Diffusion-limited Electrochemical Oxidation of H₂/CO on Ni-Anode Catalyst in a CH₄/CO₂-Solid Oxide Fuel Cell

Ali Modjtahedi^a, Nader Hedayat^a and Steven S.C. Chuang^{b,*}

^aDepartment of Chemical and Biomolecular Engineering, ^bDepartment of Polymer Science, FirstEnergy Advanced Energy Research Center, The University of Akron, 170 University Ave., Akron, OH 44325-3909, USA

* Corresponding author. Tel: +1 330 972 6993, Fax: +1 330 972 5856

E-mail address: chuang@uakron.edu (Steven S.C. Chuang)

E-mail address: sm141@zips.uakron.edu (Ali Modjtahedi)

E-mail address: nh17@zips.uakron.edu (Nader Hedayat)

Abstract

CH₄/CO₂-solid oxide fuel cell (SOFC) and CH₄-SOFC have been studied at 750, 800 and 850 °C using a Ni anode, which is comprised of a porous Ni/ScSZ (Scandium-Stabilized Zirconia) catalyst interlayer and a porous Ni/YSZ (Yttrium-Stabilized Zirconia) anode support. CH₄/CO₂-SOFC denotes direct feeding CH₄/CO₂ to the anode chamber; and CH₄-SOFC denotes direct feeding CH₄. At open circuit, CH₄/CO₂-SOFC gave a lower anode activation loss (i.e., polarization) than CH₄-SOFC. Analysis of product profiles revealed that CH₄- and CH₄/CO₂-SOFC produced electricity from different reaction pathways. The performance of an anode-supported CH₄/CO₂-SOFC was diffusion-limited at temperatures above 800 °C. H₂/CO produced from CH₄ dry reforming on the Ni/YSZ support became limiting reactants for electrochemical oxidation on the Ni/ScSZ catalyst interlayer. Electrochemical oxidation of CO is more diffusion-limited than that of H₂ because of its molecular size.

Key words: SOFC; CH₄ dry reforming; activation polarization; concentration polarization; diffusion limitation; limiting current density.

1. Introduction

CH₄ and CO₂ have been recognized as the major greenhouse gases [1-9]. One potentially effective way to use CH₄/CO₂ is the production of syngas (H₂/CO) and electricity through direct feeding CH₄/CO₂ to a SOFC with a Ni-anode catalyst. Ni is known to be an excellent catalyst for both dry reforming (reaction (1)) and the electrochemical oxidation of H₂ and CO (reaction (2) and (3)).

CH₄/CO₂-SOFC directly fed with CH₄/CO₂ provides attractive features of (i) eliminating reformers [10, 11] and (ii) producing syngas. Syngas from methane reforming has been used as a feedstock for the Fischer-Tropsch process as well as for the production of H₂, hydrocarbons, methanol, ethanol, and dimethylether (DME) [1, 12, 13]. Elimination of reformers will simplify the overall SOFC system, reducing both capital and operating costs. Furthermore, CH₄ and CO₂ are known as major components of biogas. The direct utilization of CH₄/CO₂ in SOFCs also constitutes a promising route to electricity generation from renewable resources [14-16]

Table 1 summarizes the electrochemical performance and impedance characteristics of CH₄/CO₂-SOFCs reported in the literature. All of these cells produced the OCV (open circuit voltage) around 1 V, in the vicinity of the theoretically reversible cell voltage for the electrochemical oxidation of CH₄, CO, and H₂ [17, 18]. Short circuit current density (SCD) obtained at near zero external resistance is governed by Ohmic and Faraday resistance. High short circuit current densities reflect high activities of anode catalysts which exhibit low Faraday resistances in impedance spectroscopy. Although high SCDs have been reported, all of these SOFCs have only been operated for a short period. It remains unclear about (i) the extent of contribution of CH₄, CO, and H₂ to electricity generation and (ii) the yields of syngas which can be produced from Ni anode catalyst in a SOFC.

