results reveal that these compositional phases are highly compatible. Analysis of X-ray photoelectron spectroscopy indicates the existence of Co^{3+} and Co^{2+} mixed valences in the composites. Compared with single-phase $Ca_3Co_2O_6$, thermal expansion coefficient of the composite is favorably low and matches better with the electrolyte of solid oxide fuel cells. Test of electrical conductivity shows that the composites are comparable to the pure $Ca_3Co_2O_6$ in charge transport capacity. Electrochemical measurements indicate that the $x = 0.5$ composite cathode exhibit the lowest area specific resistance and produces the maximum power density. In the electrolyte-supported single cell along with Ni-SDC cermet as anode and pure H_2 gas as fuel, power density peak of 680 $mWcm^{-2}$ is achieved from the $x = 0.5$ composite cathode at 800 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) are efficient, environmentally friendly, and fuel-extendable reactors for conversion of chemical to electrical and heat energy [1–4]. However at current state, they are still unable to compete with the sophisticated traditional combustion systems in terms of cost and durability. Lowering the operating temperature can bring SOFCs new opportunities owing to the less degradation of its components and wider range of material selection. But once the operation temperature is reduced, sluggish kinetics of oxygen reduction reaction (ORR) on the cathode soon become the bottleneck due to reluctant splitting of molecular oxygen. It is not easy work to find an applicable cathode material with the balanced properties to replace the conventional high-temperatured one, i.e. (La,Sr)MnO_3 (LSM). In SOFCs, oxygen is reduced in electrochemical way on cathode. So, the cathode materials must have [5]: (1) favorable electronic conductivity; (2) a matched thermal expansion coefficient (TEC) and chemical compatibility with the adjacent components; (3) adequate porosity for gaseous oxygen diffusion; (4) stability under an oxidizing atmosphere; (5) high catalytic activity; and (6) cost effectiveness.

In the last decades, cobalt containing compounds with ABO_3 perovskite crystal structures have been widely studied as the most promising candidate cathode materials for intermediate-temperature SOFCs (IT-SOFCs) because of their outstanding electro-catalytic activity and impressive electrical conductivity, such as $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, $La_{1-x}Sr_xCoO_{3-\delta}$, $Sr_{1-x}RE_xCoO_{3-\delta}$ (RE = rare earth metal), $REBaCo_2O_{5+\delta}$, and their derivatives [6–17]. Unfortunately, their thermal expansion coefficients (TECs) are usually rather high, which render them poor sinterability with those most common solid oxide electrolytes, such as $Y_{2x}Zr_{1-2x}O_{2-x}$ (YSZ), $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM), $Ce_{1-x}Sm_xO_{2-\delta}$ (SDC), etc. Moreover, poor lattice thermo-stability or low electrical conductivity or segregation/enrichment of surface elements is yet another problem with some of the Co-based oxides [18–21]. In this context, it is naturally proposed that, if the key electro-catalytic activity of cobaltite perovskites which comes from the cobalt's unique redox

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couples can still be essentially retained, finding other less cobalt contained materials with likewise robust lattices would be another strategy.

In this regard, $Ca_3Co_2O_6$ (CCO) came as a good candidate which was recently explored in our group as a promising cathode material with relatively low TEC [22]. Moreover, this attractive material can show an additional thermoelectric potential generated by the temperature gradient in the waste heat [23]. Nevertheless, our subsequent study reveals that this material also confronts with great challenge. Working as a mere cathode, its ionic conductivity is questionable due to its hexagonal nature of atomic topology, and as a result its catalytic activity is not on a par with the common cubic or quasi-cubic pervoskites. In our previous work, we tried to improve CCO's electrochemical performance by ion doping or by making composite with other cobalt contained pervoskites. But each method has drawbacks or limitations of one kind or another. For example, doping brings only very limited changes on the intrinsic properties of the compound [24,25], and introducing the perovsikes lead to the higher cobalt content and in turn higher apparent TEC of the cathode [26].

In this work, to promote the electrochemical activity of hexagonal CCO cathode, we chose to introduce in the fast ion conductor $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) as the second cobalt-free phase and thus developed a special binary composite cathode. Our purpose of it is to overcome the drawback of the CCO in oxygen-ion transporting property. Rationale behind this intention is that the more triple-phase boundaries could be generated and thus the more effective electrode structure could be achieved since the faster ion transport paths could be provided in presence of SDC. The composites were generalized as $(1\text{-}x)Ca_3Co_2O_6/xCe_{0.8}Sm_{0.2}O_{1.9}$ (x is nominal mole fraction of SDC) in nominal formula. Then, effects of the phase compositions x on structure, thermal expansion, electrical conductivity and electro-catalytic activity were systematically investigated.

