

Imaging of CH₄ decomposition around the Ni/YSZ interfaces under anodic polarization

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Abstract

The catalytic activities of Ni-mesh/YSZ samples for CH₄ decomposition and reaction with reformed gases were compared under voltage-applied condition (fuel cell operation condition) by imaging analysis of labeled gases with secondary ion mass spectrometry (SIMS). The effect of applied voltages was compared in the mixture of CH₄, D₂O, and ¹⁸O₂ to label the movements of hydrogen and oxygen. A significant carbon deposition was observed at the Ni-mesh under zero-voltage condition. However, the applied voltage formed a thin oxide layer on the Ni surface and eliminated the deposited carbon on the Ni surface. Oxygen spill-over around the Ni/YSZ interfaces could effectively eliminate the deposited carbon. A possible reaction mechanism was considered for the optimum metal–oxide interfaces of SOFCs.

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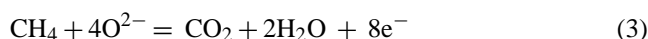
1. Introduction

Because of their high operation temperature (1073–1273 K), solid oxide fuel cells (SOFCs) can utilize hydrocarbons with internal reforming. Steam reforming is one of the promising methods to utilize hydrocarbons in SOFCs as follows:



where Eqs. (1) and (2) are called the steam reforming and shift reactions, respectively. At 1273 K, the steam reforming reaction and shift reaction proceed very fast, and relatively high performances have been reported in SOFC stacks. When the operation temperature of SOFCs is reduced to lower than 1073 K, the steam/carbon ratio should be high enough (more

than 2) to prevent carbon deposition. On the other hand, the amounts of steam should be as small as possible in terms of the efficiency of the SOFC systems. Therefore, minimum steam partial pressure and electrochemical oxidation of CH₄ must be considered in the following equation:



where O²⁻ is conducted oxide ions through the electrolyte from cathode to anode. Eq. (3) does not normally proceed quickly with Ni/YSZ anodes and a number of papers have been written on this (for example, see reference [1]). In order to realize a SOFC system with internal steam reforming at lower than 1073 K, it is desirable to optimize the electrode/electrolyte interface materials and structures. In recent years, several authors reported active metal–oxide combinations, such as Ni–CeO₂ based oxide and Cu–CeO₂ based oxide [2–5]. However, a porous metal–oxide mixture (that is called “cermet”) was difficult in determining the effect factors for CH₄ decomposition and electrochemical oxidation. The effective factors for the electrochemical reaction of CH₄ have not been clarified yet.

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The present study aims to clarify the role of metal and oxide on the decomposition and steam reforming of CH_4 under low steam partial pressures. We have reported the effect of oxides [6] and metals [7] on the decomposition and/or steam reforming of CH_4 by isotope labeling/secondary ion mass spectrometry (SIMS) imaging analyses. The active parts for carbon deposition and reaction with light elements are clearly imaged by SIMS analyses. However, the analyzed images were taken only at the non-current flow condition. The effects of anodic polarization have not been clarified yet. Thus, in this paper, we report the effects of anodic polarization on the CH_4 decomposition and carbon deposition at the Ni-mesh/YSZ interfaces.

2. Experimental

2.1. Samples and isotope labeling experiments

Fig. 1 shows schematic diagram of isotope labeling experiments under voltage application (under anodic polarization). We have chosen nickel (Ni) as the test anode because Ni is a typical metal for porous anode material [8,9]. The Ni-mesh/YSZ samples were fabricated by the mechanical pressing of grid mesh. The bottom part of Fig. 1 shows the microstructure of the Ni-mesh/YSZ sample through the YSZ electrolyte. The thickness of the Ni-mesh was about $20\ \mu\text{m}$

in this experiment. As an oxide substrate, a single crystal of Y_2O_3 -stabilized ZrO_2 (YSZ, 8 mol% Y_2O_3 -doped) was applied. As shown in Fig. 1, the Ni-mesh/YSZ interface shows clear boundaries with no voids and cracks, suggesting a perfect contact between Ni-mesh and YSZ substrates.

