Short communication

High-performance cathode-supported solid oxide fuel cells with copper cermet anodes

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ABSTRACT

Thin film solid oxide fuel cells, composed of thin coatings of 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ), thick substrates of infiltrated $La_{0.8}S_{0.2}FeO_3$ (LSF)–YSZ cathodes and CuO–SDC ($Ce_{0.85}Sm_{0.15}O_{1.925}$)–ceria anodes, are fabricated using the conventional tape casting and infiltration methods. Infiltrated LSF–YSZ cathodes exhibit a much lower interfacial polarization resistance than $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (LSM)–YSZ cathodes due to the mixed ionic and electronic conducting behavior of LSF, especially at low operation temperatures. The single cell has shown good and stable performance in hydrogen and hydrocarbon fuels. Maximum power densities for hydrogen, propane, dodecane and low sulfur diesel at 800 °C are 0.62 W cm^{-2}, 0.40 W cm^{-2}, 0.37 W cm^{-2} and 0.36 W cm^{-2}, respectively.

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1. Introduction

Solid oxide fuel cells (SOFCs) show great promise for efficient and benign conversion of chemical energy into electricity from a range of fuels such as hydrogen, natural gas and heavier hydrocarbons. Despite that hydrocarbons can be externally reformed to produce hydrogen-rich fuels for SOFCs operation, it is more desirable to directly introduce hydrocarbons into the SOFC anodes without pre-reforming since it could reduce power plant size, weight and complexity. The primary challenge is to find effective means through which anode-coking could be suppressed or avoided. The state-of-the-art SOFCs typically utilize thin electrolyte films of yttrium-stabilized zirconia supported on 1–2 mm thick Ni–YSZ anode substrates and operate at temperatures above 750 °C [1]. However, nickel is highly susceptible to coking when exposed to hydrocarbon fuels at elevated temperatures. While some progress has been made on the direction utilization of hydrocarbons in nickel anodes via controlling the operation conditions or adding an adjacent catalyst layer [2–4], alternative anodes with much less catalytic activity for coking formation might provide an important approach for direct hydrocarbon SOFCs.

Electronic oxides such as lanthanum strontium titanate [5], LaCrO$_3$ based perovskite oxide [6], $Sr_2Mg_{1-x}Mn_xMoO_{6-\delta}$ [7] and so on have been examined as anodes for SOFCs directly operating on hydrocarbon fuels. Note that these materials were generally cho-

sen based upon their electronic conductivity and stability in fuels. Their relatively poor catalysis for electrochemical oxidation of fuels, especially for heavy hydrocarbons, makes it difficult to achieve reasonably high power densities. In contrast, the Cu/YSZ/CeO$_2$ anodes showed substantially enhanced resistance to deactivation from carbon deposition and sulfur poisoning while maintaining good catalytic activity for the anodic oxidation of various heavy hydrocarbon fuels due to the mixed ionic and electronic conduction behavior of ceria in reducing atmosphere [8]. However, the low melting temperatures of copper and copper oxides do not allow them to be fabricated with the typical method used for Ni–YSZ anodes which usually require firing temperatures above 1200 °C. Up to date, the copper cermet anodes have been prepared using a unique two-step process, consisting of formation of porous YSZ skeleton on the electrolyte and the addition of copper oxide and ceria by impregnation of nitrate solutions with subsequent low temperature calcinations.

Recently, we have shown that Cu–YSZ anodes could be easily applied using screen-printing method onto the $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (LSM)–YSZ cathode supported SOFCs, yielding maximum power densities of 0.26 W cm^{-2} and 0.17 W cm^{-2} at 800 °C for hydrogen and propane, respectively. The substitution of SDC, a mixed ionic and electronic conductor, for YSZ in the copper anode could further increase the maximum power densities, e.g., 0.35 W cm^{-2} for hydrogen and 0.22 W cm^{-2} for propane [9]. In addition to advantages of high reproducibility, improved quality and reduced cost of fabrication, the conventional ceramic processing enables high loadings of copper oxides and three dimensional distribution of copper oxide within the composite anodes, which can help suppress the

coarsening of copper at operating temperatures and thus improve the long-term stability of the anode microstructure and performance. Nonetheless, the impedance analysis indicated that the cell performance was largely limited by the poor catalysis for oxygen reduction reactions of LSM–YSZ cathodes sintered at 1275 °C, as required to densify the electrolyte layer during the co-firing procedure.