In this study, we carried out a comprehensive study of a CH₄/CO₂-SOFC with a Ni anode catalyst. We measured electrical output (voltage and current) as well as the effluent compositions, aiming at (i) evaluating the catalytic activity of Ni anode for simultaneous generation of electricity and syngas and (ii) elucidating the reaction pathway on the Ni-anode of CH₄/CO₂-SOFC. For the first time, we found that the structure of the Ni-anode catalyst interlayer has a strong influence on the diffusion of H₂ and CO produced from Ni/YSZ anode support layer, thereby, affecting the rate of electrochemical oxidation of H₂ and CO. Despite the presence of high concentration of CH₄ in the anode chamber, electrochemical oxidation CO and H₂ on the Ni/ScSZ interlayer is the key pathway for electricity generation. Ni/YSZ support provides the catalytic site for the dry reforming of CH₄.

2. Experimental

2.1. Fuel cell fabrication

The anode-supported SOFC was fabricated by co-tape casting technique. NiO (AEE Co.) and YSZ (Ytria-Stabilized Zirconia, Tosoh) powders were mixed with the solvents and dispersant and then ball-milled for 3 h. The co-tape casting slips were prepared by adding binders and plasticizers to the NiO/YSZ mixture and further ball-milling for 20 h. Prior to tape casting, the mixture was de-aired in less than 5 torr vacuum. The slips containing 10ScSZ (Scandia-Stabilized Zirconia, Daiichi) electrolyte layer, NiO/10ScSZ anode interlayer (60 wt% NiO), and NiO/3YSZ anode support (65 wt% NiO) were casted successively on a polymer-based sheet. The tapes were dried at 25 °C for 48 h, cut into discs of 22 mm in diameter, and sintered at 1400 °C for 2 h. The thickness of anode support, anode interlayer and electrolyte were 850, 18, and 15

μm , respectively, obtained by adjusting the height of doctor blade during the tape casting procedure. A 25 μm LSM (lanthanum strontium manganite)/8YSZ cathode interlayer (60 wt % LSM, Heraeus CL86-8706A) and a 35 μm LSM cathode layer (Heraeus CL86-8706) with the active area of 0.5 cm^2 were screen printed on the YSZ side of the sintered disc and fired at 1150 $^{\circ}\text{C}$ for 1 h.

2.2. Fuel cell testing

The SOFC was sealed with the aid of alumina-based ceramic seal to the iron-based housing which serves as anode chamber and anode current collector. The dimension of this housing is 25 cm height and 3.5 cm inner diameter with 85% filled volume. Cathode current collection was carried on by a Fe/Cr alloy strip attached to SOFC cathode surface. Figure 1 shows the experimental apparatus including mass flow controllers (5850E, Brooks), electrical furnace, cell test unit with an impedance spectrometer (Solartron 1470E and 1400 CellTest System), and a mass spectrometer (MS, GSD-301 Pfeiffer).

The NiO/YSZ anode was reduced to Ni/YSZ in 100 sccm Ar/H_2 (1:1) flow at 750 $^{\circ}\text{C}$ for 24 h prior to testing. The fuel cell electrochemical performance was studied by feeding 100 sccm Ar/CH_4 (1:1) and CH_4/CO_2 (1:1) at 750, 800 and 850 $^{\circ}\text{C}$. The voltage - current curves, electrochemical impedance spectra, potentiostatic and potentiodynamic performance of the SOFC were recorded along with the MS profile of the exhaust gases from anode chamber. The MS signals of each feed streams can be converted to molar flow rate using the calibration curves obtaining from flowing different gas flows with known composition inside the SOFC anode chamber. Water saturator, shown in Figure 1, was used to add to 3 - 4 % H_2O vapor in the H_2 feed, a typical composition in H_2 -SOFC. In this study, H_2O saturator was not employed for CH_4 - and CH_4/CO_2 -SOFC to minimize the occurrence of the steam-reforming reaction.

