Short communication

Nanostructured palladium–La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$/Y$_2$O$_3$–ZrO$_2$ composite anodes for direct methane and ethanol solid oxide fuel cells

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A B S T R A C T

A palladium-impregnated La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_{3-\delta}$/yttria-stabilized zirconia (LSCM/YSZ) composite anode is investigated for the direct utilization of methane and ethanol fuels in solid oxide fuel cells (SOFCs). Impregnation of Pd nanoparticles significantly enhances the electrocatalytic activity of LSCM/YSZ composite anodes for the methane and ethanol electrooxidation reaction. At 800 °C, the maximum power density is increased by two and eight times with methane and ethanol fuels, respectively, for a cell with the Pd-impregnated LSCM/YSZ composite anode, as compared with that using a pure LSCM/YSZ anode. No carbon deposition is observed during the reaction of methane and ethanol fuels on the Pd-impregnated LSCM/YSZ composite anode. The results show the promises of nanostructured Pd-impregnated LSCM/YSZ composites as effective anodes for direct methane and ethanol SOFCs.

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1. Introduction

The solid oxide fuel cell (SOFC) is a promising power generation system due to its high overall electric power efficiency, great fuel flexibility, and low pollution. In particular, the possibility of direct utilization of hydrocarbon fuels and renewable fuels (e.g., methane and ethanol) will significantly reduce the cost of SOFC technologies. Ethanol is an interesting fuel as it is a biofuel and can be produced via fermentation of biomass in large quantity. To achieve a high electrochemical performance in direct hydrocarbon fuel-based SOFC, it does, however, place severe demands on the anode. A state-of-the art Ni/Y$_2$O$_3$–ZrO$_2$ (Ni/YSZ) cermet anode has excellent electrocatalytic activity for the H$_2$ oxidation reaction. Unfortunately, Ni-based anodes are not stable in hydrocarbon fuels such as methane and ethanol due to carbon deposition.

Tao and Irvine [1] have shown that the performance of La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_{3-\delta}$ (LSCM) anodes is comparable with that of the Ni/YSZ cermet anodes. LSCM is chemically stable with YSZ in reducing atmosphere at high temperatures, and has a conductivity of ~29 S cm^{-1} in air and 0.22 S cm^{-1} in 10% H$_2$ at 800 °C [2]. On the other hand, the catalytic activity of LSCM for methane steam reforming is low [3]. Our studies [4] have shown that the electrocatalytic activity of LSCM-based materials is also low in methane.

One strategy to improve the performance of SOFC electrodes is catalytic promotion with the addition of nanosized oxides or metals. We have shown that introduction of Gd-doped CeO$_2$ (GDC) nanoparticles substantially enhances the activity of LSCM and Ni for methane oxidation [5,6]. McIntosh and Gorte [7] have intensively investigated the impregnation of Cu and ceria to form a Cu–ceria–YSZ composite anode for the direct utilization of methane, methanol and *n*-butane fuels [7]. In the work presented here, nanostructured Pd–LSCM/YSZ composite anodes are prepared by the impregnation of Pd nanoparticles. These nanoparticles significantly promote the electrocatalytic activity of the LSCM/YSZ composite anode for the electrochemical oxidation of CH$_4$ and C$_2$H$_5$OH fuels.

2. Experiments

Y$_2$O$_3$–ZrO$_2$ (YSZ) electrolyte substrates and La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_{3-\delta}$/YSZ (LSCM/YSZ, 50/50 wt%) composite anodes were prepared as described previously [4]. The anode was sintered at 1200 °C in air for 2 h. The surface area of the anode was 0.4 cm^2 and the thickness of the YSZ electrolyte was kept constant as 1.0 ± 0.03 mm by grinding. Impregnation of palladium was performed by dripping 0.25 M Pd(NO$_3$)$_2$ solution on to the surface of a LSCM/YSZ composite anode; the solution infiltrated the porous anode under capillary action. The resulting anode was heated at 700 °C in air for 1 h to form PdO. The PdO loading in the anode was kept within the range 0.36–0.46 mg cm^{-2}.

