Short communication

Effect of addition method of gadolinia-doped ceria-added FeCr gas diffusion layer on performance of direct-methane solid oxide fuel cells

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ABSTRACT

A solid oxide fuel cell (SOFC) was set up with a porous disk of gadolinia-doped ceria (GDC)-added FeCr as a gas diffusion layer under direct-methane feeding. The addition of GDC was done by mixing GDC powder with FeCr powder before disk fabrication, or by coating GDC powder or impregnating GDC precursor to the surface of the porous FeCr disk. When GDC was added by mixing, the direct-methane SOFC (DM-SOFC) performance degraded very rapidly. When GDC was added by either powder coating or impregnating, the DM-SOFC performance can be relatively stable. Both the current density and the CO_2 selectivity with GDC addition by impregnating are larger than those by powder coating.

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1. Introduction

Methane is an important fuel for the solid oxide fuel cells (SOFCs). A great deal of research efforts have been put on the conversion of methane fuel into hydrogen-rich gas as required for the electrochemical reaction on the anode. Recently, the SOFCs with internal reforming, either direct or indirect internal reforming [1–3], have attracted much attention since the requirement for a separate fuel reformer can thus be eliminated and the efficiency is increased by effective utilization of the waste heat. Depending on the operating conditions, the heat consumed by internal reforming can vary from 40 to 70% of the total heat produced in a fuel cell [1]. Therefore, internal reforming SOFC is energy efficient. However, over the usual Ni anode, coking is a well-known problem when methane is used as the fuel. Although the coking problem may be overcome by adding enough steam into the fuel stream, the dilution of the fuel by the steam becomes a problem [1] in addition to the extra heating energy required to produce the steam. The direct-methane SOFCs (DM-SOFCs) with either an inert porous layer [4] or a catalytic layer [5] placed between the anode and the fuel stream is promising to reduce or even solve the coking problem.

Methane decomposition occurs over the Ni anode in DM-SOFCs [6–9]. At high temperatures, methane may decompose to produce the C species, the reaction being $CH_4 \rightarrow C + 2H_2$. The deposition of the C species over Ni may cause coking [10], which can cause very

rapid deactivation of the SOFC anode; consequently, the removal of the deposited carbon should be important. However, a carbon SOFC has been proposed to utilize the deposited carbon as a fuel [11]. Huang and Huang [12] have confirmed that the deposited carbon can be fully utilized for the generation of the electrical current in DM-SOFCs.

The FeCr alloy can be used as the interconnect materials for intermediate temperature SOFCs [13]. Thus, FeCr can be utilized as the current collector over the SOFC anode. A porous FeCr disk has been used as the gas diffusion layer (GDL) and also as the current collector over the anode side of a DM-SOFC to achieve a stable SOFC performance [14]. Additionally, the surface of the FeCr disk has been modified by adding powders of yttria-stabilized zirconia (YSZ) and Ni-YSZ; these surface-modified FeCr disks result in an improved DM-SOFC performance than that without surface modification [14].

The doped ceria-coated Ni anode has been used for direct utilization of methane in low-temperature SOFCs [15]; the coating of Sm-doped ceria with the impregnating method to a porous Ni anode layer enhances the anode performance. Therefore, the addition of doped ceria by impregnating onto the surface of the porous FeCr GDL would be beneficial in association with direct-methane feeding. However, the method of addition can also be powder coating onto the surface [14] or mixing into the bulk of the FeCr disk; thus, it would be interesting to study the effect of the method of addition of doped ceria.

In the work, various gadolinia-doped ceria (GDC)-added FeCr disks were used as the GDL and also as the current collector over the anode of the DM-SOFCs. The method of GDC addition to the porous FeCr disk showed a large effect on the DM-SOFC performance.

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2. Experimental

2.1. Preparation of GDC-added FeCr disk

The GDC powders were prepared by a co-precipitation method. The details of the method have been reported elsewhere [16]. The calcination of the GDC powders was performed by heating in air at a rate of $10\,°C\,min^{-1}$ to $300\,°C$ and held for 2 h, and then to $700\,°C$ and held for 4 h, and then slowly cooled down to room temperature. GDC of this work is $(GdO_{1.5})_{0.1}(CeO_2)_{0.9}$.