The mixed-conducting oxide $La_{0.8}Sr_{0.2}FeO_3$ (LSF), exhibiting a high oxygen ionic conductivity in addition to a high electronic conductivity, is one of promising alternative cathode materials for SOFCs operation below 800 °C with advantages of enhanced surface exchange kinetics and increased surface area for oxygen reduction reactions. Nonetheless, interfacial diffusion between LSF and YSZ at high temperatures resulted in a pronounced increase in the cathode polarization resistance, making it necessary to reduce the sintering temperature of the cathode or introduce an interlayer between LSF and YSZ [10,11]. Outstanding performance was achieved for LSF–YSZ cathodes prepared by impregnation of a porous YSZ skeleton with La, Sr and Fe nitrate solutions followed by low temperature calcinations to form LSF perovskite, thus avoiding the high temperature interfacial diffusion [12]. In this paper, porous YSZ substrates infiltrated with LSF were thus adopted as the cathodes for thin film SOFCs to further exploit the merit of direct fabrication of copper cermet anodes.

2. Experimental

The LSF infiltrated YSZ cathode supported fuel cells were fabricated by first preparing tri-layers of highly porous thick YSZ support, less porous thin YSZ interlayer and dense thin YSZ film. The tri-layer structure was produced by laminating three tape-casted ceramic green tapes, with varied fugitive materials for the two porous YSZ layers. The laminated green tapes were co-fired at 1400 °C to produce the final ceramic structures. The mercury porosimetry measurement indicated that the average pore diameters of the YSZ substrate and interlayer were, respectively, 11 μm and 2 μm with porosities of 70% for the former and 60% for the latter. The copper anodes were prepared by mixing CuO powder (Alfa), SDC ($Ce_{0.85}Sm_{0.15}O_{1.925}$, 7 m^2 g^{-1}, Praxair) powder and rice starch in a weight ratio of 45:45:10. A screen printing vehicle (Electro-Science Laboratory) was added to the mixed powder to make a slurry. The slurry was applied onto the YSZ electrolyte coatings of half-cells by screen-printing and fired at 900 °C for 4 h.

The active cathode catalyst, LSF, was then added into the porous scaffold via impregnation of nitrate solutions containing $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ in an appropriate ratio, followed by calcinations at 850 °C for 4 h to produce the perovskite structure. Fig. 1 is a diffraction pattern of the decomposition products of the precursors and demonstrates that the LSF–YSZ composite cathode has the proper structure. The procedure of impregnation and calcinations was repeated until a loading of 40 wt.% LSF was achieved. The impregnation of 10 wt.% ceria into the copper anodes was the final step in the cell fabrication. The microstructure of the cathode supported SOFCs was examined using the scanning electron microscopy (JSM6390LV, JEOL).

For fuel cell tests, the anode sides of the cells were sealed to alumina tubes using a ceramic adhesive (Aremco, Ultra-Temp 552). Au and Ag current collectors were painted on the anode and cathode sides, respectively. Single SOFCs were tested in a tube furnace at temperatures from 700 °C to 800 °C, using hydrogen, propane, dodecane or low sulfur diesel as the fuel. Ambient air was maintained on the cathode side. Electrochemical impedances were measured using a Gamry Instruments Model EIS300 impedance spectrometer with a frequency range from 0.1 Hz to 100 kHz. Symmetrical cells, consisting of two LSF infiltrated YSZ electrodes
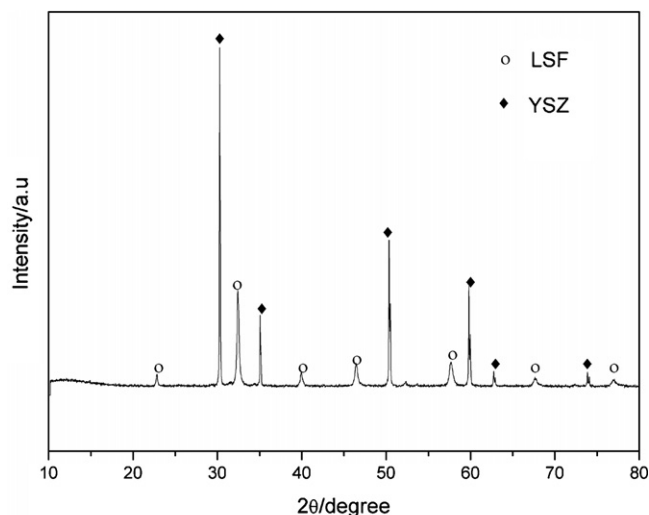

