

# Temperature effect on electrochemical promotion of syngas cogeneration in direct-methane solid oxide fuel cells

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## Abstract

Syngas cogeneration in direct-methane solid oxide fuel cells with Ni–yttria-stabilized zirconia (YSZ) anodes was studied with temperature varying from 700 to 900 °C. A phenomenon of electrochemical promotion of bulk lattice-oxygen extraction from the YSZ electrolyte was observed. With increasing temperature, this promotion effect increases while both the rate enhancement ratios of CO and CO<sub>2</sub> formations decrease. The activation energy of CO and CO<sub>2</sub> formation under close circuit is lower than that under open circuit. The activation energy for the lattice-oxygen extraction from the YSZ bulk is higher than that for the oxygen transport through the YSZ bulk. The process of lattice-oxygen extraction from YSZ is rate determining in direct-methane oxidation under the condition of either close circuit or open circuit. The dependence of CO formation rate on the oxygen supply rate is stronger than that of CO<sub>2</sub> formation rate. Electrochemical promotion of bulk lattice-oxygen extraction enhances syngas cogeneration.

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**Keywords:** Temperature effect; Electrochemical promotion; Lattice-oxygen extraction; Syngas cogeneration; Solid oxide fuel cell

## 1. Introduction

The cogeneration of synthesis gas and electrical power can be carried out by electrochemical methane oxidation in a solid oxide fuel cell (SOFC) [1–6]. The oxygen species needed for the partial oxidation of methane over the anode comes from the cathode three-phase boundary (TPB) via the bulk lattice of the oxygen-ion conducting electrolyte. This process of syngas cogeneration combines the concepts of a catalytic reactor and a power generator. In this process, a newly observed effect is the electrochemical promotion of bulk lattice-oxygen extraction, which enhances the syngas cogeneration [7,8]. This effect has been applied to an operation with intermittent methane supply for the cogeneration of synthesis gas and electricity, in which a continuous generation of the electrical current is obtained with a methane supply time of only one fifth of the total operation time [9].

The electrochemical promotion or non-Faradaic electrochemical modification of catalytic activity (NEMCA) effect

has been studied extensively [10–19]. This effect is due to the electrochemically controlled migration of ionic species from the solid electrolyte onto the gas-exposed electrode surface. Upon application of an external potential, the migration of ionic species onto the gas-exposed electrode surface causes a change in catalyst work function [12], which corresponds to a change in activation energy so as to affect the catalytic rate.

The Faradaic efficiency,  $\Lambda$ , for electrochemical promotion with O<sup>2-</sup>-conducting supports is defined as

$$\Lambda = \frac{\Delta r}{I/2F} \quad (1)$$

where  $\Delta r$  is the current- or potential-induced change in catalytic rate,  $I$  is the applied current and  $F$  is Faraday's constant [18]. It is pointed out that only a fraction ( $1/\Lambda$ ) of the oxygen species from the support will be found in the reaction products [15]. This fraction becomes significant only at elevated temperature, i.e.  $T > 550$  °C, where  $\Lambda$  approaches unity and the phenomenon of electrochemical promotion disappears. In other words, when a positive (anodic) current  $I$  is applied, O<sup>2-</sup> is supplied to the catalyst at a rate  $I/2F$ ; this support-supplied lattice oxygen species can act as a reactant but the reaction rate due to this oxygen is limited by  $I/2F$  [17], i.e. limited by the current. However,

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in an operating direct-methane SOFC with power generation instead of power consumption, the electrochemical promotion of bulk lattice-oxygen extraction leads to a markedly higher amount of oxygen consumed in the anodic reaction than that associated with the measured current [7,8]. This reveals a difference between the electrochemical promotion or NEMCA effect with anode-side gaseous oxygen under applied voltage and that without anode-side gaseous oxygen under generated voltage. Thus, it is interesting to study the temperature effect on electrochemical promotion in an operating direct-methane SOFC to see whether the phenomenon of electrochemical promotion disappears at elevated temperature.

For direct-methane SOFCs [20,21], methane decomposition over the Ni cermet anode is a major reaction, which generally causes carbon deposition (coking) [22]. The deposited carbon can cover the whole anode surface and cause cell failure [21]. Nevertheless, the deposited carbon species can be removed by the oxygen species from the bulk, i.e. without the presence of oxygen in the gas phase; this carbon removal has been termed “self de-coking” [23–25]. In the case of direct-methane SOFC, self de-coking can be a major reaction, which is carried out by the oxygen species transported from the cathode TPB to the anode surface via the bulk lattice of the oxygen-ion conducting materials [9]. Consequently, the removal of the deposited carbon species via self de-coking may solve the coking problem of direct-methane SOFC.

During the operation of direct-methane SOFC, the formation of only CO but not CO<sub>2</sub> should lead to a large difference in SOFC performance. This is due to that the electrochemical formation of CO<sub>2</sub> involves four electrons while that of CO involves only two electrons, with each oxygen ion carrying two electrons; as a consequence, the current density associated with CO<sub>2</sub> formation is double that associated with CO formation. If the direct-methane SOFC is used for the cogeneration of syngas, i.e. CO + H<sub>2</sub>, the formation of only CO but not CO<sub>2</sub> should help the selectivity for syngas. As for SOFC with the deposited carbon as fuel [26], the formation of only CO but not CO<sub>2</sub> would lead to a two-time difference in the total current density.

On the other hand, the study of temperature effect is frequently associated with the activation energy. For SOFCs, the activation energy of hydrogen oxidation has been studied by various techniques, including the galvanostatic current interruption [27] and the electrochemical impedance spectroscopy [28,29], and also by a method using the current densities measured at constant overpotentials [28]. However, the activation energy of methane oxidation over the SOFC anodes has seldom been studied and those of CO and CO<sub>2</sub> formations in direct-methane SOFCs have not yet been studied. For syngas cogeneration, the kinetics of CO and CO<sub>2</sub> formations is important and thus the study of their activation energies in direct-methane SOFCs is desirable.