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A three-electrode arrangement was used for electrochemical measurements. Platinum paste was painted on to the opposite side of the LSCM/YSZ composite anode as the counter electrode and to the edge of the YSZ substrate to form a ring reference electrode. Hydrogen and methane humidified at room temperature (97% H_2/3% H_2O, 97% CH_4/3% H_2O) and ethanol-saturated nitrogen (obtained by passing the gas through absolute ethanol at 40 °C) were used as the fuel. Air served as the oxidant. The ethanol content in the ethanol-saturated nitrogen at 40 °C was calculated to be ~17.48%. The fuel flow rate was controlled at 80 mL min^{-1}. Electrochemical impedance spectroscopy (EIS) was carried out using a Solartron 1260 frequency response analyzer coupled to a Solartron 1287 electrochemical interface. The impedance spectra of the cell were recorded at open-circuit potential with an amplitude of 20 mV over the frequency range from 0.01 Hz to 1 MHz. The electrode polarization (interface) resistance, R_E was determined by the difference between the low and high frequency intercepts on the impedance curves. The polarization curves were measured by sweeping the potential at a scan rate of 5 mV s^{-1}. For comparison, LSCM/YSZ composite anodes without Pd impregnation were examined under the same conditions.

The phases of synthesized LSCM powder and LSCM/YSZ composite anodes with and without Pd impregnation were identified by powder X-ray diffraction (XRD, Philips, PW 1050). The microstructure of the anodes before and after testing was inspected by scanning electron microscopy (SEM, JEOL JSM-6340F, Japan).

3. Results and discussion

The XRD patterns of LSCM powder and LSCM/YSZ composite powder with and without Pd impregnation are shown in Fig. 1. There is no chemical reaction between LSCM and YSZ in the LSCM/YSZ composite anode as no Bragg peaks are detected other than those expected for LSCM and YSZ. As seen in Fig. 1c, the impregnated palladium exists in the form of PdO.
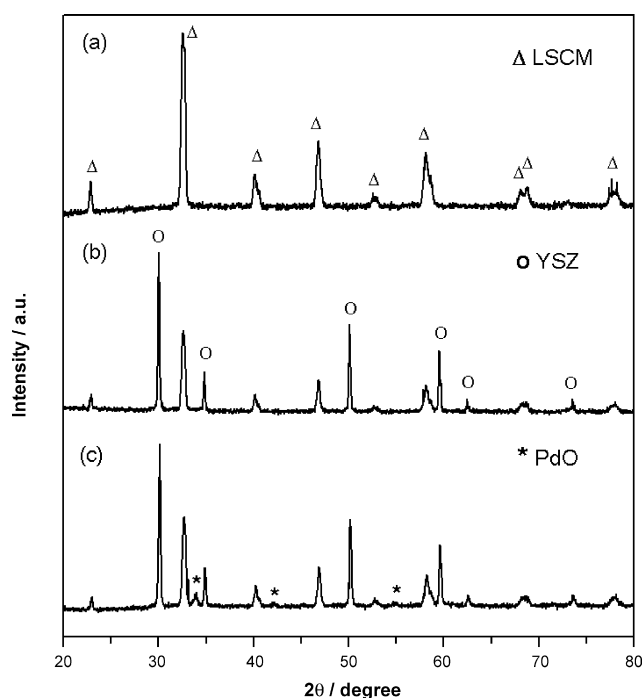

Fig. 1. XRD patterns of: (a) LSCM powder, (b) LSCM (50 wt%)/YSZ (50 wt.%) composite; (c) Pd-impregnated LSCM/YSZ composite.
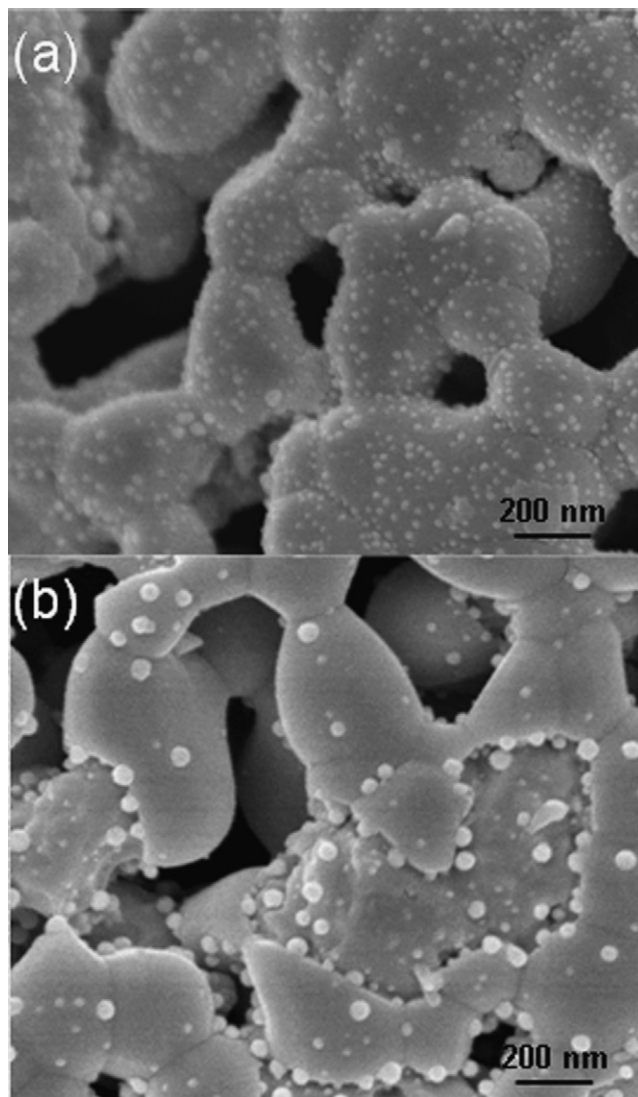

