

Powering Solid Oxide Fuel Cells with Syngas Using $\text{La}_{0.4}\text{Sr}_{0.5}\text{Ba}_{0.1}\text{TiO}_3$ Anode Infiltrated with Nano-composite

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Abstract

$\text{La}_{0.4}\text{Sr}_{0.5}\text{Ba}_{0.1}\text{TiO}_3$ (LSBT) is a promising anode candidate with perovskite structure, due to its excellent chemical stability even in sour hydrocarbons. Infiltrating nano-composite catalysts into the perovskite substrate can further enhance the electrochemical activity without undermining the robustness of the anode in light hydrocarbon fuels. This paper focuses on developing a new LSBT anode with enhanced catalytic performance and chemical stability in syngas and hydrogen fuel by infiltrating the substrate with Cu+Co and

CeO_2 +Cu+Co nano-composite catalysts. It was found that CeO_2 +Cu+Co significantly improved the chemical and thermal stabilities of the anode. However, an excess of infiltration reduced the active sites. The SOFC cell with the LSBT anode, which was infiltrated with 9.0 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.% Co, exhibited much improved electrochemical performance in syngas environments.

Keywords: Catalysis, EIS, Electrode, Fuel Cell, Infiltration, Solid Oxide Fuel Cell

1 Introduction

In the past decades, the quality of life has significantly improved along with the revolution in energy generation technologies. Novel applicable energy generation technologies are urgently needed to address the increasing public concerns on energy supply, pollution management, potential hazard control, economic efficiency and fuel feeds availability [1]. Compared to conventional combustion-based power generation system, solid oxide fuel cell (SOFC) exhibits the benefits of higher energy efficiency, lower pollutant emission and more fuel flexibility by turning chemical energy directly into electrical energy using an electrochemical process at elevated temperatures [2,3]. In addition, there are also several advantages of using fuel cells in comparison with batteries. Different from battery systems, SOFCs can be refueled continuously, and be scaled up to an industrial-application set-up in a relatively simple and flexible fashion [3]. However, the successful deployment of SOFC is still hindered by some technical barriers, including lower economical competitiveness compared to existing combustion engines, and poor chemical stability in hydrocarbon-fueled environments [4].

Compared with pure H_2 , the direct oxidation of light hydrocarbons (such as syngas, methane, etc.) in SOFCs can provide more economic benefits and has garnered extensive attention, since these readily available fuels are cheaper, naturally-abundant and more feasible for use [5–7]. Ni/yttria-stabilized zirconia (YSZ) cermet has been widely applied as the anode in H_2 -fueled SOFCs because of its excellent catalytic activity and electrical conductivity [3,8,9]. However, this anode is not suitable for operating in syngas, particularly the coal-derived syngas which is rich in CO. Since Ni can catalyze the formation of graphite, the resulted metal-dusting effect will disintegrate the structure of the anode [5, 10–12]. One approach to enhance carbon and sulfur resistance of an anode is to replace Ni with other alternatives, including ceramic-metal composites (such as Cu-ceria and Pd-ceria) [13, 14] and complex oxides (such as perovskite oxide) [15,16]. Lanthanum substituted strontium titanate (LST) has a perovskite structure, which is a promising anode material since it has exhibited excellent chemical stability even in sour hydrocarbons [17, 18].

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With 40% of Sr sites occupied by La, a proportion of Ti^{4+} is reduced to Ti^{3+} to maintain the charge balance [19], leading to an increase in both electronic and ionic conductivities. Moreover, the substitution of Sr with Ba (LSBT) can further improve the ionic conductivity [20, 21]. However, the catalytic activity of this catalyst is insufficient to provide a satisfactory performance compared to metallic catalysts.

