A new phenomenon of a fuel-free current during intermittent fuel flow over Ni-YSZ anode in direct methane SOFCs

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Abstract

A solid oxide fuel cell (SOFC) test unit was constructed with YSZ electrolyte as the support, and with Ni-YSZ anode (Ni:YSZ = 3:5 in weight) and Pt cathode. Direct methane SOFC operation at $800\,^\circ C$ with 10% CH_4 in argon was carried out. A new phenomenon of the generation of the electrical current without the fuel was observed and termed the fuel-free current. An operation of intermittent methane supply was designed to take advantage of three driving forces, i.e. methane in the gas phase, the deposited carbon at the anode surface, and a deficiency of the bulk lattice-oxygen concentration on the anode side, for the generation of the electrical current. A continuous generation of the electrical current is obtained with a methane pulse of only one-fifth of the total operation time. The operation of intermittent methane flow can reduce or even avoid SOFC deactivation by the carbon deposition; at the same time, the deposited carbon can be fully utilized for the power generation. It was also found that hydrogen from methane has been mostly evolved to the outlet gaseous product and the amount of CO formation is much higher than that of CO_2; the operation of intermittent methane flow can further increase the amount of CO over that of CO_2; these are beneficial for the co-generation of synthesis gas.
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Keywords: Lattice oxygen; Fuel-free current; Intermittent flow; Methane oxidation; Solid oxide fuel cell; Synthesis gas

1. Introduction

Methane decomposition occurs over the Ni anode in a direct methane solid oxide fuel cell (SOFC) [1,2]. Methane decomposition over Ni is usually considered as $CH_4 \rightarrow CH_3 + H \rightarrow CH_2 + H_2 \rightarrow CH + H + H_2 \rightarrow C + 2H_2$. At high temperatures, such as $800\,^\circ C$, $CH_4 \rightarrow C + 2H_2$ may occur in one step, similar to thermal cracking of methane. Thus, methane decomposition over Ni generally causes the carbon deposition (coking) [3], which may cause very rapid deactivation of the anode; consequently, the removal of the deposited carbon should be important. Nevertheless, the deposited carbon can be utilized as a fuel and this has led to the proposal of a carbon SOFC [4]. On the other hand, the deposited C species may lift the Ni species off the surface [5] and thus the amount of C deposition should be controlled; this may be done by a low concentration of methane, a short feeding time of methane, and a continuous removal of the deposited C species.

It is well known that the deposited carbon due to methane decomposition can be removed via gasification by steam [6] or carbon dioxide [5]. Recently, Huang et al. [7–9] have shown that, with the oxygen-ion conducting materials as the support, the nickel catalyst may exhibit a self de-coking capability, that is, the gasification of the deposited carbon by the O species supplemented from the bulk lattice. Notably, in an SOFC, self de-coking is equivalent to an operation with the deposited carbon as the fuel. In this work, the generally used Ni-YSZ, i.e. nickel associated with the oxygen-ion conducting YSZ, was employed as the anode materials to study its self de-coking capability during an operation of intermittent methane flow for the direct methane SOFCs.

During an SOFC operation with either the methane or the deposited carbon as the fuel, the formation of carbon oxides, i.e. CO and CO_2, is equivalent to the consumption of the oxygen species, which should eventually come from the cathode-side gas phase oxygen via the oxygen-ion conducting electrolyte. This leads to the generation of the electrical current. For the formation of carbon oxides, bulk lattice oxygen plays a very important role [10]. During self de-coking, the concentration of bulk lattice oxygen on the anode side may become deficient;

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this is indeed the case in this work, and a new phenomenon of "fuel-free current" is observed. This fuel-free current is a measured electrical current generated, in the absence of any fuel, by the replenishment of oxygen from the cathode-side three-phase boundary (TPB) to return the deficient bulk lattice-oxygen concentration on the anode side to its initial state. This fuel-free current is considered to be due to an effect of electrochemical promotion of bulk lattice-oxygen extraction [11].

In this work, an operation with intermittent methane flow was designed to take advantage of three driving forces for the generation of the electrical current, that is, methane in the gas phase, the deposited carbon at the anode surface, and a deficiency of the bulk lattice-oxygen concentration on the anode side. With a cyclic operation of intermittent methane flow, maximum utilization of the fuel can be achieved with a reduced coking problem and with the generation of a continuous electrical current by the methane pulses.