In this work, syngas cogeneration in a direct-methane SOFC with Ni–yttria-stabilized zirconia (YSZ) anode was studied with temperature varying from 700 to 900 °C. The phenomenon of electrochemical promotion of bulk lattice-oxygen extraction from the YSZ electrolyte was observed. The activation energies for CO and CO<sub>2</sub> formations in direct-methane SOFCs, the

lattice-oxygen extraction from the YSZ bulk, as well as the oxygen transport through the YSZ bulk were obtained. Some discussions were performed to lead to answers for the above-mentioned questions, that is, whether the reaction rate due to the support-supplied lattice oxygen is limited by the electrical current and whether the phenomenon of electrochemical promotion disappears at elevated temperature. Additionally, the effect of electrochemical promotion of bulk lattice-oxygen extraction on syngas cogeneration in direct-methane SOFCs was investigated.

## 2. Experimental

### 2.1. Preparation of Ni–YSZ powder

The Ni–YSZ powder for the anode was prepared by impregnating the YSZ (8 mol% yttria) powder (1.68 μm) with an aqueous solution of nickel nitrate (98% purity) in a ratio to make 60 wt% Ni with respect to YSZ. The mixture was heated with stirring to remove excess water and then placed in a vacuum oven to be dried overnight. The dried Ni–YSZ powder was 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 SOFC unit cell

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 anode layer was coated by spinning coating the Ni–YSZ paste 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<sup>-1</sup>, to 300 °C, held for 2 h, then to 500 °C, held for 2 h, and then to 1400 °C, held for 2 h. The thus-prepared unit cell has an anode area of 1 cm<sup>2</sup>, an anode thickness of about 30 μm, an electrolyte thickness of 156 μm, a cathode area of 1 cm<sup>2</sup>, and a cathode thickness of about 5 μm. These thicknesses were measured from a scanning electron micrograph of the cross section of the unit cell.

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 test of direct-methane oxidation

A voltage of 0.61 V was maintained for all close-circuit tests with methane flow as feed over the anode in this work. The test temperature varied from 700 to 900 °C. The methane flow

was 10% CH<sub>4</sub> in argon. The flow rate was always 100 ml min<sup>-1</sup> passing the anode side.

The test under close-circuit condition started with anode reduction at 400 °C in 10% H<sub>2</sub> for 2 h. Then, argon flow was passed for 2 h to purge the system. The test unit was then heated in argon to the designated temperature at a rate of 5 °C min<sup>-1</sup>. Then, 10% H<sub>2</sub> was introduced for 30 min and argon flow was followed until the measured electrical current came down to that of a leakage current [30]. The direct-methane oxidation test was then carried out by introducing methane flow as feed over the anode for 5 min. Then, the gaseous feed was switched to pure argon until CO and CO<sub>2</sub> in the effluent flow became zero and the measured current came down to that of a leakage current.

The procedure for the test under open-circuit condition was the same as that of close circuit until the direct-methane oxidation test, but all under open circuit. The direct-methane oxidation test was carried out by introducing methane flow for 5 min under open circuit. After supplying methane flow for 5 min, the gaseous feed over the anode was switched to pure argon and the external circuit was closed at the same time. The argon flow persisted until CO and CO<sub>2</sub> in the effluent flow became zero and the measured current came down to that of a leakage current.

Through out the test, electrical current, voltage, and outlet gas compositions were always measured. CO and CO<sub>2</sub> compositions were measured by CO-NDIR (non-dispersive infrared analyzer, Beckman 880) and CO<sub>2</sub>-NDIR (Beckman 880), respectively. Other gas compositions were measured by two gas chromatographs (GCs, China Chromatography 8900) in series.

### 3. Results

#### 3.1. Temperature effect

Table 1 presents the results on the study of the temperature effect during close-circuit measurement with methane feeding over the anode. A typical result for this measurement is shown in Fig. 1. The oxygen amount consumed for the formation of CO and CO<sub>2</sub>, as represented by the equivalent current, can be

Table 1  
Temperature effect on current density, the amounts of oxygen transported from cathode TPB and extracted from anode-side bulk during 5 min CH<sub>4</sub> feeding under close circuit

Temperature (°C)	Current density <sup>a</sup> (mA cm <sup>-2</sup> )	O species transported <sup>b</sup> (μmol cm <sup>-2</sup> )	Lattice O extracted <sup>c</sup> (μmol cm <sup>-2</sup> )
700	5.97	9.28	6.43
750	14.16	22.0	17.0
800	26.26	40.8	34.4
850	40.47	62.9	58.2
900	54.86	85.3	88.4

<sup>a</sup> Average value of the measured current density during 5 min CH<sub>4</sub> feeding. The area is in terms of the anode area.

<sup>b</sup> The amount of oxygen species transported from cathode TPB for the generation of the measured current.

<sup>c</sup> The amount of lattice oxygen species additionally extracted from anode-side bulk.

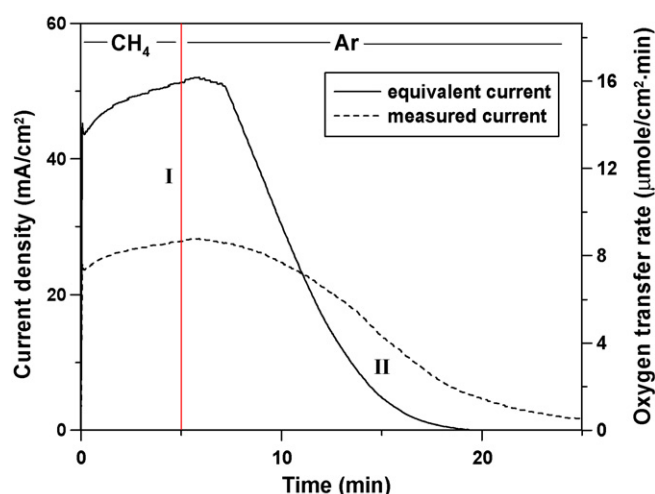


Fig. 1. Profiles of current densities vs. time. Close-circuit measurement at 800 °C. Zone I denotes the area between the curves of equivalent current and measured current and extends from time zero until these two curves meet; zone II denotes the area under the curve of measured current and to the right of the curve of equivalent current.

much higher than that from the cathode-side gas phase, as represented by the measured current. Notably, a measured current can occur only when the oxygen species, with each carrying two electrons, are transported from the cathode TPB to the anode TPB via the electrolyte; the oxygen species extracted only from the anode-side bulk lattice would not contribute to the measured current. Notably, also, in Fig. 1, zone I denotes the area between the curves of equivalent current and measured current and extends from time zero until these two curves meet; zone II denotes the area under the curve of measured current and to the right of the curve of equivalent current. Since there is no gaseous oxygen feed over the anode, additional amount of lattice oxygen should have been extracted, shown as zone I; these lattice oxygen species should come from the anode-side bulk. This is a phenomenon of electrochemical promotion of bulk lattice-oxygen extraction [7,8].

