

Electric-Field Effect on the Surface Process of Platinum-Coated Yttria-Stabilized Zirconia

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Thermionic emission of O^- ions was studied using platinum-coated Yttria-Stabilized Zirconia (YSZ). Electric field up to about 450×10^3 V/m was applied on the YSZ surface. Emission current was investigated at the temperature ranging from 750 to 850 °C under a pressure of about 1×10^{-3} Pa. Experimental results showed that negative charged particles were emitted from the YSZ surface. Emission current was confirmed to increase with temperature and applied voltage. Terminal voltage between an emission surface and an air electrode was measured; at low electric field, the ohmic relation between emission current and $\Delta V = V_{emf} - V_{terminal}$ held, while, at high electric field, it did not hold. Electrochemical oxygen pumping proved to slightly affect emission current, which would be attributed to the variation in work function of platinum on the YSZ surface.

Key words: YSZ, surface process, electric field, thermionic emission, negative ion

1. INTRODUCTION

Oxygen radical anions, O^- , play important roles in some chemical processes, such as combustion, CVD, and biological processes [1]. Grabowski et al. revealed that O^- anions have bond-breaking and bond-making effects, acting to synthesize many intermediate anions in organic chemistry [2]. In chemical processes, therefore, it is significant to control the production and introduction of O^- radical anions. Generally, O^- anions are produced by discharge of gases [3]. However, it is difficult to produce O^- radical anions efficiently and selectively.

In 1997, Torimoto et al. demonstrated that O^- ions are emitted from a gold-coated surface of yttria-stabilized zirconia (YSZ), proposing a new method for producing O^- radical anions using YSZ [4]. They measured emission of O^- ions with a mass analyzer for detecting negative ions over the temperature range from 460 to 580 °C. In terms of application, the method using YSZ will have many advantages. One of expected advantages is high selectivity of produced ions. Since only oxygen anions migrate across YSZ, produced ions will be only oxygen radical anions. Another expected advantage is cost down. Similar to electrochemical reactions in an air electrode of solid oxide fuel cells (SOFC), oxygen radical anions will be generated spontaneously from air, so that pure oxygen gas is not necessary. Hence, the method with solid oxide electrolytes like YSZ seems very rational.

However, the emission process of O^- ions from the surface of solid oxide electrolytes has not well understood. For this reason, we have

started an experimental study on O^- emission by means of a platinum-coated YSZ tube with a closed end. To obtain higher emission current, temperature of the YSZ tube was increased up to 850 °C. In the present study, we investigated emission characteristics such as applied voltage dependence and temperature dependence. Next, we measured variation in terminal voltage between the platinum-coated emission surface and an air electrode. Moreover, using a potentiostat, we measured the effect of electrochemical oxygen pumping on emission current.

2. EXPERIMENTAL APPARATUS

Figure 1 shows an experimental apparatus for measuring emission current from the surface of a platinum-coated YSZ tube. It consists of the YSZ tube with a closed end, a SiO_2 -glass chamber, an extraction electrode, a cylindrical ion collector and a high-voltage power supply.

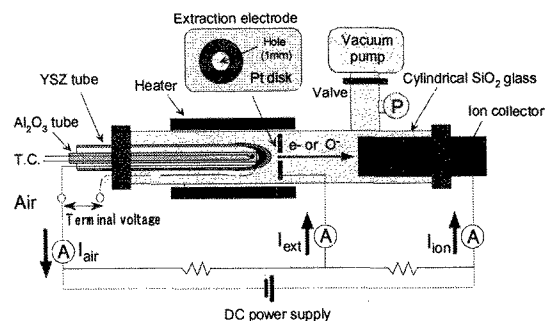


Fig.1 Schematic diagram of the experimental apparatus.

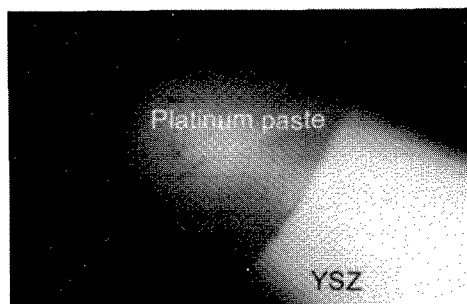


Fig.2 A picture of the platinum-coated YSZ tube.

The YSZ tube has an inner diameter of 5 mm, an outer diameter of 8 mm, and a length of 300 mm. The inner surface of the closed end of the YSZ tube, which works as an air electrode, was coated with platinum paste and fired at 950 °C for 1 h in air. The air electrode is connected to the power supply by a platinum wire. The outer surface was also coated with platinum paste and fired at 950 °C for 1 h. Figure 2 is a picture of the closed end of the platinum-coated YSZ tube.

