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Oscillation of electrical current during direct methane oxidation over Ni-added LSCF–GDC anode of solid oxide fuel cells

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ABSTRACT

Solid oxide fuel cells are studied under direct methane feeding with 10–70% CH_4. When either $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)–$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) or Ni-added LSCF–GDC composite is used as the anode, the oscillations of the electrical current and the formation rates of CO and CO_2 occur. The oscillation of the electrical current can be explained by a mechanism of periodic oxidation–reduction of the bulk lattice of the anode, with the determining factor being the build-up of the concentration of the oxygen vacancies to a certain extent. As the methane concentration increases, the current density increases and becomes larger with Ni addition. Higher methane concentration leads to higher possibility to induce the oscillation, to start it earlier, and to result in a larger amplitude. Ni addition inhibites the occurrence of the oscillation of the electrical current but promotes that of the CO_2 formation rate.

1. Introduction

Natural gas, with methane as the major component, is an important fuel for solid oxide fuel cells (SOFCs). Direct-methane SOFCs have simplest operation and highest fuel efficiency. Methane decomposition occurs over the Ni cermet anodes in direct-methane SOFCs [1,2]. At the operating temperatures of SOFCs, such as 800 °C, methane decomposition over Ni can be $CH_4 \rightarrow C + 2H_2$ [3]. Thus, methane decomposition over Ni generally causes the carbon deposition (coking) [4], which may cause very rapid deactivation of the SOFC anode. On the other hand, a carbon SOFC has been proposed to utilize the deposited carbon as the fuel [5]. Huang and Huang [6] have confirmed that the deposited carbon can be fully utilized for the power generation.

Methane oxidation over the Ni catalysts has resulted in an oscillatory behavior of the oxidation rate [7–10]. This rate oscillation has been considered to be thermokinetic due to periodic oxidation–reduction of the Ni surface [11]. The oxygen content of the bulk Ni phase and a significant amount of the deposited carbon have been demonstrated to be involved in these oscillations [12]. A substantial amount of oxygen and carbon is stored and evolved by the catalysts during the oscillatory process [9]. On the other hand, the oscillation of the potential during methane oxidation has been observed in an SOFC with lanthanum chromite-based perovskite oxide as the anode and fueled with weakly humidified methane [13]. These studies of the oscillatory behavior can help the understanding of the mechanism of methane oxidation reactions over the catalysts or the electrodes.

In this work, the performance of direct-methane SOFCs was studied with the variations of the methane concentration from 10 to 70% CH_4 in argon and of the anode materials of either $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)–$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) or Ni-added LSCF–GDC. The oscillations of the electrical current and the formation rates of CO_2 and CO were observed. Both the methane concentration and the addition of Ni onto the anode showed strong effects on these oscillations. A mechanism of periodic oxidation–reduction of the bulk lattice of the anode was proposed to explain the occurrence of the oscillation of the electrical current, with the determining factor being the build-up of the concentration of the oxygen vacancies to a certain extent.

2. Experimental

2.1. Preparation of Ni-added LSCF–GDC powder

LSCF was prepared by glycine–nitrate process. Appropriate amounts of reagent-grade (Showa, Japan) metal nitrates $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in de-ionized water. Glycine (Sigma, USA) was also dissolved in de-ionized water. Then, these two solutions were mixed with glycine to NO_3 ratio of 1:0.8. The mixture was heated under stirring until combustion occurred. The product was ground to powders and then calcined by heating at 10 °C/min to 400 °C and

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held for 2 h, then at 5 °C/min to 850 °C and held for 2 h. LSCF of this work is $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$.

Gadolinia-doped ceria (GDC) was prepared by co-precipitation. The details of the method have been presented elsewhere [14]. The GDC powders were calcined by heating at 10 °C/min to 500 °C and held for 2 h, and then at 5 °C/min to 1000 °C and held for 2 h. GDC of this work is $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$.

The LSCF–GDC composite was prepared by mixing the above-prepared LSCF and GDC powders at LSCF:GDC = 60:100 in weight. The mixture was ground for 24 h, then calcined by heating at 5 °C/min to 500 °C and held for 2 h, and then at 5 °C/min to 900 °C, held for 10 h.

The addition of Ni onto LSCF–GDC was done by impregnation. The details of the method have been presented elsewhere [15]. After drying, the powders were calcined by heating at 10 °C/min to 400 °C and held for 2 h, and then at 5 °C/min to 850 °C and held for 2 h. Ni-added LSCF–GDC of this work has a Ni loading of 3 wt% with respect to the weight of LSCF in the LSCF–GDC composite, designated as Ni-LSCF–GDC.