As the temperature increases from 700 to 900 °C, the measured current density and the amount of additionally extracted lattice O species increase markedly, as Table 1 reveals. The O species transported from the cathode TPB generate electrical current and synthesis gas. Additional synthesis gas is generated by the electrochemically promoted extraction of bulk lattice oxygen, indicated by the amount of lattice O extracted as zone I. On the other hand, as shown by comparing Fig. 1 with Fig. 2, the latter being a typical result of the profiles of CO and CO<sub>2</sub> formation rates, the occurrence of zone II current is not accompanied by syngas generation. This is because the occurrence of zone II current is not due to the oxidation of any fuel; consequently, the measured zone II current has been termed “fuel-free current” [9]. This zone II current has been attributed to the replenishment of the oxygen species from the cathode-side gas phase. This replenishment occurs due to a concentration deficiency generated by the electrochemically promoted extraction of bulk lattice oxygen from the anode side during the oxidation of the fuel [9]. Notably, the process of replenishment becomes slower as the concentration deficiency becomes smaller. For the test of Fig. 1,

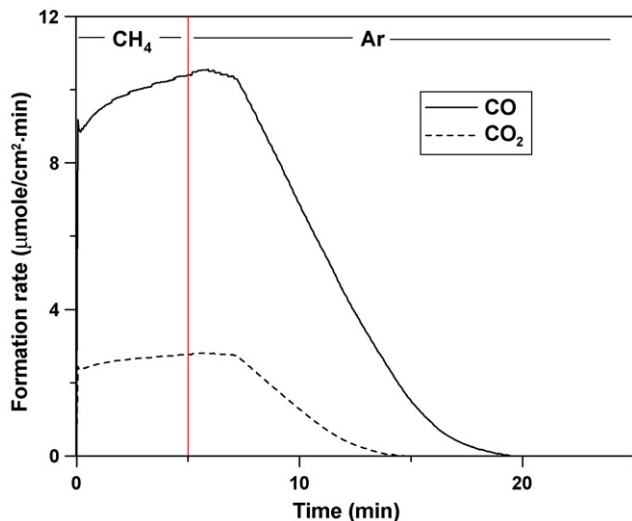


Fig. 2. Profiles of CO and CO<sub>2</sub> formation rates vs. time. Close-circuit measurement at 800 °C.

after switching to argon flow for 60 min, the residual current density was 0.5 mA cm<sup>-2</sup>; this current is considered to consist of both the fuel-free current and the leakage current [30].

In Fig. 1, the oxygen amount for the production of CO<sub>x</sub>, i.e. CO and CO<sub>2</sub>, is indicated by the equivalent current and also revealed by the oxygen-transfer rate. Notably, the current density and the oxygen-transfer rate, the left and right ordinate of Fig. 1, is related by 1 mA cm<sup>-2</sup> to 0.31088 μmol O<sup>2-</sup> cm<sup>-2</sup> min<sup>-1</sup>. As revealed above, the oxygen species for methane oxidation can come from either the cathode-side gas phase or the anode-side bulk. Since NiO can be completely reduced to Ni at 400 °C [31], the oxygen species from the anode-side bulk should come only from YSZ in this work, noting that the NiO–YSZ anode has been reduced at a temperature of 700 °C or higher.

The “equivalent current” indicates the current which would be produced if the O species for CO<sub>x</sub> formations at the anode TPB come from the cathode TPB. This CO<sub>x</sub> equivalent current is calculated with the total amount of the O species in forming CO and CO<sub>2</sub>, with each O species carrying two electrons, that is, [(CO formation amount) + (CO<sub>2</sub> formation amount) × 2]/0.31088. Notably, the equivalent current in this work is equivalent to the formation rate of CO<sub>x</sub> only; it should be equivalent to the total rate of formation of all the oxidation products. Therefore, the formation rate of other detectable oxidation product, which is only H<sub>2</sub>O in this work, is included to calculate the total amount of lattice oxygen extracted for oxidation. Nevertheless, the amount of H<sub>2</sub>O formed from CH<sub>4</sub> reactions was quite small during all the tests of this work. Thus, although H<sub>2</sub>O was measured by GC whose accuracy is less than that of NDIR to measure CO<sub>x</sub>, the total amount of lattice oxygen extracted can be calculated with sufficient accuracy.

During the methane feeding period, a comparison of Fig. 2 with Fig. 3 indicates that the rates of CO and CO<sub>2</sub> formations can be markedly promoted with electrical current relative to that without it. Notably, electrical current exists under close circuit and there is no electrical current under open circuit. Notably, also, Fig. 3 is a typical result of the profiles of CO and CO<sub>2</sub>