The SiO₂-glass chamber has an inner diameter of 29 mm, an outer diameter of 33 mm, and a length of 300 mm. Capacity of the power supply is DC 650 V, 100 mA. The extraction electrode is made of platinum. The dimension of the extraction electrode is 10 mm in diameter and 0.1 mm thick. The gap length between the closed-end surface and the extraction electrode is about 1 mm. The ion collector is made of copper, which is 150 mm long, 21 mm in outer diameter and 18 mm in inner diameter. The ion collector is located about 10 cm downstream from the extraction electrode. Positive high voltage is applied on the extraction electrode and the ion collector, forming an electric field; negative charge particles emitted from the YSZ surface are attracted by the electric field. The extraction electrode has a hole of 1 mm in diameter so that negative charge particles may pass through the extraction electrode. As shown in Fig. 3, the currents flowing through the electric circuits are measured with electrometers (ADVANTEST R8240).

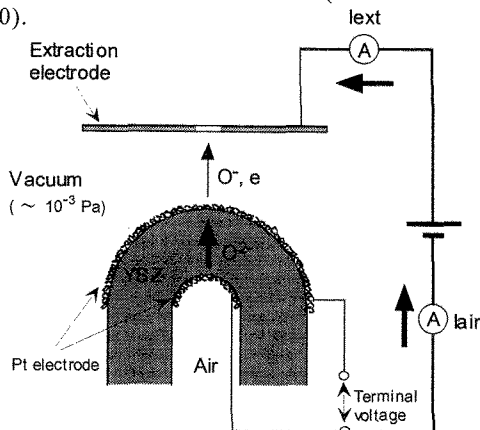


Fig.3 Schematic illustration around the closed end of the YSZ tube.

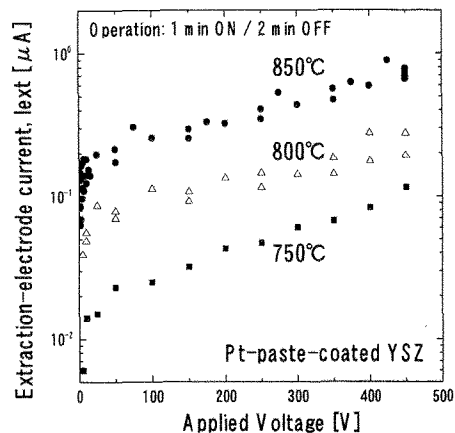


Fig.4 Applied voltage and temperature dependence of I_{ext} .

An electric furnace enables us to regulate the temperature of the YSZ tube. To monitor a temperature around the closed end of the YSZ tube, a thermocouple is placed near the air electrode inside of the YSZ tube. With alumina tubes, the thermocouple is insulated from the platinum wire connected to the DC power supply.

The chamber is evacuated with a diaphragm vacuum pump and a turbo-molecular pump. Gas pressure inside the chamber is measured with a pirani gauge and an ionization vacuum gauge. In the present experiment, typical gas pressure was around 1×10^{-3} Pa.

3. RESULTS AND DISCUSSION

3.1 Emission current characteristics

(A) Applied voltage and temperature dependence

Figure 4 shows applied voltage and temperature dependence of extraction-electrode current, I_{ext} . Temperature of the YSZ tube was changed from 750 to 850 °C. In the measurement, positive voltage was applied to the extraction electrode for 1 min every 2-min intervals; I_{ext} was obtained at the end of 1-min pulse. Positive value of I_{ext} indicates that negative charged particles were emitted from the YSZ surface. It can be seen that I_{ext} increased with applied voltage and temperature.

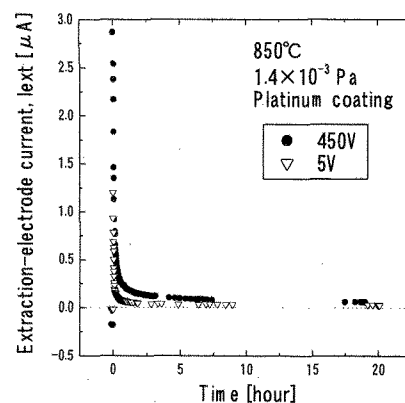


Fig.5 Time-dependent behavior of I_{ext} at the voltage of 5 and 450 V.

