Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Diffusion-limited electrochemical oxidation of H_2/CO on Ni-anode catalyst in a CH_4/CO_2-solid oxide fuel cell

Ali Modjtahedi [a], Nader Hedayat [a], Steven S.C. Chuang [b,*]

[a] Department of Chemical and Biomolecular Engineering, First Energy Advanced Energy Research Center, The University of Akron, 170 University Ave., Akron, OH 44325-3909, USA
[b] Department of Polymer Science, First Energy Advanced Energy Research Center, The University of Akron, 170 University Ave., Akron, OH 44325-3909, USA

ARTICLE INFO

Article history:
Received 21 October 2015
Received in revised form
23 December 2015
Accepted 24 December 2015
Available online xxx

Keywords:
SOFC
CH_4 dry reforming
Activation polarization
Concentration polarization
Diffusion limitation
Limiting current density

ABSTRACT

CH_4/CO_2-solid oxide fuel cell (SOFC) and CH_4-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. CH_4/CO_2-SOFC denotes direct feeding CH_4/CO_2 to the anode chamber; and CH_4-SOFC denotes direct feeding CH_4. At open circuit, CH_4/CO_2-SOFC gave a lower anode activation loss (i.e., polarization) than CH_4-SOFC. Analysis of product profiles revealed that CH_4- and CH_4/CO_2-SOFC produced electricity from different reaction pathways. The performance of an anode-supported CH_4/CO_2-SOFC was diffusion-limited at temperatures above 800 °C. H_2/CO produced from CH_4 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 H_2 because of its molecular size.

Published by Elsevier B.V.

1. Introduction

CH_4 and CO_2 have been recognized as the major greenhouse gases [1–9]. One potentially effective way to use CH_4/CO_2 is the production of syngas (H_2/CO) and electricity through direct feeding CH_4/CO_2 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 H_2 and CO (Reactions (2) and (3)).

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H^0_{298} = 247 kJ/mol \tag{1}$$

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

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{3}$$

CH_4/CO_2-SOFC directly fed with CH_4/CO_2 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 H_2, 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, CH_4 and CO_2 are known as major components of biogas. The direct utilization of CH_4/CO_2 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 CH_4/CO_2-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 CH_4, CO, and H_2 [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 CH_4, CO, and H_2 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 CH_4/CO_2-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 CH_4/CO_2-SOFC. For the first time, we found that the structure of the Ni-anode catalyst interlayer has a strong influence on the diffusion of H_2 and CO produced

* Corresponding author. Fax: +1 330 972 5856.
E-mail addresses: sm141@zips.uakron.edu (A. Modjtahedi), nh17@zips.uakron.edu (N. Hedayat), chuang@uakron.edu (S.S.C. Chuang).

http://dx.doi.org/10.1016/j.cattod.2015.12.026
0920-5861/Published by Elsevier B.V.

Table 1
Review of literatures for CH_4/CO_2-SOFC electrochemical performance.

Anode	Fuel	Temperature (°C)	SCD[a] (mA/cm^2)	Ohmic R (Ω cm^2)	Faraday R (Ω cm^2)	Refs.
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	$CH_4/CO_2/H_2O$ 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.

from Ni/YSZ anode support layer, thereby, affecting the rate of electrochemical oxidation of H_2 and CO. Despite the presence of high concentration of CH_4 in the anode chamber, electrochemical oxidation CO and H_2 on the Ni/ScSZ interlayer is the key pathway for electricity generation. Ni/YSZ support provides the catalytic site for the dry reforming of CH_4.

2. Experimental

2.1. Fuel cell fabrication

The anode-supported SOFC was fabricated by co-tape casting technique. NiO (AEE Co.) and YSZ (Yttria-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 °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. Fig. 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 °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 °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 Fig. 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

Fig. 2 shows the voltage–current curves and electrochemical impedance spectra of CH_4- and CH_4/CO_2-SOFCs at 750, 800, and 850 °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 Fig. 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 °C

Please cite this article in press as: A. Modjtahedi, et al., Diffusion-limited electrochemical oxidation of H_2/CO on Ni-anode catalyst in a CH_4/CO_2-solid oxide fuel cell, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2015.12.026