IN SITU OBSERVATION OF DEPOSITED CARBON ON ANODE FOR SOLID OXIDE FUEL CELLS

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ABSTRACT

We have developed a new measurement technique combining electrochemical measurement with Raman microspectroscopy at high temperatures. In situ observation of carbon deposition on the anode for solid oxide fuel cells was attempted by Raman microspectroscopy. It was found that the form of deposited carbon was amorphous carbon in dry butane/Pt/8YSZ and graphite in humid methane/Ni/8YSZ, respectively. The deposited carbon on Ni surface could not be burned electrochemically.

INTRODUCTION

In recent years, environmental pollution from consumption of fossil fuels has been recognized as a serious problem. This problem may be solved if a new efficient power generation system can be developed. Solid oxide fuel cells (SOFCs) are one of the promising candidates due to their high efficiency and low emissions. Ideally, SOFCs use hydrogen as fuel. There has been, however, no economical method to produce hydrogen from water. SOFCs are operated at high temperatures, so hydrocarbons can be used as a fuel by internal reforming. In this case, carbon deposition on an anode may occur in some conditions depending on temperature, the combination of electrode and electrolyte, and the ratio of steam to carbon. Carbon deposition is considered a critical problem because it causes drastic deterioration of anode performance. Therefore, it is necessary to elucidate the mechanism of carbon deposition to improve tolerance for hydrocarbon fuel.

The influence of carbon deposition on electrode reaction has been reported (1,2). Most of those reports were, however, indirect information such as electrode kinetics getting slower in a hydrocarbon atmosphere investigated by conventional electrochemical measurements, i.e. steady-state polarization measurement and impedance spectroscopy. It is difficult to find the details of the problem in this case. The reason for this difficulty is lack of direct information about the reaction. Using only the electrochemical method, we cannot examine the condition of carbon deposition correctly. In situ observation of the electrode is necessary to obtain more precise information about the electrode reaction.

In this study, an attempt was made to carry out in situ observation of carbon deposition at high temperatures by Raman microspectroscopy. Raman spectroscopy is widely used as an
effective technique to characterize various carbon materials (3-6). With a micro-Raman spectroscope, it is possible to observe the site of carbon deposition and oxidation and to characterize deposited carbon in the microscopic area. The purpose of this study was to establish the technique for in situ observation of carbon deposition on the electrode and electrolyte at high temperatures by advanced electrochemical setup combined with Raman microspectroscopy.

EXPERIMENTAL

Sample Preparation

Pt paste/YSZ/Pt paste. 8 mol% yttria stabilized zirconia powder (Tosoh, TZ-8Y) was pressed into a pellet and sintered at 1400°C for 3 h. The pellet was ~5 mm diameter and 0.5 mm thick. As working and counter electrodes, Pt paste was fired at 1400°C for 3 h.

Ni mesh/YSZ/Pt paste. The electrolyte was an 8YSZ single crystal (Nakazumi Crystal Laboratory, 8YSZ 111). The crystal was cut into the 5 x 0.5-mm pellet and polished. As a working electrode, Ni mesh (Veco grid, 400 mesh/in., 3 mm x 5 μm) was sintered at 1400°C for 1 h in reducing atm to be attached completely to the electrolyte. Platinum electrode was formed on the other side as a counter electrode and fired at 900°C for 1 h.

Experimental Setup

Figure 1 shows the quartz chamber for simultaneous measurement of electrochemical properties and Raman microspectroscopy at high temperatures. The chamber was divided into two compartments by Pyrex® glass sealing: fuel gases were fed into the compartment of the working electrode. Air was introduced into the other side. In the case of the Pt/YSZ cell, CH₄-H₂O-Ar and dry C₄H₁₀ systems were used as fuel gas, while Ni mesh electrode was exposed to CH₄-H₂O-Ar. Steam partial pressure was controlled by a water bubbler and a temperature-controlled cold trap. An electric furnace was composed of a Pyromax® heating element. The sample temperature was controlled within ±1°C from the target. The furnace power was small enough not to damage the Raman optical system.

Electrochemical measurement and Raman microspectroscopy were conducted through a potentiostat/galvanostat (Toho, PS-14) and Raman microspectroscopic system (Jovin-Yvon, T64000), respectively. The excitation line was Ar ion laser of 488 nm (NEC, GLG3200). Steady-state polarization measurements were performed through a two-terminal configuration. Surface observations with optical microscope and Raman spectroscopy were carried out on the top of the sample through a quartz window.