2. Experimental

2.1. Preparation of Ni-YSZ powder

The Ni-YSZ powder for the anode is prepared by impregnating the YSZ (8 mol% yttria) powder (1.68 μm, 99.9%, Sigma–Aldrich Inc., USA) with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (98.0% purity, Showa Chemical Co., Japan) in a ratio to make 60 wt% Ni with respect to YSZ. The mixture is heated with stirring to remove excess water and then place in a vacuum oven to dry overnight. The dried Ni-YSZ powder is heated to 900 °C and then cooled down to room temperature. After milling, the Ni-YSZ powder with Ni:YSZ = 3:5 in weight was obtained.

2.2. Construction of test unit

The commercial 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 tape. One side of the disk was coated with the Ni-YSZ paste, which was made of the above Ni-YSZ powder, coin oil, polyvinyl butyral, and ethanol. The other side of the disk was screen-printed with a thin layer of Pt paste (C3605P, Heraeus) to make the cathode layer.

The coating of the Ni-YSZ paste to make the anode layer was carried out by spinning coating with 2000 rpm for nine times. Then, the both side-coated unit cell was heated in an oven, with a heating rate of 5 °C min^{-1}, to 300 °C, which temperature was held for 2 h, then to 500 °C, which temperature was held for 2 h, and then to 1400 °C, which temperature was held for 2 h. The thus-prepared unit cell has an area of 1 cm^2, an anode thickness of about 30 μm, an electrolyte thickness of 156 μm, and a cathode thickness of about 5 μm.

Both sides of the completed unit cell were closely connected with gold mesh wires (100 mesh) for the current collection, and then with the 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. Test of unit cell

A circuit resistance of 1 Ω, which is the lowest adjustable resistance of the load circuit in this work, was employed. The test temperature is 800 °C throughout this work. The feed was 10% CH_4 in argon. The flow rate was always 100 ml min^{-1} passing the anode side.

The test started with the anode reduction at 400 °C with 10% H_2 for 2 h. Then, an 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^{-1}. Then, 10% H_2 was introduced for 30 min and the argon flow was followed until the measured electrical current became zero. Methane test was then carried out with introducing a CH_4 flow for a designated time, followed by the argon flow until both CO and CO_2 formations as well as the measured current became zero. Then, 20% O_2 was introduced until the CO and CO_2 formations became zero. Finally, an argon flow was passed for 30 min to purge the system.

A new test started with the above-described introduction of 10% H_2 for 30 min at 800 °C and with following argon flow until the measured electrical current became zero. However, if this H_2 test result showed a deactivation of the used unit cell, a fresh unit cell would be used and the new test started with the above-described anode reduction at 400 °C.

Through out the test, the electrical current, the voltage, and the outlet gas compositions were always measured. 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) on line.

3. Results and discussion

3.1. Phenomenon of a fuel-free current

Fig. 1 shows the profiles of measured and equivalent current densities versus time with 30 min CH_4 flow. The equivalent current indicates the current which would be produced if the O species for CO_x, i.e. CO and CO_2, formations at the anode three-phase boundary (TPB) come from the cathode TPB. This CO_x equivalent current is calculated with the total amount of O species in forming CO and CO_2, with each O species carrying two electrons. Notably, the equivalent current as shown in this work is equivalent to the formation rates of CO_x only; it should be equivalent to the total formation rates of all the oxidation products and thus the formation rate of other detectable oxidation product, only H_2O in this work, will be included if the total amount of oxygen consumption is to be calculated. Nevertheless, H_2O formation was quite small during all the experiments of this work and thus the amount of oxygen consumed by H_2O formation is negligibly small.