(B) Time dependence

Figures 5 shows the variation in I_{ext} as a function of time at a temperature of 850 °C. Positive voltages of 5 V and 450 V were applied, respectively, at a time of zero, and then being kept continuously. By applying positive voltage, both I_{ext} rose rapidly, reaching a maximum; and then it decreased gradually with the passage of time, finally approaching zero.

3.2 Variation in terminal voltage between the air electrode and the emission surface

Figure 6 shows one-dimensional conditions where ideal solid oxide electrolytes are placed between air and vacuum. Since the electronic conductivity of YSZ is much smaller than its ionic conductivity, the electronic conductivity is not taken into account in the following calculation. If local equilibrium holds, current density is given by

$$J_{O^{2-}} = \frac{\sigma_{O^{2-}}}{2F} \frac{d\eta_{O^{2-}}}{dx} = \frac{\sigma_{O^{2-}}}{2F} \left(\frac{d\mu_O}{dx} + 2 \frac{d\eta_e}{dx} \right), \quad (1)$$

where $\sigma_{O^{2-}}$ represents conductivity of oxide ions, $\eta_{O^{2-}}$ and η_e are electrochemical potential of oxide ions and electrons, respectively, and μ_O is chemical potential of oxygen atoms.

Suppose oxide ion conductivity, $\sigma_{O^{2-}}$, is independent of oxygen partial pressure; terminal voltage between an air side and a vacuum side is obtained by integrating Eq. 1,

$$\int_0^L J_{O^{2-}} dx = \sigma_{O^{2-}} \left(\frac{1}{2F} \int_0^L \frac{d\mu_O}{dx} dx + \frac{1}{F} \int_0^L \frac{d\eta_e}{dx} dx \right). \quad (2)$$

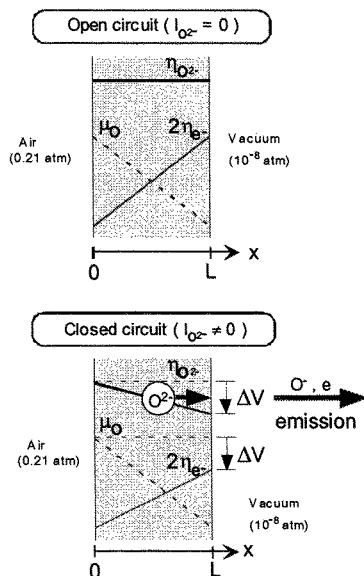


Fig. 6. Schematic diagrams of potential profile in ideal electrolytes.

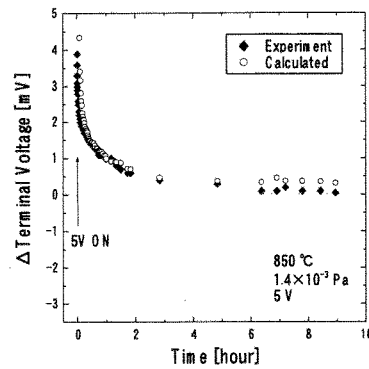


Fig. 7. Variation in the terminal voltage at 5V.

Since current density is independent of x, Eq. 2 can be rewritten as

$$J_{O^{2-}} L = \sigma_{O^{2-}} \left\{ \frac{RT}{4F} \ln \left(\frac{p_{O_2}^{vacuum}}{p_{O_2}^{air}} \right) + \frac{1}{F} \int \eta_e^{vacuum} d\eta_e \right\}. \quad (3)$$

In Eq. 3, the first term in the right side is e.m.f of a concentration cell, and the second term is the terminal voltage [5]. Then, we obtain

$$J_{O^{2-}} L = \sigma_{O^{2-}} (V_{emf} - V_{terminal}). \quad (4)$$

Equation 4 gives the ohmic relation between $J_{O^{2-}}$ and the $\Delta V = V_{emf} - V_{terminal}$.

From the continuity of current, emission current will be equal to current through the YSZ from the air side to the vacuum side. Hence, in the emission surface, Eq. 5 will hold as follows:

$$I_{emission} = C (V_{emf} - V_{terminal}), \quad (5)$$

where $I_{emission}$ is emission current, C is $(\sigma_{O^{2-}} \times S)/L$, and S is emission area.

Figure 7 shows the variation in terminal voltage between the air electrode and the platinum-coated emission surface as a function of time, when positive voltages of 5 V was applied on the extraction electrode. In the Fig. 7, open circles are values calculated using Eq. 5 and I_{ext} in Fig. 5, when V_{emf} and C are assumed to be -412.8 mV, $0.5 \times 10^{-4} \text{ A} \cdot \text{V}^{-1}$, respectively. It can be seen that the calculated values of $V_{terminal}$ agree well with experimental data. Assuming that $\sigma_{O^{2-}}$ and L are $4.65 \times 10^{-2} \text{ S/cm}$ and 0.15 cm, respectively, effective emission area, S, is estimated to be $1.6 \times 10^{-4} \text{ cm}^2$.

