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Emission characteristics of negative oxygen ions into vacuum from cerium oxide

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Abstract

The oxygen ion emission characteristics of CeO_2 were studied under electric field in a vacuum chamber to find a candidate material for a novel ion source, “solid oxide ion source (SOIS)”. The emission current was observed from CeO_2 under a pressure of around 10^{-3} Pa, at the temperature ranging from 973 K to 1173 K. It was found that the emission current increased with temperature and applied voltage. The ions emitted from CeO_2 were confirmed to be oxygen negative ions (O^-) by the use of quadrupole mass spectrometer. The emission current decreased with time as was observed in the earlier works with other oxide ion conductors such as stabilized zirconia [1,2] or other materials [3]. To enhance the emission current from CeO_2, an introduction of donor into CeO_2 was tested using $Ce_{0.992}Nb_{0.008}O_2$. For comparison, effect of acceptor doping was also tested using $Ce_{0.9}Gd_{0.1}O_{1.95}$. The emission current from $Ce_{0.9}Gd_{0.1}O_{1.95}$ was smaller than that from donor-doped and pure CeO_2. Clear enhancement of the emission current was not observed with $Ce_{0.992}Nb_{0.008}O_2$.

Keywords: CeO_2; Ionic conduction; Surface and interface; Thermionic emission

1. Introduction

Oxygen ion beams are widely used in many fields such as material processing and material analyses [4,5]. From the practical point of view, negative oxygen ions are more useful than the positive ions since the former will cause less problem of charging up when they are irradiated on an insulator surface [6]. However, the production of negative oxygen ions has a difficulty because the conventional discharge plasma method that is used for producing the positive ions is not suitable to produce the negative ions. Recently, Fujiwara et al. [1,2] proposed a new ion source named Solid Oxide Ion Source (SOIS), that utilizes oxide-ionic conductors such as Y_2O_3-stabilized ZrO_2(YSZ).

The concept of SOIS is shown in Fig. 1. In the air electrode, oxygen molecules accept electrons and change into oxide ions (O^{2-}), and then migrate to emission surface across the ionic conductor by a gradient of electrochemical potential of oxide ions. In the emission surface, O^{2-} change into absorbed oxygen species. Some of them may still have negative charges. When positive electric fields are applied to the emission surface, the oxygen negative ions are emitted to vacuum.

As in the earlier work by Torimoto et al. [7], O^- ions were emitted when a high voltage of 100–450 V was applied between the YSZ surface and the counter electrode through vacuum. However, the emission current density from YSZ was very low.

Until now, we have explored various oxides to find a new candidate for SOIS. We considered that the material that has oxygen nonstoichiometry at high temperatures is suitable for SOIS. CeO_2 has catalytic activity as well as nonstoichiometry and is used for purification of CO and NO_x [8]. For this reason, the emission characteristics of CeO_2 were studied in this work.

In several works, it was reported that ion emission current from an oxide is affected by the work function of the oxide.

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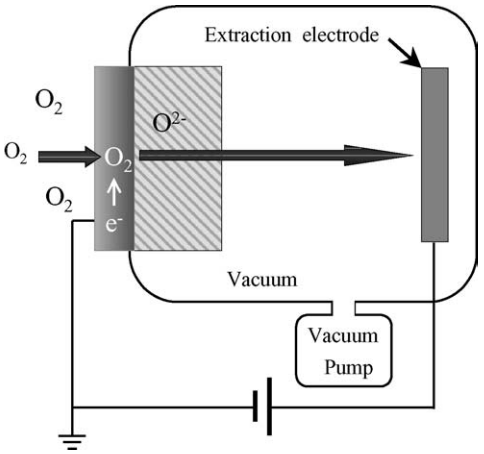

Fig. 1. Illustration of solid oxide ion source.

The probability of thermionic emission of positive ion from an oxide with a high work function was reported to be larger than that from an oxide with a low work function [9,10]. This idea suggests that, for negative ions, an introduction of donor will enhance the emission due to the decrease in work function. In this work, the effect of donor doping on emission current from CeO_2 was tested using $Ce_{0.992}Nb_{0.008}O_2$. For comparison, the effect of acceptor doping (which cause the increase in the work function) was also tested using $Ce_{0.9}Gd_{0.1}O_{1.95}$.

