



Characterization of Cu, Ag and Pt added $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and gadolinia-doped ceria as solid oxide fuel cell electrodes by temperature-programmed techniques

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ABSTRACT

Cu, Ag and Pt added $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and gadolinia-doped ceria (GDC) were analyzed by the temperature-programmed techniques for their characteristics as either the cathode or the anode of the solid oxide fuel cells (SOFCs). Temperature-programmed oxidation using CO_2 was used to characterize the cathode materials while temperature-programmed reduction (TPR) using H_2 and TPR using CO were used to characterize the anode materials. These techniques can offer an easy screening of the materials as the SOFC electrodes. The effects of adding Cu, Ag and Pt to LSCF for the cathodic reduction activity and the anodic oxidation activity are different—Cu > Ag > Pt for reduction and Pt > Cu > Ag for oxidation. The CO oxidation activities are higher than the H_2 oxidation activities. Adding GDC to LSCF can increase both reduction and oxidation activities. The LSCF–GDC composite has a maximum activity for either reduction or oxidation when LSCF/GDC is 2 in weight.

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1. Introduction

The $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) perovskites have been considered as the cathode materials for the solid oxide fuel cells (SOFCs) to replace the conventional $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) materials [1–4]. This is attributed to the high catalytic activity of LSCF for oxygen reduction. The oxygen reduction activity of LSCF can be one order of magnitude higher than that of LSM [5], especially of the A-site deficient $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite [6]. This is an important characteristic for SOFCs when the operating temperature is reduced. However, as the operating temperature of an SOFC is decreasing, a higher activity of oxygen reduction becomes increasingly important and thus the adding of metals into the cathode material to increase its oxygen reduction activity has been the subject of numerous studies; the metals which have been studied include Pt [7–10], Pd [11], Ag [9,12–14] and Cu [15–17]. Copper has also been studied as a component in the perovskite materials as the SOFC cathodes [18,19].

The LSCF perovskites have also been considered as the SOFC anode materials [20]. Other La and Sr based perovskites have also been studied as the SOFC anode materials so as to have an enhanced anodic activity [21,22]. The anodic activity can also be enhanced

with the addition of metals, such as Pt [23] and Cu [24]; these metals are used especially for suppressing coking, which is a serious problem during direct oxidation of methane in SOFCs [25]. Nevertheless, Ag is seldom used in the SOFC anode materials.

Gadolinia-doped ceria (GDC) is the well-known materials in the SOFC anodes [26]. The mixing of GDC with LSCF to form the LSCF–GDC composite has been shown to increase the adhesion of the cathode materials to the YSZ electrolyte [27]. With LSCF being $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and GDC being $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, the LSCF–GDC composite can perform better than pure LSCF as the SOFC cathode [10]. The addition of 50 vol.% GDC to LSCF has resulted in a decrease of the polarization resistance with a factor of about 10 compared to that of the LSCF cathode [28]. On the other hand, LSCF–GDC has also been used as anode materials for the direct oxidation of methane in intermediate-temperature SOFCs and shown to have no formation of carbon deposits [29].

The characterization of the SOFC cathode materials is frequently performed by the impedance spectroscopic measurements [5,10,28]. This impedance spectroscopic result is usually quite complex, since there coexist many resistances, such as the resistance for the oxygen exchange reaction at the electrode surface, the oxygen-ion transfer resistance at the electrode/electrolyte interface, and the oxygen-ion conducting resistance in the electrolyte [30]. Thus, the impedance result may not be directly related to the oxygen reduction activity of the cathode materials.

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A measurement of temperature-programmed oxidation using carbon dioxide (CO₂-TPO) [31] may be applicable to analyze the characteristics of the SOFC cathode materials. This can be a relatively direct analysis of the SOFC cathode characteristics since the reaction of CO₂-TPO is the dissociative adsorption of CO₂, CO₂ → CO + O, and the produced O species can fill into the surface oxygen vacancy or transport into the oxygen vacancy in the bulk lattice [32,33]. Since the oxygen reduction mechanism consists of oxygen adsorption, charge transfer reaction and oxygen incorporation into the oxygen vacancy [17], the oxygen reduction activity may be analyzed by the CO₂-TPO measurements.

In this work, Cu, Ag and Pt added LSCF and GDC as well as various LSCF–GDC composites, all in the powder forms, were analyzed by CO₂-TPO for their characteristics as the SOFC cathodes. Current–voltage and AC impedance measurements in SOFC unit cells were performed to confirm the feasibility of the CO₂-TPO characterization for the cathode materials. These materials were also analyzed by temperature-programmed reduction (TPR) using H₂ and TPR using CO for their characteristics as the SOFC anodes. It was shown that these temperature-programmed techniques can offer an easy screening of the materials as the SOFC electrodes.

2. Experimental

2.1. Preparation of LSCF and GDC and metal addition

LSCF was prepared by the glycine–nitrate process with a composition of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3–δ}. The A-site deficient LSCF was also prepared and its composition was La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3–δ}, denoted as L58SCF. Appropriate amounts of reagent-grade (Showa, Japan) metal nitrates La(NO₃)₃·6H₂O, Sr(NO₃)₂, Co(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in de-ionized water. Glycine (Sigma, USA) was also dissolved in de-ionized water. Then, these two solutions were mixed together with a glycine to NO₃ ratio of 1:0.8. The mixture was then heated under stirring at 110 °C until combustion occurred. The obtained product was ground to powders. The LSCF powders were calcined by heating in air at a rate of 5 °C min⁻¹ to 500 °C and held for 2 h, then to 900 °C and held for 4 h, and then slowly cooled down to room temperature.

