

Performance stability of strontium-doped lanthanum cobaltite ceramic cathode synthesized by a wet chemical method



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ABSTRACT

Porous strontium-doped lanthanum cobaltite ($\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, LSC) thin film electrodes were deposited by a metal-organic chemical solution deposition method. These films were used as cathodic electrodes replacing precious metal electrodes for low-temperature solid oxide fuel cell (LT-SOFC) applications. They were characterized electrochemically and compared with devices that had platinum (Pt) cathodes. Pt was prepared by a DC magnetron sputtering method and LSC-YSZ-Pt and Pt-YSZ-Pt (cathode-electrolyte-anode) SOFC unit cells were fabricated. The performance of each cell was continuously evaluated under operating conditions and the performance of fuel cells with a Pt cathode was superior to those using a LSC cathode at the initial stages of operation; however, the output power density started to decrease as a function of time due to the degradation that comes from the heat vulnerability of Pt. As a consequence, the performance of Pt-YSZ-Pt was significantly lower than LSC-YSZ-Pt, and the electrode resistance grew to be about four times larger compared to before operation. In contrast, neither the output power density nor the electrode resistance of LSC-YSZ-Pt changed during operation. These results imply that LSC has better long-term performance stability compared to Pt and feasibility of using ceramic electrode for low-temperature solid oxide fuel cells.

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1. Introduction

Solid oxide fuel cells (SOFCs) are compelling energy conversion systems that have been intensively investigated due to their high efficiency, diverse fuel compatibility, and environmental friendliness. SOFCs are essentially solid-state devices. This signifies that high operation temperatures are generally required because the ionic conductivity and oxygen reduction reaction (ORR) rate are sluggish in typical solid materials. In general, temperatures above 800 °C are usually adopted in order to achieve reasonable performance. Thus, the thermal stability and chemical compatibility requirements of the component materials of SOFC systems are stringent, thereby inducing costly and uneconomical fabrication [1,2]. For these reason, various attempts have been made to lower the operating temperature of SOFCs. In recent years, these have been reduced to intermediate ranges (500–800 °C) [3–5], and continuous research has been conducted to further lower the operating temperature regime (below 500 °C) [6–8]. The main obstacles to lower the operating temperature have been related to

the resistance; low operating temperatures significantly increase the ohmic and electrode interface resistances of SOFCs, which reduce the performance and efficiency.

To diminish these losses, studies investigating methods to decrease the thickness of the electrolyte to a submicrometer-scale have been conducted [9–14]. Additionally, attempts to decrease ohmic losses, including ionic transport, have been effectively carried out by minimizing the transport path. Another attempt focused on minimizing the losses of electrodes; for example, the cathodic interface resistance was reduced by introducing a functional layer between the electrolyte and cathode [15–18]. This improved the surface exchange coefficient, thereby improving the performance of the cell by facilitating the surface oxygen kinetics.

Modifying the nanometer-scale structure and increasing the electrochemical reaction area was another approach used to improve the performance of SOFCs in the low-temperature regime [19,20]. The output power was increased proportionally with the active area, and some researchers have demonstrated considerably high output power densities below 500 °C.

For effective energy production in the low-temperature regime, thin-film electrodes with high catalytic activity are essential to further improve the performance. A decent number of studies have employed noble metals [21–24]; these materials show prominent catalytic activity, even at low temperatures. Also, in order

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to generate a high density of output power, nanoscale pores can be formed at these electrodes. These pores allow the electrolyte, which is contacted with the catalyst, to be exposed to gas. Electrochemical reactions occur only at the sites that electrolyte, electrically connected catalyst, and gas are all physically connected with. Referred to as triple phase boundaries (TPBs), the porosity of the electrode is an important factor that influences the cell performance [25]. However, because the melting point of noble metals is relatively low, and because these nanoscale pores have poor thermal stability, aging effects can occur under continuous heating. Platinum is widely accepted as the representative catalyst material for electrodes in hydrogen fuel cells in the low-temperature regime; however, the aging effect remains as a major problem, especially above 450 °C [26]. Moreover, extremely high price of precious metals including Pt is another major challenge for adopting those as catalytic electrodes.

On account of this issue, several studies have tried to find an alternative to noble metals. Due to their remarkable thermal stability, ceramics with high ionic and electronic conductivities are potential candidates. Lanthanum perovskites, such as LSM ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$), LSC ($\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$), and LSCF ($\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$), have been frequently used as the cathodic electrodes of SOFCs [27,28]. However, because lanthanum perovskites are essentially ceramics, the activation energies for their catalytic activities are larger than those of noble metals. Furthermore, because LSM shows poor conductivity at temperatures below 600 °C [29], some lanthanum perovskites are inappropriate for this application. Several studies have employed LSC thin films as a replacement for Pt in the low-temperature regime (below 500 °C) [29–31]; however, most of these studies have fabricated LSC thin films with physical vapor deposition (PVD) technique such as a pulsed laser deposition (PLD) method. Unfortunately, the PLD method has many limitations, including large-scale deposition issues and economic feasibility; a more practical approach is required.

