Short communication

Reactions of low and middle concentration dry methane over Ni/YSZ anode of solid oxide fuel cell

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Abstract

Directly using methane in solid oxide fuel cells (SOFC) requires the knowledge of the reaction of methane over the anode. The reactions of low and middle concentration dry methane were studied over the anode of solid oxide fuel cell with Ni/yttria-stabilized zirconia (YSZ) anode and YSZ electrolyte. The production rates of different types of gas at anode outlet were measured at different current density. Mass balance and relationships between production rates and reaction rates were used to analyze the chemical and electrochemical reactions that took place in parallel. When dry methane is in low concentration, methane decomposition and deposited carbon oxidation occurs at low current density with the overall reaction being partial oxidation of methane (POM). With increased current density, hydrogen oxidation and carbon monoxide oxidizing to carbon dioxide take place simultaneously, and the overall reaction becomes the direct oxidation of methane (DOM). When DOM occurs, a portion of methane participates the POM. However, the rate of POM decreases with increased current density. At medium methane concentration, only partial oxidation of methane takes place. Carbon deposition was found in all the tests across the concentration range investigated.
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Keywords: Solid oxide fuel cells; Methane; Reaction; Anode

1. Introduction

Direct electrochemical oxidation of hydrocarbon fuels in solid oxide fuel cell (SOFC) offers the possibility to generate electrical power without upstream fuel processing, such as reforming. Natural gas whose main composition is methane is considered as a suitable hydrocarbon fuel used in SOFC. As the pure methane enters the anode of SOFCs, H_2, CO, CO_2, and H_2O are formed by partial electrochemical oxidation of methane (POM) and direct electrochemical oxidation of methane (DOM). The partial oxidation gives a higher voltage as well as a higher gradient with temperature than the full oxidation. The resulting gas mixture ($CO + H_2$) can be either used to generate more electrical power or in other applications. The direct oxidation of methane to CO_2 can effectively prevent carbon deposition without steam reforming and improve fuel efficiency. POM and DOM are different not only in terms of their reaction prod-

ucts, but also in their power generating performance, such as open-circuit voltage (OCV) [1].

The reaction of dry methane over Cu-yttria-stabilized zirconia (YSZ) anode is DOM [2].

$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$

DOM also took place over the anode of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$/Pt at given current density [3]. Between 700 °C and 900 °C, POM takes place over nickel cermet anode containing 5% cerium oxide [4].

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$
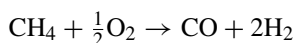
Pure methane gives open-circuit voltage which was consistent with that calculated from the Nernst equation with partial oxidation. Synthesis gases were obtained from dry methane at 700–800 °C and within the current density 0–100 mA cm^{-2} over the anode of Ni-SDC [5]. The speculated reaction mechanism was that methane cracking reaction took place at Ni particles in the Ni-SDC anode, i.e.,

$$CH_4 + Ni \rightarrow C–Ni + 2H_2$$
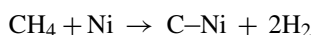
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Nomenclature

F	faraday constant ($C\,mol^{-1}$)
I	current (A)
r_i	reaction rate of reaction i ($mol\,s^{-1}$)
ν	produce rate of the some kinds material ($mol\,s^{-1}$)

Subscripts

C	deposited carbon
dep	deposited
fH	from hydrogen balance
fO	from oxygen balance
i	reaction i
in	inlet
m	reacted methane
O	oxygen ion take part in reaction
out	outlet

The reaction led carbon deposition. The carbon then reacted with the oxygen species pumped to anode side from the cathode side, that the OCV is 1.29 V.

$$C–Ni + O^{2-} \Leftrightarrow CO + Ni + 2e^-$$
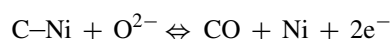
The reason for the fact that various studies coducted by different researchers on dry methane reacting over the anode of SOFCs give different results may be that anodes in the studies are different and testing conditions including current density were also not the same. This calls for a study on reactions take place over the anode of SOFC when current densities change continuously.In this paper, the conversation of dry methane at different concentrations over the anode of Ni-YSZ and YSZ electrolyte at continuously changed current density was investigated. The effect of current density on the electrochemical reactions and chemical reactions of dry methane was also studied.