3. Results and discussion

3.1. Fuel cell testing

Figure 2 shows the voltage – current curves and electrochemical impedance spectra of CH_4 - and CH_4/CO_2 -SOFCs at 750, 800 and 850 $^{\circ}\text{C}$. CH_4 -SOFC produced a higher OCV than CH_4/CO_2 -SOFC. This is because (i) CH_4/CO_2 -SOFC generated electricity through electrochemical oxidation of CO and H_2 which was produced from dry reforming reaction of CH_4 and (ii) the reversible voltage of CH_4 electrochemical oxidation is higher than that of CO electrochemical oxidation. The electrochemical oxidation of CO and H_2 will be further discussed in Figure 3. The V-I curve of CH_4/CO_2 -SOFC showed a sharp drop and a limiting current around 480 mA/cm^2 at 800 $^{\circ}\text{C}$ and 700 mA/cm^2 at 850 $^{\circ}\text{C}$. These different V-I behaviors suggest that CH_4 - and CH_4/CO_2 -SOFC were operated with different reaction pathways for electricity generation. The difference in reaction pathway for electricity generation in these SOFCs with different fuels will be further discussed in the light of impedance spectra in Figure 2 and the compositions of the effluents from the anode chambers in Figure 3.

Electrochemical impedance spectra collected at temperatures from 750 to 850 °C with external DC loading at OCV and ~SCD (50 mV) in Figure 2 (c) – (f) exhibited low and high frequency intercepts with the real impedance axis. The low frequency intercept represents the total SOFC resistance at a given operating condition and the high frequency intercept expresses the SOFC Ohmic resistance. The SOFC's non-Ohmic resistance (i.e., Faraday resistance) can be determined by subtracting the high frequency intercept from low frequency one. Table 1 summarizes Faraday resistances obtained from Figure 2. Faraday resistance is resulted from electrochemical reactions on anode and cathode. High activity of the catalyst would lead to low Faraday resistance. Table 2 summarizes the electrochemical impedance frequencies at important points collected in OCV.

Impedance spectra obtained at OCV revealed the kinetic behavior of electrochemical reactions. These impedance spectra consist of two vague arcs. These arcs are resulted from kinetics of electrochemical reactions on the catalysts in the electrodes. Reactions on cathode catalyst led to the high frequency arc; reactions on anode catalyst gave the low frequency arc [29-31]. CH₄/CO₂-SOFC showed small impedance arcs and lower Faraday resistance than that for CH₄-SOFC, reflecting the difference in kinetics of reactions of CH₄, H₂ and CO over Ni catalyst. The effluent composition of SOFCs in Table 3 shows that Ar/CH₄ produced mainly H₂ at OCV. The CH₄-SOFC consumed H₂ and increased the production of CO at SCD (i.e., short circuit condition), indicating the occurrence of the follow reactions:

In contrast, CH₄/CO₂-SOFC produced mainly H₂ and CO at OCV and consumed both species at SCD, showing that the electrochemical oxidation reactions of H₂ and CO, reaction (2) and (3), are major pathways for electricity generation. The low activation polarization and Faraday resistance of CH₄/CO₂-SOFC can be attributed to high activity of Ni/ScSZ catalyst for the electrochemical oxidation of H₂ and CO when compared to that of CH₄ in CH₄-SOFC. This low activation polarization could also be related to a much higher adsorption rate and binding energy of CO than those of H₂ and CH₄ on Ni catalyst [32-37].

Raising temperature increased the rate of the overall reaction process for both producing electricity and syngas. The rates of H₂ and CO formation are summarized in Table 3. The specific effects of temperature on the rates of electrochemical oxidation and diffusion on the anode catalyst can be further unraveled by examining the dependence of impedance spectra and Faraday resistance on temperature. Increasing the operating temperature decreased the impedance as shown by shrinking impedance arc and lowering Faraday resistance at both OCV and SCD conditions.