A strategy for achieving the excellent electrochemical performance of an anode without losing its structural integrity in hydrocarbons is to combine the above mentioned two types of catalysts through introducing an active nano-scale catalyst into the perovskite-based substrate [22–25]. Infiltrating metallic catalysts into a sintered porous perovskite-based skeleton holds great potential for achieving this goal [26, 27]. Compared with conventional solid state synthesis, the wet infiltration method is a low cost and highly efficient process, which produces a uniform dispersion of infiltrates over the substrate materials surface to reach a high redox and chemical stability in hydrocarbons [28, 29]. Herein, we introduce three types of infiltrates (Co, Cu and CeO_2). It is expected that the addition of Co and Cu can enhance the catalytic activity and carbon resistance, respectively [30–32]. CeO_2 not only can increase the redox and thermal stabilities of the infiltrated Co or Cu, but also behave as an oxygen reservoir to enhance the carbon resistance of the anode.

2 Experimental

2.1 Fabrication of SOFCs

$\text{La}_{0.4}\text{Sr}_{0.5}\text{Ba}_{0.1}\text{TiO}_3$ (LSBT) was prepared using the solid state synthesis method. The starting materials were La_2O_3 (Alfa 99.99%), SrCO_3 (Fisher 99.0%), BaCO_3 (Fisher 99.4%) and TiO_2 (BDH 98%) powders. The powders were weighed in the molar ratio and mixed uniformly. The mixed powders were sequentially pressed uniaxially into pellet at 200 MPa, calcined at 1,200 °C for 10 h and ball milled into powders.

Fuel cells were fabricated using commercial YSZ (8 mol.% Y-doped ZrO_2) disks of 300 μm thickness and 25 mm diameter as the electrolyte (provided by FCM, fuelcellmaterials company, <http://fuelcellmaterials.com>). The anode was made of equal weights of YSZ and the as-prepared LSBT powders, while the cathode was the mixture of equal weights of YSZ and LSM ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) powders. In the electrode membrane fabrication, the powders were initially mixed with 10 wt.% of polymethylmethacrylate (CA 6, microbeads) was the pore-former. The resulting mixture was then mixed with a homemade gel containing terpineol and isopropanol (2:1 in volume ratio, the gel also contains 5 wt.% polyvinyl butyral-co-vinyl alcohol-co-vinyl acetate, PVB, MW = 70,000–100,000, Aldrich, and 5 wt.% ethyl cellulose) to form electrode inks. The electrode inks were deposited onto the YSZ electrolyte disc using screen printing on both sides of the YSZ disks and sintered in air for 2 h at 350 °C and 2 h at 1,200 °C to form the fuel cell.

After sintering, infiltrations were performed on the porous anode. Two types of infiltrates were used for investigation: Cu+Co and CeO_2 +Cu+Co. The specific chemical compositions of different infiltrates are listed in Table 1. The infiltrating solution was prepared by mixing nitrates with de-ionized water: a cerium nitrate solution was made at a concentration of 4.0 mol L^{-1} ; a copper-cobalt nitrate solution was made at a molar ratio of 2:3 at a total metal concentration of 3.0 mol L^{-1} . For the infiltration of Cu+Co, copper-cobalt nitrate solution was dropped slowly on the surface of the LSBT-YSZ electrode and calcinated at 400 °C for 2 h. For the infiltration containing CeO_2 , ceria nitrate solution was first slowly dropped in the anode structures and then calcinated in air at 800 °C for 2 h. Then the copper-cobalt solution was added in the anode and then calcinated at 400 °C for 2 h. The morphology of cross-section and surface of cells were observed at room temperature by a Hitachi S-2700 SEM.

2.2 Fuel Cell Setup and Electrochemical Characterization

In a Thermolyne F79300 vertical furnace, single cell tests were carried out with a coaxial set-up with both inlet and outlet tubes. To avoid the leakage of flue gas and oxygen, the outlet tube was sealed by ceramic paste (Ceramabond 503, Aremco) to the outer edge of the anode side. The fuel cell was heated at a heating rate of 2 K min^{-1} to the designed operating temperature (850, 900, or 950 °C). Then, the fuel gas, including H_2 or syngas (40% CO + 60% H_2), was fed into the anode chamber at a flow rate of 25 mL min^{-1} , while air was supplied to the cathode chamber by exposing the cathode

Table 1 Chemical composition of the infiltrates.