2. Experimental

Disks of 8 mol 5%Y_2O_3–ZrO_2 (8-YSZ; 20 mm diameter; manufactured by Tosoh Company) were used as electrolytes. The anodes were prepared by coating one side of the disk with a mixture of NiO powder (particle size 7 μm, Soekawa Company), 8-YSZ (particle size 0.2 μm, Tosoh Company), ethylcellulose, and α-terpineol. The disks were calcined at 1400 °C in air for 5 h. Using a similar calcination method, the opposite side of the disk was coated with $La_{0.85}Sr_{0.15}MnO_3$ as a cathode material. The anode and cathode are of the same size and were placed in the centre of the disk. The calcination temperature and calcination time for the cathode were 1200 °C and 3 h, respectively. The cathode was calcined after the calcination of anode.

The configuration of the cell is shown in Fig. 1. Two soft glass rings were used as sealing gaskets to avoid the leakage of reactant gases. Platinum mesh was used to collect current over each electrode. The furnace was heated up to 1000 °C electrically. Prior to measurements, the anode was reduced in pure hydro-
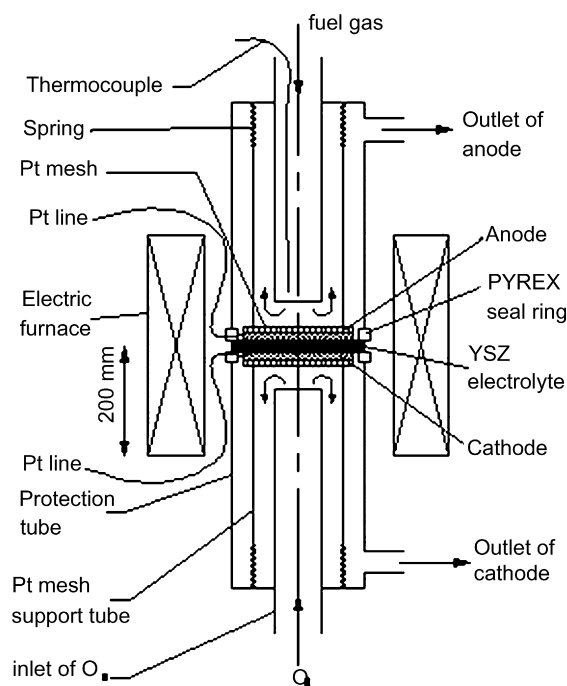

Fig. 1. Schematic of the SOFC used in this work.

gen. After the reduction, hydrogen in the experiment had been purged with argon. Pure O_2 was used as an oxide whose feed rate was 50 mL STP min^{-1}. The gaseous mixture of CH_4 and Ar was fed to the anode side of the reactor at a rate of 65 mL STP min^{-1}.The concentrations of methane used in experiments were 4.2% and 29.2%, respectively. The thicknesses of electrolyte and anode were 0.5 mm and 0.14 mm when methane's concentration was 29.2% while for 4.2% methane the thicknesses were 1 mm and 0.07 mm. The current across the cells was controlled by a Galvan stat (Hokuto Denko, HA-151). Gas chromatograph was used to characterize the exit gas in order to determine the production rates in the anode. Each measurement was conducted 15 min after current was changed. The production rates of each gas were calculated by the flow rate of Ar and the partial pressure of each gas (Ar, CO, CO_2, CH_4, H_2, and other HCs) measured by the chromatograph.

The mass balances were used to determine the deposited carbon and water. The amount of water formed in reactions can be calculated by hydrogen balance or oxygen balance.

Experiments were performed at the atmospheric in the temperature 1000 °C. The deposited carbon was removed by pure oxygen at open-circuit condition. Power generation experiments were done with pure hydrogen before changing the methane concentration in order to evaluate the deterioration of the cell. When the current density was changed, the compositions were measured after mixed gases were fed for 15 min.

