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Carbon Deposition and Sulfur Tolerant $La_{0.4}Sr_{0.5}Ba_{0.1}TiO_3–La_{0.4}Ce_{0.6}O_{1.8}$ Anode Catalysts for Solid Oxide Fuel Cells

Yi-Fei Sun [a], Jian-Hui Li [b,*], Shao-Hua Cui [a,c], Karl T. Chuang [a], Jing-Li Luo [a,*]

[a] *Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada*
[b] *National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*
[c] *Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, China,*

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ABSTRACT

In this work, LSBT–LDC ($La_{0.4}Sr_{0.5}Ba_{0.1}TiO_3–La_{0.4}Ce_{0.6}O_{1.8}$) was successfully prepared by impregnating LSBT and LDC solutions on porous YSZ matrix. The prepared anode material exhibited higher catalytic performance and better resistance against carbon deposition than LSBT anode material in 5000 ppm H_2S containing methane. Electrochemical impedance spectra (EIS) characterizations revealed that the addition of LDC significantly reduces the activation polarization resistance. Energy-dispersive X-ray spectroscopy (EDX) results indicated that the distribution of impregnated oxides in the matrix was uniform. The results of X-ray photoelectron spectroscopy (XPS) and temperature-programed oxidation (TPO) indicated that LSBT–LDC anode could enhance the tolerance against carbon deposition. The gas chromatography (GC) analysis proved that the modification of LDC could effectively promote the activation of methane and contribute to remove carbon deposition formed on the catalyst simultaneously.

1. Introduction

With the continuous exploration and discovery of natural gas reserves worldwide, the solid oxide fuel cell (SOFC) directly using hydrocarbon as feed, rather than expensive H_2, has drawn increasing attentions in recent years [1–3]. The Ni-YSZ cermet is the most wildly used anode material which shows excellent electronic conductivity and catalytic activity [4–6]. However, many problems of Ni-YSZ cermets remain to be solved before successfully using hydrocarbon from natural gas as fuel in SOFC. For example, the carbon deposition generated at higher temperature may block the active sites and reduce the length of triple phase boundary (TPB) [7], thus decreasing the performances of the cells significantly [8]. Another severe problem from utilizing hydrocarbon feed is the impurities contained in feed. Even trace amount of H_2S in the feed may cause serious and irreversible poisoning on the anode catalysts [9]. It has been shown that nickel-based cermets will react with H_2S in the feed at the concentration as low as 10 ppm [10], resulting in the formation of irreversible metal sulfide with the concentration of H_2S higher than 100 ppm.

So far, much effort has been dedicated to developing doping perovskite structure (ABO_3) materials that can function effectively and stably in reducing environment. The high capacity of lattice vacancies of these anode materials allows them to have mixed ionic and electronic conductivity [11]. Further the perovskite oxides exhibit promising resistance against carbon deposition and H_2S [12,13]. So far, La-doped $SrTiO_3$ (LST) anode materials have been paid much attention because the doping of high valance cation of La^{3+} can create more oxygen vacancies that can facilitate the transportation of oxygen ions [14–18], increase the ionic conductivity and improve the fuel cell performance. The previous work done by Adrien et al. [16,19] in our group showed that the partial substitution of Ba for Sr in LST ($La_{0.4}Sr_{0.6-x}Ba_xTiO_3$, $0 < x < 0.2$ (LSBT)) prepared by solid state method [16] could increase its ionic conductivity, catalytic activity to the oxidation of CH_4 and improve the stability of the LST structure. Besides, the fuel cell performance was significantly enhanced when H_2S was present in either CH_4 or H_2 fuel.

For the preparation of catalysts, the impregnation or infiltration method has been widely used [20–22]. Also, the impregnation technology could be regarded as a promising method for fabrication of high performance electrode materials for SOFCs. The anode catalyst prepared by impregnation method showed much small particle size with larger BET surface and obviously

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* Corresponding authors. Tel.: +1 780 492 2232; fax: +1 780 492 2881.
E-mail addresses: jhli@xmu.edu.cn (J.-H. Li), Jingli.Luo@ualberta.ca (J.-L. Luo).

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higher electrochemical performance than anode with same composition prepared by traditional solid-state method. For example, the performance of LSBT prepared by impregnation was several times higher than that by solid state method, which exhibited the maximum power density of 84 mW cm^{-2} when the feed was CH_4 + 0.5% H_2S [14]. Even so, its electrochemical performance still needs to be further enhanced, and its resistance against carbon deposition is still questionable.

Previous researches have showed that the cerium based oxides could be applied as the effective promoter for anode catalysts. The solutions of $Ce(NO_3)_2$ with other metal nitrates could be infiltrated to the porous matrix of anode through capillary effect to form doped cerium oxides [23,24], and the anode performance and its resistance against carbon deposition could thus be enhanced [25]. The researches showed that the addition of GDC speeded up the process of oxygen diffusion, which reduced the activation energy of the reaction [26]. However, the not too many reports about the promotion effect of GDC on LST-based anode have been shown because it will probably introduce new Ga-rich phase. On the other hand, the lanthanum-doped ceria was widely investigated as an interlayer between the electrolyte and anode material to minimize reactions and inter-diffusion. The $La_{0.4}Ce_{0.6}O_{1.8}$ (LDC) with the composition of La:Ce = 2:3 has been widely reported and investigated [27–32]. LDC is selected as the second component in the composite anode, considering it as an MIEC with excellent tolerance to sulfur contaminants in the fuel. Since LDC has substantial catalytic activity for fuel oxidation, it is expected to improve the anode performance.