Infiltrates type	Composition / wt.%		
	CeO_2	Cu	Co
Cu+Co	–	3.6	5.4
CeO_2 +Cu+Co	9.0	0.6	0.8
	9.0	3.6	5.4
	9.0	4.5	6.7

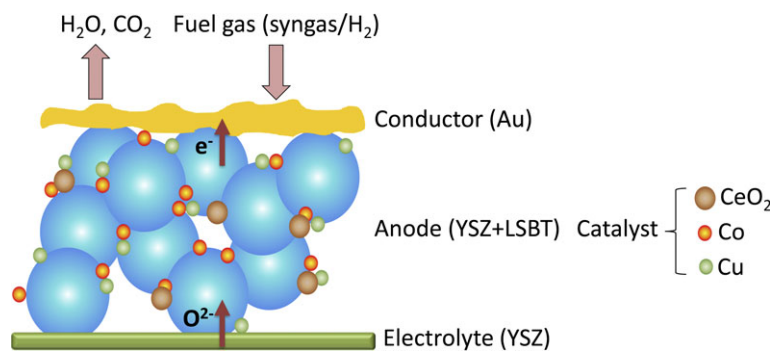


Fig. 1 Schematic diagram of the infiltrated anode.

side to air. The dwelling time at each temperature point is less than 2 h.

Electrochemical performances were measured using an electrochemical workstation of a Solartron 1287 potentiostat and a Solartron 1255 frequency response analyzer. The polarization resistance of the cell was then estimated based on electrochemical impedance spectroscopy (EIS), recorded in the frequency range from 10^6 to 1 Hz, with AC perturbation of ± 20 mV based on open circuit voltage (OCV).

The current density (j) vs. voltage (V) and power density (P) curves were measured with a potentiodynamic mode. The V was scanned from OCV to zero voltage at a rate of 5 mV s^{-1} . A four-point probe measurement was carried out to ensure that the resistance of interconnect was not included in the voltage losses of the cell. After measuring the j vs. V curve, P was acquired by multiplying j and V and then plotted as a function of j .

3 Results and Discussion

3.1 Morphology of Fabricated SOFCs

Figure 2 shows the cross-sectional SEM image of a fabricated SOFC cell with a porous LSBT+YSZ anode on the left and a LSM+YSZ cathode on the right before anode infiltration. It was found that both electrodes were firmly bonded to the dense YSZ electrolyte. The thicknesses of the anode and cathode were both around $60 \mu\text{m}$. The visible morphological changes at each surface of the electrodes represent gold and platinum pastes as the current collectors for the anode and the cathode, respectively.

Figure 3 is the image of the cross-section of the anode both before infiltration and after the infiltration with 9 wt.% CeO_2 +3.6 wt.% Cu+5.4 wt.% Co. It is shown that the white nano-particles, which were supposed to be the infiltrated metal and oxides, homogeneously distributed on the anode after infiltration. Such fine microstructure with the open porosity of the anode should be favorable for a high-performance anode. Further SEM examination on other infiltrated structures indicates that the microstructures of the infiltrated anode remained consistent from sample to sample.

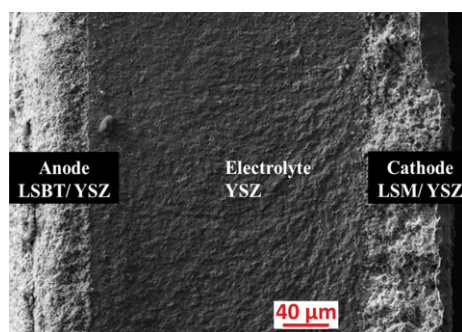


Fig. 2 SEM image of the cross-section of SOFC with LSBT+YSZ/YSZ/LSM+YSZ.