Accordingly, in this study, a metal-organic chemical solution deposition (MOCSD) method was employed for the deposition of LSC. By employing this wet chemical method, porous and nanoscale-thick LSC thin films can be fabricated by using La, Sr, and Co with organic ligand precursors. SOFCs with LSC as the cathodic electrode can be fabricated and operated at the low-temperature regime. We also measured the performance of another SOFC with Pt as the cathode; this served as a reference cell. The performance characteristics of these cells were evaluated at 450 °C by using a thermal stability-oriented approach. The output current that comes from the electrochemical reaction was continuously collected at a constant probe bias, and microstructural analysis was conducted to look at the expected morphological change that comes from the heat vulnerability of Pt.

2. Experimental details

Two different types of electrolyte-supported SOFCs were prepared, as depicted in Fig. 1(a). Pt-YSZ-Pt and LSC-YSZ-Pt SOFCs were fabricated using 300- μm -thick 8 mol% polycrystalline YSZ (MTI Corp.) as the electrolyte support.

In the case of Pt-YSZ-Pt, porous platinum electrodes (for the cathode and anode) were deposited on both sides of the YSZ with an angle-resolved DC magnetron sputtering system with a DC power of 100 W and a current of 0.25 A under 75 mTorr at room temperature. The sputtering target of platinum used in this study had a diameter of 2 in. and was 0.125-in.-thick (Kurt J. Lesker Company). The sputtering process proceeded for 230 s to obtain the desired thickness. As a consequence, a ~ 150 -nm-thick porous electrode was deposited. The microstructure of this electrode was analyzed using field-emission scanning electron microscopy (FE-

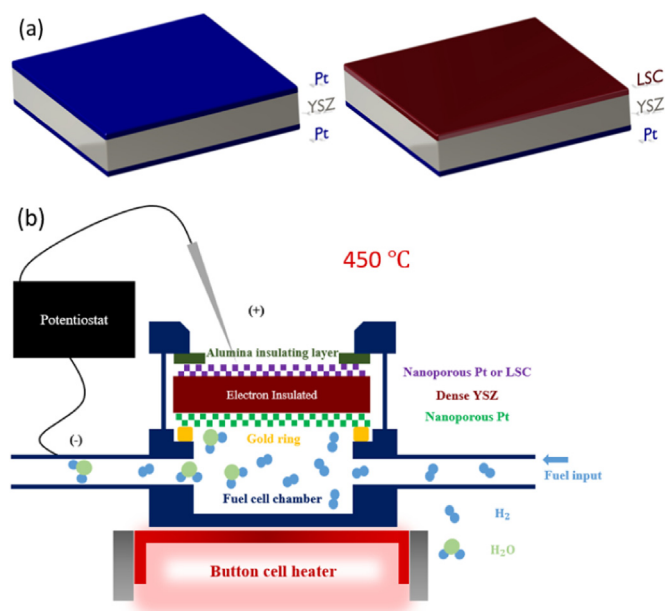


Fig. 1. (a) Schematic of fabricated samples (Pt-YSZ-Pt and LSC-YSZ-Pt) and (b) cross view of the fuel cell test station.

SEM) with JSM-6701F (JEOL Ltd.). Because the hydrogen oxidation reaction (HOR) rate is much faster than the oxygen oxidation rate (ORR), the cathode should be deposited on the polished side of the YSZ.

For the other type of SOFC, a strontium-doped lanthanum cobaltite (LSC) thin film was deposited on the polished side of the YSZ. LSC was synthesized and fabricated by a wet chemical method and used lanthanum nitrate hexahydrate [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] (Fluka), strontium acetate [$\text{Sr}(\text{CH}_3\text{COO})_2$] (Aldrich), and cobalt (II) acetate tetrahydrate [$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] (Sigma-Aldrich) as precursors. Lanthanum precursors were dissolved by stirring in deionized water at room temperature and the strontium and cobalt were dissolved separately in acetic acid [CH_3COOH] (Sigma-Aldrich) with a hotplate. The atomic ratio of lanthanum to strontium was set at 50:50 in order to obtain high conductivities. The cobalt atomic ratio is equal to the sum of La and Sr. After several hours, these solutions were mixed together and stirred at a constant rate. This precursor solution was filtered to get rid of any remaining precipitates and impurities; these can impede proper film formation. LSC was coated on the YSZ substrate by spin-coating at ~ 3000 rpm for 30 s. The coated films were dried at 200 °C for 3 min and pyrolyzed at 400 °C for 5 min to ensure thermal decomposition of the organics. Annealing was conducted at 650 °C in ambient air using a halogen furnace for 30 min. The deposited thickness of the LSC thin film was around 50 nm, as determined by electron microscopy; this deposition process was repeated twice more to obtain a 150-nm-thick film. Platinum was then deposited on the opposite side using the same sputtering process that is described above. The surface morphologies of SOFCs were observed with FE-SEM to allow for the comparison of the surface before and after electrochemical operation. Top view images were taken by an in-lens detector with an acceleration voltage of 15 kV. These images were imported to MATLAB for quantitative analysis.

To operate these SOFCs in the low-temperature regime, the fuel cell station shown in Fig. 1(b) is employed. The cathodic side is exposed to ambient air and 25 sccm of hydrogen is supplied at the opposite side of the chamber. A gold ring was put between the cell and the fuel cell chamber; this serves to seal the fuel and acts as the current collector for the anode.

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