

Short communication

Potential oscillation of methane oxidation reaction on $(\text{La}_{0.75}\text{Sr}_{0.25})(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$ electrodes of solid oxide fuel cells

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Abstract

Oscillation of open circuit potential (OCP) and potential is observed for the methane oxidation reaction on $(\text{La}_{0.75}\text{Sr}_{0.25})(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$ (LSCM) and LSCM/YSZ composite electrodes of solid oxide fuel cells (SOFCs) in weakly humidified methane (i.e., 97%CH₄/3%H₂O). In dry methane (i.e., 100%CH₄), the potential oscillation is reduced significantly. The oscillation behaviour of OCP is also found to be strongly related to the temperature, the microstructure of the composite electrode and the fuel composition. The results indicate that the potential oscillation is thermally activated and is most likely associated with the adsorbed oxygen species on the electrode surface.

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Keywords: Solid oxide fuel cell; Methane reaction; Lanthanum strontium chromium manganite electrode; Oxidation; Potential oscillation

1. Introduction

Development of Ni-free oxides such as ceria, titanate and lanthanum chromite based oxides as alternative anodes for solid oxide fuel cells (SOFCs) has attracted a great attention recently. Lanthanum chromite based perovskite oxide is an interesting class of materials as potential electrodes for SOFCs as they are stable in both oxidation and reducing environment. Substitution on the A and B sites with alkali earth and transition metal elements can significantly modify the electronic as well as catalytic properties of the lanthanum chromite perovskite oxides [1,2]. Vernoux et al. [3] studied the catalytic properties of LaCrO₃ (LC) and $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Cr}_{0.8}\text{Mn}_{0.2})\text{O}_3$ (LSCM) for the methane steam reforming at 800 °C. LC was almost inert for the steam reforming of methane at 800 °C and the catalytic activity of LSCM was also very low. On the other hand, Tao and Irvine [4] showed a good performance of $(\text{La}_{0.75}\text{Sr}_{0.25})(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$ (LSCM) electrode for the oxidation reaction in wet CH₄ and H₂ at 900 °C. No coke formation in CH₄ was observed on LSCM anodes [5]. This indicates the enhanced catalytic activity of LSCM-based materials

under anodic polarization potentials. In this paper we studied the oxidation reaction of methane on LSCM-based anodes in weakly humidified methane under open circuit conditions. A potential oscillation was observed and the magnitude and frequencies of the oscillation are strongly affected by the SOFC operating conditions.

2. Experimental

$(\text{La}_{0.75}\text{Sr}_{0.25})(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$ (LSCM) was synthesized by a solid-state reaction method from La₂O₃, SrCO₃, Cr₂O₃ and MnCO₃ (all from Sigma–Aldrich). The powders were weighed, mixed with propanol and ball-milled for 4 h, followed by calcination at 1200 °C for 20 h in air. XRD analysis indicated the formation of perovskite phase of LSCM. LSCM electrodes were applied to the Y₂O₃–ZrO₂ (YSZ) electrolyte disk by slurry painting and sintered at 1200 °C in air for 2 h. The LSCM coating thickness was ~40 μm. LSCM (50 wt%)/YSZ (50 wt%) composites (LSCM/YSZ) with the addition of 5 wt% graphite were also prepared by single or double slurry coatings. The thickness of the single slurry coating was ~15 μm (LSCM/YSZ-1) and for double slurry coatings, it was ~35 μm (LSCM/YSZ-2). Impregnation solution of Ce_{0.8}Gd_{0.2}(NO₃)_x was prepared from Gd(NO₃)₃·6H₂O (99.9%, Aldrich) and Ce(NO₃)₃·6H₂O