3. Results and discussion

The results of power generation experiments for low and medium concentration methane are presented in Fig. 2. When 29.2% methane was present in the gas, the overall performance of the cell is better than the case when 4.2% methane was used.
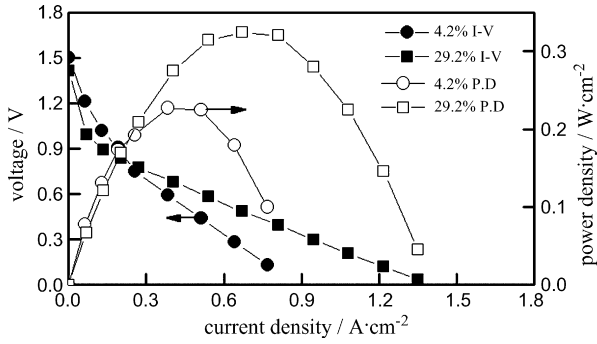
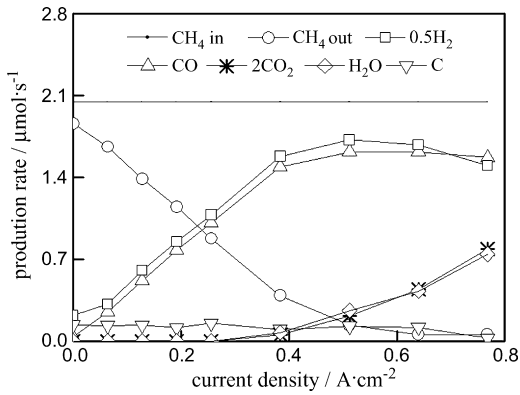Fig. 2. I-V characteristics and power density.

Fig. 3. The production rates for 4.2% methane.

This is because the cell has thinner electrolyte, thicker anode and operated with higher concentration of methane.

3.1. Anode outlet gases

Figs. 3 and 4 show the production rates of anode outlet gases for methane concentrations of 4.2% and 29.2%, respectively. The carbon deposition rate is calculated by carbon balance:

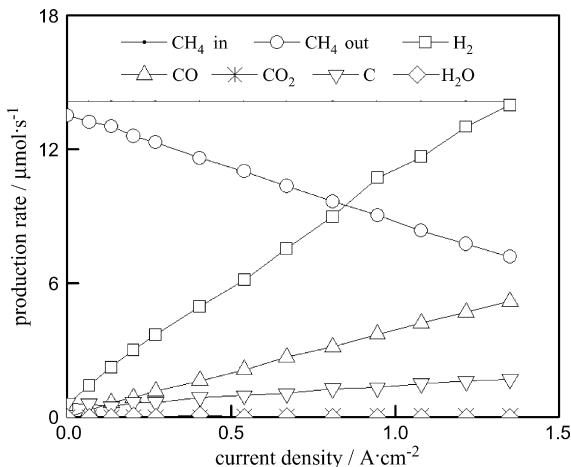$$\nu(C)_{dep} = \nu(CH_4)_{in} - \nu(CH_4)_{out} - \nu(CO)_{out} - \nu(CO_2)_{out} \tag{1}$$

Fig. 4. The production rates for 29.2% methane.

where $\nu(C)_{dep}$ is the flux of deposited carbon per second, $\nu(CH_4)_{in}$ the inlet flux of CH_4, $\nu(CH_4)_{out}$, $\nu(CO)_{out}$ and $\nu(CO_2)_{out}$ are the outlet fluxes of CH_4, CO, and CO_2. The flux of water is calculated from oxygen balance by following equation:

$$\nu(H_2O)_{fO} = \nu(O^{2-}) - \nu(CO)_{out} - 2\nu(CO_2)_{out} \tag{2}$$

where $\nu(O^{2-})$ is the O^{2-} flux calculated from the current (I) passed though the electrolyte. The relation between the $\nu(O^{2-})$ and I is

$$\nu(O^{2-}) = \frac{I}{2F} \tag{3}$$

Also hydrogen balance can be used to calculated the amount of water, $\nu(H_2O)_{fH}$ can be obtained by the following equation:

$$\nu(H_2O)_{fH} = 2\{\nu(CH_4)_{in} - \nu(CH_4)_{out}\} - \nu(H_2)_{out} \tag{4}$$
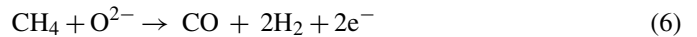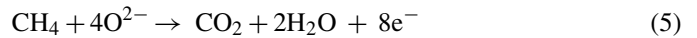
Comparison of the water determined from oxygen balance and hydrogen balance can provide a reliable estimation on H_2O production rate. There were less than 20% differences between them in our results, which can be attributed to the experimental error [6]. The results from oxygen balance were used here, because the current could be measured more accurately [7].