At SCD, low external resistance allowed electrons produced in the electrochemical oxidation of fuel molecules to be rapidly removed from the anode. If the rate of conversion of fuel molecules on the catalyst interlayer is higher than the rate of supplying fuel molecules to the anode catalyst interlayer, the fuel molecules adsorbed on the catalyst interlayer will be depleted. Thus, the overall reaction process on the anode catalyst interlayer will be limited by the availability of fuel molecules. Such a limited availability of fuel molecules was observed in CH₄/CO₂-SOFC at 800 and 850 °C, shown in Figure 2 which shows a sharp drop in V-I and V-P. The corresponding impedance spectra showed a nearly straight line in the low frequency region, reflecting the contribution of a Warburg element which describes a diffusion-limited process. The observed V-I and impedance spectra in Figure 2(b) and (f) depict a scheme that CH₄/CO₂ dry reforming takes place at Ni-anode support, producing CO/H₂ that further diffuse into Ni/ScSZ interlayer for electrochemical oxidation. It can be concluded that the overall electrochemical oxidation of H₂/CO in CH₄/CO₂-SOFC at 800 and 850 °C is diffusion-limited.

3.2. CH₄-fed SOFCs potentiostatic study

Figure 3 shows the change in MS profiles of the effluents from the anode chamber of CH₄- and CH₄/CO₂-SOFCs during switching the fuel cell load from OCV to ~SCD (50 mV) at 750, 800 and 850 °C. Switching the fuel cell load from OCV to ~SCD allowed the electrochemical oxidation of fuel molecules to occur, producing electric current. The decrease in CH₄/H₂ and the increase in CO/CO₂/H₂O MS profiles, shown in Figure 3(a), indicate that electricity is generated from the electrochemical oxidation of CH₄ and H₂ to CO, CO₂ and H₂O in CH₄-SOFC.

Figure 3(b) shows the CH₄/CO₂-SOFC produced high MS intensity profiles of CO and H₂ at OCV. Both CO and H₂ profiles showed significant decreases when switching to SCD, a mode for producing the maximum current. These results revealed that the electrochemical oxidation reactions of CO and H₂ are the main pathways for electricity generation. Although the MS level of CH₄ in anode effluents from both CH₄- and CH₄/CO₂-SOFC are comparable, CH₄ did not play a current generating role in CH₄/CO₂-SOFC. CO produced from dry reforming could block CH₄ from electrochemical oxidation on the Ni/ScSZ interlayer.

Figure 4 shows the results of the potentiodynamic study of CH₄- and CH₄/CO₂-SOFCs at 850 °C. Fuel cell voltage was gradually decreased from OCV to zero as the current density and conversion of fuel molecules increased. The levelling off in the current density, CO₂, CO, and H₂ in Figure 4(b) indicate that the performance of CH₄/CO₂-SOFC approached limiting current conditions. The comparison of Figure 4(a) and (b) shows a sharp contrast, further supported the previous proposition that CH₄- and CH₄/CO₂-SOFCs operated with different reaction pathways. The absence of significant variations in the CH₄ profile in Figure 4(b) further confirmed that CH₄ did not play a direct role in electricity generation in CH₄/CO₂-SOFCs.

3.3. Analysis of diffusion limitation in CH₄/CO₂-SOFC

The overall reaction process is diffusion-limited (or diffusion-controlled) when the reactant concentration inside the catalyst drops to zero. In other words, the diffusion of the reactants onto catalytic sites controls the rate of the overall reaction process, specifically, limiting the performance of a fuel cell. The maximum current density in the presence of diffusion limitation is called limiting current density ($i_L - A/cm^2$), which can be estimated by Fick's first law. In the steady-state condition Fick's first law can be written as equation (1).

$$J = -D_{eff} \frac{C_r^* - C_r^0}{\delta} \quad (1)$$

, where D_{eff} is the effective diffusion coefficient (cm^2/s), C_r^* and C_r^0 are the reactant molar concentration (mol/cm^3) at catalyst interface and bulk flow, respectively, and δ is the thickness of diffusion layer (cm). In this specific study, C_r^0 is considered as the concentration of CO and H₂ in the anode effluent measured by MS. At steady-state condition, current density ($i - A/cm^2$) can be calculated by $i = Z \times F \times J$, where, Z is the number of transferred electrons, F is the Faraday's constant (C/mol), and J is the diffusion molar flux (mol/cm^2s) obtained from Fick's first law. Thus, the current density generated in a fuel cell can be calculated by equation (2).