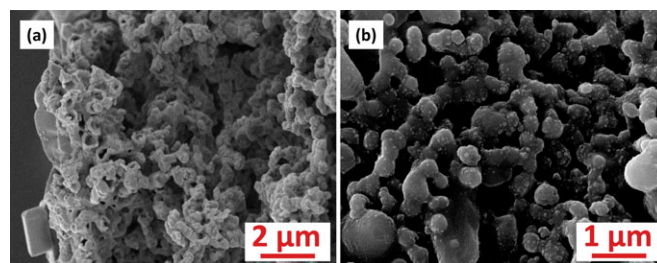


Fig. 3 SEM image of the LSBT anode (a) before infiltration and (b) after infiltration with 9 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.% Co.

3.2 Electrochemical Characterization

3.2.1 Electrochemical Analyses of Cu+Co Infiltration in LSBT Anode

SOFCs with the LSBT+YSZ anode infiltrated with 3.6 wt.% Cu + 5.4 wt.% Co are tested in H_2 at 950, 900, and 850 °C, respectively. The primary purpose of using the high-temperature test is to evaluate the thermal stability of the infiltrates. After the first cycle of tests, the temperature was maintained at 850 °C for 30 min and then was set back to 950 °C for the next cycle of tests to determine the thermal stability of the anode catalyst in H_2 as a function of time. Figure 4 is the electrochemical impedance spectroscopy of the SOFC at different temperatures and exposure time. The spectra were composed of two capacitance arcs which showed the activity polarization resistance of the catalysts. It was difficult to identify the individual activation polarization resistance of the cathode and the anode as there was no clear boundary between the two arcs. Nonetheless, an obvious increase in activation polarization occurred in the second test, reaching $1.2 \Omega \text{ cm}^{-2}$ at 850 °C. The change in activation polarization loss as a function of time was a good indication of the loss of catalytic activity in the infiltrated anode. The degradation of the activation polarization performance, determined from the spectra, was clear and remarkable.

Potentiodynamic tests were also conducted to identify the electrochemical performance of the anode catalyst co-infiltrated with Cu and Co, and the results are shown in Figure 5. The ohmic resistance of the cell was mainly determined by the resistance of YSZ electrolyte, and the theoretical value should be around $0.2 \Omega \text{ cm}^{-2}$ at 850 °C. However, the acquired ohmic resistance of the operating fuel cells was noticeably higher than $0.2 \Omega \text{ cm}^{-2}$. For the purpose of comparing the performance of the fuel cells, the ohmic resistances are all compensated in this paper. It was observed that the j - V curve of the cell had two linear regions with different slopes that divided the j - V curve into a high voltage part and a low voltage part, with the slope change point at around 0.6 V. There was a sudden decrease in current density at the low voltage part. As shown in Figure 5, the power output was reduced in the second test compared with that in the first run. A possible explanation for the decrease in current density is the oxidation of Co and Cu at a low partial pressure of H_2 . During the test at high temperature, the possible agglomeration of Co and Cu

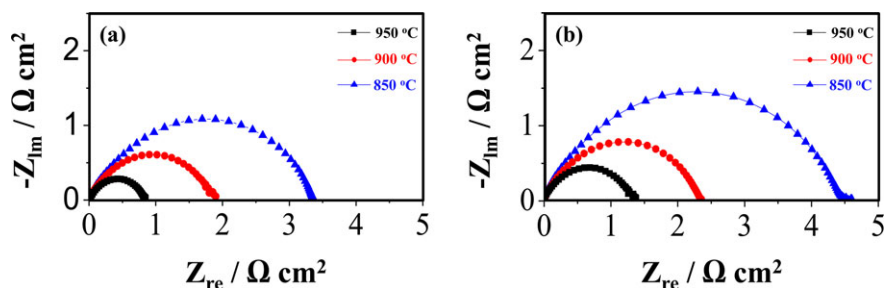


Fig. 4 EIS spectra of an SOFC with 3.6 wt.% Cu + 5.4 wt.% Co infiltration in LSBT anode in H_2 : a. first cycle, b. second cycle.

