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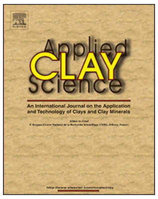

Research Paper

Palygorskite mixed with Ho-based perovskite as a promising cathode material for solid oxide fuel cell

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ABSTRACT

Porous palygorskite (Pal) was mixed with $Ho_{0.9}Sr_{0.1}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (HSCF) perovskite to prepare a novel cathode material for SOFC due to large specific surface area and nano-scaled internal channels. Calcination of HSCF was preceded under 1000 °C by Thermogravimetry and differential scanning calorimetry techniques (TG-DSC) and X-ray diffraction (XRD) analysis. Field emission scanning electron microscopy (FESEM) and IR manifested that Pal was mixed homogeneously with HSCF. Brunauer-Emmett-Teller (BET) analysis proved that surface areas of cathode increased from $0.18\ m^2\ g^{-1}$ to $4.23\ m^2 g^{-1}$after mixing with palygorskite. In addition, the performances of the single cell (NiO-GDC|GDC|HSCF-GDC and NiO-GDC|GDC|HSCF-Pal-GDC) were also measured at 450–550 °C when the 99% H_2 and ambient air were fuels of anode and cathode, respectively. Corresponding the maximum power density were $14.32\ mW\cdot cm^{-2}$ and $28.43\ mW\cdot cm^{-2}$ at 500 °C. When the single cell operating temperature was raised to 550 °C, the performance of single cell NiO-GDC|GDC|HSCF-GDC continues to enhance, while another ome decreased sharply. BET values of the cathode with mixing Pal after cell test declined from $4.23\ m^2\ g^{-1}$ to $0.11\ m^2\ g^{-1}$, which indicated the collapsing of the pores in Pal at the cell operating temperature and impeded the performance of the cell. The operating temperature of the single cell after mixing Pal in electrode couldn't exceed 500 °C. The electrochemical impedance spectra (EIS) was also used to analysis the factors influencing cell performance. Therefore, HSCF-Pal as a promising cathode can be used as low temperature solid oxide fuel cell.

1. Introduction

Solid oxide fuel cells (SOFC) were regarded as a promising clean energy conversion-storage system for their high-energy conversion efficiency, efficient reclamation of waste heat, environmental friendly, and extensive fuel flexibility over other fuel cells (Jun et al., 2015; Fan et al., 2018; Shao et al., 2012; Sengodan et al., 2014; Joo et al., 2016). However, even with these advantages, the high operating temperature (800–1000 °C) causes several problems, e.g., higher energy expenditure, cell materials degradation, and material compatibility challenges (Steele and Heinzel, 2001). An approach to overcome these obstacles is to reduce the operating temperature of the SOFC to the intermediate-temperature (IT) range (400–800 °C) (Wachsman and Lee, 2011; Nie et al., 2010; Ding et al., 2013). In order to operate at intermediate temperature, new cathode materials with high electrochemical properties are required, which as an important part to SOFC could boost its performance.

In the past decade, many cathodes have attracted more attention for their highly mixed ionic-electronic conductivity and good oxygen reduction reaction (ORR) activity at low temperature. Among the various functional materials ABO_3-type perovskite or double perovskite, composed of alkali or rare earth metals in A-site and transition metals in B-site, was a good electrode for the high oxygen kinetics, oxygen capacity and structure stability, for example, $PrLa_{0.4}Ba_{0.6}Fe_{0.8}Zn_{0.2}O_{5+\delta}$, $PrBaCo_2O_{5+\delta}$, $SmBaCo_2O_{5+\delta}$, and their derivatives (Lynch et al., 2011; Zhang et al., 2018; Bu et al., 2015; Bu et al., 2016a, 2016b; Grimaud et al., 2013; Shao and Haile, 2004; Ishihara et al., 1999). In perovskite oxides, ionic defects could be formed from protons by bonding with oxygen, and diffused with Grotthuss mechanism including the fast rotational diffusion of the protonic defects and the proton transfer to neighboring oxygen ions. Such diffusion requires local lattice distortions such as elongation and bending of the B-O bong (Zhou et al., 2016). However, these materials are still restricted for