Fig. 1 indicates that there is a region, designated as zone II, for the generation of electrical current in the absence of any fuel, either methane in the gas phase or deposited carbon at
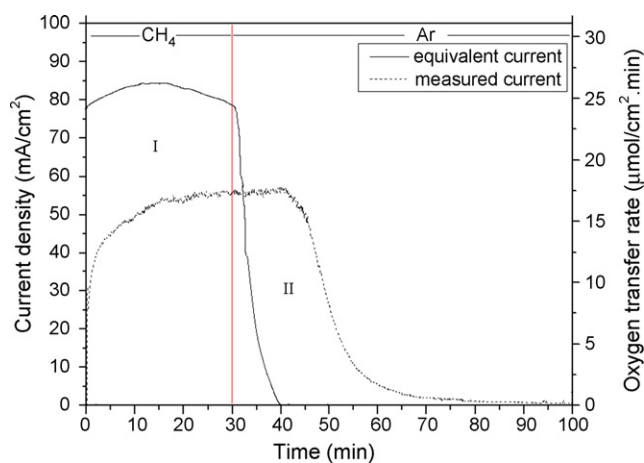
Fig. 1. Profiles of current densities vs. time with 30 min CH_4 flow. Zone I denotes the area between the curves of equivalent and measured currents and extends from time zero until these two curves meet. Zone II denotes the area under the curve of the measured current and to the right of the curve of the equivalent current.

the anode surface. Notably, zone II denotes the area under the curve of the measured current and to the right of the curve of the equivalent current. The evidence for the absence of any fuel is shown in Fig. 2, which presents the outlet gas composition from the anode side, i.e. the fuel side. It is seen that CH_4 conversion and H_2 concentration become zero well before switching to the Ar flow. Separate gas chromatographic measurements show that the CH_4 concentration becomes zero in less than 2 min after switching to the Ar flow, which means a very quick purge with 100 ml min^{-1} of Ar flow. On the other hand, there is no any fuel-oxidation product, i.e. CO, CO_2, or H_2O as detected in this work, associated with the occurrence of zone II. Thus, the electrical current as designated by zone II is indeed a current generated in the absence of any fuel and can be termed a "fuel-free current".

In this work, the fuel means both the methane and the deposited carbon species from the decomposition of methane. The evidence for the existence of the deposited carbon species can be seen in Fig. 2, where the amounts of CO and CO_2 formations exceed that allowed by the methane conversion after about
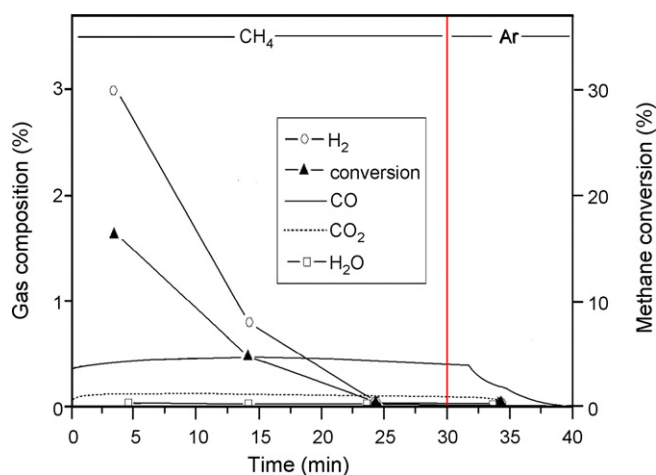

Fig. 2. Outlet gas composition and methane conversion with 30 min CH_4 flow.

15 min of CH_4 flow. The exceeding amounts of CO and CO_2 formations should be due to the oxidation of the deposited carbon species. These carbon species are usually considered to be surface CH_x ($x = 0$–3) species, which are intermediates of CH_4 decomposition [12]. Notably, before about 15 min of CH_4 flow, the amount of CO_x formations are lower or much lower than that allowed by the methane conversion, indicating the occurrence of some methane decomposition without oxidation, which produces the deposited carbon species. However, since the amount of H_2O production after about 25 min of CH_4 flow becomes zero, the CH_x species should be mostly the C species, which may cause the coking problem and should be removed the sooner the better. Notably, also, with an anode thickness of about 30 μm in this work, the whole anode can be effective to utilize the deposited C species to generate the electrical current so that the deposited C species is removed continuously; this can lessen the problem of coking to the anode. Abudula et al. [13] has reported an effective anode thickness of 70 μm for 4.6% of dry methane fuel in an SOFC.