The porous FeCr disk was prepared by mixing FeCr powder (Goodfellow, Fe 87.5% and Cr 12.5%, particle size $45\,\mu m$) and graphite powder (Aldrich, synthetic, particle size $<20\,\mu m$) in a weight ratio of graphite:FeCr of 3:4. 0.5 g of the mixture powders were compressed with 10 ton into a disk. Then, the disk was calcined at $1200\,°C$ to make it porous. The FeCr disk has a porosity of 78%, an area of $1\,cm^2$ and a thickness of 0.22 cm.

The GDC-added FeCr disk was prepared by three methods of GDC addition:

(1) Mixing: this modifies the bulk property of the FeCr disk. The FeCr powder, the graphite powder and the GDC powder were mixed in a weight ratio of graphite:FeCr:GDC of 3:4:1.05, resulting in 26% GDC with respect to the weight of FeCr. 0.575 g of the mixture powders were compressed with 10 ton into a disk. Then, the disk was calcined at $1200\,°C$ to make it porous. This GDC-added FeCr disk has a porosity of 78%, an area of $1\,cm^2$ and a thickness of 0.25 cm.
(2) Powder coating: this modifies the surface property of the FeCr disk. 0.075 g of the GDC powder was mixed physically into the porous FeCr disk, resulting in 26% GDC with respect to the weight of FeCr. Intensive shaking was done in an effort to make the powders distributing uniformly in the pores of the FeCr disk. Then, the disk was calcined at $800\,°C$ to fix the powders to the surface of the porous disk.
(3) Impregnating: this also modifies the surface property of the FeCr disk. The porous FeCr disk was impregnated with a solution of GDC precursor equivalent to 26% GDC with respect to the weight of FeCr. After drying, the disk was heated to $800\,°C$ to form GDC over the surface of the porous disk.

2.2. Construction of the SOFC unit

The commercial YSZ tape ($156\,\mu m$ 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 60 wt% Ni-YSZ powder, corn oil, polyvinyl butyral and ethanol. The other side of the disk was screen-printed with a thin layer of Pt paste (Heraeus, C3605P) to make the cathode layer.

The method of the coating of the Ni-YSZ paste to make the anode layer has been described elsewhere [12]. The thus-prepared unit cell has an anode area of $1\,cm^2$, an anode thickness of about $30\,\mu m$, an electrolyte thickness of $156\,\mu m$, a cathode area of $1\,cm^2$ and a cathode thickness of about $5\,\mu m$. These thicknesses were measured from a scanning electron micrograph plot of the cross section of the unit cell.

The unit cells were closely connected with the GDC-added FeCr disk on the anode side for current collection and then with the Pt wires to the current and voltage measurement unit. 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 was sealed in the quartz tube and the cathode side was exposed to the stagnant air.

2.3. Activity tests of unit cell

A voltage of 0.61 V was maintained for all tests in this work. The test temperature was fixed at $800\,°C$. For reduction, the feed to the anode side was 10% H_2 in argon. For the H_2 test, the fuel to the anode side was 10% H_2 in argon. For the direct-methane test, the fuel to the anode side was 10.5–70% methane in argon. The flow rate was always 100 ml/min 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 $5\,°C\,min^{-1}$. Then, 10% H_2 was introduced for 30 min to carry out the H_2 test; pure argon flow was then introduced until the measured electrical current became zero. The DM-SOFC test was then carried out with introducing methane fuel flow for 360 min. Then, the anode-side flow was switched to pure argon.

During 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 (nondispersive 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. Effect of addition method on current density

Fig. 1 shows the H_2-test results of the SOFCs with various GDC-added FeCr disks as GDLs. The steady-state current densities were obtained in all cases and had the same value. This indicates that the method of GDC addition to modify the FeCr GDLs does not affect the performance of the hydrogen-fed SOFCs. This is due to the fact that the SOFCs with hydrogen as the fuel do not need fuel processing. Therefore, the FeCr GDLs functioned only as the current collector. It is also confirmed that the method of GDC addition does not affect the property of the FeCr GDLs for the current collection.