$$i = -Z F D_{eff} \frac{C_r^* - C_r^0}{\delta} \quad (2)$$

The limiting current density (i_L) can be obtained by setting $C_r^* = 0$ in equation (2):

$$i_L = Z F D_{eff} \frac{C_r^0}{\delta} \quad (3)$$

The diffusion layer thickness (δ) and fuel concentration profiles across the anode porous structure in the CH₄/CO₂-SOFC at 850 °C can be estimated with known values for i_L in Figure 2, C_r^0 obtained from Figure 4(b) and a calculated value of D_{eff} .

The first step to calculate D_{eff} is to estimate porosity (ε) and tortuosity (τ) of anode support and interlayer by examining SOFC layers micrograph along with the filtered version of SEM images in Figure 5. The SEM micrographs revealed that the SOFC anode support and anode interlayer porosity were 35% and 16% with average pore diameter of 340 and 180 nm and Ni particle size of 3.25 and 1.45 μm , respectively. Their tortuosities were around 3.5 and 10, respectively. The results are in a very good agreement with the literature data for the similar fuel cells [41-44].

The next step is to estimate the diffusion coefficients of CO and H₂. The Knudsen diffusion coefficient for a specific gas, A, can be calculated based on the electrode pore diameter, the gas A molecular weight and operating temperature. The results are listed in Table 4.

The diffusion coefficient of hydrogen, D_{H_2} , and carbon monoxide, D_{CO} , for a system of five gases (CH_4 , CO_2 , H_2 , CO and H_2O) can be obtained with the equations (4) and (5) by considering contribution of Knudson diffusion and effect of other gasses [45].

$$\frac{1}{D_{H_2}} = \frac{1}{D_{K,H_2}} + \frac{x_{CH_4}}{D_{CH_4,H_2}} + \frac{x_{CO_2}}{D_{CO_2,H_2}} + \frac{x_{CO}}{D_{CO,H_2}} + \frac{1 - (x_{CH_4} + x_{CO_2} + x_{CO})}{D_{H_2O,H_2}} \quad (4)$$

$$\frac{1}{D_{CO}} = \frac{1}{D_{K,CO}} + \frac{x_{CH_4}}{D_{CH_4,CO}} + \frac{x_{CO_2}}{D_{CO_2,CO}} + \frac{x_{H_2}}{D_{H_2,CO}} + \frac{1 - (x_{CH_4} + x_{CO_2} + x_{H_2})}{D_{H_2O,CO}} \quad (5)$$

where, $D_{K,A}$ is the Knudsen diffusion coefficient for species A , $D_{B,A}$ is the binary diffusion coefficient (cm^2/s) for gas A in gas B , and x_A is the mole fraction of gas A in the in gases mixture at fuel cell anode chamber. Binary diffusion coefficient is a function of pressure, temperature and molecular weights of both gas species. In the non-polar gas system with low operating pressure, the binary diffusion coefficient can be calculated by equation (6).

$$D_{B,A} = \frac{2.745 \times 10^{-4}}{P} \left(\frac{T}{\sqrt{T_{cA} T_{cB}}} \right)^{1.823} (P_{cA} P_{cB})^{\frac{1}{3}} (T_{cA} T_{cB})^{\frac{5}{12}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} \quad (6)$$

where, P and T are the operating pressure and temperature in (atm) and (K); T_{cA} , T_{cB} , P_{cA} and P_{cB} are the critical temperatures and pressures of species A and B ; M_A and M_B are the gas species molecular weights (g/mol). Table 5 summarizes the calculated diffusion coefficients for CH_4/CO_2 -SOFC fuels (H_2 and CO) at 750, 800 and 850 °C.