RESULTS AND DISCUSSION

Raman Spectra at High Temperatures

First we checked whether the Raman setup would work properly at high temperature. Pt/YSZ cell was put into the chamber, which was detached from electrochemical setup. In the stream of 1% CH₄-2.3% H₂O-Ar, Raman spectra were examined at 500°C to 800°C.
Figure 1. Experimental setup for advanced electrochemical measurement combined with Raman microspectroscopy.

Figure 2. Raman spectra on (A) 8YSZ and (B) Pt at high temperatures from 500° to 800°C in 1% CH₄-2.3% H₂O-Ar.

Figure 2 (A) and (B) show the temperature dependence of in situ Raman spectra. We found that background level gradually increases with increase in temperature, especially in the region of high Raman shift. There is no obvious peak on platinum surface. On the other hand, the peak was found around 600 cm⁻¹ on zirconia, which is derived from YSZ (7). The result shows that Raman spectra can be obtained with our setup even at temperatures as high as 800°C.

In Situ Observation of Carbon Deposition at High Temperatures

Concerning the Pt electrode system, no Raman spectrum characteristic of carbon was observed at 800°C in 1% CH₄-H₂O, even in the range of steam/carbon <1. To cause carbon deposition, the gas mixture was changed to a more reactive specie, dry butane. Some time
after the gas was introduced, something black was deposited on Pt (Figure 3). To characterize it, Raman spectrum on Pt was measured (Figure 4). In Figure 4, two broad peaks appeared that were identified as disordered carbon (1355 cm$^{-1}$) and graphite (1590 cm$^{-1}$), respectively (6). This indicates that the form of the deposited carbon was amorphous. The measurement confirmed that the form of deposited carbon could be determined by in situ Raman microspectroscopy.

![Figure 3. Optical microscopic images of Pt electrode before and after carbon deposition in dry butane.](image)

Electrochemical Measurement Combined with Raman Microspectroscopy

To check the performance of the electrochemical cell, Ni mesh/8YSZ/Pt, steady-state polarization was measured in the CH$_4$-H$_2$O-Ar system at 800°C (Figure 5). The anodic current was relatively small compared with the cathodic current, possibly because the polarization of the counter electrode was unexpectedly large. It should be better to apply a three-terminal cell to cancel the influence of counter electrode polarization. Anyway, the combined electrochemical and Raman microspectroscopic measurement was applied to the cell. The steam concentration was fixed at 2.3%, while the concentration of methane gradually increased from 1%. Then, at more than 40% CH$_4$, carbon was found deposited on the Ni surface by Raman microspectroscopy. The deposited carbon was identified as graphite because of the sharp peak at 1560 cm$^{-1}$ (Figure 6).
Another Ni mesh/8YSZ cell was under anodic polarization of +170 mV (11 μA/cm²) in 50% CH₄-2.3% H₂O-Ar after the deposition (60 min) to make it clear whether the deposit carbon could be burned out by electrochemically permeated oxygen. The result is shown in Figure 7. After the anodic polarization, there is no obvious change in the peak (1564 cm⁻¹). This means that the deposited carbon could not be burned electrochemically.

CONCLUSIONS

The advanced measurement technique was developed to investigate carbon deposition on the anode for SOFCs. The technique is electrochemical measurement combined with Raman microspectroscopy. The following results were drawn from this study:

- The form of deposited carbon is amorphous carbon in dry butane/Pt/8YSZ and graphite in humid methane/Ni/8YSZ, respectively.
- The deposited carbon on Ni surface could not be burned electrochemically.
Figure 7. Raman spectra of deposited carbon on Ni mesh before and after polarization. The cell was anodically polarized [+170 mV, 11 µA/cm²] from 60 min after humid methane introduction.

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REFERENCES

1. J.-H. Koh, Y.-S. Yoo, J.-W. Park, and H.-C. Lim, Solid State Ionics, 149, 157 (2002).
2. C. M. Finnerty, N. J. Coe, R.H. Cunningham, and R. M. Ormerod, Catalysis Today, 46, 137 (1998).
3. Y. Hattori, Y. Watanabe, S. Kawasaki, F. Okinno, B. K. Paradhan, T. Kyotani, A. Tomita, and H. Touhara, Carbon, 37, 137 (1999).
4. T. Nakajima, M. Koh, and T. Katsuze, Solid State Science, 2, 17 (2000).
5. M. Yudasaka, R. Kikuti, T. Matsui, Y. Ohki, M. Bexendale, S. Yoshihara, and E. Ota, Thin Solid Films, 305, 351 (1997).
6. S. M. Mominuzzaman, K. M. Krishna, T. Soga, T. Jimbo, and M. Ueno, Carbon, 38, 127 (2000).
7. K. Nomura, Y. Mizutani, M. Kawai, Y. Nakamura and O. Yamamoto, Solid State Ionics, 132, 235 (2000).