The occurrence of fuel-free current is considered to be due to the deficiency of the bulk lattice-oxygen concentration on the anode side after oxidations of methane and deposited carbon species, which have extracted additional amount of lattice oxygen from the anode bulk without replenishment from the cathode TPB. Consequently, a deficiency of the bulk lattice-oxygen concentration on the anode side occurs and is build up during the oxidation of fuel and thus the oxygen species migrate from the cathode TPB to the anode side to replenish the bulk lattice-oxygen concentration on the anode side to its initial state, which generates an electrical current. In copper oxide, the oxygen vacancy may be created via the lattice oxygen reduction and migration when the lattice oxygen overcomes the energy barrier by a specific electrical field [14]; this is a type of electrochemical promotion [15], that is, the work function and thus the activation energy of the lattice oxygen reduction is reduced under a potential (an electrical field) [16]. Similarly, the oxygen vacancy in YSZ can be produced at 800 °C under the operating potential (voltage), since a decreased activation energy of the YSZ lattice-oxygen reduction can make the YSZ bulk reducible at this temperature. Since the deficiency of bulk lattice-oxygen concentration is a consequence of electrochemically promoted bulk lattice-oxygen extraction [11], it can be concluded that the occurrence of fuel-free current is due to the effect of electrochemical promotion of bulk lattice-oxygen extraction.

The quantity of fuel-free current is represented by the area of zone II. Zone II indicates the amount of the O species which have been replenished with the oxygen species coming from the cathode TPB, considering that one oxygen ion carries two electrons. Since the concentration difference becomes smaller as the replenishing process is going on, the rate of replenishment, which causes the fuel-free current, becomes increasingly smaller. This is indicated by a long tail of the measured current as shown in Fig. 1.

Fig. 1 shows also that the equivalent current can reach a maximum rate very fast while the measured current needs some time to reach the maximum. This is attributed to both the mobility of lattice oxygen in the bulk of oxygen-ion conducting materials

and the distance from the cathode TPB to the anode TPB. Additionally, zone I indicates the amount of lattice oxygen species which have been extracted from the anode-side bulk but have not been replenished from the cathode TPB; thus, the measured current is lower than it should be if all the O species used for the oxidation come from the cathode TPB. Notably, a measured current can occur only with the oxygen species, with each carrying two electrons, transported from the cathode TPB to the anode TPB. The current density and the oxygen transfer rate, i.e. the left and the right coordinate, respectively, as shown in Fig. 1, is related by $1 \, mA \, cm^{-2}$ to $0.31088 \, \mu mol \, O^{2-} \, cm^{-2} \, min$.

3.2. Self de-coking

The oxidation of the deposited carbon species by the lattice oxygen species is termed "self de-coking" [10], i.e. de-coking by the O species of the catalyst itself. As noted before, self de-coking is equivalent to an operation with the deposited carbon as the fuel. Self de-coking may be considered to have started when the amount of CO_x production exceeds that allowed by the methane conversion and ended when CO_x becomes zero. Nevertheless, some carbon species cannot be self de-coked and thus have to be removed by oxidation with 20% oxygen, with the results shown in Table 1. The removal of the carbon species by the lattice oxygen is termed "self de-coking" in this work in order to discriminate it from the de-coking operation by a simulated air (20% O_2), which is termed "O_2 de-coking". Notably, there is power generation during self de-coking but no power generation during O_2 de-coking. This is because the O species for self de-coking can come from the cathode TPB but those for O_2 de-coking come entirely from the anode-side gas phase.

Fig. 2 shows also that the methane conversion becomes zero after 25 min CH_4 flow, indicating a complete deactivation of the anode. Although the anode activity can be fully or partially recovered after O_2 de-coking, the amount of deposited carbon is better to be controlled. A shortening of the methane flow time during the process of intermittent methane flow, i.e. a CH_4 flow followed by an Ar flow, not only produces a smaller amount of deposited carbon but also results in a faster removal of the deposited carbon. Notably, a methane flow with a relatively short duration can be termed a methane pulse.

Table 1 reveals that the amount of CO_x formation, which is equivalent to the amount of the deposited carbon removed during O_2 de-coking, decreases with decreasing methane flow time.