For the gas with 4.2% methane, the production rates of CO and H_2 increased with current density linearly at first. Then they slowly decreased after reaching the maximum. CO_2 and H_2O did not exist at small current density. When current was high enough, CO_2 and H_2O were formed simultaneously with the decrease of CO and H_2.
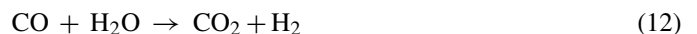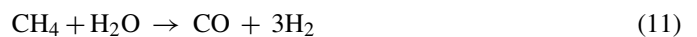
For the gas with 29.2% methane, the production rates of outlet gases increased with the increasing current density. Only when the current density reached 0.54 A cm^{-2}, small amount of CO_2 were detected.
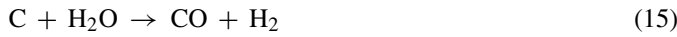
3.2. Reactions on anode

There are six chemical species on the anode: H_2, CO, CO_2, CH_4, H_2O, and deposited carbon. Chemical and electrochemical reactions may take place among the six species and the O^{2-} could transfer to the anode. The electrochemical reactions may be listed as below [1,5,8–9]:

$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^- \tag{5}$$

$$CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e^- \tag{6}$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{7}$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{8}$$

$$C + O^{2-} \rightarrow CO + 2e^- \tag{9}$$

Following chemical reactions may also take place [1,5,8–10]:

$$CH_4 \rightarrow C + 2H_2 \tag{10}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{11}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{12}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{13}$$

$$2CO \rightarrow C + CO_2 \tag{14}$$

$$C + H_2O \rightarrow CO + H_2 \tag{15}$$

In Refs. [6,7], a method about how to determine the rates of electrochemical reactions taking place in parallel in a CH_4–H_2O system was proposed. This method can also be used here to analyze the reactions of dry methane over the anode of SOFC similarly.

It is particularly noteworthy that some above reactions are not independent. For instance, reaction (6) is the sum of reaction (10) and reaction (9), and reaction (5) may be considered as the appropriate combination of reaction (10), (9), (8), and (7).

The relationships among the six chemical species of H_2, CO, CO_2, CH_4, H_2O, and C have been established by mass balances of hydrogen, H, oxygen, O, and carbon, C. The balance of oxygen connected the electrochemical reactions (7)–(9). Therefore, only three more independent equations are needed to describe the variation in the flux of these species. Since all the six chemical species are included in the chemical reactions (10)–(12), the chemical reactions (10)–(12) are employed at here.

In order to determine the chemical and electrochemical reactions taking place over the anode of dry methane, the relations of the production rates and the reaction rates, r_i, of reactions (7)–(12) are analyzed in the following equations:

$$v(C)_{dep} = r_{10} - r_9 \tag{16}$$

$$v(CO_2)_{out} = r_8 + r_{12} \tag{17}$$

$$v(CO)_{out} = r_9 - r_8 + r_{11} \tag{18}$$

$$v(CH_4)_{in} - v(CH_4)_{out} = r_{10} + r_{11} \tag{19}$$

$$v(O^{2-})_{fO} = r_7 + r_8 + r_9 \tag{20}$$

$$v(H_2O) = r_7 - r_{11} - r_{12} \tag{21}$$

Using Eq. (17) under the open-circuit condition, i.e., no O^{2-} transferring, it is shown that CO_2 and H_2O did not exist in the outlet gas for the methane content of 4.2% and 29.2%, which proved that the reaction (12) did not take place, i.e., $r_{12} = 0$. Also Fig. 4 suggested that CO_2 and H_2O did not exist at low current density. From Fig. 4, it can also be seen that changing the content of CH_4, CO, and H_2 either that reactions (11) and (12) do not take place or the CO_2 and H_2O produced are consumed by some reactions. We assume that reactions (11) and (12) did not take place in the methane concentration range and current density covered by this study. So