2.2. Construction of the SOFC unit

The commercial yttria-stabilized zirconia (YSZ) tape (156 μm thickness, Jiuhow, Taiwan) was employed to make an electrolyte-supported cell. A disk of 1.25 cm diameter was cut from the YSZ tape. One side of the disk was spin-coated with the paste made of various anode materials. The other side of the disk was spin-coated with 100LSCF–50GDC and then 2Ag–100LSCF–50GDC powders to make the cathode layer. The details of the construction of the SOFC unit cell have been presented elsewhere [6]. The thus-prepared unit cell has an anode area of 1 cm^2, an anode thickness of about 30 μm, an electrolyte thickness of 156 μm, a cathode area of 1 cm^2, and a cathode thickness of about 12 μm. These thicknesses were measured from a scanning electron micrograph plot of the cross-section of the unit cell.

Fig. 1 shows a sketch of the reactor setup of the SOFC unit cell and a scanning electron microscope (SEM) view of the cathode/electrolyte cross-section. Both sides of the completed unit cell were closely connected with gold mesh wires (100 mesh) for current collection and then with Pt wires to the current and voltage measurement units. The ceramic paste was used to seal the unit cell in a quartz tube with a heat treatment of 400 °C for 1.5 h so as to complete the preparation of the test unit with a single cell. The anode side of the unit cell is sealed in the quartz tube and the cathode side is exposed to stagnant air.

2.3. Activity tests of unit cell

A fixed voltage of 0.61 V was maintained for all tests in this work. The test temperature was fixed at 800 °C. The fuel to the anode side was 10–70% methane (CH_4) in argon; for reduction, the feed to the anode side was 10% H_2 in argon. The flow rate was always 100 $cm^3\ min^{-1}$ passing the anode side.

The test started with the reduction of the anode at 400 °C in 10% H_2 for 1 h. Then, pure argon flow was passed for 2 h to purge the system. The test unit was then heated in argon to 800 °C at a rate of 5 °C/min. Then, 10% H_2 was introduced for 30 min and argon flow was followed until the measured electrical current became zero. Direct-methane SOFC test was then carried out with introducing 10–70% CH_4 flow for 220 min, respectively. Then, the anode-side flow was switched to argon.

All the results with either LSCF–GDC or Ni-LSCF–GDC as the anode were obtained using the same cell. After the test with 10% CH_4, a flow of 20% O_2 in argon passed the anode side of the cell to remove the deposited carbon. It has been confirmed that the cell performance can be recovered after the O_2 treatment. This procedure was repeated after each test of 10–70% CH_4.

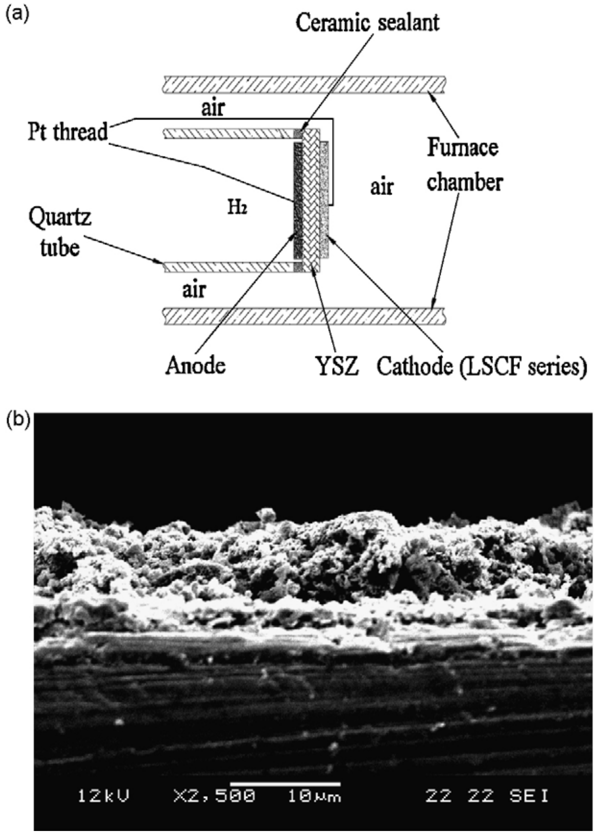

Fig. 1. The SOFC unit cell: (a) a sketch of the reactor setup, with YSZ electrolyte and (b) an SEM view of cathode/electrolyte cross-section.