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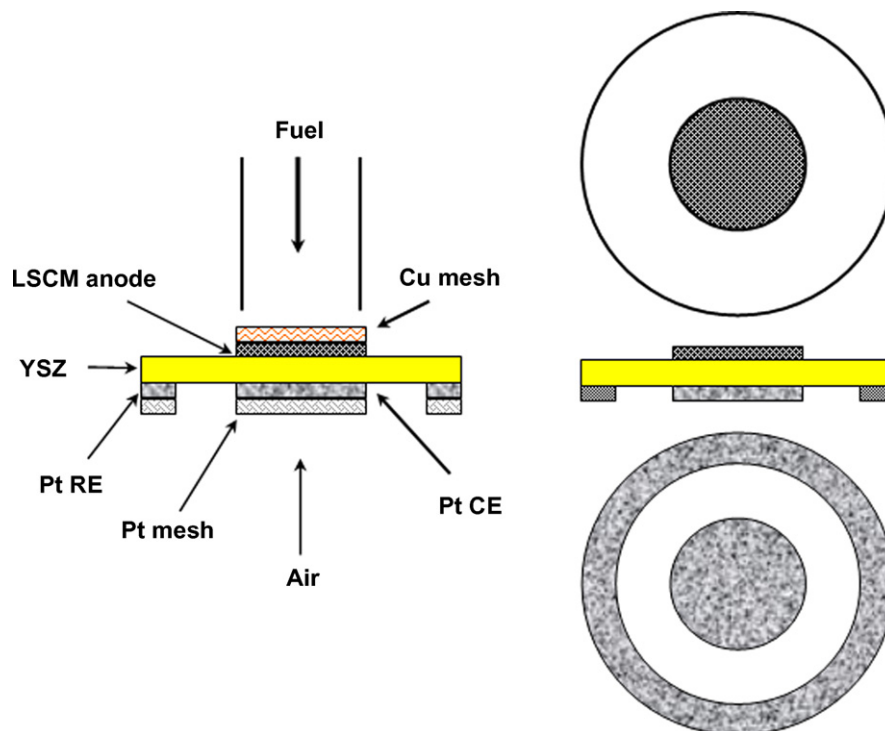


Fig. 1. Schematic diagram of the cell configuration used in this study.

(99.9%, Aldrich). Impregnation of the electrode coating was carried out by placing a drop of the solution on top of the LSCM/YSZ electrode which infiltrated the porous coating by capillary action. The electrode was fired at 850 °C in air for 1 h and the GDC loading was $\sim 1.0 \text{ mg cm}^{-2}$. A recent study shows that the electrocatalytic activity of the LSCM electrodes for the oxidation reaction of H_2 and methane fuels is improved by the GDC impregnation [6].

Platinum paste was painted onto the other side of the YSZ electrolyte substrate as the counter and reference electrodes (CE & RE). Copper mesh was used as the current collector. Copper is inert to hydrogen and hydrocarbon oxidation and has no catalytic activity for the cleavage of C–C bonds [7], thus having negligible interferences to the reaction in methane fuel on LSCM-based electrodes. Dry methane and methane humidified at room temperature ($97\% \text{CH}_4/3\% \text{H}_2\text{O}$) were used as fuel and air was used as oxidant. In comparison $97\% \text{H}_2/3\% \text{H}_2\text{O}$ and mixture of CO and H_2 were also used as a fuel. The fuel flow rate was 100 mL min^{-1} . Fig. 1 shows the schematic diagram of the cell configuration used in this study. The open circuit potential (OCP) and polarization measurements were carried out in the temperature range of 700–950 °C using a Solartron 1260 electrochemical system.

3. Results and discussion

OCP measured on a pure LSCM anode measured at different temperatures in wet and dry methane is shown in Fig. 2. In comparison the OCP measured in wet H_2 is also shown in the figure. In wet H_2 , OCP is stable and increases with the decrease of temperature. At 850 °C, OCP is 1.077 V, which is

close to the theoretical value of 1.089 V (Fig. 2a). In the case of methane, the OCP increases with the increase in temperature, consistent with the thermodynamics of the $\text{CH}_4\text{--H}_2\text{O}$ system [8]. However, OCP is not stable and fluctuated periodically in both wet and dry CH_4 . The oscillation is much more pronounced in wet CH_4 than that in dry CH_4 . For example, for the reaction at 850 °C in wet CH_4 , the magnitude of the OCP change was 30 mV while in dry CH_4 , the magnitude decreased significantly to 7 mV. The potential oscillation also became much less frequent in dry CH_4 (Fig. 2c). Under similar experimental conditions, we did not observe potential or OCP oscillation for the reaction on Ni-based electrode. Also, no such potential or OCP oscillation is reported for the reaction in methane fuel on Ni-based anodes [9,10]. No carbon deposits were found for the reaction in methane fuel on the surface of LSCM-based electrodes after test in the present study, consistent with that reported by Wan et al. [5].