2. Experimental

2.1. Material and cell preparation

$(1\text{-}x)Ca_3Co_2O_6/xCe_{0.8}Sm_{0.2}O_{1.9}$ composite powder was synthesized by one-pot method via a combined ethylenediaminetetraacetic acid (EDTA)-citrate complexing process. $Ce(NO_3)_2{\cdot}6H_2O$, Sm_2O_3, $Ca((NO_3)_2{\cdot}4H_2O$, $C_4H_6O_4Co{\cdot}4H_2O$ (cobalt acetate) were used as the raw materials of metallic ion sources. Stoichiometric amounts of these metallic salts were mixed in deionized water and Sm_2O_3 metallic oxide was dissolved in concentrated nitric acid, and then solutions of all metallic ions were merged. EDTA and anhydrous citric acid were then added as the complexing agents. The molar ratio of total metallic ions, EDTA, and citric acid in the solution was set as 1:1:1. Solution pH was adjusted to ~8 by NH_3 aqueous solution. This mixture solution was then put on a plate heater for evaporation till a homogeneous gel was formed. The gel was further dried thoroughly in oven at 150 °C for hours (about 2–3 h), decomposed at 450 °C for 5 h and annealed at 900–1050 °C for 10 h in air furnace with interment grinding between decomposition and annealing.

$La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM) dense electrolyte discs were prepared via solid state reaction, as described elsewhere [23,27]. The composite anode of NiO-SDC was made by thoroughly mixing NiO and SDC fine powders in weight ratio of 65:35.

Button-sized single cells and symmetrical electrodes were fabricated for electrochemical performance tests, and the detailed fabrication procedures are similar to our previous work [26]. Routinely, the composite cathodes were fabricated into electrolyte-supported single cells with 230(±5) μm thick LSGM electrolyte disc, NiO-SDC anode, and SDC the buffer layer between the anode and the electrolyte. In fabrication, the SDC slurry was screen-printed onto LSGM disc and sintered at 1300 °C for 2 h in stagnant air. The anode layer (~30 μm) was attained by screen-printing the "NiO-SDC" slurry on the electrolyte and successively baking at 1250 °C for 4 h. The cathode ink was screen-printed onto another side of the electrolyte with an exposure area of $5 \times 5\ mm^2$ and fired at 960 °C for 5 h to achieve porous texture with layer thickness of 20–30 μm. Ag grids were used as the collector and the single cell was mounted onto an alumina tube and carefully sealed by Ag paste. H_2 was fed to the anode side as a fuel at a flow rate of $60\ mL\ min^{-1}$ (STP) while the cathode side was exposed to the ambient air. The fabrication method of symmetric cells had no difference from that of single cells except that the cathode ink was simultaneously screen-printed onto both sides of LSGM disc.

2.2. Structure and performance characterization

Phase impurity of the samples was checked by X-ray powder diffraction (XRD, Rigaku Ultima-IV) in Bragg-Brentano geometry with Cu-Kα radiation. The diffraction patterns were collected in the 2θ range of 10–90° with the scan rate of $5°\ min^{-1}$, and cell parameters were calculated by MDI Jade 5.0 software [28]. Morphologies of the composites were observed by a scanning electron microscope (SEM, FEI: Sirion 200). Binding state of compositional elements in the composites was analyzed using X-ray Photoelectron Spectrometer, and narrow high-resolution scans were run to obtain O1s and Co2p level spectra with 0.05 eV steps.

Test of thermal expansion was carried out on the rectangular-shaped bar specimens (5 mm × 5 mm × 25 mm) from room temperature to 950 °C at a heating rate of $5\ °C\ min^{-1}$ by using a dilatometer (NETZSCH STA449c/3/G). Electrical conductivity of the composites was measured according to four-probe method. To prepare both of these specimens, the as-prepared raw powders were pressed into pellets (13 mm in diameter and 1 mm in thickness) or bars under a pressure of 100 MPa followed by sintering at highest allowable temperature 1020 °C for 10 h.

Electrochemical measurements were performed on 2273 electrochemical workstation. Electrochemical impedance spectroscopy (EIS) of symmetrical electrodes were measured around open circuit voltage (E_{OCV}) using a voltage disturbance signal of 10 mV amplitude, and the frequency was modulated from 100 kHz to 10 mHz, and I-V curve was measured on the single cell to demonstrate the power density output and the polarization extent.

3. Results and discussion

3.1. Structural investigation

To get accurate instruction on how to choose an optimum temperature for sintering cathode material onto electrolyte, the precise range of temperature for CCO crystallization were studied. The CCO precursor oxides after decomposition at 450 °C were firstly annealed for 10 h in air and then the products were investigated by XRD, and results were shown in Fig. 1a. Here, stress is placed on the temperature dependence of phase formation and thermal-resistance of the hexagonal structure. It is observed that the pure phase CCO with hexagonal crystal structure is only attained in the temperature range of 960–1020 °C. Below 960 °C, precursory compounds, such as $Ca_3Co_4O_9$ or $Ca_2Co_2O_5$m, are unable to be completely suppressed. Exceeding 1040 °C, CCO tends to decompose into CaO and CoO, as reflected by the presence of identified impurities' peaks. In our previous study, it has been demonstrated that CCO lattice is quite stable below the annealing temperature once it has been established from crystallization [22]. Result of this