During the test, electrical current, voltage, and outlet gas compositions were always measured. The current density was obtained by dividing the measured electrical current by the anode area of 1 cm^2. The compositions of CO and CO_2 were measured by CO-NDIR and CO_2-NDIR (non-dispersive infrared analyzer, Beckman 880), respectively. Other gas compositions were measured by two gas chromatographs (China Chromatography 8900) in series.

3. Results and discussion

3.1. Oscillation of the electrical current

Fig. 2(a) shows that the oscillation of the current density occurs over the LSCF–GDC anode with 10–70% CH_4 as the fuel. However, Fig. 2(b) shows that the oscillation of the current density occurs over the Ni-LSCF–GDC anode only with 50 and 70% CH_4. Additionally, the oscillation over the LSCF–GDC anode has a larger amplitude than that over the Ni-LSCF–GDC anode and also starts earlier. Thus, the addition of Ni reduces the possibility for the occurrence of the oscillation of the electrical current and also the strength of the oscillation. However, the oscillation of the electrical current over the Ni-added LSCF–GDC anode is regular but that over the LSCF–GDC anode is irregular.

Fig. 2(b) also shows that the current density can attain a steady or stable state after an induction period. However, both the behavior and the length of the induction period vary with the methane concentration. With 50% CH_4 over the Ni-LSCF–GDC anode, the induction period is relatively long, about 160 min of operation, before attaining a stable state when an oscillation occurs; with 70% CH_4, a steady state without an oscillation occurs first and an

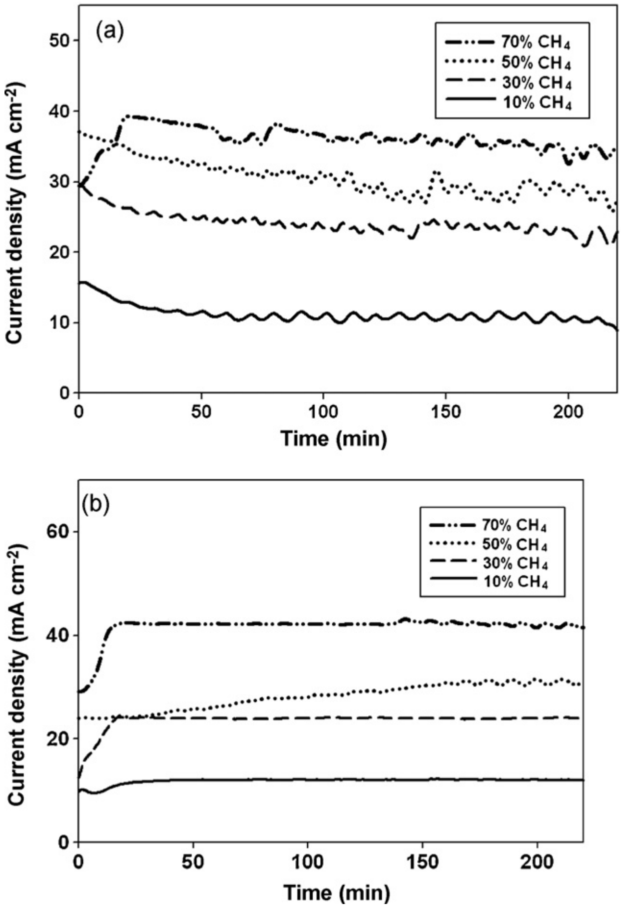

Fig. 2. Effect of CH_4 concentration on current density profiles of direct methane oxidation over anode of (a) LSCF–GDC and (b) Ni-LSCF–GDC.

oscillation occurs after about 140 min of operation, which is earlier than that with 50% CH_4. Therefore, the methane concentration has an effect on the occurrence of the oscillation. Higher methane concentration leads to higher possibility to induce an oscillation of the electrical current. Additionally, as the methane concentration increases from 10 to 70%, the current density increases considerably either without or with Ni addition, as also shown in Table 1; the current density with Ni addition is always larger than that without Ni addition.

3.2. *Periodic oxidation–reduction of anode bulk lattice*

For methane oxidation over the Ni catalysts, the oscillatory behavior of the oxidation rate has been frequently observed [7–10]. This rate oscillation has been attributed to periodic oxidation–reduction of the Ni surface [11], with the involvement of the oxygen content of the bulk Ni phase and the deposited carbon [12]. This is in agreement with the observation that a substantial amount of oxygen and carbon is stored and evolved by the catalysts during the oscillatory process [9]. Therefore, for methane oxidation over the SOFC anodes, the occurrence of the oscillation of the electrical current may be attributed to periodic oxidation–reduction of the bulk lattice of the anode.

