

## In situ Fourier Transform Infrared Spectroscopy of Oxygen Species on Pt/YSZ Electrodes at High Temperature

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In order to reveal details of electrode reactions on solid electrolytes, in situ chemical analyses of the reactive surface are necessary in addition to conventional electrochemical measurement. Thus we applied one of the advanced Fourier transform infrared spectroscopy (FT-IR) called polarization modulated reflection adsorption FT-IR (PM-IR), which can detect only surface species with extremely high sensitivity without background measurement at high temperatures. The adsorption and desorption of oxygen was measured in situ on a Pt/YSZ (Yttria-Stabilized Zirconia) cell. Experiments were performed under oxygen partial pressure,  $P_{O_2}$ , of  $1 \times 10^5$  Pa in temperature range from 18 °C to 500 °C. PM-IR spectra of adsorbed oxygen species were found at  $960\text{cm}^{-1}$  and  $1090\text{cm}^{-1}$ . Though the former peak disappeared at 500 °C, the latter peak didn't disappear until the voltage of  $-100$  mV was applied on the electrode. These results show PM-IR is a powerful tool to detect surface species on electrodes, to investigate electrochemical reactions at high temperatures.

Key words: electrode reactions, infrared spectroscopy, photo-elastic modulation, high temperature

### 1. INTRODUCTION

There is an immediate demand for developing electrochemical devices with solid oxide electrolytes as gas sensors, hydrogen production system, and solid oxide fuel cells (SOFC). The properties of these systems have been investigated to some extent by electrochemical methods like impedance spectroscopy and steady state polarization analysis. In some cases of them, it has been proved that the chemical reactions on the electrode surface or triple phase boundaries (TPB) play important roles [1]. In order to reveal the electrode reactions completely, studies are carried out in the following procedure:

- 1) Determination of the reaction pathways.
- 2) Decision of rate determining step (RDS).
- 3) Determination of the reaction model and elicitation of the kinetic equations.

It is, however, difficult to elucidate electrode reaction mechanism by conventional electrochemical techniques only, because of a lack of direct information about electrochemical reaction. To this end, spectroscopic analyses such as Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and so on have been introduced into in situ measurements in recent years. For instance, carbon deposition on the anode in humid  $\text{CH}_4$ , Ni/yttria-stabilized zirconia (YSZ)/Pt cell at 800 °C was observed through Raman micro-spectroscopy. This measurement confirmed that the form of deposited carbon was graphite [2]. FT-IR can be also expected as a

useful way to identify the surface species because it can acquire the vibration modes of molecule bonds. Recently, Lu et al. applied potential dependent FT-IR emission spectroscopy (pd-FTIRS) to in situ study of SOFC electrode reactions [3]. It was clearly observed that the concentration of adsorbed oxygen was changed against applied voltage on oxygen electrode,  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3.5}$ . Whereas, more complicated reaction such as the  $\text{CH}_4$  oxidation on a SOFC anode (Ni-SDC) appeared to be difficult to measure because of the interferences by the  $\text{H}_2\text{O}$  or  $\text{CO}_2$  in the gas phase.

This study aims to establish an in situ observation of electrode surface species at high temperature by the advanced FT-IR. Infrared reflection adsorption spectroscopy (IRRAS) is a popular technique to detect adsorbed species sensitively [4]. If FT-IR is applied to high temperature measurements, some complex problems are expected. Infrared radiation from a specimen itself especially causes much noise on spectrum. Therefore we adopted polarization modulated IRRAS (PM-IR) [5]. This technique can detect only surface species with high sensitivity since the incident light is modulated. In this paper, the adsorbed oxygen on Pt/YSZ surface was observed to confirm the validity of PM-IR at high temperatures. Then we tried to implement PM-IR and electrochemical measurement simultaneously to observe adsorption and desorption of oxygen on a model Pt/YSZ/Pt cell.