2. Experimental

2.1. Sample preparation

In this study, the pellet type samples were used for the emission current measurement and the mass spectrum analysis. CeO_2 powder (99.99% CeO_2, Rare Metallic Co., Ltd.) was pressed to a pellet and sintered at 1673 K for 5 h in air. The dimension of the pellets was 13 mm in diameter and 4.7 mm in thickness for the emission current measurement, and was 8.9 mm in diameter and 2.4 mm in thickness for the mass spectrum analysis. $Ce_{0.992}Nb_{0.008}O_2$ and $Ce_{0.9}Gd_{0.1}O_{1.95}$ powders were synthesized by solid-state reaction method and co-precipitation method using oxalic acid, respectively. They were pressed and sintered at 1873 K for 5 h to pellets of 13 mm in diameter and 4.7–4.8 mm in thickness. The opposite surface of the emission surface of each pellet was coated with Pt paste and sintered at 1253 K for 1 h in air, which works as the electrode to provide electrons. The difference from our previous work [1,2] using YSZ tube was that the samples were not contacting with air. In the case of pellet-type samples, negative ions are produced by electrolysis with variation of oxygen nonstoichiometry of the samples.

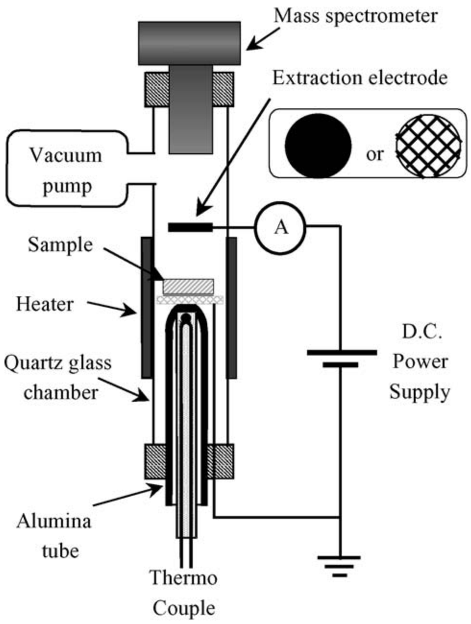

Fig. 2. Experimental apparatus of negative ions emission from CeO_2 pellets.

2.2. Experimental apparatus

The configuration of the experimental apparatus for negative ion emission experiment from CeO_2 pellets is shown in Fig. 2. The vacuum chamber is made of a quartz glass, and the inside of the chamber is evacuated using turbomolecular vacuum pump to maintain the gas pressure around 10^{3-} Pa. The samples are heated by radiant heat of the external heater. The temperature around the samples is monitored using a thermocouple covered with an alumina tube. In the case of a measurement of the emission current from CeO_2, a 7 mm gap exists between the emission surface of the samples and the platinum-disk extraction electrode. The extraction electrode is connected to a positive output of the dc power supply, and on the other hand, the platinum net contacting with the platinum-pasted surface (a opposite surface of the emission surface) of the samples is connected to a ground of the dc power supply. When positive voltage is applied to the extraction electrode, an electric field is formed between the extraction electrode and the emission surface of the samples, and negative ions and electrons are emitted as an emission current from the emission surface to the extraction electrode. The current that flows from the extraction electrode into the dc power supply is measured using an electrometer (ADVANTEST Co., R8240).

A quadrupole mass spectrometer (HidenPSM003) is used to detect negative ions emitted from the samples. In this case, a mesh-type extraction electrode is used so that negative ions emitted from the emission surfaces can pass through the extraction electrode. The gap between the mesh-type extraction electrode and the emission surface of the samples is approximately 3 mm.

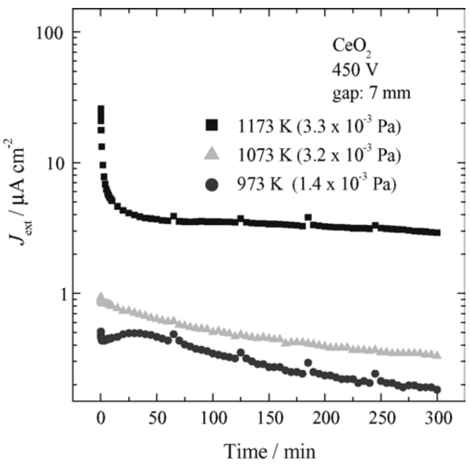

Fig. 3. Time and temperature dependence of emission current from CeO_2 pellet.

3. Result and discussion

3.1. *The time dependence and temperature dependence of emission current*

Fig. 3 shows the time dependence of emission current from CeO_2 at each temperature (973 K, 1073 K and 1173 K), when the positive voltage of 450 V was applied to the extraction electrode. As shown in Fig. 3, emission current from CeO_2 pellets decreased gradually with the passage of time. The decay of emission current from solid oxides was reported not only for negative ion emission from ionic conductor (YSZ) [1,2], but also for positive and negative ion emission from alkali halide (KF) [3]. In these reports, the decay of emission current has been discussed in terms of the surface adsorption and accumulation of charged species. However, clear reason of this phenomenon is not revealed yet. The emission current from CeO_2 increased with temperature. Similar temperature dependence of emission current from solid oxides was also reported by some researchers [1–3,9–11].