Table 1
Variation of average[a] current density (mA cm^{-2}) with CH_4 concentration and anode materials.

CH_4 concentration	Anode	
	LSCF–GDC	Ni-LSCF–GDC
10% CH_4	10.76	12.09
30% CH_4	23.43	23.99
50% CH_4	28.96	29.98
70% CH_4	35.64	42.31

[a] The averaged value of the data taken during the SOFC operation from 100 to 200 min.

The reduction of the anode bulk is due to the extraction of the lattice oxygen from the bulk of the oxygen-ion containing materials, LSCF–GDC in this work, for the oxidation of the surface C species produced by the dissociation of methane; this is a phenomenon similar to self de-coking [16]. Notably, in direct-methane SOFCs and via comparison of open circuit voltages with Nerst potentials, the formation of surface C species from methane and its partial oxidation have been proposed as the main anode reactions [17]. Notably, also, the reduction of the anode bulk results in the formation of the oxygen vacancies. Then, the oxidation of the anode bulk is due to the replenishment of the O species from the cathode side, which generates the electrical current; these O species fill the oxygen vacancies in the anode bulk so as to recover the concentration of the lattice oxygen to its original level. Thus, the occurrence of the oscillation of the electrical current during direct methane oxidation is associated with an anode reaction mechanism of:

1. Methane dissociation to produce the surface C species.
2. The oxidation of the surface C species. The needed O species is suplied by extracting from the bulk lattice of the anode; this extraction produces the oxygen vacancies in the anode bulk. The O species is also supplied by transporting from the cathode side via the electrolyte.
3. Build-up of the concentration of the oxygen vacancies in the anode bulk.
4. The replenishment of the O species from the cathode side to fill the oxygen vacancies in the anode bulk so as to recover the concentration of the lattice oxygen of the anode bulk to its original level.

Since the above steps 1, 2 and 4 always occur but the oscillation of the electrical current may not occur, the step 3 should be determining. Thus, the build-up of the concentration of the oxygen vacancies in the anode bulk to a certain extent should be a determining factor for a measurable oscillation of the electrical current. This extent depends on the rate of the reduction of the anode bulk, which in turn depends on the concentration of the surface C species. This is in agreement with the above observation that higher methane concentration, which results in higher rate of formation of the surface C species, has higher possibility to induce an oscillation of the electrical current. Thus, the occurrence of the oscillation of the electrical current should be due to the build-up of the concentration of the oxygen vacancies to a certain extent in the above mechanism of periodic oxidation–reduction of the anode bulk lattice. Notably, the oscillation starts with an increase of the current density, as shown in Fig. 2(b) with 70% CH_4 for example—that is, the oxidation of the anode bulk, the step 4 in the above mechanism, starts first. This is an evidence supporting the above mechanism with the determining factor for the oscillation of the electrical current. Then, the extraction of lattice oxygen from the anode bulk, the step 2 in the above mechanism, occurs; this does not generate an electrical current and thus the current density decreases to the steady state value, as also shown in Fig. 2.

LSCF used as the anode may be reduced after initial contact with the fuel; this is the extraction of the O species from the bulk lattice of the anode according to the step 2 of the above mechanism. However, LSCF is re-oxidized by the oxygen coming from the cathode side during the SOFC operation; this is the replenishment of the O species from the cathode side as in the step 4 of the above mechanism. Therefore, LSCF would not be totally reduced under the fuel atmosphere. Notably, LSCF has been used as the anode for a study of the coal syngas reactivity [15]. Brunaccini el al. [18] have reported that, when Ni-doped $La_{0.58}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ is used as the anode in a hydrogen-fed SOFC, an extensive reduction of perovskite is prevented by keeping the voltage at a fixed value of 0.5 V.

Higher methane concentration results in higher concentration of the surface C species. Notably, the surface C species did not accumulate to an extent to deactivate the SOFC performance, as indicated by the existence of steady-state current density shown in Fig. 2. As the concentration of the surface C species increases, the rate of the lattice oxygen extraction from the anode bulk increases. Within a certain limit, the extracted lattice oxygen can be quickly replenished to attain a steady state and thus no oscillation would occur, as shown in Fig. 2(b) for the cases of 10 and 30% CH_4. When the amount of the extracted lattice oxygen exceeds this limit, a certain extent of the deficiency of the lattice oxygen concentration in the anode bulk is built up and an oscillation can start. Notably, when the concentration deficiency exists, the filling of the oxygen vacancies via the replenishment of oxygen from the cathode side should occur, which results in an electrical current; this is why the oscillation starts with an increase of the current density. When the oxygen vacancies are filled to reduce the extent of the concentration deficiency, the rate of oxygen replenishment decreases and thus the associated current density decreases.

