A comparative study of $La_{0.8}Sr_{0.2}MnO_3$ and $La_{0.8}Sr_{0.2}Sc_{0.1}Mn_{0.9}O_3$ as cathode materials of single-chamber SOFCs operating on a methane–air mixture

Chunming Zhang[a], Yao Zheng[a], Ye Lin[a], Ran Ran[a], Zongping Shao[a,*], David Farrusseng[b]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology No.5 Xin Mofan Road, Nanjing, JiangSu 210009, PR China
[b] IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Unit′e Mixte de Recherche 5256 CNRS-Universit′e de Lyon 1, 2 avenue Albert Einstein, F-69626 Villeurbanne Cedex, France

ABSTRACT
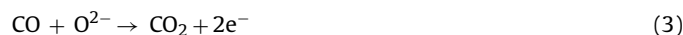
As candidates of cathode materials for single-chamber solid oxide fuel cells, $La_{0.8}Sr_{0.2}MnO_3$ (LSM) and $La_{0.8}Sr_{0.2}Sc_{0.1}Mn_{0.9}O_3$ (LSSM) were synthesized by a combined EDTA-citrate complexing sol–gel process. The solid precursors of LSM and LSSM were calcined at 1000 and 1150 °C, respectively, to obtain products with similar specific surface area. LSSM was found to have higher activity for methane oxidization than LSM due to LSSM's higher catalytic activity for oxygen reduction. Single cells with these two cathodes initialized by ex situ reduction had similar peak power densities of around 220 mW cm^{-2} at 825 °C. The cell using the LSM cathode showed higher open-circuit-voltage (OCV) at corresponding temperatures due to its reduced activity for methane oxidation relative to LSSM. A negligible effect of methane and CO_2 on the cathode performance was observed for both LSM and LSSM via electrochemical impedance spectroscopy analysis. The high phase stability of LSSM under reducing atmosphere allows a more convenient in situ reduction for fuel cell initiation. The resultant cell with LSSM cathode delivered a peak power density of ~200 mW cm^{-2} at 825 °C, comparable to that from ex situ reduction.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, single-chamber solid oxide fuel cells (SC-SOFCs) have been receiving attention for their simplified reactor configuration and capability for quick start-up. They have potential application as micropower generator for portable devices. Because they operate on fuel–air mixture, one way to minimize the gas phase reaction that would reduce the electrical efficiency is to adopt fuels with high chemical stability such as hydrocarbons with low carbon numbers, especially methane [1–7]; another way is to reduce the operation temperature.

The operation principle of methane-fueled SC-SOFCs relies on different chemical catalytic and electro-catalytic activities of anode and cathode materials in the methane–air mixture [8–10]. Ideally, the cathode is inert to the oxidation of methane but highly efficient for oxygen reduction (Eq. (1)), while the anode possesses high catalytic activity and selectivity towards partial oxidation of methane, forming CO and H_2 (Eq. (2)). During operation, the oxygen anion is pumped from the cathode side through electrolyte and reacted with CO and H_2 at the anode to produce electricity (Eqs. (3) and (4)).

$$0.5O_2 + 2e^- \rightarrow O^{2-} \quad (1)$$

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \quad (2)$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (3)$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (4)$$

Because of their large number of bulk oxygen vacancies, cobalt-based perovskite oxides like $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC), $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF), $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), have been extensively investigated as cathode materials in dual-chamber SOFCs (DC-SOFCs) [11–15]. Good performance at intermediate temperature has been achieved in many reports. However, such materials are intrinsically unstable in reducing atmosphere. For example, BSCF can be reduced to metallic Co, Fe and $BaO/Ba(OH)_2 \cdot xH_2O$, $SrO/(Sr(OH)_2 \cdot xH_2O$ under hydrogen atmosphere [16]. If these materials are applied as the cathode of SC-SOFCs, an additional ex situ reduction step is preferred to avoid destruction of the perovskite lattice structure by the reducing atmosphere during the initialization process [17–19]. The so-called ex situ reduction is a pre-reducing process for the anode substrate, mostly from NiO to Ni, before the deposition of cathode on the electrolyte layer. When applying the ex situ reduction process, to avoid the re-oxidation of the Ni-based anode, after the cathode deposition is completed, the three layered cell must be fired under an inert atmosphere to adhere the cathode onto the electrolyte surface firmly. However, such a SC-SOFC fabrication process is time consuming and expensive.