$$v(CO_2)_{out} = r_8 \tag{22}$$

$$v(CO)_{out} = r_9 - r_8 \tag{23}$$

$$v(CH_4)_{in} - v(CH_4)_{out} = r_{10} \tag{24}$$

$$v(O^{2-})_{fO} = r_7 + r_8 + r_9 \tag{25}$$

$$v(H_2O) = r_7 \tag{26}$$

Changing (22)–(26), we get

$$v(C)_{dep} = v(CH_4)_{in} - v(CH_4)_{out} - v(CO)_{out} - v(CO_2)_{out} \tag{27}$$

$$r_8 = v(CO_2)_{out} \tag{28}$$

$$r_9 = v(CO)_{out} + v(CO_2)_{out} \tag{29}$$

$$r_{10} = v(CH_4)_{in} - v(CH_4)_{out} \tag{30}$$

$$v(O^{2-})_{fO} = v(H_2O) + v(CO)_{out} + 2v(CO_2)_{out} \tag{31}$$

$$r_7 = v(H_2O) \tag{32}$$

It is clear that Eqs. (27) and (31) have the same form with Eqs. (1) and (2), respectively. Eqs. (27) and (31) are obtained from the analysis of reaction rates while Eqs. (1) and (2) are derived from mass balances. If reactions (11) and (12) take place, then it is not possible for Eqs. (1) and (27) to be in the same form, which also applies to Eqs. (2) and (31). These indicate that reactions (11) and (12) really do not take place.

Under the open-circuit and low current density condition for gas 4.2% methane, no CO_2 exists, i.e., $v(CO_2)_{out} = r_8 = 0$, $r_9 = v(CO)_{out}$. The generated CO is related with electrochemical reaction (9) taking place over three phase boundary. The oxygen ion, O^{2-}, only reacted with deposited carbon to generate CO, because no CO_2 and H_2O were detected. By reaction (10) the deposited carbon reacted with oxygen ion. The overall reaction of reaction (9) and (10) is partial oxidation of methane (POM), i.e., reaction (6).

Under higher current density condition for gas with 4.2% methane, the generated CO_2 suggested that reaction (8) takes place, and $r_8 = v(CO_2)_{out}$. Reaction (9) and (10) must also have taken place in advance of the reaction (8). Otherwise, reaction (8) could never take place. Part of the deposited carbon produced by reaction (10) is oxidized by reaction (9) at three phase boundary, and part generated CO is oxidized to CO_2 sequentially according reaction (8). In Fig. 2, CO_2 and H_2O were formed at the same time, and the production rates of CO_2 and H_2O is in the ratio of 0.5. With the increasing of current density, hydrogen oxidation and carbon monoxide oxidizing to carbon dioxide take place at the same time, and the overall reaction is direct oxidation of methane. When the reaction of DOM occurs, a portion of methane still take part in POM reaction, but the rate of POM decreases with the increasing current density.

For gas with 29.2% methane, a small quantity of CO_2 were found when current density was larger than $0.5\,A\,cm^{-2}$, and $r_9 = v(CO)_{out}$, which was similar to low concentration dry methane. The CO generated here is from the reaction (9) over three phase boundary of methane. The C reacted with oxygen ion is generated by reaction (10). The overall reaction at low current is POM. The small quantities of CO_2 are generated from reaction (8).