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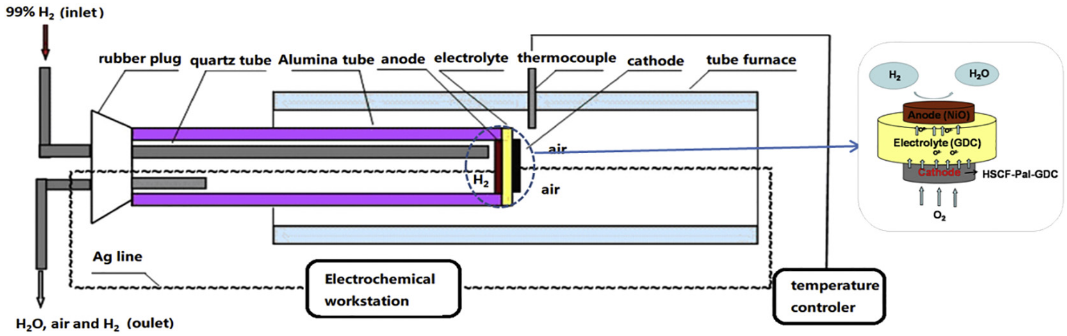

Fig. 1. Schematic diagram of single solid oxide fuel cell.

their compatibility with the electrolyte materials and/or other cell components. IT-SOFC operating at low temperature requires little polarization resistance. In recent years, many researchers devoted themselves to find out the highly efficient electrode backbone through mixing of active material or surface modification. Among them, an effective cathode consisting of a porous mixed-conductivity architectures offers good ionic and electronic conductivity. An active catalyst can provide high catalytic activity and stability, such as $La_{0.4}Ba_{0.6}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ + $Sm_{0.2}Ce_{0.8}O_{1.9}$, $Pr_{1-x}Ba_xCo_2O_{5+\delta}$($x = 0.1$–$0.4$) and $PrBaCo_2O_{5+\delta}$ + $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (Bu et al., 2016a, 2016b; Bu et al., 2017; Pelosato et al., 2015; Fu et al., 2016). Perovskite $HoCrO_3$ as magnetic materials has been studied by different methods (Yin et al., 2017a, 2017b; Yin and Jain, 2016; Herb et al., 2017). The interaction of Ho and Cr ions shows electrons are splitted in spin-allowed d-d transition. In this paper, Sr and Fe were doped in A-site and B-site respectively to increase the oxygen vacancies thus can produce more itinerant electrons. Electrolyte mixed with electrode materials can improve the oxygen permeability due to the existence of an interfacial phase of cerate that forms during the sintering of the mixture (GDC and cathode material). This interfacial phase can effectively maintain the structural integrity of the composition by limiting the interfacial diffusion of some ions between GDC and cathode (Wang et al., 2004; Gong and Hong, 2011; Sun et al., 2013).

Palygorskite (Pal) is a non-metallic mineral, exhibiting high adsorption capacity for many gases (Chen et al., 2011; Cao et al., 2008; Choudalakis, 2009; Goettler et al., 2007; Gallégo et al., 2008; Kiliaris and Papaspyrides, 2010) meanwhile possessing many advantageous properties, such as low cost, nontoxicity and chemical/physical stability. In this paper, the porous Pal, as the surface modification, was mixed with HSCF as a part of cathode material for solid oxide fuel cells. After adding Pal, the BET of the cathode increased and further affected the performance of the single cell.