Fig. 2(b) also shows that, with 70% CH_4 over the Ni-LSCF–GDC anode and before about 140 min of operation, a steady state is observed. This and other steady states are attributed to the fact that the surface C species can be oxidized by the O species not only extracted from the anode bulk but also supplied by transporting from the cathode side. However, a deficiency of the lattice-oxygen concentration on the anode side is built up during the period before about 140 min of operation and thus the behavior during this period should be a pseudo-steady state, when the extent of the deficiency of the lattice-oxygen concentration is not large enough to result in a measurable oscillation of the electrical current.

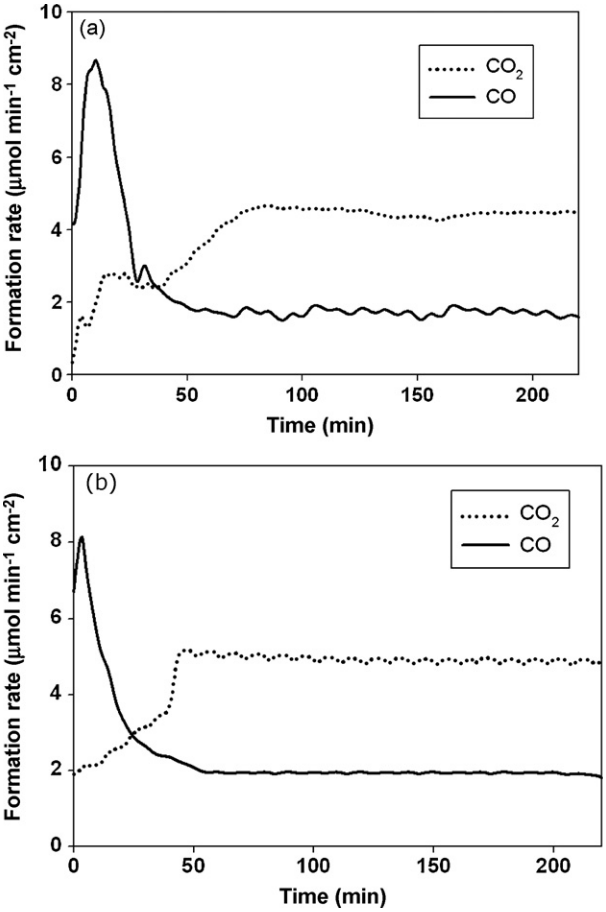

Fig. 3. CO_2 and CO formation profiles of direct methane oxidation with 10% CH_4 over anode of (a) LSCF–GDC and (b) Ni-LSCF–GDC.

3.3. Oscillation of CO and CO_2 formation rates

The generation of the electrical current is accompanied by the formation of CO_2 and/or CO. Thus, the oscillation of the formation rate of CO_2 and/or CO should occur; Fig. 3(a) shows the oscillation of the formation rate of CO and Fig. 3(b) shows that of CO_2. Notably, the hydrogen atoms from methane recombine into H_2 instead of being oxidized to form water; this direct-methane SOFC operation without H_2O formation has been observed previously [3,6]; this is attributed to a stronger interaction of the C species with the Ni surface than that of hydrogen; restated, hydrogen cannot compete with the C species to be adsorbed onto the Ni surface of the anode [3]. However, the formation of CO_2 and/or CO would not generate an electrical current if the O species were extracted from the anode bulk lattice. This may explain the observations that, with 10% CH_4 over the Ni-LSCF–GDC anode, there is no oscillation of the electrical current but there exists the oscillation of the CO_2 rate. This may also explain the observations that, with 10% CH_4 over the LSCF–GDC anode, no peak occurs for the current density, as shown in Fig. 2(a), but a peak occurs for the formation rate of CO initially, as shown in Fig. 3(a). The occurrence of the CO peak, the jumping up and down of the formation rate of CO, is attributed to the fact that the concentration of the lattice oxygen in the anode bulk is high initially and thus the rate of the lattice oxygen extraction can be high. Notably, the extracted lattice oxygen can result in the oxidation of the surface C species to produce CO; thus, the formation rate of CO can jump up.