According reaction (5) and (6), without considering the water, there is a corresponding relation between the quantity of electrons according to produced CO, CO_2 and the quantity of electrons calculated from current. Figs. 5 and 6 show the relation for methane concentration 4.2% and 29.2%, respectively, which indicate that the quantity of electrons obtained by the different methods above agree with each other well. So, it can be concluded that there is neglectable leak in the fuel cell.
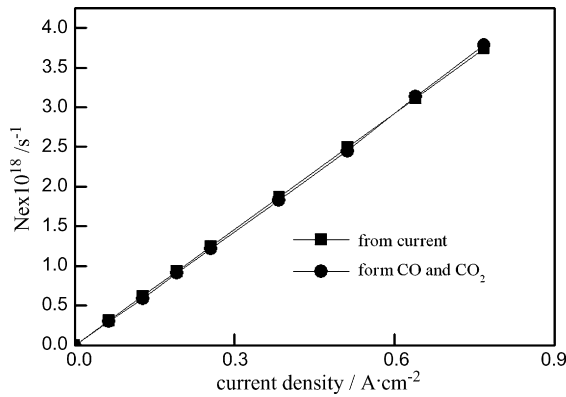
Fig. 5. The electrons calculated from CO/CO_2 and current for 4.2% methane.

3.3. Analysis of hydrogen

The ratios of H_2 to CO production rate, $\nu(H_2)/\nu(CO)$, for the gases with different content dry methane are out of our expectation. Under low current density, the ratio should be 2 according the reaction of POM. For the gas with 29.2% methane, the ratio is 2.38 at maximum current density $1.35\,\mathrm{A\,cm^{-2}}$. And the ratio is 2.13 at current density $0.256\,\mathrm{A\,cm^{-2}}$ for 4.2% methane.

Under low current density, reaction of POM took place on three phase boundary for different methane contents. But according to the carbon balance, deposited carbon was generated by reaction (10).

It is considered that the hydrogen detected at anode outlet came from two sources. One part of the hydrogen was generated from the electrochemical reactions of methane on three phase boundary; the other part was from the reaction of thermal decomposition of methane, i.e. (10), at non-three phase boundary. The reaction of thermal decomposition of methane may also have taken place over the entire anode, but on three phase boundary the carbon formed from reaction (10) can take part in the electrochemical oxidation reaction (9).

The hydrogen from methane may be transformed to dissociated hydrogen gas for medium methane concentration, but for low concentration methane the hydrogen in water must be included.
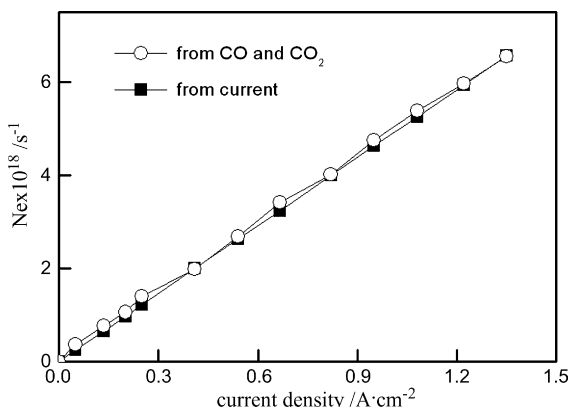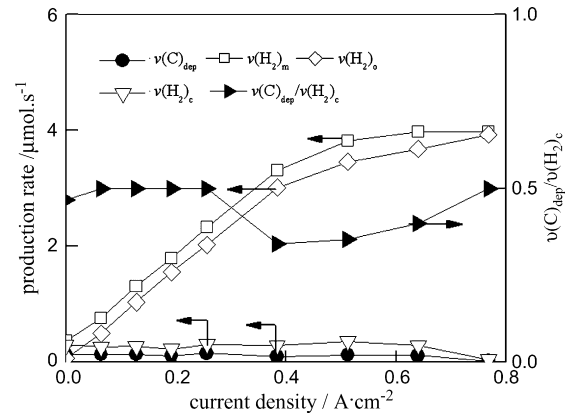

Fig. 7. The hydrogen analysis for 4.2% methane.

The hydrogen generated from methane, $\nu(H_2)_m$ can be obtained from the following equation:

$$\nu(H_2)_m = 2\{\nu(CH_4)_{in} - \nu(CH_4)_{out}\} \tag{33}$$

The hydrogen generated from methane by electrochemical reaction on three phase boundary, $\nu(H_2)_O$, is calculated by following equation:

$$\nu(H_2)_O = 2\{\nu(CO)_{out} + \nu(CO_2)_{out}\} \tag{34}$$

The difference between $\nu(H_2)_m$ and $\nu(H_2)_O$ is the hydrogen generated on non-three phase boundary, $\nu(H_2)_C$:

$$\nu(H_2)_C = \nu(H_2)_m - \nu(H_2)_O \tag{35}$$

The reaction that can generate hydrogen on non-three phase boundary is only reaction (10).