A voltage was applied so that oxide ions (O^{2-}) were supplied to the Ni-mesh/YSZ interfaces. In this experiment, the voltage at the anode was set from 0 to 0.3 V versus a counter electrode (Pt). The current densities observed were from 0 to $20\ \text{mA cm}^{-2}$. Under anodic polarization, the isotope labeling was examined for the duration of 300 s, which corresponded to the following amount of oxygen conducted through the YSZ: $2 \times 10^{-5}\ \text{mol cm}^{-2}$. The amount of oxygen molecules is sufficient to cover the whole surface of Ni-mesh. Under this condition, atmospheric $^{18}\text{O}_2$ can conduct through the YSZ electrolyte and oxidize the deposited carbon on the Ni-mesh anode.

The current–voltage characteristic was measured under the mixtures of CH_4 , D_2O , $^{18}\text{O}_2$, and Ar to simulate the steam reforming and direct-feeding of CH_4 into SOFCs. The total gas pressure was 0.35 bar, and the partial pressures of the mixed gases were in the following ratios: $p(\text{CH}_4)/p(\text{D}_2\text{O})/p(^{18}\text{O}_2) = 0.29/0.02/0.04$ bar. D_2O and $^{18}\text{O}_2$ were used to label the movements of hydrogen and oxygen, respectively. The thermodynamic equilibrium oxygen partial pressure is calculated to be around 10^{-23} bar, and the reformed gas composition is calculated

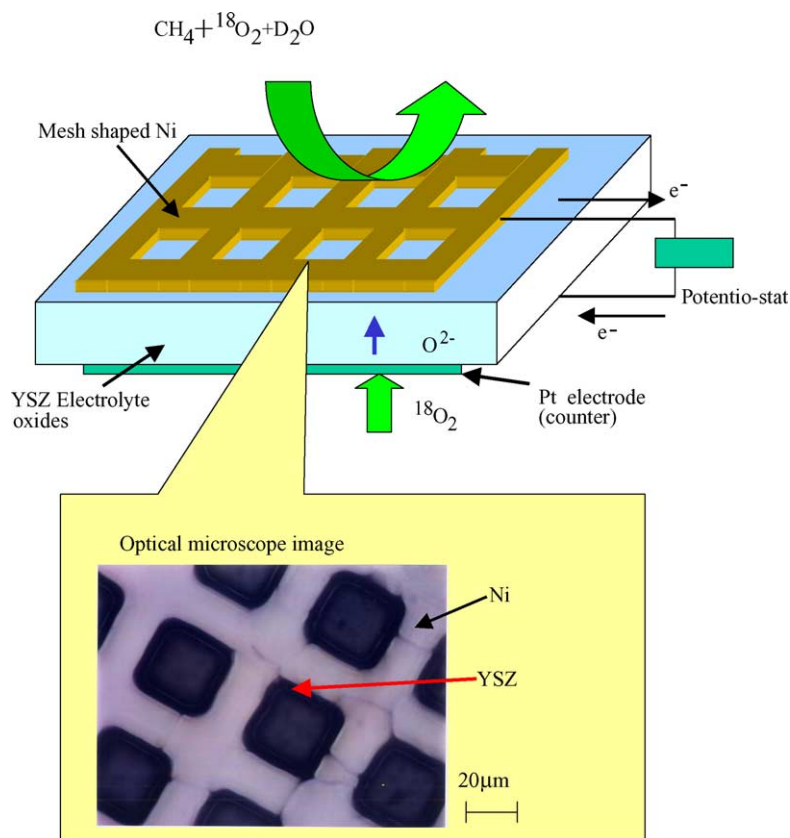


Fig. 1. Schematic diagram of isotope labeling experiment under voltage-applied condition.

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