Fig. 1. An XRD pattern of an LSF–YSZ composite with 40 wt.% LSF, produced by infiltration into the porous YSZ scaffold.

separated by a dense YSZ electrolyte layer, were constructed and analyzed in air using ac impedance so as to determine the interfacial polarization resistances, given by the difference between the real-axis intercepts of the impedance plots. For comparison, similar analysis was also performed on the symmetric electrolyte supported SOFCs with LSM–YSZ cathodes fired at 1150 °C.

3. Results and discussion

LSM–YSZ composites have been the most widely used materials for SOFC cathodes due to their high electronic conductivity, reasonable catalysis for electrochemical reduction of oxygen, thermal compatibility with adjacent cell components as well as good chemical and structural stability. As shown in Fig. 2, the interfacial polarization resistance values for LSM–YSZ fired at 1150 °C, as typical used in the state-of-the-art nickel anode supported SOFCs, were 0.2 Ω cm^2 and 0.5 Ω cm^2 at 800 and 700 °C, respectively. However, firing LSM–YSZ cathodes at 1275 °C, as previously used in the thin film SOFCs with copper anodes, would remarkably reduce their catalytic activity for oxygen reduction reactions and thus produce enlarged interfacial polarization resistance values, e.g., 0.5 Ω cm^2
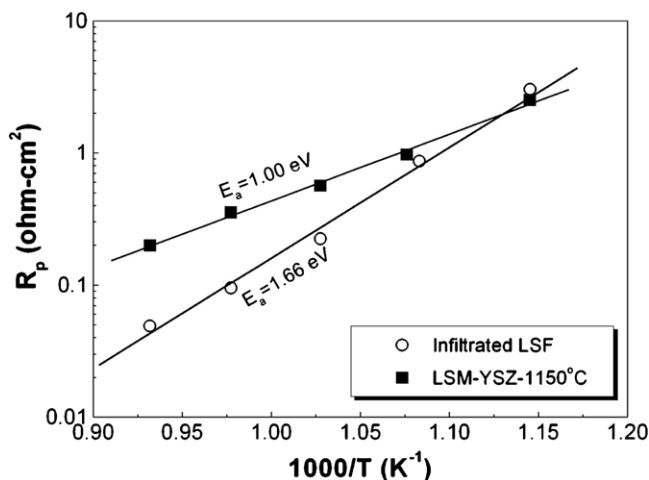

Fig. 2. Temperature dependence of the interfacial polarization resistances over a temperature range of 600–800 °C in air for LSF–YSZ cathodes prepared via impregnation and LSM–YSZ cathodes fired at 1150 °C.
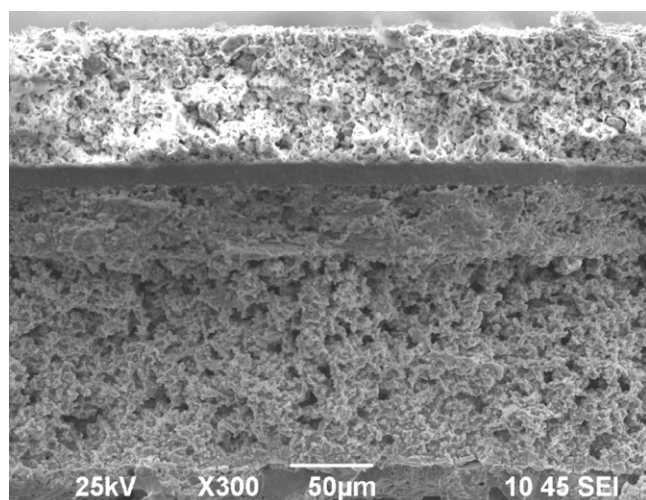
Fig. 3. The cross-sectional SEM image of the cathode supported SOFC (LSF–YSZ|YSZ|Cu–SDC–CeO$_2$).

at 800 °C, due to formation of insulating phases like La$_2$Zr$_2$O$_7$ or SrZrO$_3$ within the electrochemical reactive zones as well as excessive coarsening of LSM particles at high temperatures [9].