GDC was prepared by the co-precipitation method with a composition of Ce_{0.8}Gd_{0.2}O_{2–δ}. The details of the method have been described elsewhere [34]. The GDC powders were calcined by heating in air at a rate of 5 °C min⁻¹ to 900 °C and held for 4 h before cooling down.

The LSCF–GDC composite was prepared by mixing the above-prepared LSCF and GDC powders. The mixture was ground for 24 h and then calcined by heating in air at a rate of 5 °C min⁻¹ to 500 °C and held for 2 h, and then to 900 °C and held for 10 h before cooling down.

The metal addition to L58SCF, LSCF, GDC and LSCF–GDC powders was done by impregnation. The Cu, Ag and Pt cation solutions were prepared by dissolving Cu(NO₃)₂·3H₂O (Showa, Japan), AgNO₃ (Hwang Long, Taiwan) and H₂Pt(OH)₆ (Aldrich, USA) in de-ionized water, respectively. After drying, the powders were calcined by heating in air at a rate of 5 °C min⁻¹ to 900 °C and held for 4 h before cooling down. The metal loading in this work was always 2 wt.% in terms of the weight of LSCF in metal-added LSCF or LSCF–GDC or the weight of GDC in metal-added GDC.

2.2. Current–voltage and AC impedance measurements in SOFC unit cell

The commercial YSZ tape (Jiuhow, Taiwan) was employed to make an electrolyte-supported SOFC cell. A disk of 1.8 cm in diameter was cut from the tape. One side of the disk was spin-coated

with the paste of Ni–GDC as the anode, being composed of 60 wt.% Ni in terms of GDC, which has been shown to have an optimum anode performance [25]. The details of the preparation of the Ni–GDC paste have been described elsewhere [35]. The other side of the disk was spin-coated with a thin LSCF–GDC interlayer to enhance adhesion and then with L58SCF or metal-added L58SCF as the cathode. The thus-prepared SOFC unit cell has an anode-layer thickness of 25 μm, an electrolyte-layer thickness of 156 μm, an interlayer thickness of 5 μm, a cathode-layer thickness of 20 μm, and a cathode area of 1.1 cm².

The measurement of current–voltage (*I*–*V*) curve was performed at 800 °C with pure hydrogen on the anode side and 20% O₂ in Ar on the cathode side, both at a flow rate of 100 ml min⁻¹. The voltage was varied by an adjustable resistor, and both the voltage and the current were measured by a Multimeter (TES 2730). The AC impedance measurement was done by an Electrochemical Analyzer (CHI608A, CH Instruments, USA) with a scanning frequency range of 1 MHz to 0.01 Hz and an amplitude of 50 mV. The working electrode was connected to the anode current collector, and both the reference electrode and the counter electrode were connected to the cathode current collector. The AC impedance measurements were performed under the same operating conditions as those of *I*–*V* curves.

2.3. CO₂-TPO measurement

The CO₂-TPO measurement was conducted under atmospheric pressure in a continuous flow reactor charged with 25 mg of sample powders. Some details of the CO₂-TPO measurement have been described elsewhere [31].

The powders were dried in the reactor, and then reduced by heating at a rate of 10 °C min⁻¹ in 30 ml min⁻¹ of 10% H₂ in Ar to 900 °C and then held at 900 °C for 30 min. Then, the powders were cooled down to room temperature in argon flow. Then, CO₂-TPO was performed with 30 ml min⁻¹ of 10% CO₂ in Ar from room temperature to 900 °C at a rate of 10 °C min⁻¹ and then held at 900 °C for 30 min before cooling down. The reactor outflow was analyzed on-line by a CO-NDIR (non-dispersive infrared analyzer, Beckman 880).

2.4. Temperature-programmed reduction using H₂ or CO

Temperature-programmed reduction using hydrogen (H₂-TPR) and temperature-programmed reduction using carbon monoxide (CO-TPR) were performed at atmospheric pressure in a continuous flow reactor charged with 25 mg of sample powders. H₂-TPR tests

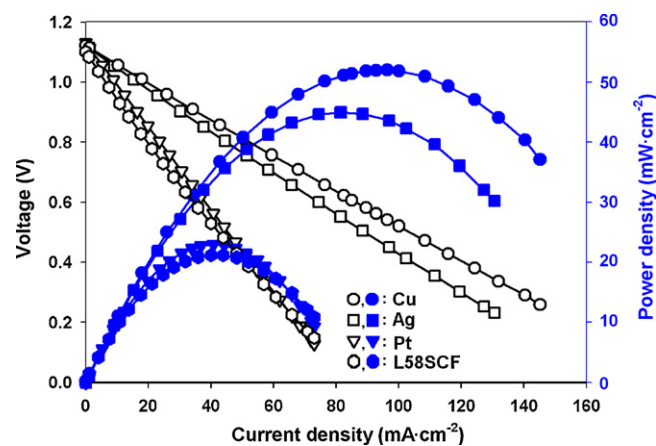


Fig. 1. Current–voltage and power density profiles of L58SCF and Cu, Ag and Pt added L58SCF as SOFC cathodes.

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