The analysis results of hydrogen are shown in Figs. 7 and 8. The carbon deposition rate, $\nu(C)_{dep}$, and the ratio of $\nu(C)_{dep}/\nu(H_2)_c$ are also illustrated in these figures.

For the gas with 29.2% methane, the ratio of $\nu(C)_{dep}/\nu(H_2)_c$ is about 0.5, which means that reaction (10) takes place on non-three phase boundary. The reason for the ratio of $\nu(H_2)/\nu(CO)$ being 2.38 at maximum current density $1.35\,\mathrm{A\,cm^{-2}}$ is that reaction (6) on three phase boundary took place at the same time as reaction (10) on non-three phase boundary.

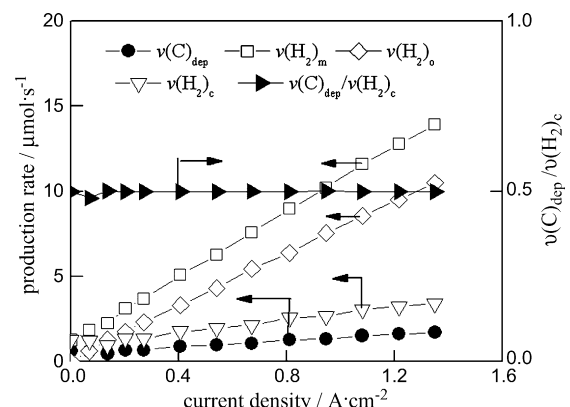
Fig. 6. The electrons calculated from CO/CO_2 and current for 29.2% methane.

Fig. 8. The hydrogen analysis for 29.2% methane.

The ratio of $v(C)_{dep}/v(H_2)_c$ was about 0.5 under current density smaller than $0.25\,A\,cm^{-2}$ for 4.2% methane, although the hydrogen production rate increased with current density. Once the hydrogen production rate deviating from linearity as shown in Fig. 3, the ratio of $v(C)_{dep}/v(H_2)_c$ is less than 0.5. It should be pointed that CO_2 was detected and H_2O was generated at this condition when current density over than $0.25\,A\,cm^{-2}$. The facts that CO_2, H_2O are generated simultaneously and $v(C)_{dep}/v(H_2)_c$ is below than 0.5 indicate that the reaction of DOM can suppress the carbon deposition. High current density has contributed to generating of CO_2, H_2O and suppressing or removing deposited carbon [3,10,11].

The behavior of carbon deposition and the influence of carbon deposition on cell performance over Ni-YSZ anode was studied by Koh [11]. There are two kinds of carbon deposition. One kind is reversible carbon deposition occurred at or near three phase boundaries which can be oxidized by electrochemical reaction with oxygen ions supplied. The other kind is irreversible carbon formation deposited mostly on Ni surface when excess methane exists. The carbon deposited with humidified methane is reversible when it is oxidized with a current density of $200\,mA\,cm^{-2}$. Yoon [10] also suggested to use carbon gasification reaction (15) for the reduction of the carbon deposition.

4. Conclusions

The production rates of different gases at anode outlet were measured at different current density for the SOFC with Ni/yttria-stabilized zirconia anode and YSZ electrolyte. The reactions of dry methane at low and medium concentrations were studied over the anode. Mass balance and relations of production rates with reaction rates were used to analyze the chemical and electrochemical reactions taking place in parallel. When dry methane was at low concentration, partial oxidation of methane occurred at low current density, direct oxidation of methane took place with the increasing current density simultaneously with POM. At middle methane concentration, only POM occurred. Based on the reactions on three phase boundary, the hydrogen analysis shows that the ratio of H_2 and CO production rate is related with the electrochemical reaction of methane on three phase boundary and methane decomposition reaction on non-three phase boundary, and high current density has contributions to the suppression or removal of deposited carbon.

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