OCP responses of LSCM/YSZ composite anodes prepared by single and double slurry coatings (LSCM/YSZ-1 and LSCM/YSZ-2) measured in wet CH_4 at different temperatures are given in Fig. 3. Oscillation behaviour was observed for the reaction on LSCM/YSZ composite electrodes with different thickness. However, the oscillation is significantly smaller for the reaction on LSCM/YSZ-1 in comparison to that on LSCM/YSZ-2. As LSCM/YSZ-1 is thinner than LSCM/YSZ-2, it would be expected that LSCM/YSZ-1 composite electrode would be more open than that of LSCM/YSZ-2 composite electrode. This indicates that oscillation behaviour for the methane oxidation on LSCM electrodes is sensitive to the microstructure of the electrodes. The oscillation frequency decreases with the decrease in temperature, similar to that on the LSCM electrode

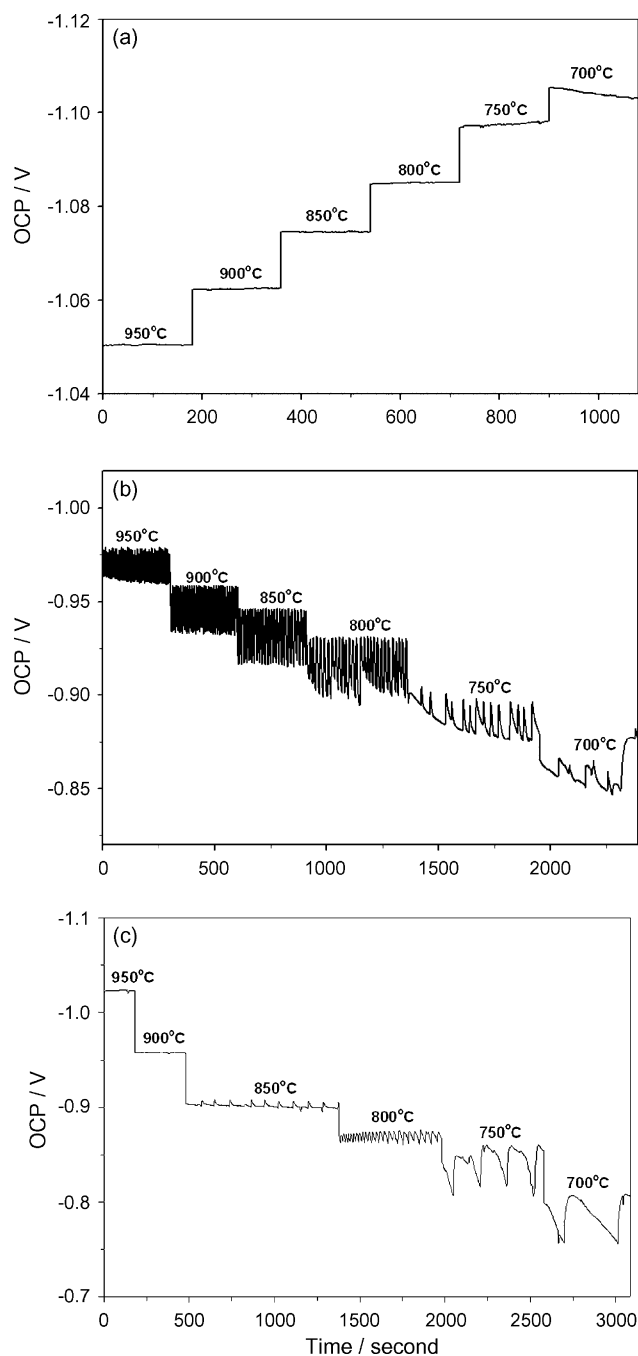


Fig. 2. OCP measured on a LSCM electrode measured in (a) wet H_2 (97% H_2 /3% H_2O), (b) wet CH_4 (97% CH_4 /3% H_2O) and (c) dry CH_4 (100% CH_4) at different temperatures.

(Fig. 2b). At 700 °C, OCP oscillation completely disappeared. This implies that the process associated with the potential oscillation is thermally activated.

Potential responses for the reaction in wet CH_4 at 800 °C were also studied as a function of CH_4 concentration and dc bias on a GDC-impregnated LSCM/YSZ-2 composite electrode (Fig. 4). The oscillation frequency decreases with the decrease in the CH_4 concentration (Fig. 4a). In the case of 100% CH_4 , the oscillation frequency is ~ 2.6 cycles min^{-1} . As the CH_4 concentration decreased to 90% (balanced by N_2), the oscillation frequency