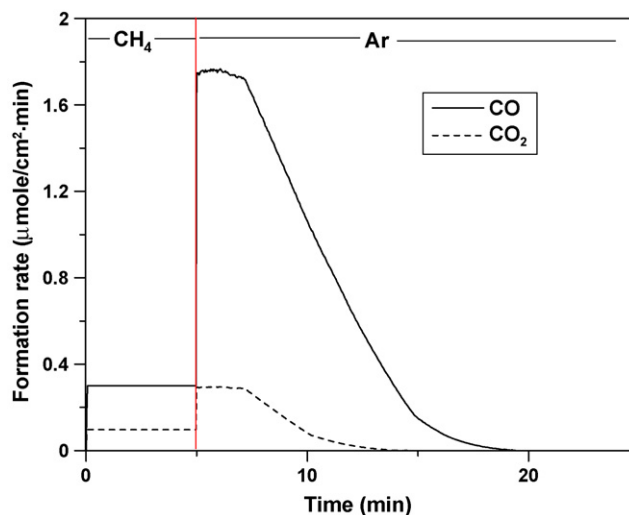


Fig. 3. Profiles of CO and CO<sub>2</sub> formation rates vs. time. Open-circuit (CH<sub>4</sub> flow) followed by close-circuit (Ar flow) measurement at 800 °C.

formation rates during 5 min methane feeding under open circuit and then with pure argon flow under close circuit. The promoted rates indicate “rate enhancement”. The rate enhancement ratio,  $\rho$ , for electrochemical promotion is defined as [18]

$$\rho = \frac{r}{r_0} \quad (2)$$

where  $r$  is the electrochemically promoted reaction rate, i.e. the close-circuit rate, and  $r_0$  is the open-circuit rate; both rates are measured during fuel flow, i.e. during methane feeding in this work. Fig. 4 shows that both rate enhancement ratios of CO and CO<sub>2</sub> formations decrease with increasing temperature; additionally, the decreasing extent of CO formation is higher than that of CO<sub>2</sub> formation.

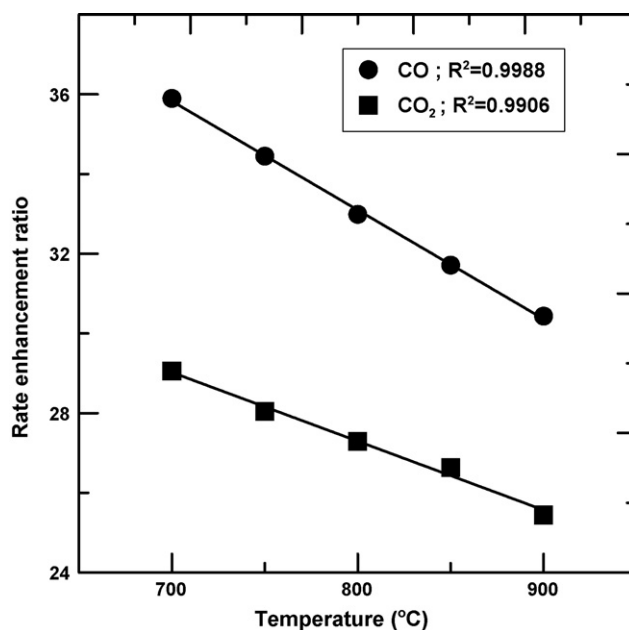


Fig. 4. Variations of the rate enhancement ratios of CO and CO<sub>2</sub> formations with temperature. Linear regression analysis.

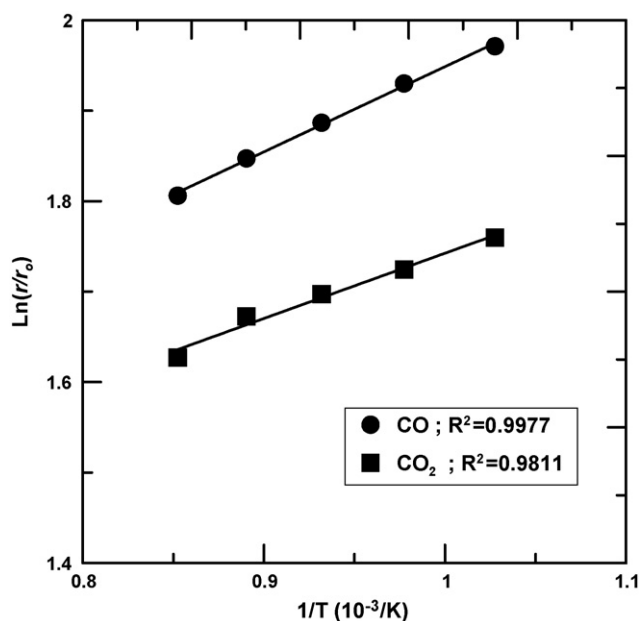


Fig. 5. Plots of  $\ln(r/r_0) = (\alpha e \xi \eta / k + \beta e / k) / T$  for CO and CO<sub>2</sub> formations.

The electrochemically promoted reaction rate can be related to the applied potential ( $\eta$ ) and temperature ( $T$ ) by an equation of the form [32]

$$\ln\left(\frac{r}{r_0}\right) = \frac{\alpha e \xi \eta}{kT} + \frac{\beta e}{kT} \quad (3)$$

where  $\alpha$  and  $\beta$  are empirically determined constants,  $e$  is the charge of an electron,  $k$  is the Boltzmann constant,  $T$  is the operating temperature. Additionally,  $\xi$  is the relationship between the change in electron extraction potential,  $\Delta\Phi$ , and the applied potential, i.e.  $\Delta\Phi = \xi\eta$ . Metcalfe [32] pointed out that  $\xi$  depends on the operating conditions and the electrode morphology. Plotting  $\ln(r/r_0)$  versus  $1/T$  according to Eq. (3), Fig. 5 shows that, for either CO or CO<sub>2</sub> formations,  $\xi$  is a constant and Eq. (3) is satisfied. Thus,  $\xi$  depends on the reaction type, noting that the operating conditions were the same for CO and CO<sub>2</sub> formations and no difference was made on the electrode morphology. This indicates that the previous theory on electrochemical promotion can be satisfied in the new phenomenon of promoted extraction of bulk lattice oxygen but additional theory may be needed for proper interpretation of this new phenomenon.