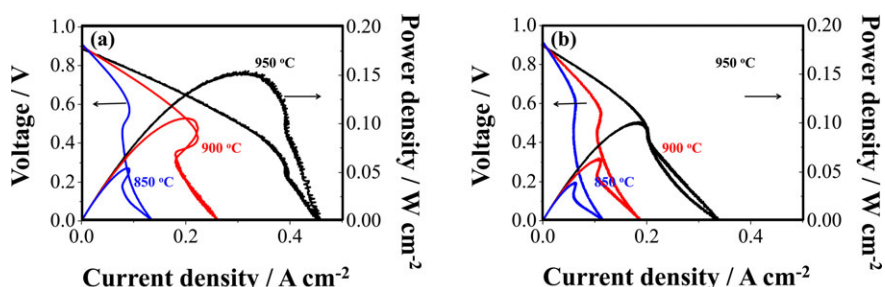


Fig. 5 Current density vs. voltage and power density curves of fuel cells of anode infiltrated with 3.6 wt.% Cu + 5.4 wt.% Co in LSBT anode in H_2 : a. first time, b. second time.

nanoparticles might block some of the pores in the electrode, which may hinder the transportation of feeding H_2 gas and contribute to higher concentration polarization resistance. Thus, a localized deficiency of H_2 is likely to happen and the oxidation of Co and Cu may take place, resulting in a decrease in current density.

3.2.2 Electrochemical Characterization of $CeO_2+Cu+Co$ Infiltration in LSBT Anode

Besides Cu and Co, CeO_2 was also infiltrated to improve the thermal stability of the SOFCs [33]. The cells with $CeO_2+Cu+Co$ infiltration on anode were tested in both H_2 and syngas environments to find the optimal amount of catalysts loading in the anode. Figures 6a, 6c, and 6e show the recorded EIS of the cells with the anode infiltrated with different amounts of $CeO_2+Cu+Co$ in H_2 , while Figures 6b, 6d and 6f exhibit the EIS results of the same cells operated in the syngas. Compared with the results in Figure 4, the activation polarization loss of the cells was significantly decreased with infiltrating 9 wt.% CeO_2 in LSBT substrates. The enhanced performance of the cells could be the result that CeO_2 is not only catalytically active, but also stabilizes the metallic infiltrates at elevated temperatures. With an increase in the amount of infiltrated Co+Cu, the activation loss of the anode decreased within the range of low infiltration amount but increased when the

infiltrates exceeded a certain amount. The best performance of the cell was achieved by infiltrating the LSBT anode with 9 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.% Co. The observed phenomenon is likely to be attributed to the increase of triple-phase boundary (TPB), due to the increase in Cu+Co. TPB is defined as the lines where the percolated ionic, electronic and gas phases meet and it has been proved that increasing nanoparticles of Cu+Co will enhance the length of TPB [23]. However, it is tentatively proposed that the infiltrated catalysts could reduce the porosity of the electrode and then block the gas diffusion pathway, resulting in the negative effects on mass transfer [33]. If there is an excess amount of metal catalyst infiltrates, the length of the boundary could also be reduced and the anode performance subsequently be restrained [34].

Figure 7 shows the current density vs. voltage and power density curves and Table 2 summarizes the maximum power