Fig. 2. Scanning electron micrographs of Pd-impregnated LSCM/YSZ composite anodes (a) before and (b) after testing at 800 °C in methane. Pd loading was 0.36 mg cm^{-2}.

Fig. 2 presents the SEM images of the surface of Pd impregnated LSCM/YSZ composite anodes before and after cell testing at 800 °C. The particle size of the LSCM/YSZ composites is ~0.5 μm, where as that of the impregnated PdO particles is 10–20 and 50–70 nm before and after the test, respectively. The Pd nanoparticles are uniformly dispersed on the surface of LSCM/YSZ grains and inside the bulk of the electrode, and are not interconnected.

Impedance curves of LSCM/YSZ composite anodes at 800 °C for reaction in H_2, CH_4 and C_2H_5OH were measured under open-circuit (Fig. 3). As seen, the impedance responses for the oxidation reaction in H_2 are not significantly affected by the impregnation of Pd nanoparticles. R_E is ~1.32 Ω cm^2 for a pure LSCM/YSZ composite anode without Pd impregnation and is reduced slightly to ~0.88 Ω cm^2 for the composite anodes with impregnated Pd nanoparticles. This indicates that for the H_2 oxidation reaction, the impregnation of Pd nanoparticles exerts a relatively small effect on the R_E of the reaction on LSCM/YSZ composite anodes.