Table 1
Variation of the carbon oxides formation and the time of O_2 de-coking with the methane flow time

Methane flow time (min)	Carbon oxides[a] formation during O_2 de-coking[b] ($\mu mol \, cm^{-2}$ anode)	O_2 de-coking time[c] (min)
5	0.47	24
10	3.62	510
30	7.23	750

[a] Carbon oxides means CO and CO_2.
[b] Removal of the remaining coke after self de-coking with $100 \, ml \, min^{-1}$ of 20% O_2 in argon at 800 °C. Only CO_2 was detected during O_2 de-coking.
[c] The time for O_2 de-coking until zero CO_2 formation.

Table 2
Variation of the self de-coking capability and the overall methane conversion with the methane flow time

Methane flow time (min)	Self de-coking capability[a] (%)	Overall methane conversion (%)
5	99.8	17.9
10	97.5	11.1
30	92.6	7.2

[a] Self de-coking capability = self de-coking amount/amount of total carbon deposition, where the amount of total carbon deposition equals the self de-coking amount plus the O_2 de-coking amount, both in terms of (amount of CO + amount of CO_2).

Additionally, the time needed for O_2 de-coking also decreases, which means an easier removal of the deposited carbon. It is also found that, after the process of O_2 de-coking, the SOFC activity can be fully recovered for the cases of 5 and 10 min methane flow, but with about 10% deactivation for the case of 30 min methane flow. These results indicate that an intermittent methane flow with a short methane pulse is beneficial not only for a better fuel utilization but also for lessening the coking problem. With a methane pulse short enough, the coking problem may be fully avoided.

As discussed above, the concentration of bulk lattice-oxygen species should have some effect on the self de-coking capability. Additionally, since the methane oxidation is also a process of extracting the bulk lattice-oxygen species, the concentration of bulk lattice-oxygen species should also have some effect on the methane conversion. Since an increase of the methane flow time results in a decrease of the bulk lattice-oxygen concentration, both the self de-coking capability and the overall methane conversion should decrease with an increased duration of methane flow, as confirmed by the results shown in Table 2.

3.3. Effect of lattice oxygen concentration

As discussed above, the variation of the bulk lattice-oxygen concentration was achieved by varying the flow time of methane. With the methane flow time decreased from 30 to 5 min, Table 3 shows that the amount of bulk lattice-oxygen extraction decreases. This would result in a decreased extent of the deficiency of the bulk lattice-oxygen concentration on the anode side. Consequently, the bulk lattice-oxygen concentration increases. With an increased bulk lattice-oxygen concentration, the self de-coking capability increases. Thus, the extent of anode deactivation decreases and the overall methane conversion increases, shown in Table 2.

Fig. 1 shows also that, after about 20 min of methane exposure, the equivalent current starts to decrease, but the measured current does not. This is due to a decrease of the CO formation rate, shown in Fig. 3. This is a consequence of the decrease of the bulk lattice-oxygen concentration on the anode side. This is according to that the CO formation needs the supply of lattice oxygen and its supply rate depends on the bulk lattice-oxygen concentration [10]. Nevertheless, for the cases of 5 and 10 min methane flow, the equivalent currents show no decrease during the methane exposure, shown in Fig. 4. For the case of 10 min

Table 3
Variation of the amounts of the lattice oxygen extracted and replenished with the methane flow time

Methane flow time (min)	Lattice oxygen extracted[a] (10^2 μmol cm^{-2} anode)	Lattice oxygen replenished[b] (10^2 μmol cm^{-2} anode)
5	1.6	1.6
10	1.9	1.8
30	3.2	3.1

[a] The total amount of the lattice oxygen extracted as in zone I, after a modification with the amount of the O species in forming H_2O.

[b] The total amount of the lattice oxygen replenished as in zone II. No H_2O formation was observed during this period.

methane flow, Fig. 4(a) shows that the equivalent current can be kept constant for some time. These are attributed to a high concentration of the bulk lattice oxygen.

Fig. 4(b) reveals that zone I extends well into the argon flow period. Notably, zone I denotes the area between the curves of equivalent and measured currents and extends from time zero until these two curves meet. This indicates that the bulk lattice-oxygen concentration on the anode side is high enough to be extracted during self de-coking. Table 3 indicates also that the amount of the replenished O species is about the same as or slightly less than that of the extracted O species, indicating that the extracted lattice oxygen can be almost fully replenished. Notably, the amount of lattice O replenished is equivalent to the quantity of fuel-free current. Thus, the advantage for utilizing the fuel-free current is not only for the generation of additional electrical current but also for the replenishment of oxygen species to the anode bulk so that the concentration of anode-side bulk lattice oxygen can be restored to its initial level. This enhances both the self de-coking capability and the overall methane conversion.