* Corresponding author. Tel.: +86 25 83172256; fax: +86 25 83172256.
 E-mail address: shaozp@njut.edu.cn (Z. Shao).

In our previous work, a simplified in situ reduction process was introduced to initialize SC-SOFCs, in which both the unreduced anode and cathode were exposed to the same reducing atmosphere of hydrogen [20]. If successful, the conventional fuel cell fabrication technique could also be applied for the SC-SOFCs, thereby greatly reducing the fabrication cost. However, the initiation by in situ reduction did not work well for SC-SOFCs with a BSCF cathode. Although a reduced BSCF cathode can be partially restored to its initial perovskite structure under a methane–air atmosphere at high temperatures, the power output of the cells was much lower than that of the cell initialized by ex situ reduction due to the altered electrode structure after the reduction/re-oxidation process. Thus, there is an urgent need for the development of a more stable cathode for the reducing atmosphere.

As a classic cathode material of DC-SOFCs, $La_{0.8}Sr_{0.2}MnO_3$ (LSM) shows good structural and chemical stability under cathodic operation condition. It has been applied as the cathode of SC-SOFC by Hibino et al., who reported a peak power density of $204\,mW\,cm^{-2}$ at a furnace temperature of $950\,°C$ for a cell with 15 wt.% MnO_2-modified $La_{0.8}Sr_{0.2}MnO_3$ as cathode when operating in a methane–air mixture [8]. The decomposition oxygen partial pressure of LSM is around 10^{-18} atm at $800\,°C$ [21], suggesting that the stability of LSM may still be a problem in SC-SOFC applications when adopting the in situ reduction process for cell initialization, since the oxygen partial pressure in a hydrogen atmosphere could be lower than 10^{-19} atm. Recently, we have developed a novel perovskite-type oxide $La_{0.8}Sr_{0.2}Sc_{0.1}Mn_{0.9}O_3$ (LSSM) which showed not only better cathode performance than LSM for electrochemical oxygen reduction [22–25] but also improved stability under reducing atmosphere [24]. Yue et al. also reported this cathode material which had better performance [26]. This suggests that LSSM may be a potential candidate for an SC-SOFC cathode.

In this paper, LSM and LSSM were prepared and their performance in SC-SOFCs operating in a methane–air mixture was systematically investigated. The cell initialization by both ex situ and in situ reduction methods for the two cells was comparatively studied.

2. Experimental

2.1. Powder synthesis and fuel cell fabrication

The fuel cells employed in this study were in an anode-supported configuration with a NiO+ScSZ anode substrate ($\sim$500 μm, NiO:ScSZ = 60:40 by wt.%), ScSZ electrolyte (20–30 μm) and an LSM or LSSM cathode ($\sim$20 μm). ScSZ, LSM and LSSM were all synthesized by a combined EDTA-citrate complexing sol–gel process. Such a preparation process has been described in detail in our previous publications [27,28]. A dry-pressing/sintering process was adopted to fabricate the anode-supported thin-film ScSZ bi-layer pellets. These green dual-layer pellets resulting from dry pressing were then fired at $1500\,°C$ for 5 h in air to achieve the densification of the electrolyte layer and a firm connection between the anode substrate and the thin-film electrolyte. The cathode was applied to the electrolyte surface by a spray deposition/sintering process. The cathode powder (LSM or LSSM) was first dispersed in a pre-mixed solution of glycerol, ethylene glycol and isopropyl alcohol to form a colloidal suspension through high-energy ball milling (Fritsch, Pulverisettle 6), at a rotational speed of 400 rpm for 1 h. The resultant slurry was spray deposited onto the electrolyte surface of fresh or pre-reduced dual-layer membranes, then calcined at $1000\,°C$ (the resulting sample was named LSM_{1000}) and $1150\,°C$ ($LSSM_{1150}$) for 2 h in air (or under a flowing nitrogen atmosphere for the cells with a pre-reduced anode) to obtain triple-layered single

cells. The resulting coin-shaped cathode had an effective geometric surface area of $0.48\,cm^2$.