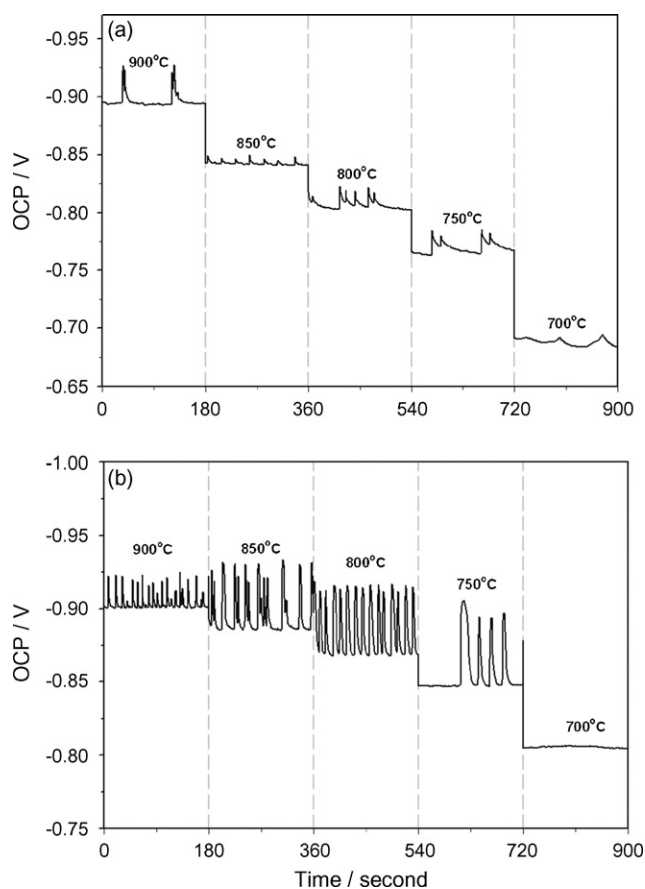


Fig. 3. OCP of (a) LSCM/YSZ-1 composite electrode and (b) LSCM/YSZ-2 composite electrode, measured in wet CH_4 at different temperatures.

decreased to ~ 1 cycle min^{-1} . When the CH_4 was reduced to 70% and 50%, the OCP oscillation almost disappeared. The magnitude of the potential oscillation is also dependent on the dc bias, which increases with the increase in dc bias (Fig. 3b). The magnitude of oscillation was ~ 46 mV at open circuit and increased to ~ 138 mV under a dc bias of 60 mA. Similar potential behaviour is also observed for the reaction on LSCM/YSZ composite electrodes without GDC-impregnation.

OCP responses for the reaction in 97% ($H_2 + CO$)/3% H_2O at 800 °C as a function of CO/ H_2 concentration on an LSCM/YSZ-2 electrode are given in Fig. 5. The OCP is stable in the CO/ H_2 concentration range studied. This indicates that the potential oscillation does not occur for the reaction in a mixed CO/ H_2 fuel on the LSCM-based electrodes. In another word, the potential oscillation at open circuit is not related to the oxidation reactions in CO, H_2 or CO/ H_2 mixed gases.

LSCM is a typical p-type conductor with total electronic conductivity in the range of 25–35 $S\ cm^{-1}$ in air [4]. In fuel reducing environment, the total conductivity decreases significantly due to the increase in the oxygen vacancy concentration. Raj et al. [11] studied the oxygen diffusion and surface exchange properties of LSCM and showed that the oxygen tracer diffusion coefficient of LSCM is two orders of magnitudes higher than that of (La, Sr)MnO₃ but is significantly lower than that of typical ionic conductors such as YSZ and Gd-doped ceria. This