Fig. 2 shows that, the method of GDC addition to the GDLs can affect the DM-SOFC performance quite largely. This is due to the fact that the SOFCs with direct-methane feeding need fuel processing, which means internal methane processing in this work, to avoid or reduce the extent of anode coking [14]. Notably, internal
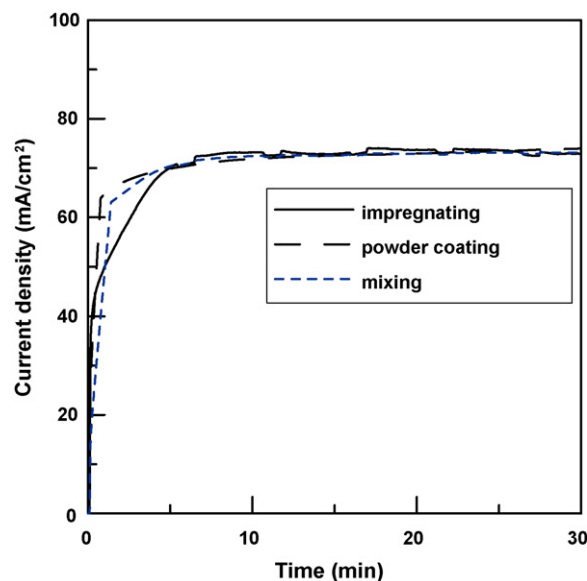

Fig. 1. Effect of the method of GDC addition on the measured currents with 10% H_2 as the fuel. Closed circuit at $800\,°C$ and constant voltage of 0.61 V.
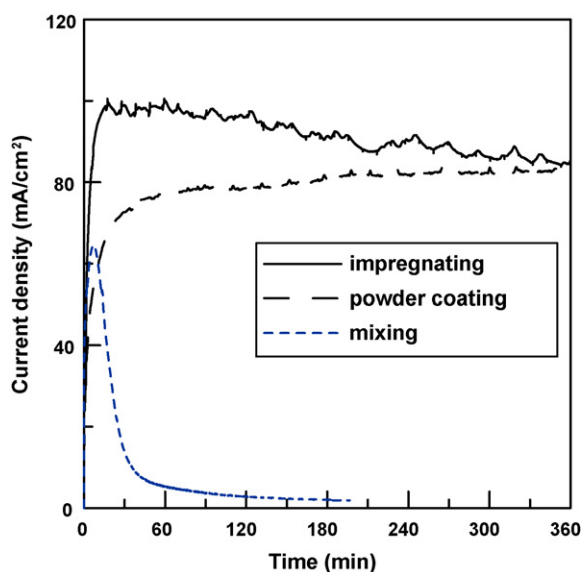
Fig. 2. Effect of the method of GDC addition on the measured currents with 10.5% CH_4 as the fuel. Closed circuit at 800 °C and constant voltage of 0.61 V.

methane processing means that methane is internally reformed by the oxidized products formed over the anode. When GDC was added by mixing, the current density decreased very rapidly after about 10 min. However, when GDC was added by either impregnating or power coating, the current density can become much higher than that by mixing and also has only a mild decrease or even a gradual increase. Notably, after 360 min of operation, the performance of the DM-SOFC with the GDL of GDC addition by impregnating may become worse than that by powder coating. However, an intermittent operation [12] has been proposed for the DM-SOFCs to produce not only continuous but also relatively stable electrical current. The operation time of 360 min CH_4 feeding in this work is much longer than that of 5 min CH_4 feeding, followed by 20 min Ar flow to form a cycle, in the above-proposed intermittent operation; thus, a much longer cycle in this intermittent operation can be considered for the DM-SOFCs of this work.

The above results indicate that modifying the surface property of the FeCr GDL with GDC addition by either powder coating or impregnating can lead to a good activity of internal methane processing and thus result in a good DM-SOFC performance. However, mixing the GDC powder into the bulk structure of the FeCr GDL did not have good methane processing activity and thus the DM-SOFC performance degrades very rapidly. Therefore, only the surface property of the FeCr GDL should be modified but not its bulk property.