In comparison, the polarization resistance values for LSF infiltrated YSZ cathodes were only ≈0.05 Ω cm^2 at 800 °C and ≈0.2 Ω cm^2 at 700 °C. Note that these values were slightly higher than previously reported by Huang et al., probably due to the difference in the porous microstructure of YSZ scaffold, but were much smaller than obtained with the above LSM–YSZ cathodes fired at 1150 °C. Note that LSM is almost a pure electronic conductor with negligible ionic conductivity. The electrochemical reactive sites for oxygen reduction reactions in the LSM–YSZ cathodes are thus limited to the triple phase boundaries where the electronic conducting phase (LSM), the oxygen ionic conducting phase (YSZ) and the gas phase (pores) meet. The superior catalysis of LSF infiltrated YSZ substrates for electrochemical reduction of oxygen could be explained by their mixed ionic and electronic conducting behavior, which can dramatically increase the number of active sites for electrochemical reactions from traditional triple phase boundaries for LSM–YSZ to the entire surface for LSF–YSZ [12]. A linear Arrhenius behavior was observed for the plots of Lg(R_p) versus 1000/T, yielding an activation energy of ~1.66 eV for the LSF infiltrated YSZ cathodes. This activation energy value was in good agreement with prior studies of lanthanum ferrite based cathodes where activation energies of 1.65 eV were reported [13].

Fig. 3 shows a typical example of a cross-sectional SEM image of the graded LSF infiltrated YSZ cathode supported SOFCs with Cu–SDC–CeO$_2$ anodes. The electrolyte layer appeared fully dense and had a uniform thickness of 15 μm. Note that good intimate contact between the electrolyte and the electrodes were achieved, which would facilitate the oxygen ionic transport across the interfaces and thus reduce the electrode polarizations. As expected, a graded cathode microstructure was observed with less porosity for the 40 μm thick active cathode interlayer. The estimated porosities for the thick cathode substrates and thin cathode interlayers were, respectively, 55% and 40% after impregnation, sufficiently high to achieve adequate oxygen transport to the electrochemically active sites and thus avoid diffusion limitation in the cell performance.

Fig. 4a shows the voltage V and power density P versus the current density J for the LSF infiltrated YSZ cathode supported SOFCs with CuO–SDC–CeO$_2$ anodes operated in dry hydrogen at 700 °C and 800 °C. Open circuit voltages decreased from 1.16 to 1.10 V with increasing temperature. The area specific resistance (ASR) values calculated from the V–J slopes were 0.49 Ω cm^2 at 800 °C and
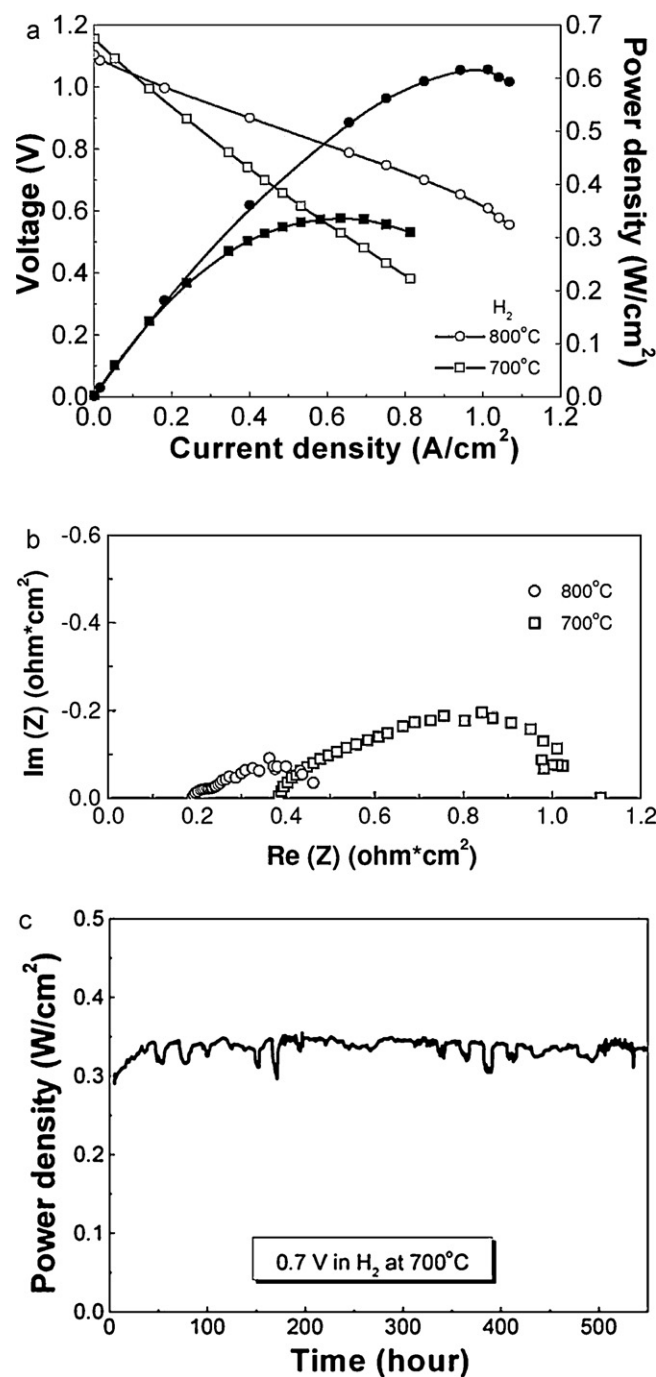