The extraction of the lattice oxygen produces the oxygen vacancy [19], which can be replenished by oxygen from the cathode side; this generates an electrical current [6]. Therefore, in association with the initial jump up of the CO rate with 10% CH_4 over the LSCF–GDC anode, the current density is at its highest point initially, as also shown in Fig. 2(a). However, some of the oxygen vacancies cannot be replenished soon enough due to the oxygen mobility and thus a build-up of the concentration of the oxygen vacancies in the anode bulk occurs. When this concentration comes to a certain extent, an oscillation of the electrical current occurs, as also shown in Fig. 2(a). This is another evidence supporting the mechanism of periodic oxidation–reduction of the anode bulk lattice with the specified determining factor for the oscillation of the electrical current. Notably, an oscillation of the CO rate also occurs, as shown in Fig. 3(a); however, there is no oscillation of the CO_2 rate. On the other hand, with 10% CH_4 over the Ni-LSCF–GDC anode, there is an oscillation of the CO_2 rate but no measurable oscillation of either the electrical current or the CO rate, as shown in Figs. 2(b) and 3(b). The oscillation of only the CO_2 rate belongs to a case similar to that of methane oxidation over the Ni catalysts [10] and thus the oscillation of the CO_2 rate may be explained by periodic oxidation–reduction of the Ni surface [11].

Since the formation of CO_2 needs two O species while that of CO needs only one, it would be easier for the oscillation of the formation rate of CO to occur than that of CO_2 when a certain extent of the deficiency of the lattice-oxygen concentration occurs. Fig. 3(a) shows that, with 10% CH_4 over the LSCF–GDC anode, the formation rate of CO has irregular oscillation but that of CO_2 does not have any oscillation. However, Fig. 3(b) shows that, over the Ni-LSCF–GDC anode, there is almost no measurable oscillation of the CO rate but a regular oscillation of the CO_2 rate occurs right after an induction

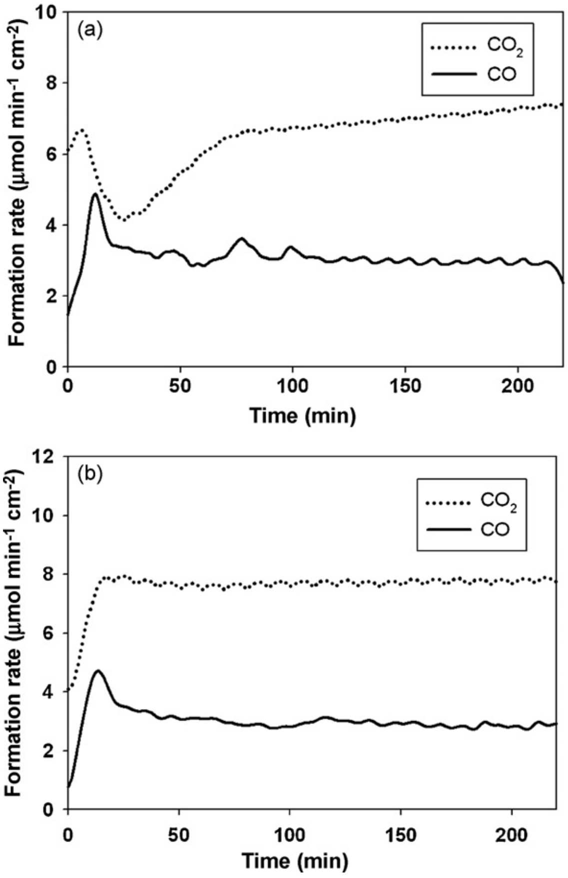

Fig. 4. CO_2 and CO formation profiles of direct methane oxidation with 30% CH_4 over anode of (a) LSCF–GDC and (b) Ni-LSCF–GDC.