3.2. Effect of addition method on methane conversion and products formation

Fig. 3 shows the product formation rates and the CH_4 conversion rate with 10.5% CH_4 as the fuel in the SOFCs with various GDC-added FeCr GDLs. Within the detection limit of the gas chromatograph used in this work, no H_2O vapor was detected in all the tests of Fig. 3. Without H_2O formation, the major CH_4 reaction during these DM-SOFC operations should be the dissociation of methane without hydrogen oxidation. Notably, the DM-SOFC operations without H_2O formation have been observed previously either in an SOFC with GDL [14] or in one without GDL [12]; this is attributed to a stronger interaction of the C species with the catalyst surface than that of hydrogen; restated, hydrogen cannot compete with the C species to be adsorbed onto the Ni surface of

the anode [14]. Additionally, the SOFC operations with the coal syngas (CO plus H_2) as the fuel has led to the observation that the reactivity of CO is higher than that of H_2; this is attributed to the stronger C-metal interaction than the H-metal interaction [17]. However, hydrogen should have some adsorption affinity on the Ni surface under the conditions of this work; the above result indi-
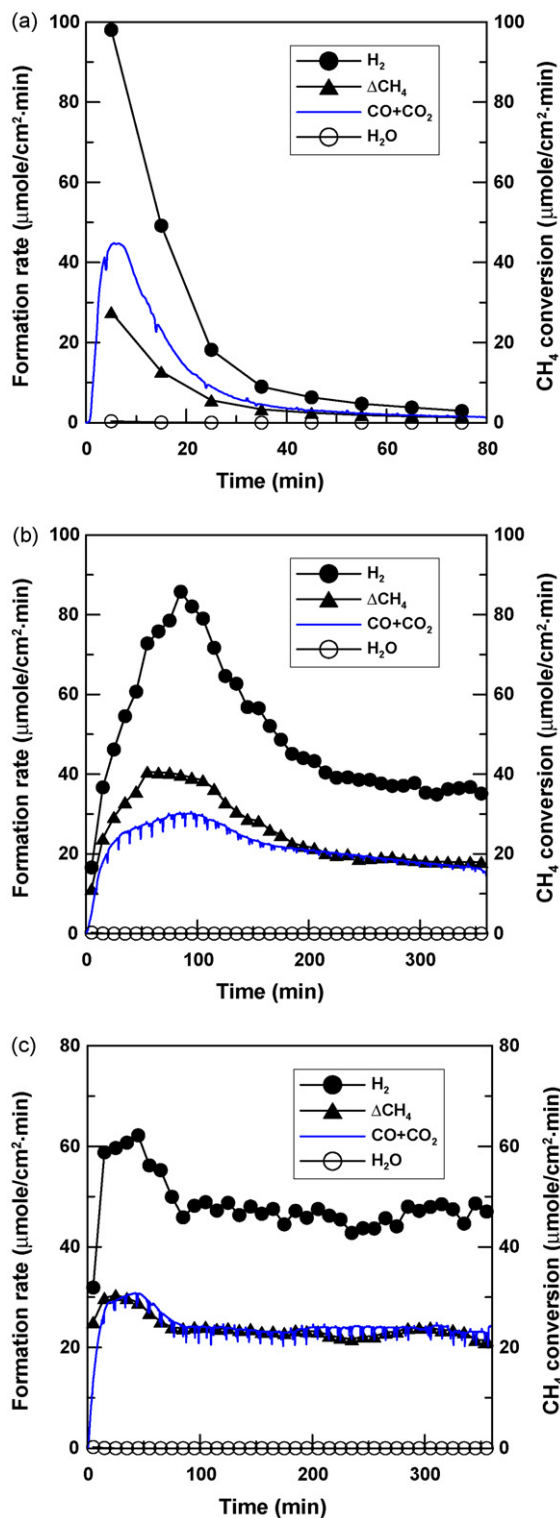

Fig. 3. Effect of the method of GDC addition on the product formation rates and the CH_4 conversion rate with 10.5% CH_4 as the fuel. GDC added to FeCr GDL by (a) mixing, (b) powder coating, and (c) impregnating. Closed circuit at 800 °C and constant voltage of 0.61 V.

cates that this adsorption affinity is small and the amount of H_2O formed by the oxidation of the adsorbed H_2 would be too small to be detectable.