Fig. 4. Electrochemical characteristics at 800 °C and 700 °C for cathode supported SOFCs, 40 wt.% LSF infiltrated YSZ|YSZ|CuO–SDC–CeO$_2$. (a) Voltage and power density versus current density, (b) Nyquist plot of the electrochemical impedance spectroscopy, and (c) power density as a function of operation time.

0.95 Ω cm^2 at 700 °C. The maximum power densities ranged from 0.33 W cm^{-2} at 700 °C to 0.62 W cm^{-2} at 800 °C, much higher than reported by Jung et al. [14]. Fig. 4b shows typical electrochemical impedance spectra for these SOFCs operated in dry hydrogen at 700 °C and 800 °C. The Nyquist plot consisted of a small higher-frequency depressed arc and a large lower-frequency arc, both of which followed Arrhenius dependence typical of electrochemical processes such as charge transfer or surface diffusion. The electrode arcs represented ≈60% of the total cell resistance, as expected for thin-electrolyte SOFCs. Note that the total interfacial polarization resistance at 800 °C was ≈0.27 Ω cm^2, in good agreement
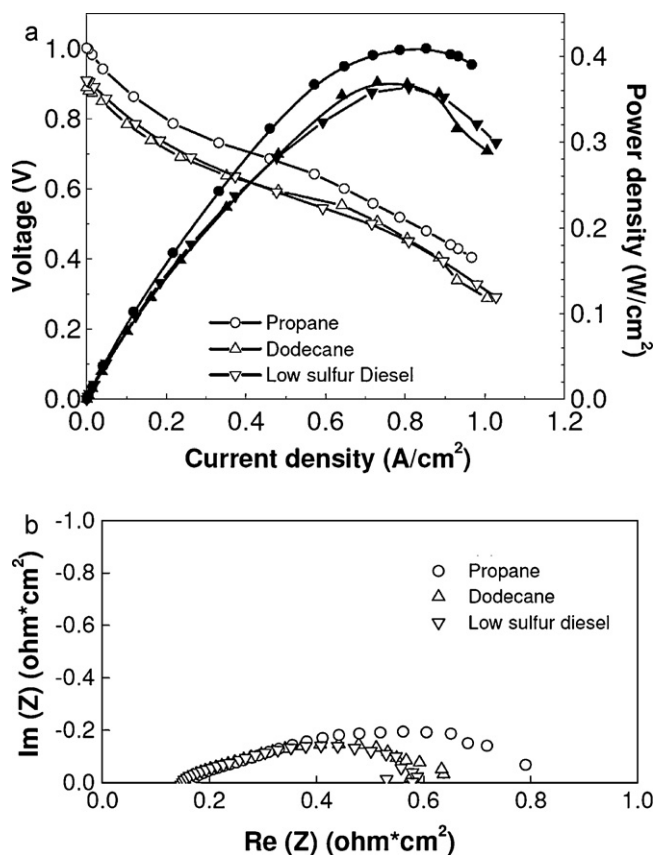
Fig. 5. Electrochemical characteristics for cathode supported SOFCs, 40 wt.% LSF infiltrated YSZ|YSZ|CuO–SDC–CeO$_2$ tested at 800 °C with propane, dodecane or low sulfur diesel as the fuel: (a) Voltage and power density versus current density and (b) Nyquist plot of the electrochemical impedance spectroscopy.