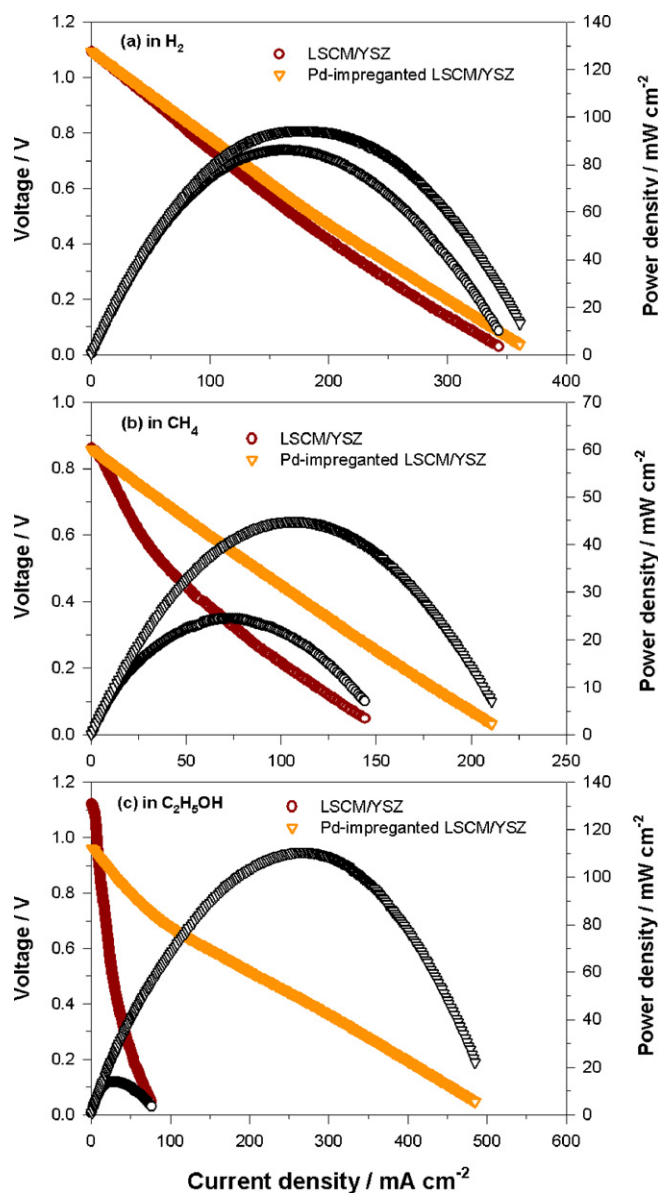
Very different to the impedance response of the H_2 oxidation reaction, the impedance arc for the reaction in CH_4 and C_2H_5OH fuels is significantly reduced with Pd impregnation, see Fig. 3(b) and (c). For methane oxidation on a pure LSCM/YSZ composite anode, R_E
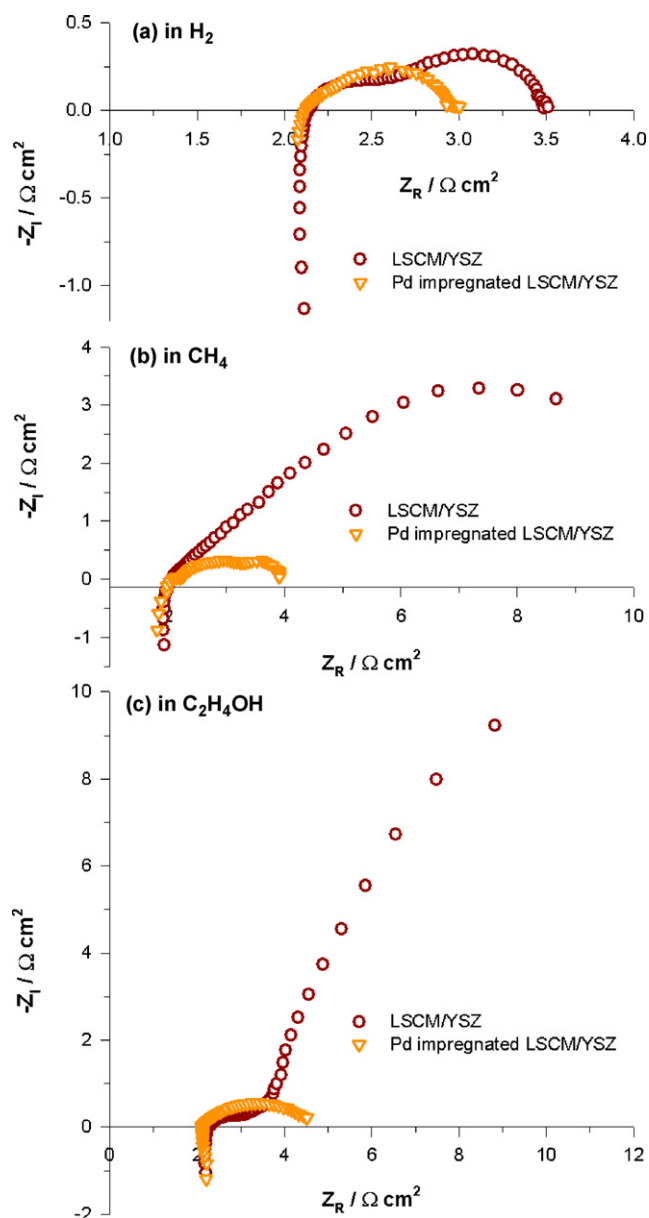
Fig. 3. Impedance responses of LSCM/YSZ composite anodes with and without Pd impregnation for reaction in different fuels at 800 °C. Impedance measured at open-circuit.

Fig. 4. Cell performances in different fuels at 800 °C (a–c).

is 9.18 $\Omega\,cm^2$, by impregnated Pd nanoparticles, R_E is reduced significantly to ~2.0 $\Omega\,cm^2$. There is also a remarkable reduction in the electrode impedance for electrochemical oxidation of ethanol on the Pd impregnated LSCM/YSZ composite anode (Fig. 3c). It is also noticed that impregnation of Pd nanoparticles primarily reduces the electrode polarization resistance associated with the low frequencies for the reaction in CH_4 and C_2H_5OH.