Fig. 3a shows that, in the SOFCs with the GDL of GDC addition by mixing, the rate of hydrogen formation can be larger than two times that of methane conversion, i.e. $\Delta H_2 > 2\Delta CH_4$, where ΔH_2 is the hydrogen formation rate and ΔCH_4 is the methane conversion rate. This is attributed to the CH_x species with $x \neq 0$ formed by CH_4 dissociation and the deposition of these CH_x species. Notably, due to the limitation of the gas chromatograph, the H_2 measurement was carried out every 10 min; thus, the profile at the very beginning for the case of Fig. 3a cannot be identified. However, the initial period for the cases of both Fig. 3b and c can be much longer due to the stability and thus the profiles at the very beginning can be identified. Both Fig. 3b and c show that, at the very beginning, the CH_x adsorption results in low H_2 production with $\Delta(H_2) < 2\Delta(CH_4)$. Within a certain period afterwards, high H_2 production with $\Delta(H_2) > 2\Delta(CH_4)$ occurs, as shown in Fig. 3a at 5 min.

After the initial deposition of the CH_x species, the simultaneous occurrence of the following reactions results in $\Delta H_2 > 2\Delta CH_4$:

$$CH_x \rightarrow C + (x/2)H_2 \tag{1}$$

$$CH_4 \rightarrow C + 2H_2 \tag{2}$$

Notably, ΔH_2 equals $2\Delta CH_4$ if only reaction (2) occurs. If ΔH_2 is much larger than $2\Delta CH_4$, a considerable amount of CH_x species should have been formed over the anode of the DM-SOFCs with the GDL of GDC addition by mixing. If either the CH_x or the C species is not oxidized to form CO and/or CO_2 soon enough, the coke could be formed. The formed coke covers the anode surface and degrades the SOFC performance. Notably, also, the deposited carbon has been observed visually in the GDL and over the anode in every used SOFC unit.

Fig. 3b shows that, in the SOFCs with the GDL of GDC addition by powder coating, ΔH_2 is smaller than $2\Delta CH_4$ before about 60 min of the SOFC operation. This indicates the formation of the CH_x species with $x \neq 0$ by CH_4 dissociation. Then, $\Delta H_2 > 2\Delta CH_4$ occurs. However, with GDC addition by powder coating, the extent of ΔH_2 being larger than $2\Delta CH_4$ is much smaller than that by mixing, indicating that the amount of CH_x formed is much smaller. This extent is even smaller with GDC addition by impregnating, as shown in Fig. 3c. According to the above discussion, the removal of the CH_x species needs one more reaction than that of the C species and thus the former would be more difficult than the latter. This may explain why the DM-SOFCs with the GDL of GDC addition by mixing degrades very rapidly but that by either powder coating or impregnating does not.

Methane can dissociate to produce the C species, via reaction (2), without forming the CH_x species. Notably, the occurrence of reaction (2) leads to $\Delta H_2 = 2\Delta CH_4$; this is confirmed by the results for the SOFCs with the GDL of GDC addition by either powder coating or impregnating, as shown in Table 1. Additionally, the above discussion indicates that the formation of the CH_x species is minor in these DM-SOFCs. Therefore, in these DM-SOFCs, methane dis-

sociation to produce the C species via reaction (2) is the major reaction.

Fig. 3b also shows that, in the SOFCs with the GDL of GDC addition by powder coating, the CH_4 conversion rate can be larger than the $(CO + CO_2)$ formation rate. This indicates the deposition of the C species, i.e. $\Delta C \neq 0$:

$$\Delta C = \Delta CH_4 - \Delta(CO + CO_2) \tag{3}$$

where ΔC is the rate of formation of the deposited C species and $\Delta(CO + CO_2)$ is the rate of formation of CO and CO_2. Notably, Fig. 3a shows that there can be $\Delta(CO + CO_2) > \Delta CH_4$; this indicates the oxidation of the previously deposited C species to form the carbon oxides.