In this paper, based on the investigation of our previous work on LSBT based anode materials, we introduce the addition of LDC into the porous YSZ matrix together with the LSBT. The electrochemical performance of this anode catalyst and its resistance against carbon deposition and sulfur were also investigated. Gas chromatography (GC) was employed to analysis the components of outlet gas from different treated samples to reveal the origin of the enhancing electrochemical performance with the addition of LDC.

2. Experimental

2.1. Electrode Catalysts and Fuel Cell Preparation

In order to achieve a high level of porosity, the YSZ powder (Tosoh) and 20 wt% polymer microspheres (polymethylmethacrylate, PMMA) (Sigma Aldrich) were thoroughly mixed by ball mill and then sintered at 1350 °C. The final materials had an approximately 55% porosity. The powder was then mixed with 5wt% poly solution (vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB, Mw = 70000–100000, Aldrich). The next step was to screen print the paste onto one side of a commercial YSZ disks (fuel cell materials) with a thickness of 300 μm and diameter of 25 mm, which were further sintered at 1200 °C for 5 h to form membrane electrode assemblies (MEA) with circular 1 cm^2 anodes.

The LSBT solution was prepared using the procedure demonstrated by Vicent et al. [19]. Certain amounts of titanium(IV) propoxide (98%, Aldrich) and triethanolamine (Aldrich) (mole ratio of 1:4) were dissolved into an aqueous solution containing the appropriate amounts of lanthanum(III) nitrate hexahydrate (99.999%, Aldrich) and the strontium nitrate (Aldrich). LDC solution was prepared by dissolving lanthanum(III) nitrate hexahydrate, ammonium cerium(IV) nitrate (99.99%, Aldrich) and glycine (Aldrich) in 0.2:0.3:1 molar ratio. The total metal ion concentration was 0.5 mol L^{-1} for both solutions. After each impregnation step, the cell was sintered at 400 °C for 4 h. Previous literature has shown that the anode of YSZ matrix infiltrated with 15 wt% of LSBT showed optimal performance than anodes with other contents [19]. LBST was impregnated three times to form electrodes having 15 wt% deposits. LDC–LBST sample was prepared by impregnating LDC twice (10 wt%) before LBST (15 wt%). The cells were denoted as LSBT and LSBT–LDC, respectively. After the anode impregnation process has been finished, the composite lanthanum strontium manganite (LSM) was employed as the cathode prepared by screen printing method and sintered at 1200 °C for 1 h.

2.2. Fuel Cell Testing

The gold and platinum pastes were applied and painted onto the anode and cathode as the current collectors. The cell was placed on a coaxial two-tube set-up and sealed with the glass sealant (Armco-seal 617), the finished set-up was then placed in the vertical furnace. CH_4 with 5000 ppm H_2S (denoted as H_2S–CH_4) flowed through the anode at the rate of 50 ml min^{-1} while the cathode counterpart was directly open to the air. The Electrochemical performances were determined, using a Solartron 1287 instrument at the scan rate of 5 mV s^{-1}. The Zplot, Zview, Corrware and Corrview software were used to perform and analyze the electrochemical tests. A Solartron 1252 A FRA was utilized to analyze the electrochemical impedance from 1 MHz to 0.1 Hz at OCV with a 10 mV amplitude. Fuel cell tests were conducted using a two electrode setup.

2.3. Materials characterization

A Rigaku RU200 powder X-ray diffraction (XRD) system with Co tube (λ=1.79026A°) was used for analysis of all synthesized powders, with a scan rate of 2°θ min^{-1}.The software Jade 5.0 was used for identification of phases in the samples.

The morphology and elemental composition of the cross-section of the cell and the MEAs were characterized by a scanning electron microscopy on fractured cells (LEO 1430) with Energy-dispersive X-ray spectroscopy (EDX) detector.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical AXIS 165. A monochromatic Al Kα source ($h\nu$ = 1486.6 eV) was used with the power of 210 W and base pressure of 3×10^{-8} Pa in the analytical chamber. Spectra were referenced to the C 1 s binding energy of 284.6 eV, and were fitted using Gaussian–Lorentzian peak shapes and Shirley baselines.

A gas chromatograph (GC) (Agilent 6890 N) equipped with thermal conductivity detector (TCD) and column of Polapak Q ($3\phi \times 2$ m) was used to analyze the exhausted gases. The Ar was applied as carrier gas for GC. The formation rate (r) of carbon was evaluated from the material balance and the formation rates of CO, CO_2, and H_2 [33]:

$$r(C) = [r(H_2) - 3r(CO) - 4r(CO_2)]/2, \quad (1)$$

The unit of r is mmol min^{-1}.

The temperature-programmed oxidation (TPO) method was employed to characterize and quantify the carbon deposition on the anode materials after various treatments. The samples were put in an alumina tube that was loaded into the TPO apparatus and exposed to a flow of 10% O_2 balanced with He at 50 ml min^{-1} for 1 h. The temperature was then increased from room temperature to 1173 K at 20 K min^{-1} and the effluents were analyzed with a mass spectrometer (Thermo star 301). The signals monitored during the TPO experiment included m/z = 44 (CO_2), m/z = 28 (CO only, excluding the contributions of the residual N_2 and CO_2), m/z = 32 (O_2), m/z = 18 (H_2O), m/z = 34 (H_2S), m/z = 60 (COS), m/z = 64 (SO_2) and m/z = 76 (CS_2). Prior to the TPO analysis, the mass spectrometer signals were calibrated using gas mixtures of known concentrations.

All the samples were treated with H_2S–CH_4 at 850 °C for 24 h. The heating and cooling processes were done in 10% H_2–N_2 with the flow rate of 20 ml min^{-1}.