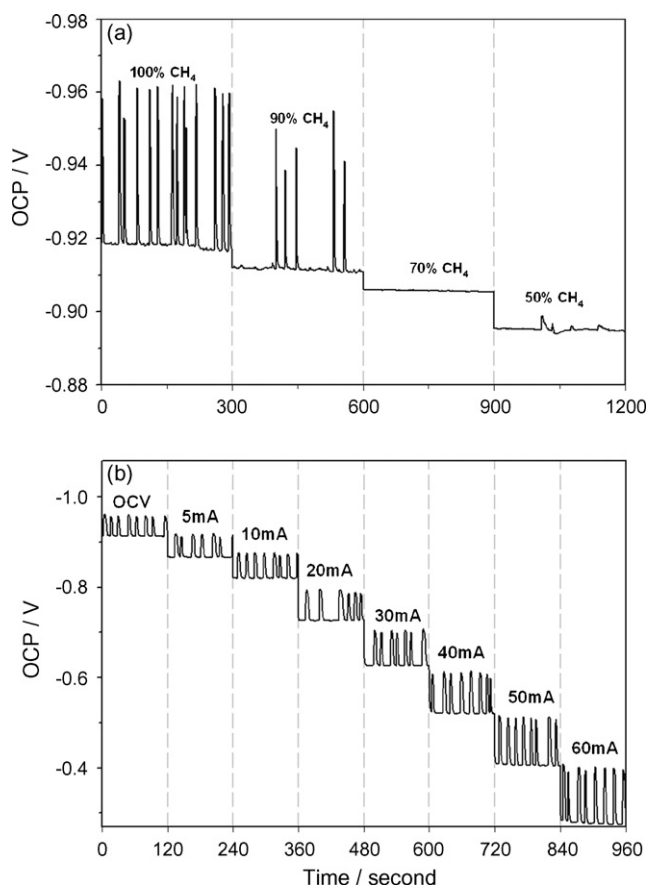


Fig. 4. OCP and potential for the reaction on GDC-impregnated LSCM/YSZ-2 composite electrodes at 800 °C in (a) wet CH₄ with different concentration of CH₄ (balanced by N₂) and (b) under different dc bias.

shows that LSCM-based material is a mixed electronic and ionic conductor with measurable oxygen ion conductivity.

Potential oscillation at open circuit or under dc bias indicates the change in the partial pressure of oxygen in a concentration cell. As the change in the oxygen partial pressure could only involve the gaseous species, this implies that the possible species which can cause the change in the oxygen partial pressure would

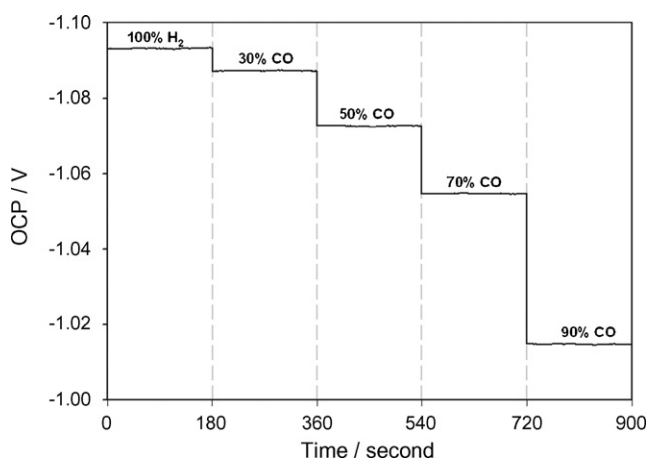


Fig. 5. OCP for the reaction on a LSCM/YSZ-2 composite electrode at 800 °C in different H₂/CO ratios. The fuel gas was humidified at room temperature.

be CH₄, H₂, H₂O, CO and CO₂. The stable OCP responses observed in wet H₂ and in H₂/CO mixed fuel shows that H₂ and CO species alone do not cause the OCP oscillation. As potential oscillation is typically associated with adsorbed species in an electrochemical system, it is most likely that the potential oscillation is originated from the adsorption and desorption of oxygen species on the reactive sites on the electrode surface. This seems to be supported by the significant effect of water on the magnitude and frequency of potential oscillation (see Fig. 2). The presence of H₂O in the methane fuel could lead to the significant increase of adsorbed oxygen species due to the possible water dissociation at high temperatures (e.g., H₂O ⇌ H₂ + O_{ads}) [12]. The strong influence of the temperature on the oscillation behaviour indicates that the concentration of the O_{ad} species is related to the exchange between the lattice O_o^x and adsorbed O_{ad} species.



where O_o^x is the lattice oxygen and V_o^{••} is the oxygen vacancy in LSCM or impregnated GDC (e.g., in the case of GDC-impregnated LSCM/YSZ electrode). The increased magnitude of the oscillation under dc bias (Fig. 4b) may be due to the increased mobility and supply of the lattice oxygen, O_o^x, which would shift the above reaction to the right. The interaction between CH₄ and adsorbed oxygen species, O_{ad}, would lead to the production of CO₂ and H₂O through the direct electrochemical oxidation reaction, or to the formation of CO and H₂ through dry reforming [13,14], then followed by the electrochemical oxidation of the CO and H₂. The exact reaction mechanism of methane oxidation under weakly humidified condition is not clear at this stage. Further work is needed to investigate in detail the nature of the potential oscillation and its implication to the reaction mechanism of the methane oxidation on LSCM-based electrodes.

4. Conclusions

The potential oscillation behaviour for the reaction in methane fuel on LSCM and LSCM/YSZ composite electrodes was investigated under various SOFC operating conditions in wet and dry CH₄. The potential oscillation has been found to be strongly related to the presence of water, the temperature, the microstructure of the composite electrode and the fuel composition. The results indicate that the potential oscillation is most likely originated from the adsorbed oxygen species on the electrode surface during the methane oxidation reaction.

Acknowledgement

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