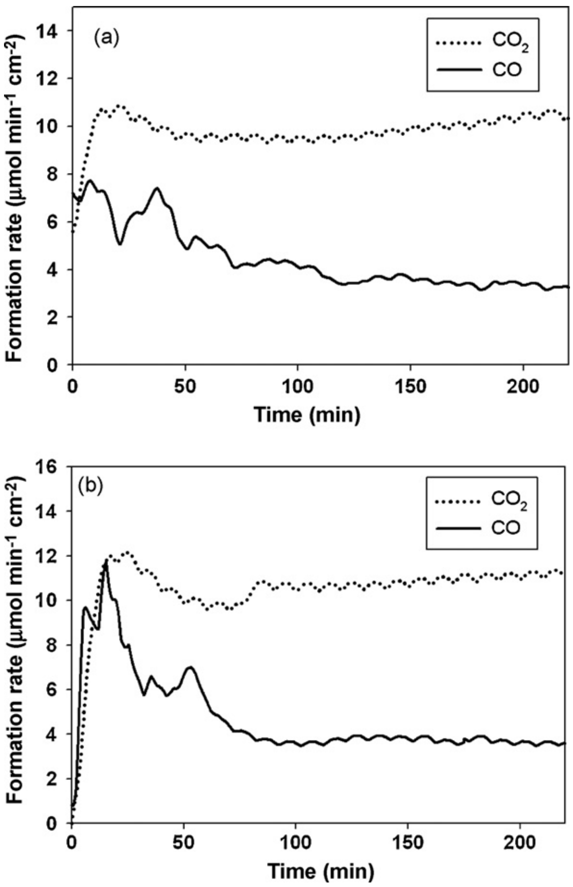

Fig. 5. CO_2 and CO formation profiles of direct methane oxidation with 50% CH_4 over anode of (a) LSCF–GDC and (b) Ni-LSCF–GDC.

period of about 45 min of operation. Therefore, the addition of Ni, a well-known metal with high activity for CH_4 dissociation to form the deposited C species, promotes the occurence of the oscillation of the rate of CO_2 formation.

Fig. 4(a) shows that, with 30% CH_4 over the LSCF–GDC anode, the rate of CO_2 formation starts to have relatively small but regular oscillation after about 75 min of operation. A comparison with that of 10% CH_4 shows an effect of the methane concentration on the occurrence of the oscillation of the CO_2 rate—that is, higher methane concentration has higher possibility to induce the oscillation of the CO_2 rate. A comparison of Fig. 4(b) with Fig. 3(b) shows that, over the Ni-LSCF–GDC anode, the oscillation of the formation rate of CO_2 starts earlier as the methane concentration becomes larger. Additionally, the oscillation of the formation rate of CO_2 is regular but that of CO is irregular.

As the CH_4 concentration increases to 50% over the LSCF–GDC anode, Fig. 5(a) shows that the oscillation of the CO_2 rate becomes stronger, i.e. with larger amplitude, and also starts earlier, both in comparison with that of 30% CH_4 as shown in Fig. 4(a). Thus, higher methane concentration induces stronger oscillation of the CO_2 rate. This is also the case over the Ni-LSCF–GDC anode, as shown by comparing Figs. 4(b) and 5(b). Additionally, higher CH_4 concentration also results in larger amplitude of the oscillation of the CO rate. However, the amplitude of the oscillation has a limit and thus, with 50% CH_4 as the fuel, the increased extent of the oscillation of the CO_2 rate over Ni-LSCF–GDC is smaller than that over LSCF–GDC since the former is stronger than the latter with 30% CH_4. This is confirmed by Fig. 6, which shows that the amplitude of the oscillation of the CO_2 rate does not increase any more as the CH_4 concentration increases to 70%. This limit on the amplitude of the oscillation is associated with that on the extent of the build-up of the concentration of the oxygen vacancies in the anode bulk before the oscillation starts.

Fig. 6(a) shows that, with 70% CH_4 over the LSCF–GDC anode, the rate of CO_2 formation has a large jump; after reaching the maximum, the CO_2 rate decreases slowly to a minimum and then increases continuously. This behavior occurs with 30–70% CH_4 over the LSCF–GDC anode; notably, both the extent of the jump and that of the continuous increase are larger with larger methane concentration. This behavior also occurs with 50–70% CH_4 over the Ni-LSCF–GDC anode, as shown in Figs. 5(b) and 6(b). The jump of the CO_2 rate is attributed to the extraction of the lattice oxygen from the LSCF–GDC bulk for the oxidation of the surface C species; then, the decrease of the concentration of the C species results in the decrease of the CO_2 rate. The larger extent of the jump and of the continuous increase of the CO_2 rate with larger methane concentration is in accordance with a larger methane concentration resulting in a larger concentration of the C species. Thus, the occurrence of this behavior indicates that methane dissociation to produce the surface C species is the major reaction over the LSCF–GDC anode without or with Ni addition. This supports the step 1 in the above mechanism.

3.4. *Effect of Ni addition*

The above results show that the addition of Ni reduces the possibility for the occurrence of the oscillation of the electrical current but promotes the occurrence of the oscillation of the rate of CO_2 formation. This is attributed to the enhancement of the rate of methane dissociation by Ni addition; thus, Ni addition results in higher amount of the surface C species than that without Ni. How-