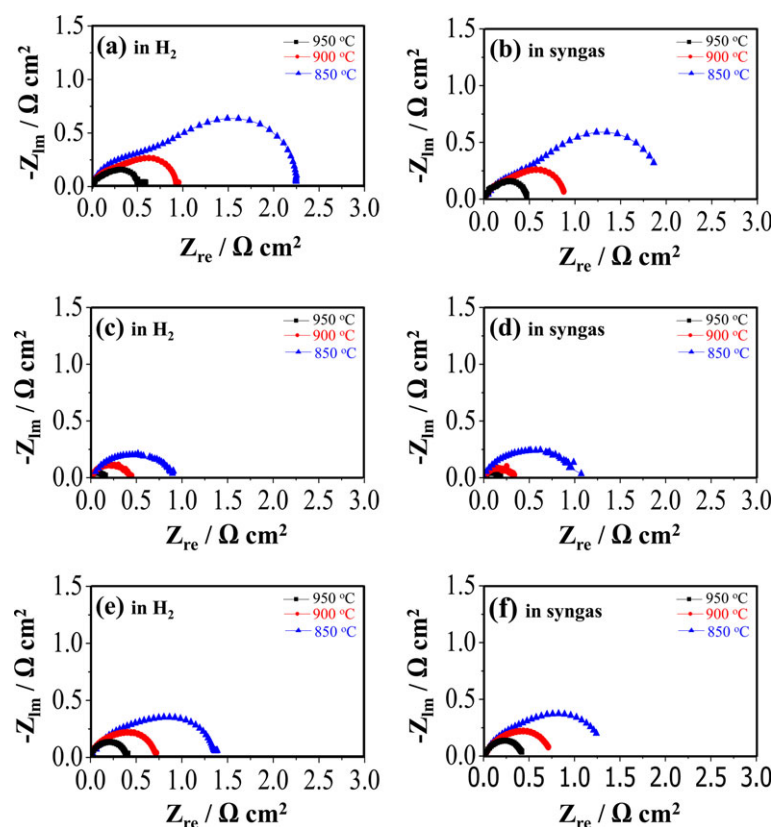


Fig. 6 EIS for SOFCs with anode infiltrated with different amounts of $CeO_2+Cu+Co$ in different fuels: 9.0 wt.% CeO_2 + 0.6 wt.% Cu + 0.8 wt.% Co in (a) H_2 , (b) syngas; 9.0 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.% Co in (c) H_2 , (d) syngas; 9.0 wt.% CeO_2 + 4.5 wt.% Cu + 6.7 wt.% Co in (e) H_2 , (f) syngas.

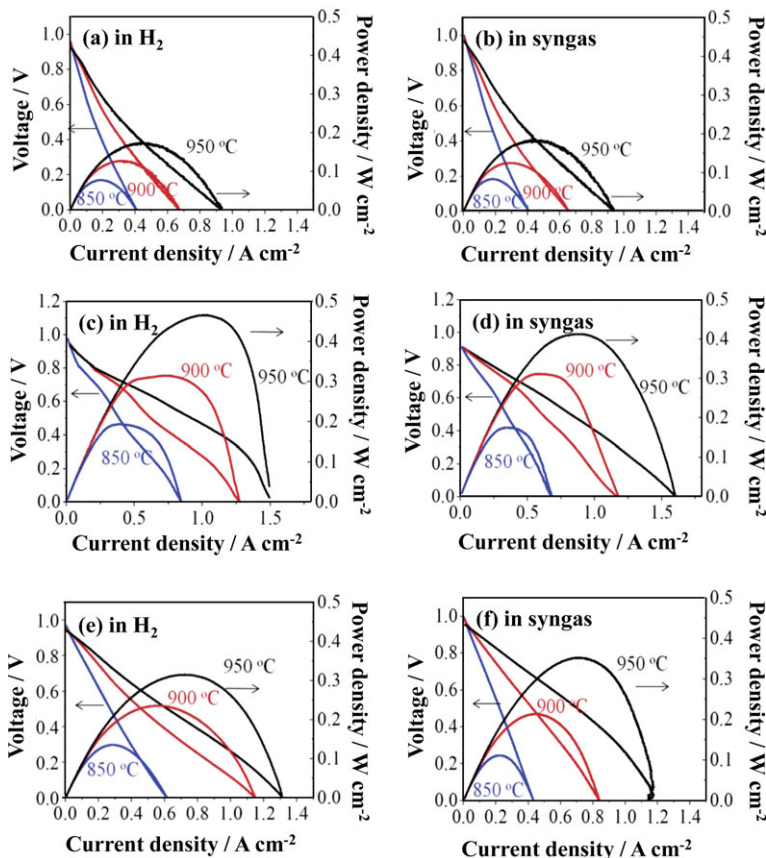


Fig. 7 Current density vs. voltage and power density curves of fuel cells of anode infiltrated with different amounts of CeO_2 +Cu+Co catalysts: (a, b) 9.0 wt.% CeO_2 + 0.6 wt.% Cu + 0.8 wt.% Co, (c, d) 9.0 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.% Co, and (e, f) 9.0 wt.% CeO_2 + 4.5 wt.% Cu + 6.7 wt.% Co at different temperatures fed with H_2 or syngas.