with the combination of previously obtained polarization value of 0.2 Ω cm^2 for Cu–SDC–CeO$_2$ anodes [9] and 0.05 Ω cm^2 for LSF infiltrated YSZ cathodes. These higher power densities than previously obtained with LSM–YSZ cathode supported SOFCs can be attributed to the substantially reduced cathode polarization resistance values as discussed above, e.g., 0.05 Ω cm^2 for LSF infiltrated YSZ versus 0.5 Ω cm^2 for LSM–YSZ fired at 1275 °C, as well as decreased pure ohmic resistance, e.g., 0.19 Ω cm^2 for LSF infiltrated YSZ cathode supported SOFCs (Fig. 4b) versus 0.3 Ω cm^2 for LSM–YSZ cathode supported SOFCs at 800 °C with the electrolyte at the same thickness [9]. Most of the above electrochemical tests were conducted over 10–30 h, but a few long-term tests showed that the LSF infiltrated YSZ cathode supported SOFCs with Cu–SDC–ceria anodes could provide stable power densities in hydrogen over 500 h, e.g., 0.33 W cm^{-2} at 0.7 V and 700 °C (Fig. 4c), indicative of negligible coarsening of copper or LSF particles.

Prior reports showed that the copper anodes were highly effective for the direct utilization of varieties of heavy hydrocarbon fuels such as propane, butane and decane without significant deactivation from coking or sulfur poisoning, which could be ascribed to the low susceptibility for coking of copper, appearing to only provide electrical conduction, and reasonably high catalytic activity of ceria for fuel oxidation due to its intrinsic mixed ionic and electronic conducting behavior in reducing atmosphere [8]. Fig. 5 shows the electrochemical characteristics for LSF infiltrated YSZ cathode supported SOFCs with Cu–SDC–CeO$_2$ anodes when operated on propane, dodecane or low sulfur diesel at 800 °C. Open circuit volt-

age values of 1.00 V, 0.89 V and 0.91 V were observed for propane, dodecane and low sulfur diesel, respectively. The relatively low OCV values were unlikely caused by gas leakage during the cell testing since the OCV values for H$_2$ were close to the thermodynamically predicted values, e.g., 1.10 V at 800 °C as shown in Fig. 4a. One possible explanation was that the electrochemical oxidation of these hydrocarbon fuels might involve partial oxidation reactions, as previously suggested by Park et al. [8]. The cell polarization curves in these hydrocarbon fuels featured a sharp decrease in terminal voltage for $J < 0.2$ A cm^{-2} and a slow drop for $J > 0.3$ A cm^{-2}, dominated, respectively, by the activation polarization and ohmic polarization. The maximum power densities, 0.36–0.40 W cm^{-2}, only changed slightly for these hydrocarbon fuels, which was reasonable given that similar electrochemical impedance spectra were observed at 800 °C, as shown in Fig. 5b. Note that these impedance spectra were collected under high polarizations in order to reduce the risk of coking formation. The typical ASR values for these hydrocarbon fuels were 0.6–0.8 Ω cm^2. Higher ASR values than obtained in hydrogen suggested that the Cu–SDC–ceria anodes had higher catalytic activity for electrochemical oxidation of hydrogen than for that of hydrocarbon fuels, probably due to heavier molecular weight of these hydrocarbons and the resulting slower gas diffusion rates.

4. Conclusions

The present results have shown that high performance can be achieved for the LSF infiltrated YSZ cathode supported solid oxide fuel cells with copper cermet anodes. In particular, the maximum power densities in hydrogen, propane, dodecane and low sulfur diesel are 0.62 W cm^{-2}, 0.40 W cm^{-2}, 0.37 W cm^{-2} and 0.36 W cm^{-2} at 800 °C, respectively. The relatively high performance could be ascribed to good catalytic activity of LSF infiltrated YSZ cathodes for electrochemical reduction reactions of oxygen. Note that fabrication of LSF infiltrated YSZ cathode supported structures required intensive infiltrations and calcinations, thus making them less attractive for commercial application. More work is thus mandatory to optimize the chemical composition and porous microstructure of the cathode substrates, so that the cathode supported fuel cells could be easily fabricated while maintaining high catalysis for oxygen reduction reactions.

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