D_{H_2} and D_{CO} represent the H_2 and CO diffusion coefficients through CH_4/CO_2 -SOFC gas mixture. Considering the effect of porous structure, the diffusion coefficient is corrected by taking account the anode porosity (ϵ) and tortuosity (τ) to give effective diffusion coefficient (D_{eff}) by equation (7).

$$D_{eff,A} = D_A \frac{\epsilon}{\tau} \quad (7)$$

Table 6 lists effective diffusion coefficients for H_2 and CO in anode support and anode interlayer of the CH_4/CO_2 -SOFC at 750, 800 and 850 °C.

The calculated values of D_{eff} in Table 6, known values of i_L in Figure 2, C_r^0 obtained from Figure 4(b) allowed us to obtain the diffusion layer thickness (δ) from equation (3). With first Fick's law equations at the steady-state condition, H_2 and CO concentration profiles across the anode porous structure in the CH_4/CO_2 -SOFC were plotted in Figure 6. Operating the CH_4/CO_2 -SOFC at 750 °C did not show limiting current density due to fuel (H_2) availability at interlayer-electrolyte interface. The concentration of CO dropped to zero prior to reaching the interlayer-

electrolyte interface while the concentration of H_2 decreased rapidly at the anode interlayer. These profiles showed H_2 fuel molecules were available for generation electricity.

Increasing the operating temperature to 800 °C resulted in limiting current generation at 476 mA/cm^2 indicating the depletion of fuels (H_2 and CO) at interlayer under SCD load.

Concentration of CO decreased to zero before reaching the SOFC anode support-interlayer interface while the concentration of H_2 dropped to a very low level at interlayer. These profiles indicate limited availability of fuel molecules for further electricity generation from their electrochemical oxidation.

Severe diffusion limitation at 850 °C in SCD is shown by dropping the concentrations of both H_2 and CO to zero far away from the interlayer. Comparing the H_2 and CO profiles in the porous structure of the CH_4/CO_2 -SOFC anode compartment showed electrochemical oxidation of CO is severely diffusion-limited because large size of CO molecule gives small diffusion coefficient. The results presented in Figure 6 revealed that the SOFC anode support thickness and porous structure played a significant role in limiting fuel cell performance. In addition to porosity (ϵ) and tortuosity (τ), the thickness of anode support should be considered in optimizing the performance of CH_4/CO_2 -SOFC.

4. Conclusion

CH_4 -SOFC generated electricity through electrochemical oxidation of carbon and hydrogen. CH_4/CO_2 -SOFC produced syngas (H_2/CO) on Ni/YSZ anode support and further electrochemical oxidized syngas on the Ni/ScSZ catalyst interlayer. Impedance spectra revealed that anode activation loss on Ni/ScSZ catalysts decreased in the following order: $CH_4 > CO > H_2$. In the other words, the activity of Ni/ScSZ for electrochemical oxidation increased in the order: $CH_4 < CO < H_2$. Severe diffusion limitation of CO and H_2 was observed when CH_4/CO_2 -SOFC operated at temperatures above 800 °C, giving the limiting currents. Diffusion limitation can be alleviated by decreasing the anode support thickness and increasing the pore size of interlayer. The overall performance of CH_4/CO_2 -SOFC for producing electricity and syngas can be improved by adding dry-reforming promoters to Ni/YSZ support and electrochemical oxidation promoters to the catalyst interlayer.

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Table 1 Review of literatures for CH₄/CO₂-SOFC electrochemical performance