Table 2 Maximum power density / mW cm^{-2} of the SOFCs with the anode infiltrated with different amounts of CeO_2 +Cu+Co catalysts at different operating temperatures and fueled gases.

Infiltration type	850 °C		900 °C		950 °C	
	H_2	Syngas	H_2	Syngas	H_2	Syngas
9.0 wt.% CeO_2 + 0.6 wt.% Cu + 0.8 wt.% Co	78	84	127	125	174	185
9.0 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.% Co	193	175	314	311	465	413
9.0 wt.% CeO_2 + 4.5 wt.% Cu + 6.7 wt.% Co	135	112	235	214	315	352

density of SOFCs with CeO_2 +Cu+Co infiltrated anodes. Generally, the power density difference in H_2 and syngas is minor compared to the literature [34,35], implying that the composite infiltrates might be active for both hydrogen and carbon monoxide, although the reaction kinetics of the latter is much sluggish [30]. The best performance was achieved on the fuel cells with the anode of 9 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.%

Co infiltration. The maximum power densities of the cell were 469 mW cm^{-2} in H_2 and 414 mW cm^{-2} in syngas at 950°C .

The electrochemical stability test was performed with the LSBT+YSZ anode infiltrated with 9 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.% Co at 850°C in syngas at the potential of 0.7 V (shown in Figure 8). For the first 10 minutes an increase in current density was observed, which was followed by a gradual degradation with the rate of 6.25 mA cm^{-2} per hour. The increase of current density may be explained by the deposition of carbon on the porous substrate and the following improvement on electrical conductivity [34]. Meanwhile, the decrease may be contributed by either carbon deposition or sintering induced morphology change, as Cu might migrate to the surface of Co [13].

4 Conclusions

The enhanced catalytic performance, thermal stability and chemical stability of perovskite materials LSBT anode in syngas/ H_2 was studied by infiltrating nano-scaled catalysts such as CeO_2 , Cu and Co. The results indicated that pre-infiltrating CeO_2 into substrate enhanced the thermal stability of the dispersed metallic catalysts. Moreover, loading more infiltrated catalysts increased the triple-phase boundary up to a limit that an excess amount of metal infiltration would reduce the active sites. The cell with a $\text{La}_{0.4}\text{Sr}_{0.5}\text{Ba}_{0.1}\text{TiO}_3$ (LSBT) anode infiltrated with 9.0 wt.% CeO_2 + 3.6 wt.% Cu + 5.4 wt.% Co exhibited excellent electrochemical performance with high power density.

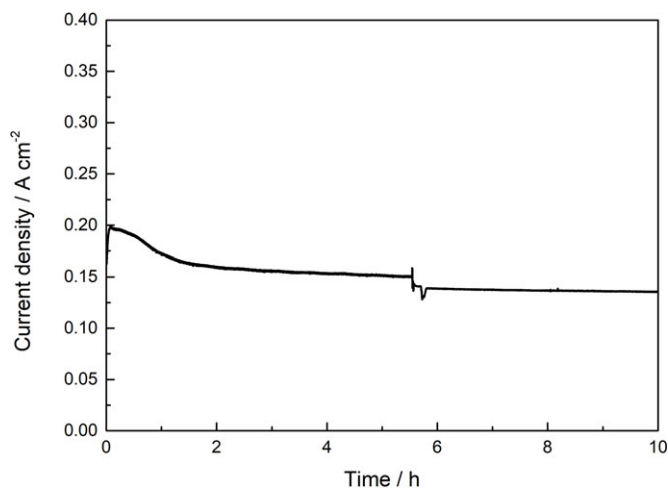


Fig. 8 The electrochemical stability test of the LSBT anode infiltrated with 9.0 wt.% CeO_2 +3.6 wt.% Cu+5.4 wt.% Co at 850°C at the potential of 0.7 V in syngas.

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