Electrochemical promotion indicates an effect which occurs due to electrochemically controlled migration of ionic species from the solid electrolyte onto the gas-exposed electrode surface [7,8,10–19]. Under close-circuit condition, the electrochemically promoted CO<sub>x</sub> formation is attributed to the promoted lattice-oxygen extraction from the anode-side bulk lattice [7,8]. The total amount of additionally extracted lattice oxygen for CO<sub>x</sub> formation is indicated by zone I, in Fig. 1 for example. On the other hand, under open-circuit condition, i.e. without electrochemical promotion, SOFC works as a conventional catalytic reactor; in the absence of gaseous oxygen, the CO<sub>x</sub> formation during methane feed as observed in Fig. 3 is due to the extrac-

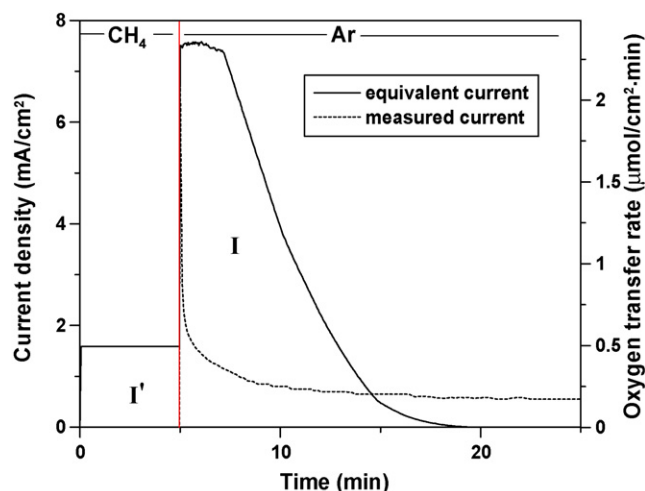


Fig. 6. Profiles of current densities vs. time. Open-circuit (CH<sub>4</sub> flow) followed by close-circuit (Ar flow) measurement at 800 °C. Zone I' denotes the area under the curve of equivalent current for time = 0–5 min; zone I denotes the area between the curves of equivalent current and measured current and extends from time = 5 min until these two curves meet.

tion of bulk lattice oxygen [33,34], as also indicated by zone I' in Fig. 6. Thus, the electrochemically promoted oxidation rate comes from both the O species associated with the electrical current and the electrochemical promotion of bulk lattice-oxygen extraction.

### 3.2. CO and CO<sub>2</sub> formations

As shown in Fig. 3, both CO and CO<sub>2</sub> formation rates increase markedly after the circuit is closed. With the circuit closed, an electrical current is generated, as shown in Fig. 6. Thus, this promotion of CO and CO<sub>2</sub> formation rates can be attributed to electrical current and is a phenomenon of electrochemical promotion. Since the gas flow was switched to pure argon at the same time as the circuit was closed, the current should be generated by the carbon species which have been deposited over the anode during the previous period of methane feeding. Notably, during the test of Fig. 6, the electrical current, after jumping up and down, decreased continuously but very slowly, being 0.5 mA cm<sup>-2</sup> after switching to argon flow for 60 min; as reported in Section 3.1, this residual current is considered to consist of both the fuel-free current [9] and the leakage current [30].

Fig. 2 shows that the formation rate of CO is much higher than that of CO<sub>2</sub> and there is a period of the formation of only CO but not CO<sub>2</sub>. This is beneficial to syngas generation. As revealed in Table 2, with increasing temperature during methane flow under either close circuit or open circuit, both amounts of CO and CO<sub>2</sub> formations increase. Nevertheless, the extent of the increase of the CO formation rate is higher than that of CO<sub>2</sub> and thus the CO selectivity increases. Additionally, although CO<sub>x</sub> formation amounts under open circuit are much smaller than those under close circuit, the CO selectivity is comparable.

Table 3 shows that, with increasing temperature, the promotion factor increases. The promotion factor ( $\sigma$ ) is defined

Table 2  
Temperature effect on total amounts of CO and CO<sub>2</sub> formations and CO selectivity during 5 min CH<sub>4</sub> feeding

Temperature (°C)	CO (μmol cm <sup>-2</sup> )	CO <sub>2</sub> (μmol cm <sup>-2</sup> )	CO selectivity <sup>a</sup>
Close circuit			
700	9.72	2.99	0.76
750	24.8	7.10	0.78
800	49.1	13.1	0.79
850	81.0	20.0	0.80
900	120	26.8	0.82
Open circuit			
700	0.271	0.103	0.72
750	0.720	0.253	0.74
800	1.49	0.479	0.76
850	2.55	0.752	0.77
900	3.94	1.05	0.79

<sup>a</sup> CO selectivity = CO formation/(CO formation + CO<sub>2</sub> formation).

as

$$\sigma = \frac{\text{amount of lattice O extracted}}{\text{amount of O species transported}} \quad (4)$$

where the “amount of lattice O extracted” denotes the total amount of the oxygen species additionally extracted from the anode-side bulk lattice and the “amount of O species transported” denotes the total amount of the oxygen species transported from cathode TPB to the anode TPB so as to generate the measured current; additionally, these amounts should be obtained during methane feeding. In other words,  $\sigma$  denotes the electrochemically promoted extraction of lattice oxygen per O species transported to generate the measured current. Notably, the amount of O species transported is equivalent to the measured current and thus the electrochemical promotion of lattice-oxygen extraction from the support bulk indicates that the amount of the support-supplied lattice oxygen for the anode reaction is not limited by the electrical current. Notably, also, the support-supplied lattice oxygen associated with the electrical current, as previously reported [17], is actually supplied from the cathode-side gas phase.

Table 3 also shows that, with increasing temperature, the Faradaic efficiency ( $\Lambda$ ) for CO formation increases but that for CO<sub>2</sub> formation decreases slightly. Additionally, the Faradaic efficiency for CO formation is greater than unity, indicating a non-Faradaic rate, and that for CO<sub>2</sub> formation is smaller than

Table 3  
Temperature effect on promotion factor and Faradaic efficiency of CO and CO<sub>2</sub> formations during 5 min CH<sub>4</sub> feeding

Temperature (°C)	Promotion factor <sup>a</sup> ( $\sigma$ )	Faradaic efficiency <sup>b</sup> ( $\Lambda$ )	
		CO	CO <sub>2</sub>
700	0.69	1.02	0.312
750	0.77	1.09	0.311
800	0.84	1.17	0.309
850	0.93	1.25	0.307
900	1.04	1.36	0.302

<sup>a</sup>  $\sigma$  = amount of lattice O extracted during CH<sub>4</sub> feeding/amount of O species transported during CH<sub>4</sub> feeding.