The performance of cells with LSCM/YSZ composite anodes and Pt cathodes for the oxidation reaction in H_2, CH_4 and C_2H_5OH at 800 °C is presented in Fig. 4. The significant changes in cell performance are most likely due to changes in the electrochemical activities of the anode as the Pt cathode and thickness of the YSZ electrolyte are kept constant in this study. Similar to the impedance behaviour, the effect of the impregnated Pd nanoparticles is most pronounced for the reaction in methane and in ethanol. The changes in the polarization behaviour in the H_2 fuel are small for the Pd-impregnated LSCM/YSZ composite anode, indicating an

insignificant effect of Pd nanoparticles on the electrocatalytic activity of the LSCM/YSZ composite anodes for the H_2 oxidation reaction (Fig. 4a). By contrast, the promoting effect of the impregnated Pd nanoparticles is substantial for the methane oxidation reaction. The maximum power output is 24 mW cm^{-2} for the cell with a pure LSCM/YSZ composite anode and is almost doubled to 45 mW cm^{-2} with the impregnation of Pd nanoparticles (Fig. 4b). For the ethanol oxidation reaction on a pure LSCM/YSZ anode, the cell power density is 14 mW cm^{-2}. After the impregnation of Pd nanoparticles, the power density reaches 111 mW cm^{-2}, an increase of eight times in power output. This is in line with the remarkable decrease in the electrode polarization resistance for the reaction on the Pd-impregnated LSCM/YSZ composite anode measured at open-circuit (Fig. 3).

No carbon deposits were detected after testing in CH_4 and C_2H_5OH on pure and Pd-impregnated LSCM/YSZ composite anodes under the conditions of the present study. Thus the cracking of methane and ethanol is not likely the main reaction path on the Pd-impregnated LSCM/YSZ composite anode. Palladium is a

well-known catalyst for partial or complete catalytic oxidation of hydrocarbons such methane, methanol and ethanol and has been extensively studied over the past 20 years in the chemical industry [8–10]. Tao et al. [11] investigated the catalytic activity of LSCM for methane oxidation and concluded that LSCM is a complete oxidation catalyst rather than a partial oxidation catalyst in methane oxidation as CO_2 dominates CO production. Hibino et al. [12] reported that addition of a small amount of Pd ($0.145\,mg\,cm^{-2}$) to the anode in a single-chamber SOFC significantly promotes the partial oxidation of methane to H_2 and CO [12].

The present study shows that impregnation of Pd nanoparticles dramatically decreases the electrode polarization resistance and increases the power output of the LSCM/YSZ composite anode. The promotion mechanism of Pd nanoparticles in the nanostructured Pd–LSCM/YSZ anode on the electrochemical oxidation reaction of methane and ethanol could be complex and is not clear at this stage. Nevertheless, the remarkable reduction in the electrode impedance at low frequencies on the Pd-impregnated LSCM/YSZ composite anode (Fig. 3) indicates the significant electrocatalytic effect of Pd nanoparticles on the dissociation, exchange and diffusion of reaction species on the surface of the LSCM/YSZ composite anodes. According to the thermodynamics of palladium oxidation, Pd could undergo reversible transformation between Pd and PdO under SOFC operation conditions which may influence the electrocatalytic behaviour [13]. We have shown recently that Pd nanoparticles can substantially enhance the O_2 reduction reaction in SOFCs [14]. Thus, under SOFC operating conditions, the co-existence and phase transformation of Pd and PdO/PdO_x may facilitate oxygen exchange and transfer and hence accelerate oxygen diffusion in the LSCM/YSZ composite, which directly enhances the electrooxidation reaction of hydrocarbon fuels such as methane and ethanol. The superior properties of Pd-based catalysts for the partial and/or complete oxidation of hydrocarbons could also play an important role in improving the electrocatalytic activity of the Pd-impregnated LSCM/YSZ composite anode under SOFC operation conditions.

4. Conclusions

Nanostructured Pd–LSCM/YSZ composite anodes have been fabricated by impregnation of Pd nanoparticles into LSCM/YSZ composite anodes. The results show that the impregnated Pd nanoparticles significantly decrease the electrode polarization resistance and increase the power output of the LSCM/YSZ composite anodes in CH_4 and C_2H_5OH. It appears that the impregnated Pd nanoparticles primarily enhance the diffusion and dissociation associated with the electrode processes at low frequencies, these by facilitating the transfer process of reaction species for the electrochemical oxidation reaction of methane and ethanol on the LSCM/YSZ composite anode. No carbon deposition is observed for the reaction in CH_4 and C_2H_5OH on the Pd-impregnated LSCM/YSZ composite anode. The results in this study demonstrate the great potential of the Pd-impregnated LSCM/YSZ composite anode for the direct use of methane and ethanol in SOFCs.

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