The above results indicate that the measured current occurs with three types of the driving forces, that is, the methane fuel in the gas phase, the deposited carbon species at the anode surface, and the deficiency of the bulk lattice-oxygen concentration on the anode side. A cyclic operation with an intermittent methane flow is thus designed to take advantage of these three driving forces for the generation of the electrical current.
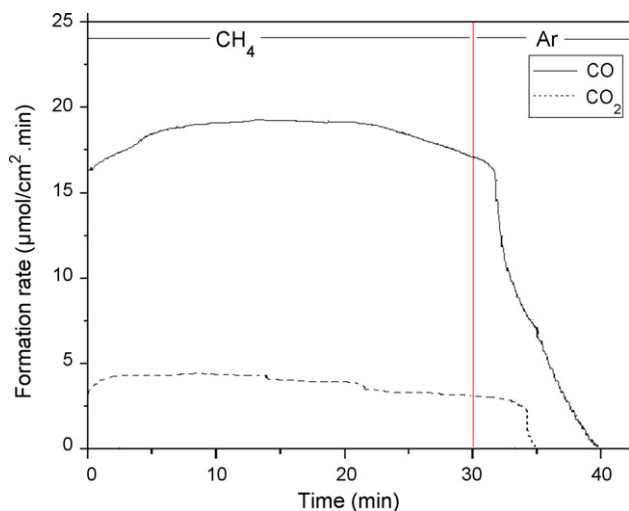

Fig. 3. Profiles of CO and CO_2 formation rates vs. time with 30 min CH_4 flow.
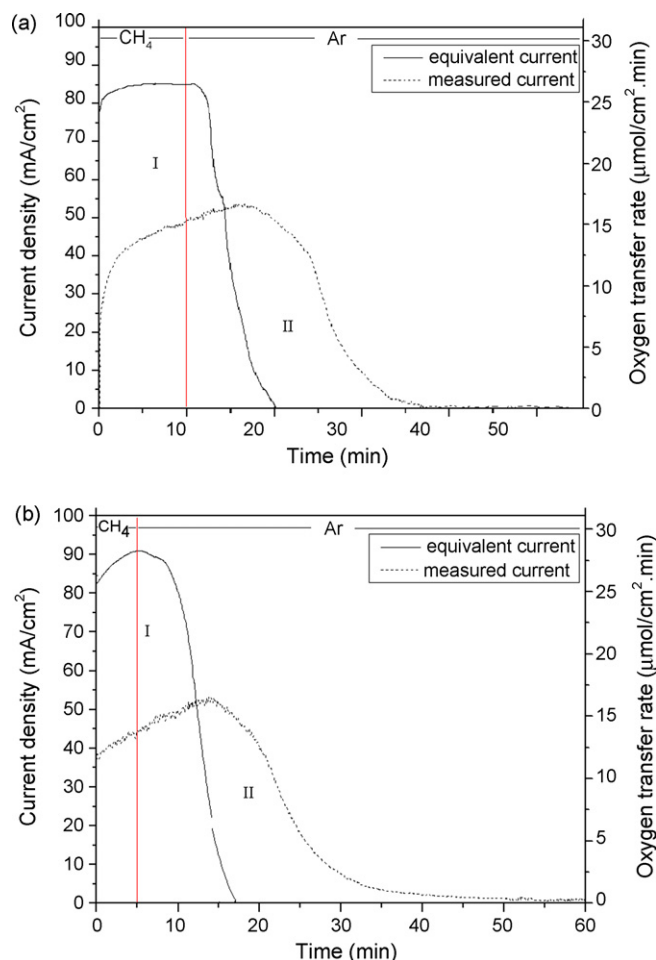

Fig. 4. Profiles of current densities vs. time: (a) with 10 min CH_4 flow; (b) with 5 min CH_4 flow. Zones I and II are defined as in Fig. 1.