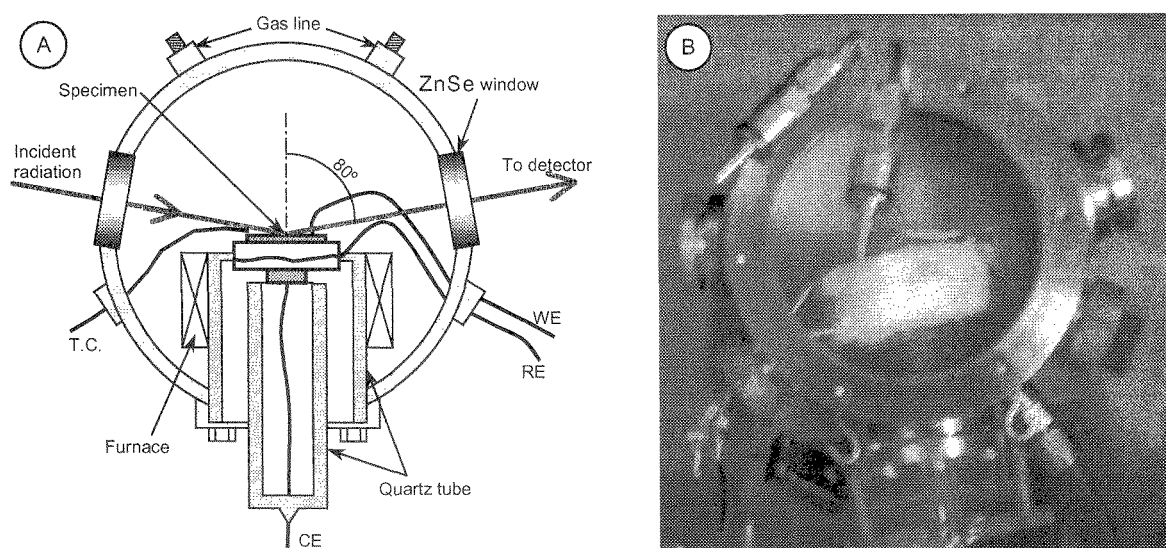


Fig. 1. Overhead schematic (A) and photograph (B) of the experimental apparatus.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

Pt/YSZ/Pt cell was prepared as following. YSZ powder (Tohso, TZ-8Y) was pressed into a pellet and sintered at 1400 °C for 3 h. The resulting pellets were 13 mm in diameter and 1 mm in thickness. The relative density was more than 95 %. Its surface was polished to achieve mirror plane. Pt thin film was fabricated on the surface as a working electrode (WE) through pulsed laser deposition (PLD) to reflect infrared light well. The film was 10mm in diameter and ~500 nm thickness. As a porous counter electrode (CE), Pt paste was fired at 700 °C for 2 h on the other side. Pt wire was wound around the side face of the pellet as a reference electrode (RE).

### 2.2 Sample holder setup

The specimen was placed on the center of the chamber supported by two quartz tubes in an electric furnace (Figs. 1A and 1B). The chamber was rotated and adjusted to obtain a good reflective position. The supportive quartz tubes were designed to avoid being subjected to infrared radiation as strong adsorption of infrared light by SiO<sub>2</sub> itself interferes the detected signal. Two optical windows (20 mm in diameter and 5 mm thickness) are made of ZnSe. Constant O<sub>2</sub>-Ar gas flow (~20 ml/min) was controlled by mass flow controller and a zirconia oxygen sensor monitored P<sub>O<sub>2</sub></sub> of the exhausted gas from the chamber. A rotary vacuum pump (ULVAC, GVD-050A) was placed on the gas line between the chamber and the zirconia sensor so that the chamber can be evacuated. A thermo couple was located near the rim of the working electrode. The three electrodes were exposed to same gas.

### 2.3 Electrochemical configuration

DC polarization measurements were carried out at 500 °C with a three terminals configuration. The overvoltage between WE and CE was controlled by a potentiostat (TOHO, PS-14) at a constant value between 0 mV and -550 mV.