Anode	Fuel	Temp. (°C)	SCD ^(a) (mA/cm ²)	Ohmic R (Ω cm ²)	Faraday R (Ω cm ²)	Ref.
Ni-Mg/YSZ	CH ₄ /CO ₂ 1:1	800	58	N/A	N/A	[5]
Ni/YSZ	CH ₄ /CO ₂ 1:1	850	245	N/A	N/A	[16]
	CH ₄ /CO ₂ 1.7:1		220			
	CH ₄ /CO ₂ 1:1.7		200			
Ni/YSZ	Wet CH ₄	700	2500	N/A	N/A	[19]
		750	3500			
		800	4100			
	CH ₄ /CO ₂ 3:1	700	2700	N/A	N/A	
		750	3100			
		800	3300	0.08	0.17	
Ni/YSZ	Wet H ₂	800	800	0.74	0.67	[20]
	Wet CH ₄ /CO ₂ 1:1		600	N/A	N/A	
Ni/GDC	CH ₄ /CO ₂ 3:2	800	1500	N/A	N/A	[21]
Ni/GDC	CH ₄ /CO ₂ 1:1	600	150	N/A	N/A	[22]
		640	250			
Ni/GDC	CH ₄ /CO ₂ 1:1	875	280	N/A	N/A	[23]
	CH ₄ /CO ₂ 2:1		225			
	CH ₄ /CO ₂ 1:2		230			
Ni/ScSZ	CH ₄ /CO ₂ /H ₂ O 39:22:1	800	200	N/A	N/A	[24]
Ni-Au/GDC	CH ₄ /CO ₂ 1:1	640	135			
Ni/YSZ	CH ₄ /CO ₂ 1:1	875	114			
Ni/GDC	CH ₄ /CO ₂ 1:1	630	90			
Ni/ScSZ	CH ₄ /CO ₂ /Air 1.5:1:1.5	800	2500	N/A	N/A	[25]
Ni/ScSZ	Ar/CH ₄ 1:1	750	440	0.66	8.56	This study
		800	850	0.54	5.04	
		850	1210	0.32	2.96	
	CH ₄ /CO ₂ 1:1	750	407	0.59	5.09	
		800	476	0.52	2.19	
		850	703	0.50	0.62	

^(a) SCD: short current density

Table 2 Frequency characteristics of Ar/CH₄- and CH₄/CO₂-SOFCs at 750, 800 and 850 °C in open circuit condition

Temp.	Fuel	High frequency intercept (Hz)	High frequency peak (Hz)	Low frequency peak (Hz)	Low frequency end point (Hz)
750 °C	Ar/CH ₄	6309	20	0.12	0.01
	CH ₄ /CO ₂	6309	63	0.10	0.01
800 °C	Ar/CH ₄	6309	2	0.32	0.01
	CH ₄ /CO ₂	6309	126	0.40	0.01
850 °C	Ar/CH ₄	5012	N/A	1.00	0.01
	CH ₄ /CO ₂	5012	N/A	199	0.10

Table 3 Chemical reaction rates in CH₄-fed SOFCs at 750, 800 and 850 °C over Ni catalyst

Reaction	Partial pressure ^(a) (atm)	Reaction rate (mol/s.g _{catalyst})			Ref.
		750 °C	800 °C	850 °C	
$CH_4 \longrightarrow C + 2H_2$	$P_{CH_4} = 1.8$	9.37	18.71	28.05	[38]
$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$	$P_{CH_4} = 1.8, P_{O_2} = 0.14$	9.53	23.66	54.17	[39]
$CH_4 + \frac{3}{2}O_2 \longrightarrow CO + 2H_2O$	$P_{CH_4} = 6.6 \times 10^{-4}$ $P_{O_2} = 1.3 \times 10^{-4}$	N/A	0.001 ^(b)	N/A	[40]
$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$	$P_{CH_4} = 1.8, P_{H_2O} = 1.8$	4.95	5.64	6.35	[39]
$CH_4 + H_2O \longrightarrow CO + 3H_2$	$P_{CH_4} = 1.8, P_{H_2O} = 0.11$	0.24	0.28	0.32	[39]
Fuel cell type	Products	Reaction rate (μmol/s.g _{catalyst})			
		750 °C	800 °C	850 °C	
CH ₄ -SOFC	H ₂	76	113	260	This study
CH ₄ /CO ₂ -SOFC	H ₂	66	73	80	
	CO	104	127	153	

^(a) The partial pressures of CH₄, CO₂, and H₂O were kept at 1.8, 1.8, and 0.11 atm, respectively, and O₂ partial pressure was calculated from the trace amount of oxygen leakage, which was around 0.14 atm.