<sup>b</sup>  $\Lambda = \Delta r/(I/2F)$ ;  $\Delta r = r - r_0$ .

Table 4  
Temperature effect on electron charge<sup>a</sup> (e<sup>-</sup>), CO and CO<sub>2</sub> formation per O species supplied for the anodic reaction during 5 min CH<sub>4</sub> feeding

Temperature (°C)	e <sup>-</sup> /O	CO/O	CO <sub>2</sub> /O
700	1.18	0.619	0.190
750	1.13	0.636	0.182
800	1.08	0.652	0.174
850	1.04	0.669	0.166
900	0.98	0.691	0.154

<sup>a</sup> Average electron charge, number of electrons transferred from cathode TPB, per O species reacted at the anode surface.

unity, indicating possibly an electrocatalytic rate. Vayenas et al. [15] have pointed out that the Faradaic efficiency decreases with increasing temperature, and electrocatalysis is limited to  $|\Lambda| \leq 1$ , which is the main distinguishing feature of electrocatalysis and electrochemical promotion. Thus, conflicting results seem to exist for either CO or CO<sub>2</sub> formation. This reveals a difference between the newly observed electrochemical promotion of bulk lattice-oxygen extraction, occurring without gas-phase oxygen, and the previously reported electrochemical promotion with gas-phase oxygen. Thus, electrochemical promotion with or without gaseous oxygen feed over the anode may need additional theory for proper interpretation.

Table 4 reveals that, with increasing temperature, the formation rate of CO per O species supplied to the anode surface increases but that of CO<sub>2</sub> decreases. This is beneficial to syn-gas generation. Notably, the amount of O species in Table 4 is a sum of those associated with the measured current and those extracted from the bulk lattice due to electrochemical promotion.

### 3.3. Kinetic analysis

Fig. 7 shows that the activation energy of CO and CO<sub>2</sub> formation under close circuit is lower than that under open circuit. This reveals that the activation energy is reduced with an application of a potential or an electrical current. This indicates an effect of electrochemical promotion. Additionally, the activation energy for the extraction of the bulk lattice oxygen, i.e. 124 kJ mol<sup>-1</sup>, is much higher than that for the transport of the O species from the cathode TPB to generate electrical current, i.e. 105 kJ mol<sup>-1</sup>.

Table 5 also shows that the activation energy for the extraction of bulk lattice oxygen under open circuit is substantially higher than that under close circuit. This is in agreement with the substantially lower CO<sub>x</sub> formation rate under open circuit than that under close circuit, as Table 2 shows.

The dependence of CO and CO<sub>2</sub> formation rates on the oxygen supply rate is obtained by a kinetic analysis as followed. Since there is no oxygen species in the gaseous feed over the anode, the transfer rate of the oxygen species, which is a sum of the oxygen species transported from the cathode TPB and the lattice oxygen species extracted from the anode-side bulk, is considered as the rate of oxygen supply for CO and CO<sub>2</sub> formations. Thus, the average formation rate ( $r$ ) of CO and CO<sub>2</sub> is

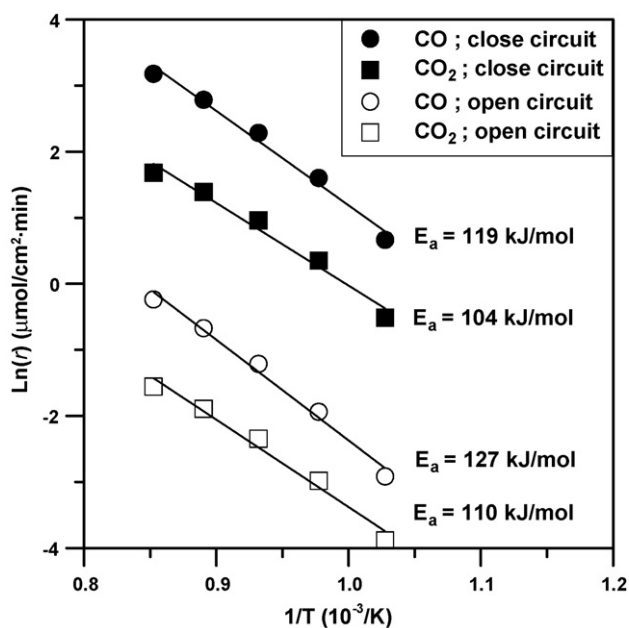


Fig. 7. Arrhenius plots for CO and CO<sub>2</sub> formations during methane feeding under close-circuit and open-circuit conditions.

Table 5  
Activation energies<sup>a</sup> ( $E_a$ ) with CH<sub>4</sub> feeding

		$E_a$ (kJ mol <sup>-1</sup> )	Standard deviation <sup>b</sup> $R^2$
Close circuit	O species transport	105	0.979
	Lattice O extraction	124	0.987
	CO	119	0.986
	CO <sub>2</sub>	104	0.978
Open circuit	Lattice O extraction	262	0.949
	CO	127	0.989
	CO <sub>2</sub>	110	0.981

<sup>a</sup> With  $r = A \exp(-E_a/RT)$  via linear regression analysis.

<sup>b</sup> Data fitting is perfect if  $R^2 = 1$ .

plotted against the oxygen supply rate ( $x$ ), i.e.

$$r = ax^n \quad (5)$$

shown in Fig. 8. The obtained constants  $a$  and  $n$  are presented in Table 6. The results show that the rate dependence of CO formation on the oxygen supply rate is much higher than that of CO<sub>2</sub> formation.