### 2.4 Optical configuration

The interferogram with PM-IR has not only the modulation that comes from the interferometer but also the polarization modulation frequency produced by the photo-elastic modulator (PEM). PEM modulates alternatively p-polarized light and s-polarized light, whose electric vectors are parallel and perpendicular respectively to the reflective surface. The spectra of the gas phase molecules, accordingly, are canceled without a background reference. The reflectance can be described as the equation (1),

$$\left(\frac{\Delta R}{R}\right)_{\text{exp}} = \left| J_2(\varphi) \left( \frac{R_p - R_s}{R_p + R_s} \right) \right| \quad (1),$$

where  $J_2(\varphi)$  is the second-order Bessel function,  $\varphi$  is the function of the maximum voltage applied on the PEM,  $R_p$  and  $R_s$  are the reflective intensity of p-polarization and s-polarization, respectively. PM-IR spectra, especially, are introduced upon some arches because of the large envelope curve of  $J_2(\varphi)$ .

The interferograms were obtained with the resolution of 4 cm<sup>-1</sup> and 1024 scans into each one using the FT-IR apparatus (Thermo Nicolet, NEXUS 670). The incident angle to the specimen was 80° and all optical paths were filled with dry air except the inside of the chamber. The polarization modulation frequency was set to 50 kHz through the PEM (Hinds, PEM90).

## 3. RESULTS AND DISCUSSION

### 3.1 Temperature and P<sub>O<sub>2</sub></sub> dependence of adsorbed oxygen

Pre-cleaning of the specimen was performed at 550 °C for 12 h in the chamber (P<sub>O<sub>2</sub></sub> = 10<sup>5</sup> Pa). Then we acquired PM-IR spectra of Pt thin film on YSZ in O<sub>2</sub> balanced Ar (P<sub>O<sub>2</sub></sub> = 3 Pa - 10<sup>5</sup> Pa) or vacuo from 18 °C to 550 °C as presented in Fig. 2. Figure 2A shows

PM-IR spectra between  $900\text{ cm}^{-1}$  and  $3750\text{ cm}^{-1}$ , in which the large envelop baseline appears as mentioned in section 2.4. It is found that the absorbance bands of  $\text{H}_2\text{O}$  ( $1300\text{ cm}^{-1} - 2000\text{ cm}^{-1}$ ,  $\sim 3000\text{ cm}^{-1}$ ) or  $\text{CO}_2$  ( $\sim 2350\text{ cm}^{-1}$ ) in the optical paths are canceled completely.

Fig. 2B is the enlarged view (between  $850\text{ cm}^{-1} \sim 1400\text{ cm}^{-1}$ ) of Fig. 2A. From this figure, at least two peaks were recognized at  $920\text{ cm}^{-1}$  and  $1080\text{ cm}^{-1}$  in  $P_{\text{O}_2}$  of 3 Pa at  $18^\circ\text{C}$ . The former disappeared with increasing temperature from  $260^\circ\text{C}$  to  $400^\circ\text{C}$ . On the contrary, the latter still remained at  $550^\circ\text{C}$  although its intensity decreased comparatively. This peak disappeared at last when the chamber was evacuated for 0.5 h. These indicate that the peaks at  $920\text{ cm}^{-1}$  and  $1080\text{ cm}^{-1}$  corresponded to surface oxygen species bonded weakly and strongly respectively. By the way, the new peak appeared near  $1160\text{ cm}^{-1}$  with additional evacuation (for 2 h). This might have been impurity that came from the thermal insulator