3.4. Cyclic operation with intermittent methane flow

With a 25 min cycle of 5 min of methane flow followed by 20 min of argon flow, the variations of the measured current and the equivalent current during 18 cycles are shown in Fig. 5, and those of CO and CO_2 formations shown in Fig. 6. It is seen that the measured current can be sustained at relatively constant-average level after an initial drop. This is a case of a continuous generation of the electrical current with a methane pulse of only one fifth of the total operation time. Notably, the generation of the fuel-free current is indicated by the region where there is measured current but no equivalent current.

Fig. 5(a) indicates that the measured current needs some time to reach the maximum for the first cycle, but it reaches the maximum very quickly in the following cycles. This is attributed to that the lattice O species needs some time to be transported from the cathode TPB to the anode TPB to produce current initially. Nevertheless, after the initial stage, the lattice O species is continuously transported from the cathode to the anode and thus the current can reach its maximum right after the introduction of methane flow.

Fig. 5(a) indicates also that the deficiency of the bulk lattice-oxygen concentration can be restored continuously, with the

production of the fuel-free current. Nevertheless, although the formation rates of carbon oxides can be kept at a constant level for some time during the first two cycles, the rates decrease right after they reach the highest point from the third cycle onward, shown in Fig. 6(a). This is considered to be due to that the bulk lattice-oxygen concentration is not fully restored and thus not enough to sustain the carbon oxides formation at a constant level. After the last cycle of the cyclic operation of 18 cycles, the replenishment has been carried out until the fuel-free current becomes zero, shown in Fig. 5(b); the amount of lattice oxygen thus replenished is 184 μmol cm^{-2} anode, higher than that for the case of 5 min methane flow as shown in Table 3. Notably, the CO_x formation behavior for the last cycle is similar to the previous ones, shown in Fig. 6(b). This confirms that the replenishment of the lattice oxygen is indeed not fully restored in the cycles before the last one, due to not enough time for the replenishment. This in turn confirms that the bulk lattice-oxygen concentration indeed has an important role in the performance of direct methane solid oxide fuel cells.

On the other hand, Fig. 6 shows that the amount of CO formation is much higher than that of CO_2, especially during the Ar flow period. This is similar to that for the case of 30 min
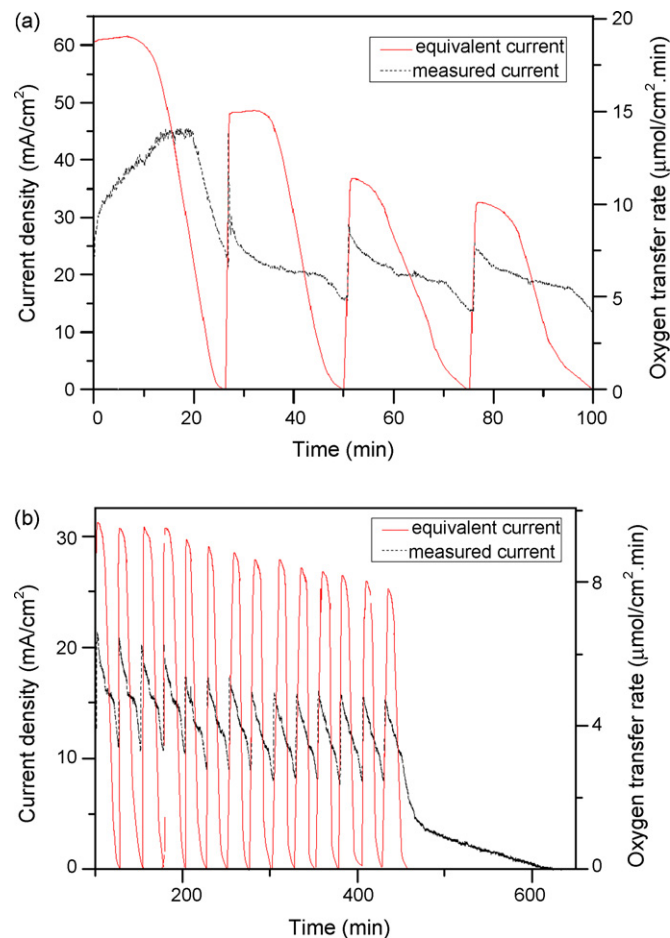