The C species produced by methane dissociation over the anode can react electrochemically with the oxygen-ion species (O^{2-}) from the cathode to produce CO_2 and CO [18]:

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \tag{4}$$

$$C + O^{2-} \rightarrow CO + 2e^- \tag{5}$$

In the GDL, the C species can be oxidized by the O species, the lattice oxygen species of GDC, via the following de-coking reactions [14]:

$$C + 2O \rightarrow CO_2 \tag{6}$$

$$C + O \rightarrow CO \tag{7}$$

Thus, the methane conversion rate can be equal to the $(CO + CO_2)$ formation rate—that is, $\Delta CH_4 = \Delta(CO + CO_2)$ and thus $\Delta C = 0$. Fig. 3c shows that this is the general case in the SOFCs with the GDL of GDC addition by impregnating. A comparison between Fig. 3b and c shows that the extent of ΔCH_4 being larger than $\Delta(CO + CO_2)$ in the GDL with GDC addition by impregnating is much smaller than that by powder coating. This indicates that the extent of carbon deposition is much smaller or the de-coking activity much larger with GDC addition by impregnating than by powder coating. Therefore, the coking problem in the SOFCs with the GDL of GDC addition by impregnating can be less than that by powder coating.

3.3. Effect of addition method on CO_2 selectivity

Fig. 4 shows the effect of the method of GDC addition on CO and CO_2 formation rates with 10.5% CH_4 as the fuel. The behavior of CO and CO_2 formations in the SOFCs with the GDL of GDC addition by powder coating is somewhat similar to that by mixing but very much different from that by impregnating. With GDC addition by either mixing or powder coating, the rate of formation of CO_2 is always larger than that of CO, as shown in Fig. 4a and b. With GDC addition by impregnating, the rate of formation of CO can be larger than that of CO_2 although only for a short period, as shown in Fig. 4c. However, the rate of formation of CO_2 with GDC addition by impregnating increases and reaches a relatively stable state while that by powder coating decreases gradually; thus, the CO_2 selectivity with GDC addition by impregnating is larger than that

Table 1
Effect of the method of GDC addition on the averaged[a] current density, methane conversion rate, product formation rates and CO_2 selectivity with 10.5% CH_4 as the fuel.

Method of GDC addition	Current density (mA/cm^2)	ΔCH_4[b]	H_2[c]	CO_2[c]	CO[c]	CO_2 selectivity[d]
Powder coating	82.16	19.5	38.9	12.63	6.68	0.654
Impregnating	88.49	22.8	45.4	16.96	6.88	0.711

[a] The averaged value of the data taken during the SOFC operation from 200 to 300 min.

[b] Methane conversion rate in μmole cm^{-2} min^{-1}.