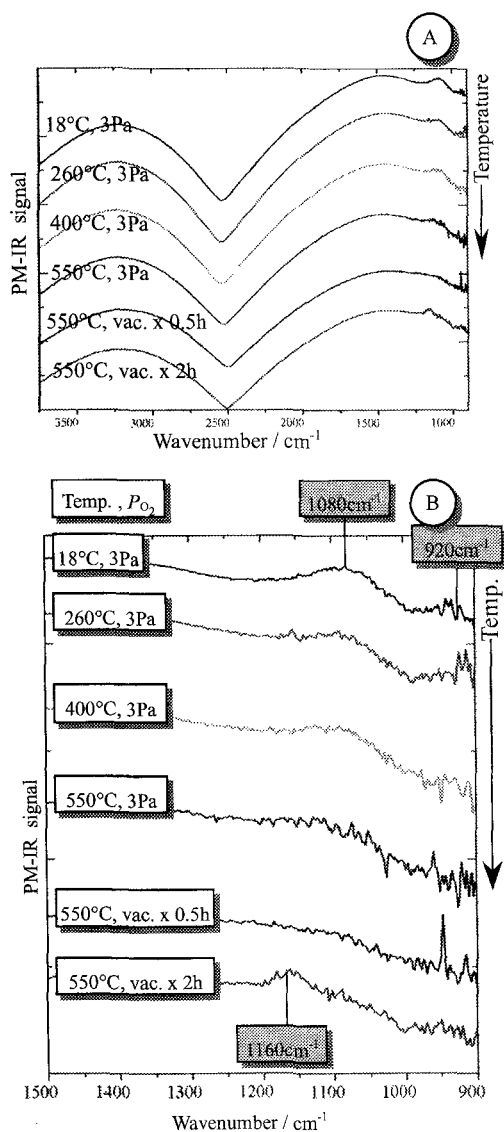


Fig. 2. The PM-IR spectra of Pt/YSZ in  $\text{O}_2$ -Ar or vacuo from  $18^\circ\text{C}$  to  $550^\circ\text{C}$ : (A)  $900\text{ cm}^{-1} - 3500\text{ cm}^{-1}$ , (B)  $900\text{ cm}^{-1} - 1500\text{ cm}^{-1}$ .

around the furnace (see Fig. 1B) in vacuo.

Absorption forms of oxygen species on Pt/YSZ can be  $\text{O}_2^{2-}$ ,  $\text{O}_2^-$ , "neutral"  $\text{O}_2$ , or the atomic adsorbates. From the viewpoint of the wavenumber showing the stretching modes of the molecular bonds, these two peaks should not be assigned to the atomic adsorbates because the chemisorbed Pt-O stretching mode appears at lower frequency ( $\sim 460\text{ cm}^{-1}$ ) [6, 7]. Unfortunately, we cannot observe that mode even if it existed, because of the limitations of our measurement system. According to this, those two peaks have the possibility to be the admolecule species. On the other hand, Matsushima et al. have reported that the dissociation of oxygen admolecules on Pt surface occurs at about 160K though this is performed in the ultra high vacuum condition [8]. From this result, these should correspond to atomic species because our experimental temperature is too high for the dissociation of the O-O bond. Thus, the obtained spectra peaks have been unclear to be the O-O stretching or Pt-O stretching of the above molecular species yet. This has been still to be investigated.

### 3.2 Oxygen reduction on electrode of Pt/YSZ/Pt cell

Table 1 shows the results of dc polarization measurement, where  $i$  and  $V$  are current density and the

Table 1. Overvoltage  $V$  vs. current density  $i$  of the Pt/YSZ/Pt cell at  $500^\circ\text{C}$  in  $P_{\text{O}_2}$  of  $3 \times 10^4\text{ Pa}$ .

| $V / \text{mV}$ | $i / \text{mA cm}^{-2}$ |
|-----------------|-------------------------|
| -100            | -22.2                   |
| -300            | -89.6                   |
| -500            | -159.3                  |