^(b) The data was reported for Pt catalyst.

Table 4 Knudsen diffusion coefficient of CH₄/CO₂-SOFC fuels as a function of fuel cell operating temperature

Fuel	Temperature (°C)	<i>D_{K,A}</i> (cm ² /s)	
		Anode support	Anode interlayer
H ₂	750	3.730	1.974
	800	3.820	2.022
	850	3.908	2.069
CO	750	0.997	0.528
	800	1.021	0.540
	850	1.044	0.553

Table 5 calculation of CH₄/CO₂-SOFC fuels diffusion coefficients for the fuel cell anode support and anode interlayer at 750, 800 and 850 °C

Temperature (°C)	D_{CH_4,H_2} (cm ² /s)	D_{CO_2,H_2} (cm ² /s)	D_{CO,H_2} (cm ² /s)	D_{H_2O,H_2} (cm ² /s)	D_{H_2} (cm ² /s)	
					Anode support	Anode interlayer
750	6.901	6.178	7.346	22.579	2.410	1.531
800	7.528	6.739	8.013	25.239	2.526	1.591
850	8.180	7.322	8.707	28.069	2.636	1.648
	$D_{CH_4,CO}$ (cm ² /s)	$D_{CO_2,CO}$ (cm ² /s)	$D_{H_2,CO}$ (cm ² /s)	$D_{H_2O,CO}$ (cm ² /s)	D_{CO} (cm ² /s)	
					Anode support	Anode interlayer
750	2.029	1.454	7.346	4.523	0.639	0.407
800	2.213	1.587	8.013	5.056	0.671	0.424
850	2.405	1.724	8.707	5.623	0.701	0.439

Table 6 H₂ and CO effective diffusion coefficients for the CH₄/CO₂-SOFC anode support and anode interlayer at 750, 800 and 850 °C

Temperature (°C)	D_{eff,H_2} (cm ² /s)		$D_{eff,CO}$ (cm ² /s)	
	Anode support	Anode interlayer	Anode support	Anode interlayer
750	0.241	0.024	0.064	0.0065
800	0.253	0.025	0.067	0.0068
850	0.264	0.026	0.070	0.0070

Figure Captions:

Figure 1 schematic of SOFC apparatus.

Figure 2 Electrochemical performance of CH₄-fed SOFCs at 750, 800 and 850 °C. (a) voltage – current curves of 100 sccm Ar/CH₄, (b) voltage – current curves of 100 sccm CH₄/CO₂, (c) electrochemical impedance spectra of Ar/CH₄ at OCV, (d) electrochemical impedance spectra of CH₄/CO₂ at OCV, (e) electrochemical impedance spectra of Ar/CH₄ at ~SCD (50 mV), (f) electrochemical impedance spectra of CH₄/CO₂ at ~SCD (50 mV).

Figure 3 MS profile of SOFC exhaust gases during static change from OCV to ~SCD (50 mV) for (a) CH₄-SOFC, (b) CH₄/CO₂-SOFC at 750, 800 and 850 °C.

Figure 4 Exhaust gases profile due to dynamic change in voltage from OCV to SCD in flowing 100 sccm (a) Ar/CH₄ 1:1 and (b) CH₄/CO₂ 1:1, at 850 °C.

Figure 5 (a) Scanning electron micrograph of anode support microstructure of SOFC, polished cross section. (b) Filtered version of anode support microstructure, showing pores selected by ImageJ. (c) SEM micrograph of SOFC cross section including cathode, electrolyte and anode interlayer. (d) Filtered version of SOFC cross section microstructure, showing anode interlayer pores selected by ImageJ (Black regions in the filtered SEM images represent the SOFC pores).

Figure 6 H₂ and CO concentration profiles across the CH₄/CO₂-SOFC anode layers at SCD condition along with the voltage – current curves at 750, 800 and 850 °C. The thickness of anode support: 850 µm; interlayer: 18, µm; and electrolyte: 15 µm

Figure

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