Table 6  
Results of regression analysis ( $r = ax^n$ ) of average formation rate<sup>a</sup> ( $r$ ) of CO and CO<sub>2</sub> vs. average oxygen supply rate<sup>b</sup> ( $x$ )

	$a$	$n$
CO formation	0.551	1.60
CO <sub>2</sub> formation	0.238	0.88

<sup>a</sup> Calculated by dividing the total formation rate of CO and CO<sub>2</sub>, respectively, during 5 min CH<sub>4</sub> feeding by 5 min.

<sup>b</sup> Calculated by dividing the total oxygen supply rate, i.e. the sum of O species transported and lattice O extracted, during 5 min CH<sub>4</sub> feeding by 5 min.

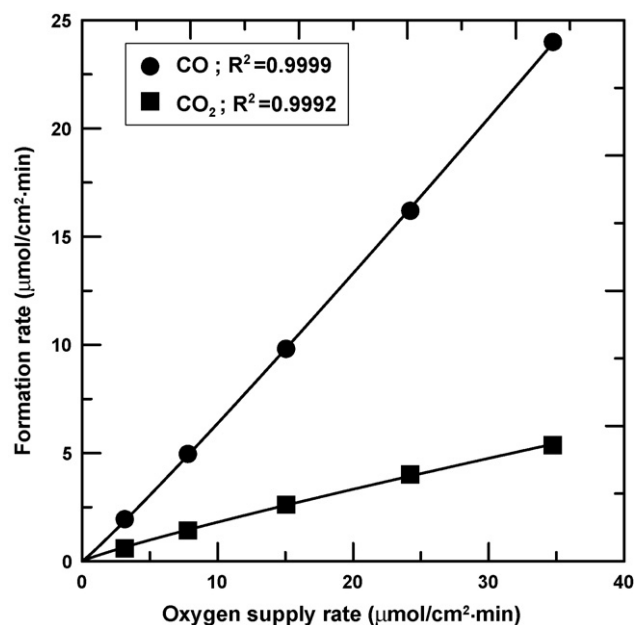


Fig. 8. Regression analysis ( $r = ax^n$ ) of average formation rate ( $r$ ) of CO and CO<sub>2</sub> vs. average oxygen supply rate ( $x$ ).

## 4. Discussion

### 4.1. Electrochemical promotion of bulk lattice-oxygen extraction

The results as presented above indicate that bulk lattice oxygen can be extracted under both the close-circuit and the open-circuit conditions. Under close circuit, the bulk lattice-oxygen extraction is electrochemically promoted; this leads to some agreements with previously reported theories of electrochemical promotion. However, additional theory may be proposed on this newly observed phenomenon of electrochemical promotion of bulk lattice-oxygen extraction. This is due to the two questions raised at the beginning of this work, that is, whether the reaction rate due to the support-supplied lattice oxygen is limited by the electrical current and whether the phenomenon of electrochemical promotion disappears at elevated temperature. The first question has been partially answered in previous reports [7,8] and additional discussion will be carried out in the following with the discussion on the second question.

The electrochemical promotion or NEMCA effect is due to electrochemically controlled migration of ionic species from the solid electrolyte onto the gas-exposed electrode surface [10–19]. With either a potential or an electrical current, the migration of ionic species onto the gas-exposed electrode surface causes a change in activation energy so as to affect the catalytic rate [12]. Since the migration of ionic species is accompanied by electron charge, an electron extraction potential is proposed. As shown in Table 4, the extraction of the bulk lattice oxygen species involves electron, and thus the theory of the electron extraction potential may be applied here; this theory is represented by Eq. (3), which can be fitted in a very good way by the data of this work, as shown in Fig. 5.

The oxygen species for generating the measured current is from the cathode-side gas phase via dissociation and charge transfer, that is,  $O_2 \rightleftharpoons 2O$  and then  $O + 2e^- \rightleftharpoons O^{2-}$ . The  $O^{2-}$  ion is usually considered to be the form of the oxygen species which can migrate in the bulk lattice of the oxygen-ion conducting materials. However, the charged oxygen species which emerge at TPB and spill over the electrode surface can be either  $O^-$  or  $O^{2-}$  [35]. Thus, when the  $O^{2-}$  ion is transported to the anode bulk, electrons may be donated to or shared with the anode-side lattice oxygen to form the  $O^{\delta-}$  ion ( $\delta = 1$  for example). This is confirmed by the results as shown in Table 4, that is, the  $O^{\delta-}$  species which are transferred in the anode-side bulk have average  $\delta$  values close to unity. Consequently, more oxygen species in the bulk phase of the oxygen-ion conducting materials become migratory and additional amount of the lattice oxygen species in the anode-side bulk can be extracted and transported to the anode surface for CO and CO<sub>2</sub> formations. Therefore, the anodic oxidation rate is promoted to become markedly higher than that by the oxygen species transported from the cathode TPB via the electrolyte. With increased temperature, the oxygen mobility increases and thus the promotion effect of bulk lattice-oxygen extraction can increase, as confirmed by Table 3. Additionally, the process of the above-described electron donation or sharing becomes faster with increasing temperature and thus the needed electron charge for the O species to be extracted and transported can decrease; this is confirmed by a decrease of the average electron charge per O species transferred for anodic reaction, as shown in Table 4.

The substantially lower CO<sub>x</sub> formation rate under open circuit than that under close circuit, as Table 2 shows, is considered to be due to the substantially higher activation energy for the extraction of bulk lattice oxygen under open circuit than that under close circuit. Additionally, Table 5 shows that the activation energy of lattice-oxygen extraction is higher than that of CO<sub>x</sub> formation under close and open circuit. Thus, in the absence of gas-phase oxygen feed over the anode, the process of lattice-oxygen extraction from the YSZ bulk can be considered to be rate determining for CO<sub>x</sub> formation under close and open circuit. This indicates that the existence of electrical current, to supply electron charge as described above, can dramatically promote the process of lattice-oxygen extraction. This is also confirmed by the result of simply closing the circuit, shown in Fig. 6.