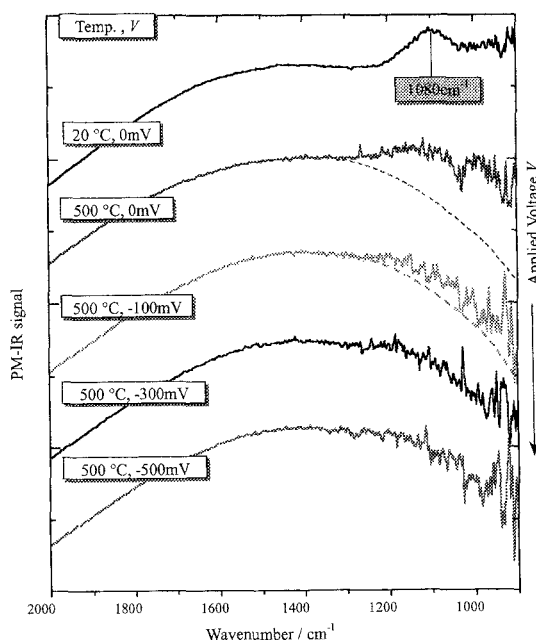
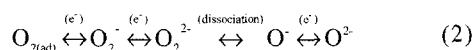


Fig. 3. PM-IR spectra of the electrode surface for the Pt/YSZ/Pt cell in  $P_{\text{O}_2}$  of  $3 \times 10^4\text{ Pa}$  at  $20^\circ\text{C}$  or  $500^\circ\text{C}$ . DC polarization measurement were performed simultaneously.

cathodic overvoltage  $V$ , respectively. Each PM-IR spectrum was measured after the equilibrium state was achieved under cathodic polarization. Fig. 3 shows the PM-IR spectra of the electrode surface under oxygen partial pressure of  $3 \times 10^4$  Pa at 20 °C or 500 °C after pre-cleaning. A peak was observed near  $1080 \text{ cm}^{-1}$  at OCV. This can be identified as the same oxygen species as the previous experiment. The intensity of the peak decreased dramatically with variation in overvoltage from 0 mV to -100 mV. It means adsorbed oxygen molecules vanished from the electrode surface under cathodic polarization. Here, the equilibrium of adsorbed oxygen species is thought as the formula (2) [9].



On the basis of this formula, possible cathodic reaction paths were depicted in Fig. 4. PM-IR results suggest that adsorbed oxygen should diffuse along the platinum surface and be incorporated into YSZ at TPB (Path I as shown in Fig. 4), because surface oxygen concentration depends on cathodic overvoltage.

PM-IR with an electrochemical measurement enabled us to obtain direct information of surface species on an electrode even at high temperatures. Consequently, it has great possibilities to become a powerful tool for the investigation of high-temperature electrode kinetics.

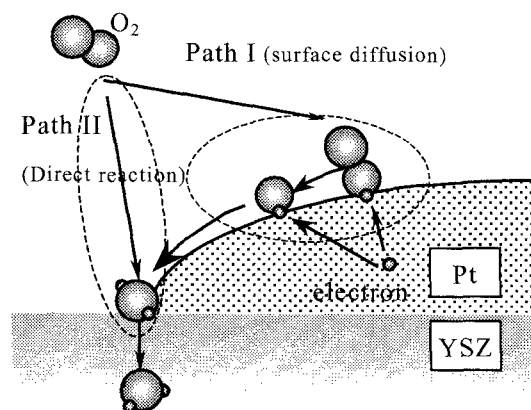


Fig. 4 Reaction pathways for oxygen reduction

#### 4. CONCLUSION

The PM-IR spectroscopy confirmed adsorbed oxygen on Pt surface at high temperature. There were at least two types of adsorbed oxygen observed at  $960 \text{ cm}^{-1}$  and  $1080 \text{ cm}^{-1}$ . The former can be a weak adsorbed species because it was easily reduced in  $P_{\text{O}_2}$  of  $10^5$  Pa at  $\sim 400$  °C. The latter is more strongly bonded and desorbed by evacuation at 550 °C.

We have achieved to combine PM-IR and steady state polarization measurement. This led in situ observation of the surface oxygen on the electrode of Pt/YSZ/Pt cell. The oxygen shown at  $1080 \text{ cm}^{-1}$  was reduced when cathodic voltage was applied in  $P_{\text{O}_2}$  of  $3 \times 10^5$  Pa at 500 °C. This has concluded PM-IR is a powerful tool for in situ study to characterize electrode kinetics.

#### 5. ACKNOWLEDGMENT

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