2. Experimental

i). Preparation

$Ho_{0.9}Sr_{0.1}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (HSCF) precursor of cathode materials was synthesized by the EDTA citric acid-nitrate combustion. Simply, stoichiometric amounts of $Ho(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Cr(NO_3)_3{\cdot}9H_2O$ and $Fe(NO_3)_2{\cdot}9H_2O$ were dissolved in distilled water with stirring. EDTA was added into $NH_3{\cdot}H_2O$ to form complexing liquid EDTA-$NH_3{\cdot}H_2O$. Then complexing liquid and citric acid were put into the mixture of metallic nitrates with proper molar ratio of EDTA:citric acid:the total metal ion =1.2:1:1. The mixture was heated with stirring at 90 °C to form sol-gel product. Then, the resultant sample was heated under 120 °C until the porous ash was obtained. Finally, the ash was calcined at 1000 °C for 12 h under air atmosphere.

Pal was purchased from Xuyi (Jiangsu province, China). Pal was treated with 1.0 $mol{\cdot}L^{-1}$ HCl for 12 h at room temperature before usage. Pal was filtrated, washed with deionized water, and dried in the drying oven at 80 °C for 12 h. The subsequent powder was ground and sifted through 100-mesh sieve. Finally, the Pal powder was obtained.

The acid-treated Pal was added into HSCF with the mass radio 1:5. The mixture was fully ground in a high speed ball mill for overnight and then calcined at 350 °C for 10 h. HSCF-Pal composite was obtained.

ii). Cell fabrication and measurements

Commercial NiO and GDC ($Ce_{0.8}Gd_{0.2}O_{1.9}$) were used as the anode and electrolyte materials of the single cells, respectively. In order to increase the thermal compatibility and reduce the interface resistance between electrode and electrolyte, mass ratio of electrode:electrolyte = 5:1 was dispersed in a hot solution containing ethyl cellulose and terpilenol. The mixtures were painted on one side of the GDC disks, another side with HSCF-GDC or HSCF-Pal-GDC. A single cell with configuration of NiO|GDC|HSCF-Pal-GDC (or NiO|GDC|HSCF-GDC) (anode|electrolyte|cathode) was as such prepared. Then the single cell (mixed with Pal) was calcined at 450 °C for 10 h. Ag mesh as a current collector was adhered to on the surface of the electrodes with Ag paste. The anode chamber of the cell was under 99% H_2 + 1% N_2 and the cathode was exposed to the air. The fuel cell tests were performed in a tube furnace which has a coaxial two-tube (inlet and outlet) setup and each face of the cell was sealed with ceramic sealant. The scheme to show the NiO|GDC|HSCF-Pal-GDC cell configuration and operation has been drawn as Fig. 1 shown:

iii). Characterisations

The surface areas of the cathode materials were measured by the Brunauer-Emmett-Teller (BET) method (Gold App V-sorb 2008p). The samples were degassed at 150 °C for 8 h before the N_2 adsorption-desorption analysis.

The crystal structure of the cathode materials was determined by X-ray diffraction with Bruker D8 Advance diffractometer equipped with Cu $K\alpha$ radiation at 35 kV and 20 mA (λ = 0.15406 nm) at room temperature. Intensity data was collected over 2 h with a 2θ range of 5-80^o and intervals of 0.02^o.

FT-IR spectra were recorded on a Nicolet 5700 Fourier transform infrared spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) from 400 to 4000 cm^{-1} using KBr discs.

The surface morphology of the cathode materials was inspected via a scanning electron microscope (SEM, S-4800II FESEM, Japan).

Symmetrical cells with the configuration of HSCF-GDC|GDC|HSCF-GDC and HSCF-Pal-GDC|GDC|HSCF-Pal-GDC were used for the impedance studies under open circuit conditions. The impedance measurements were performed using a Solartron 1255 HF frequency response analyzer, interfaced with an EG&G PAR model 273A with an amplitude of 10 mV in the frequency range from 0.1 Hz to 100 kHz.

3. Results and discussion

The TG-DSC curves of the precursor HSCF is shown in Fig. 2(a). The