The question on whether the reaction rate due to the support-supplied lattice oxygen is limited by the electrical current can now be discussed in association with the above-obtained activation energy. As shown in Table 5, the activation energy for lattice O extraction is much higher than that for O species transport; this means that the bulk lattice O transport can be much faster than the extraction of bulk lattice oxygen. When gaseous oxygen species exist over the anode, which is the case for the previously reported electrochemical promotion with gas-phase oxygen, there is no need for the extraction of bulk lattice oxygen. Instead, the need is to transport some support-supplied lattice oxygen species in the bulk. Notably, these support-supplied O species are considered as “sacrificial promoter” [15] whose amount is much smaller than that of the total O species consumed for the anodic oxidation reaction. Consequently, a small electrical current can

be enough to transport these O species. Therefore, the needed amount of support-supplied lattice oxygen is only that equivalent to the oxygen ion transported from the cathode TPB in association with the electrical current. This leads to a phenomenon that the support-supplied lattice oxygen is limited by the electrical current; this is actually due to the much higher activation energy for bulk lattice-oxygen extraction.

The question on whether the phenomenon of electrochemical promotion disappears at elevated temperature is discussed in the following. For the previously defined electrochemical promotion, indicated by the rate enhancement ratio, Fig. 4 shows that both enhancement ratios of CO and CO<sub>2</sub> formations decrease with increasing temperature. This is due to higher activation energy for CO and CO<sub>2</sub> formation under open circuit than that under close circuit. Consequently, the phenomenon of electrochemical promotion can disappear at elevated temperature. However, for the newly observed electrochemical promotion of bulk lattice-oxygen extraction [7,8], the promotion factor increases with increasing temperature; additionally, the Faradaic efficiency increases for CO formation but decreases slightly for CO<sub>2</sub> formation, shown in Table 3. This indicates that the newly observed phenomenon of electrochemical promotion of bulk lattice-oxygen extraction needs additional theory for proper interpretation. It is proposed that the above-described hypothesis of electron donation or sharing is further studied.

#### 4.2. Promotion of syngas cogeneration

The above results indicate that higher CO<sub>x</sub> formation rate, which is equivalent to higher methane conversion, lead to higher CO selectivity. Moreover, the electrochemically promoted extraction of bulk lattice oxygen results in higher CO selectivity. These are beneficial for syngas generation. With methane decomposition in the absence of gaseous oxygen, the formations of CO and CO<sub>2</sub> occur by oxidation with the oxygen species migrating from the support lattice to the metal surface via the metal-support interface [36]. Since electrochemical promotion of bulk lattice-oxygen extraction increases the supply rate of the oxygen species to the anode surface, the rates of CO and CO<sub>2</sub> formations are promoted. This promotion of the CO and CO<sub>2</sub> formation rates is due to an increased supply rate of the oxygen species by both the increased electrical current and the electrochemically promoted extraction of bulk lattice oxygen. As shown in Table 4, with increasing temperature, CO formation increases but CO<sub>2</sub> formation decreases per O species supplied for anodic reaction. Thus, higher supply rate of the oxygen species is beneficial to the formation of CO but detrimental to that of CO<sub>2</sub>; consequently, CO selectivity increases. Therefore, electrochemical promotion of bulk lattice-oxygen extraction enhances the syngas generation.

Fig. 4 reveals that the effects of electrochemical promotion, i.e. the rate enhancement ratios, of CO and CO<sub>2</sub> formations are different. This is attributed to that the dependences of CO and CO<sub>2</sub> formation rates on the oxygen supply rate are different, as shown in Table 6. Since the CO formation rate depends on the oxygen supply rate to a higher extent than the CO<sub>2</sub> rate does, the promoted oxygen supply rate should result in a higher rate



of CO formation than that of CO<sub>2</sub> formation per oxygen species transferred.

As shown above, higher oxygen supply rate is beneficial to CO formation but detrimental to CO<sub>2</sub> formation. This is attributable to that CO<sub>2</sub> formation requires two O species in the neighborhood of the C species. If there is only one O species in the neighborhood of the C species, only CO can be formed. As the oxygen supply rate increases, which means an increased migrating rate of the O species through the anode TPB, the probability of only one O species in the neighborhood of the C species during its reaction time should increase; this probability increases as the reaction time becomes shorter. A higher temperature leads to a higher migrating rate of the O species through the anode TPB, which results in a shorter reaction time for the oxidation of the C species; consequently, CO formation is favored. Thus, it can be concluded that SOFC operation at higher temperature favors syngas generation in both the production rate and the CO selectivity.

Moreover, the above-observed phenomenon of higher CO selectivity associated with higher oxygen supply rate via the oxygen-ion conducting materials is quite different from that associated with higher oxygen supply rate from the anode-side gas phase, which lowers the CO selectivity. Therefore, the effect of electrochemical promotion of bulk lattice-oxygen extraction on syngas cogeneration in direct-methane SOFC is worthy of further investigation.

## 5. Conclusions

A phenomenon of electrochemical promotion of bulk lattice-oxygen extraction from the YSZ electrolyte has been observed. In the absence of gaseous oxygen feed over the anode, markedly higher amount of oxygen than that equivalent to the measured current is supplied for anodic oxidation. The electrochemical promotion effect increases as the temperature increases. It is also influenced by the reaction type, i.e. CO and CO<sub>2</sub> formations; the effect on CO formation can be much higher than that on CO<sub>2</sub> formation. With increasing temperature, both rate enhancement ratios of CO and CO<sub>2</sub> formations decrease.

The activation energy of CO and CO<sub>2</sub> formation under close circuit is lower than that under open circuit. Additionally, the activation energy for lattice-oxygen extraction from YSZ bulk is 124 kJ mol<sup>-1</sup>, which is much higher than that for oxygen transport through YSZ bulk, i.e. 105 kJ mol<sup>-1</sup>. Thus, the process of lattice-oxygen extraction from YSZ bulk is rate determining for direct-methane oxidation to produce CO and CO<sub>2</sub> under close and open circuit.

The dependence of CO formation rate on the oxygen supply rate is stronger than that of CO<sub>2</sub> formation rate. Electrochemical

promotion of bulk lattice-oxygen extraction enhances the syngas generation. SOFC operation at higher temperature favors syngas generation in both the production rate and the CO selectivity.

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