However, as shown in Fig. 8, the variation in terminal voltage at a high voltage of 450 V cannot be explained using Eq. 5; that is, the ohmic relation like Eq. 5 did not hold at a high voltage of 450 V. The discrepancy may imply that emission process will change with electric-field strength. Further studies will be necessary to clarify the emission process from the YSZ surface.

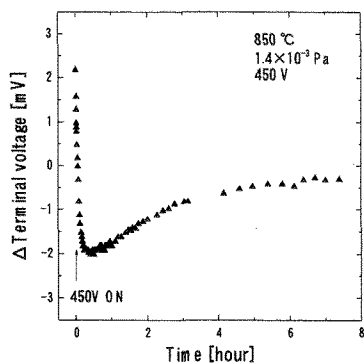


Fig. 8. Variation in the terminal voltage at 450V.

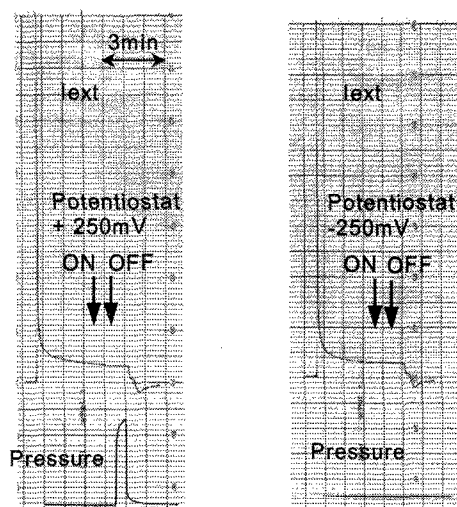
3.3 The effect of electrochemical oxygen pumping on emission current

Using a potentiostat, potential voltage between the air electrode and the platinum-coated emission surface was changed; in other words, oxygen pumping was electrochemically performed. Figure 9 is waveforms showing the variations in I_{ext} and pressure inside of the chamber at 450 V. The waveforms on the left were measured when voltage between the air electrode and the emission surface was deviated from natural potential by + 250 mV; oxygen was exhaled to the vacuum chamber. Those on the right were measured when the voltage was deviated by - 250 mV; oxygen was inhaled from the vacuum chamber. Before the experiment, we had expected that emission current would change drastically with potential between the air electrode and the emission surface. However, experimental results showed that emission current did not change significantly with the potential.

Furthermore, after I_{ext} became stable near zero, the effect of electrochemical oxygen pumping on I_{ext} was investigated. Figure 10 shows waveforms of I_{ext} and inside pressure. Change in the potential voltage between the air electrode and the emission surface proved to affect I_{ext} slightly. It has been reported that work function of catalysts on the solid electrolytes is varied with polarization [6 -8]; thus, the behavior of I_{ext} will be explained by the variation in the work function of platinum on the emission surface. That is, work function of platinum will be decreased at - 500 mV, so that I_{ext} increased; while, at 250 mV, the work function will be increased, so that I_{ext} decreased.

4. SUMMARY AND CONCLUSITON

To clarify the effect of high electric field on the surface process on a platinum-coated YSZ surface, we have started an experimental study using a YSZ tube with a closed end. Experimental results showed that negative charged particles were emitted from the surface, increasing with applied voltage and temperature. Experimental results in continuous operations showed that emission current decreased with the passage of time, approaching zero. The observation of the terminal voltage between the



Figs.9 Waveforms of I_{ext} at 450V and pressure inside of the chamber.

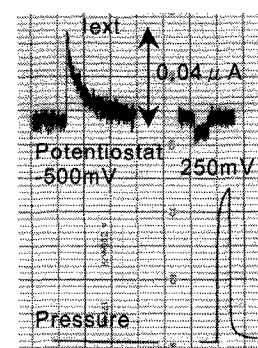


Fig.10. Waveforms of I_{ext} . After I_{ext} approached zero, its variation was studied with a potentiostat.

air electrode and the emission surface suggested that the emission process would change with electric-field strength. Electrochemical oxygen pumping proved to slightly affect emission current, which would result from the variation in work function of platinum on the YSZ surface; however, those phenomena have not been well understood. For more detailed understanding of the emission process, further research will be required.

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