[c] Formation rate in μmole cm^{-2} min^{-1}.
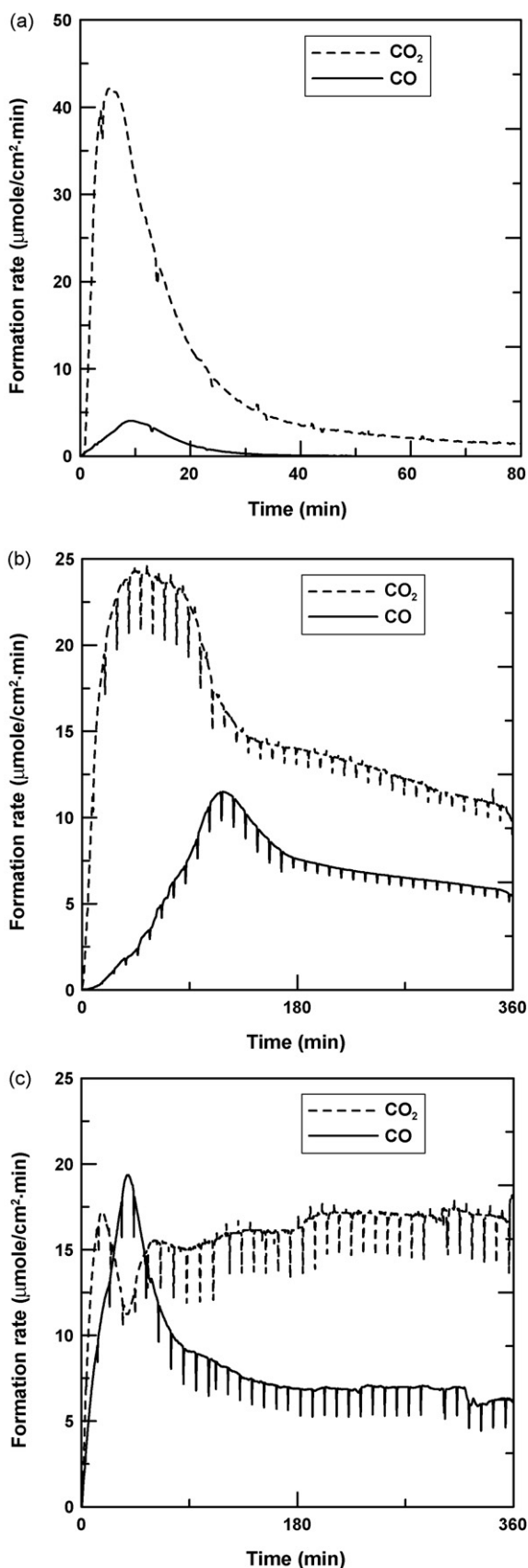
[d] Defined as $CO_2/(CO + CO_2)$.

Fig. 4. Effect of the method of GDC addition on the formation rates of CO and CO_2 with 10.5% CH_4 as the fuel. GDC added to FeCr GDL by (a) mixing, (b) powder coating, and (c) impregnating. Closed circuit at 800 °C and constant voltage of 0.61 V.

by powder coating, as shown in Table 1. Notably, with GDC addition by mixing, the DM-SOFC performance degraded very rapidly, as also shown in Fig. 4a, and thus no averaged value was reported for this case in Table 1. In any case, the overall rate of formation of CO_2 is much larger than that of CO; notably, the overall rate of formation of CO is much larger than that of CO_2 in the DM-SOFCs without a GDL [14].

The electrochemical formation of CO involves two electrons while that of CO_2 involves four electrons, with each oxygen ion carrying two electrons; thus, the current density with the formation of CO_2 is two times that of CO in terms of the utilization of carbon in methane. Thus, for the DM-SOFCs, a larger CO_2 selectivity should mean better fuel efficiency. Table 1 shows that the averaged rate of formation of CO_2 is much larger than that of CO. Huang and Huang [14] have reported that, in an SOFC with FeCr GDL surface modified by coating with YSZ powders, the averaged rate of formation of CO is larger than that of CO_2. Therefore, adding GDC to the FeCr GDL showed a better fuel efficiency than that of adding YSZ. Additionally, the generated current density with the former is larger than that with the latter. This is due to the fact that GDC has a larger oxygen storage capacity than that of YSZ.

The addition of GDC by impregnating can result in a higher extent of the dispersion of the GDC species than that by powder coating. Higher extent of GDC dispersion can result in larger amount of the Fe-GDC interface, which can act as the active site for the dissociation of methane and also for the supply of the O species to gasify the deposited carbon. Notably, the surface lattice oxygen of GDC alone can act as the active site for the dissociative adsorption of CH_4 [19]. Thus, higher extent of GDC dispersion can result in larger amount of the active sites and increase the de-coking capability; consequently, the DM-SOFC performance can be enhanced. Therefore, the current density, the methane conversion rate, the product formation rates and the CO_2 selectivity of the SOFCs with the GDL of GDC addition by impregnating are all larger than those by powder coating, as shown in Table 1. This indicates that the method of GDC addition by impregnating can be better than that by powder coating for the DM-SOFC performance.

4. Conclusions

In an SOFC with the FeCr GDL of GDC addition by mixing, the performance of direct-methane operation degraded very rapidly. In those by either powder coating or impregnating, the DM-SOFC performance can be relatively stable. Both the current density and the CO_2 selectivity with GDC addition by impregnating are larger than those by powder coating.

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