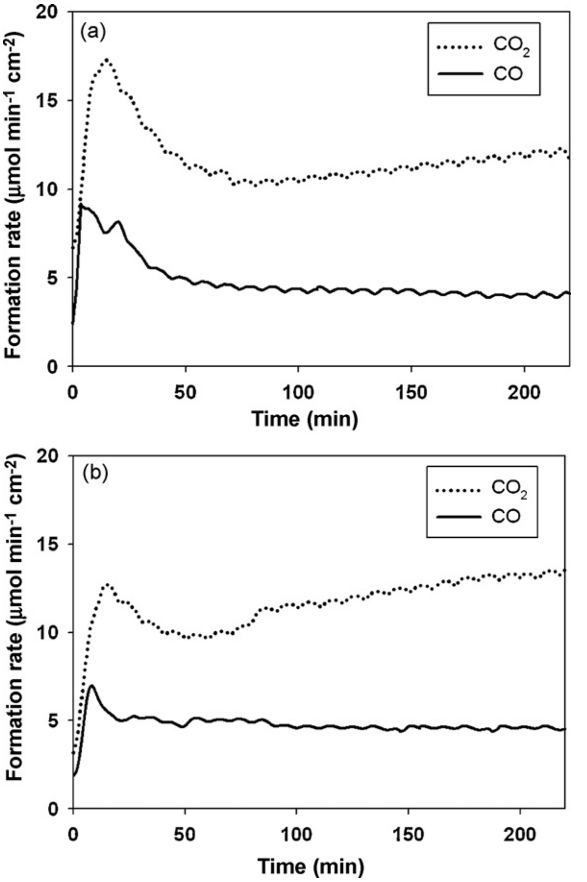

Fig. 6. CO_2 and CO formation profiles of direct methane oxidation with 70% CH_4 over anode of (a) LSCF–GDC and (b) Ni-LSCF–GDC.

Table 2
Variation of average[a] formation rates of CO and CO_2 with CH_4 concentration and anode materials.

CH_4 concentration	Anode	
	LSCF–GDC	Ni-LSCF–GDC
CO formation rate (μmol min^{-1} cm^{-2})		
10% CH_4	1.75	1.94
30% CH_4	3.00	2.91
50% CH_4	3.56	3.74
70% CH_4	4.20	4.59
CO_2 formation rate (μmol min^{-1} cm^{-2})		
10% CH_4	4.45	4.90
30% CH_4	6.99	7.74
50% CH_4	9.88	10.85
70% CH_4	11.25	12.45

[a] The averaged value of the data taken during the SOFC operation from 100 to 200 min.

ever, the active surface area of LSCF–GDC would be reduced with the addition of Ni over it and thus the amount of the C species over LSCF–GDC decreases, especially when a considerable amount of the C species are produced over the Ni surface. This decreases the possibility for the occurrence of the oscillation of the electrical current. This is also evidence supporting the mechanism of periodic oxidation–reduction of the bulk lattice of the anode with the determining factor being the build-up of the concentration of the oxygen vacancies to a certain extent for the oscillation of the electrical current.

Table 1 shows that, as the CH_4 concentration increases, the current density increases. However, the current density with the Ni-added LSCF–GDC anode is always larger than that with the LSCF–GDC anode. Table 2 shows that the formation rates of CO and CO_2 also increases as the CH_4 concentration increases; the formation rate of CO_2 with the Ni-added LSCF–GDC anode is always larger than that with the LSCF–GDC anode and that of CO is generally larger. This is also attributed to the enhancement of the rate of methane dissociation by Ni addition. This indicates again that methane dissociation to produce the surface C species is the major reaction over the Ni-added LSCF–GDC anode.

4. Conclusions

(1) When either LSCF–GDC or Ni-added LSCF–GDC was used as the anode, the oscillations of the electrical current and the formation rates of CO and CO_2 occur.
(2) The occurrence of the oscillation of the electrical current can be explained by a mechanism of periodic oxidation–reduction of the bulk lattice of the anode, with the determining factor being the build-up of the concentration of the oxygen vacancies to a certain extent.
(3) Methane dissociation to produce the surface C species is the major reaction over the LSCF–GDC anode without or with Ni addition.
(4) The oscillation of the electrical current over the Ni-added LSCF–GDC anode is regular but that over the LSCF–GDC anode is irregular.
(5) The oscillation of the formation rate of CO_2 is regular but that of CO is irregular.
(6) As the methane concentration increases, the current density increases. The current density with the Ni-added LSCF–GDC anode is always larger than that with the LSCF–GDC anode.
(7) Higher methane concentration leads to higher possibility to induce the oscillations of both the electrical current and the CO_2 formation rate and also to start them earlier. It can also result in a larger amplitude of the oscillation.
(8) The addition of Ni onto LSCF–GDC reduces the possibility for the occurrence of the oscillation of the electricl current but promotes that of the rate of CO_2 formation.

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