2.2. Catalytic characterization

The catalytic activity of the LSM or LSSM for methane oxidation was evaluated in a flow-through fixed bed reactor, which is composed of a quartz tube with an inner diameter of $\sim$8 mm. About 0.02 g of catalyst (60–80 mesh LSM or LSSM particulates) was put in the center of the reactor. A K-type thermocouple with the protection of a small quartz tube was immersed into the catalyst bed to monitor the reaction temperature. A tube furnace was applied to sustain the temperature required for the reaction. Methane–oxygen–helium mixed gas in a ratio of 1.3:1:4 was introduced from the top of the reactor. The effluent gas from the bottom of the reactor was introduced to a Varian 3800 gas chromatograph, which was equipped with Poraplot Q and 5 Å molecular sieve capillary columns for the separation of H_2, O_2, CO, CO_2 and CH_4. Before introduction into the reactor, water was adsorbed by a cooling trap. The methane and oxygen conversions were calculated based on:

$$\%conversion_{CH_4} = \frac{[CO]+[CO_2]}{[CO]+[CO_2]+[CH_4]_{outlet}} \times 100$$

$$\%conversion_{O_2} = \frac{0.5[CO]+[CO_2]+0.5[H_2O]}{0.5[CO]+[CO_2]+0.5[H_2O]+[O_2]_{outlet}} \times 100$$

2.3. Fuel cell performance test

Fuel cell polarization curves were obtained at furnace temperatures of 750–$850\,°C$. The gas was composed of methane, oxygen and nitrogen at flow rates of 110, 85 and $340\,ml\,min^{-1}$ [STP], respectively. *I–V* polarization curves were collected using a Keithley 2420 source meter based on the four-terminal configuration.

Electrochemical characterization of LSM and LSSM as cathode materials on a ScSZ electrolyte was conducted based on a three-electrode configuration using an electrochemical workstation composed of a Solartron 1287 Potentiostat and a Solartron 1260A Frequency Response Analyzer. The frequency applied ranged from 0.1 Hz to 100 kHz, and the signal amplitude was 10 mV. The thickness and diameter of the sintered electrolyte disks were $\sim$0.3 and 16 mm, respectively. Isopropyl alcohol-based LSM or LSSM slurry was applied to one side of electrolyte substrate by spray deposition and then calcined at 1000 or $1150\,°C$ in air for 2 h to act as the working electrode. An Ag paste was adopted as the current collector of the working electrode. Silver paste was also used as the reference electrode by painting a ring around the Pt counter electrode on the other side of the electrolyte pellet. The gap between the counter and reference electrodes was $\sim$4 mm. The areas of the working, counter and reference electrodes were 0.26, 0.26 and $0.3\,cm^2$, respectively. The cathodic resistances were tested under a constant cathodic current of $400\,mA\,cm^{-2}$.

2.4. Other characterization

The BET (Brunauer–Emmett–Teller) surface area of the samples was characterized by N_2 adsorption at the temperature of liquid nitrogen using a BELSORP II instrument. Prior to analysis, the samples were put in vacuum at $200\,°C$ for 3–5 h to remove the surface adsorbed species. An X-ray diffractometer (XRD, Bruker D8 Advance) was used to analyze the stability of LSM and LSSM against a reducing atmosphere during the process of in situ reduction. The diffractometer operated at 40 kV and 30 mA using Cu Kα radiation with a wavelength of 1.5418 Å, with a scanning angle (Bragg angle 2θ) ranging from $20°$ to $80°$ at a rate of $0.05°\,s^{-1}$. The microscopic features of the electrodes were characterized using an environmental scanning electron microscope (ESEM, JSM-5610LV).