Fig. 5. Variations of measured current and equivalent current with time during cyclic operation of intermittent methane flow: (a) first four cycles; (b) next 14 cycles until test ends. A cycle is 25 min, i.e. 5 min CH$_4$ flow followed by 20 min Ar flow.
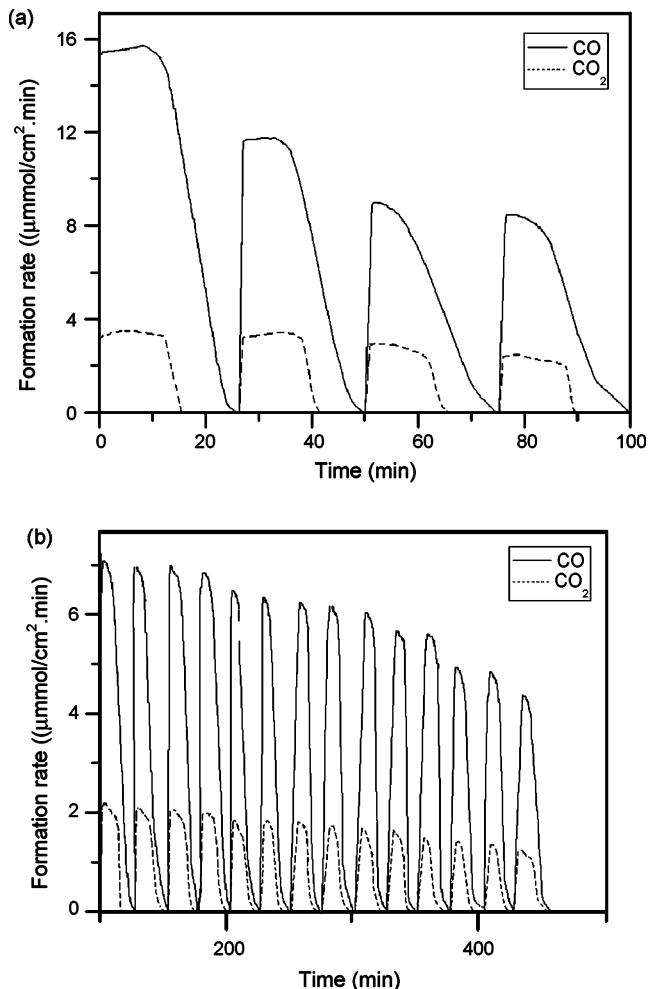

Fig. 6. Variations of CO and CO$_2$ formation rates with time during cyclic operation of intermittent methane flow: (a) first four cycles; (b) next 14 cycles. A cycle is 25 min, i.e. 5 min CH$_4$ flow followed by 20 min Ar flow.

CH$_4$ flow, shown in Fig. 3. Additionally, with very little H$_2$O formation as shown in Fig. 2, most hydrogen dissociated from methane is evolved to the outlet gas phase without being oxidized. This is also in agreement with that the mole percent of H$_2$ formation is about two times the CH$_4$ conversion in accordance to CH$_4 \rightarrow$ C + 2H$_2$. Thus, the direct methane SOFC with an operation of CH$_4$ flow followed by Ar flow favors the CO formation and thus is beneficial for the co-generation of the synthesis gas.

4. Conclusions

A new phenomenon of the generation of electrical current without the fuel was observed and this current has been termed the fuel-free current. The occurrence of the fuel-free current is attributed to the deficiency of the bulk lattice-oxygen concentration on the anode side by the before-hand fuel oxidation. An operation of an intermittent methane supply was designed to take advantage of three driving forces for the generation of the electrical current, that is, the methane in the gas phase, the deposited carbon at anode, and the deficiency of the lattice oxygen

concentration on the anode side. A continuous generation of the electrical current is obtained with a methane pulse of only one-fifth of the series time. The operation of intermittent methane flow can reduce or even avoid the SOFC deactivation by the carbon deposition; at the same time, the deposited carbon can be fully utilized as the fuel for the generation of electrical current, which leads to a high utilization efficiency of methane fuel. It was also found that hydrogen from methane has been mostly evolved to the outlet gaseous product and the amount of CO production is much higher than that of CO_2; the operation of intermittent methane flow can further increase the amount of CO production over that of CO_2; these are beneficial for the co-generation of synthesis gas.

Acknowledgements

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