After the emission experiment, all samples used in this study were totally blackened and reduced. In addition, in the case of CeO_2, the blackness of the opposite surface of emission surface and the rim of samples was deeper than that of emission surface. This result indicates a possibility that the opposite surface and the rim of the samples were reduced more strongly than that of emission surface because oxygen ions inside the bulk were collected into the emission surface during the emission experiment.

3.2. *Mass spectrum of emission current from CeO_2*

Fig. 4 shows the mass spectrum of the emitted ions from CeO_2 pellet at 1173 K when positive voltage of 300 V was applied to the mesh-type extraction electrode. High intensity peak was observed at the mass to charge ratio of 16. This result indicates that O^- ions were emitted from CeO_2 surface. Although the emission current must contain a certain amount of electrons besides O^- ions, the mass spectrum of electrons was not obtained with the present equipment. The ratio of O^- ions to the total negative charges is to be determined in a future work.

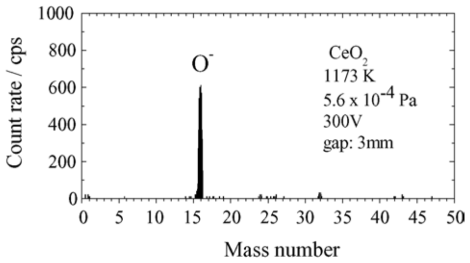

Fig. 4. Mass spectrum of emission current from CeO_2 pellet.

3.3. *Applied voltage dependence of emission current*

The applied voltage dependence of emission current at each temperature is shown in Fig. 5. The emission current from CeO_2 increased with applied voltage. The dependence of the emission current on the applied voltage is explained by the change in the potential barrier height, which is termed the Schottky effect [2,3]. In this case, emission current density, J, is described as follows:

$$J = \frac{I}{S} = AT^2 \exp\left(-\frac{E_{p0} - \Delta E_p}{kT}\right), \quad (1)$$

$$\Delta E_p = \left(\frac{e^3 V}{4\pi\varepsilon_0 d}\right)^{1/2}, \quad (2)$$

where A is a constant, S area of emission surface, T temperature of emitter, E_p potential barrier of thermionic emission from emitter, k Boltzmann's constant, e elemental charge of electron, V applied voltage, ε_0 dielectric constant of vacuum and d is gap length between extraction electrode and emission surface. The emission current density J_0 caused by only thermal excitation at zero electric field is described as fol-

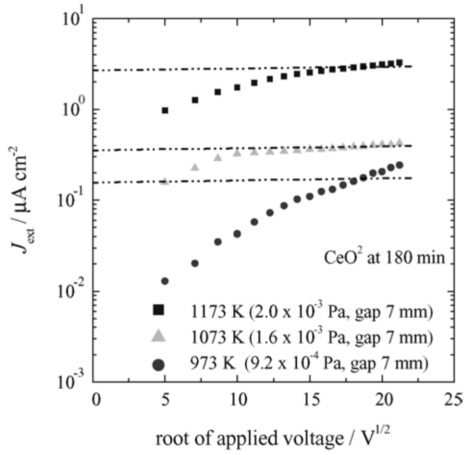

Fig. 5. Applied voltage dependence of emission current from CeO_2.

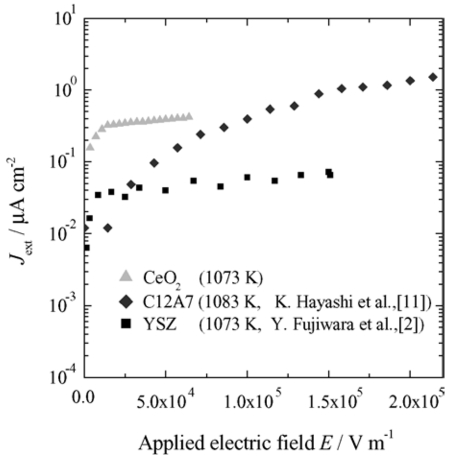

Fig. 6. Comparison of emission current from CeO_2, C12A7 and YSZ.

lows:

$$J_0 = \frac{I_0}{S} = AT^2 \exp\left(-\frac{E_p}{kT}\right). \tag{3}$$

From Eq. (3), Eq. (1) is rewritten as follows:

$$\log J = \log J_0 + 0.434\left(\frac{e^3}{4\pi\varepsilon_0 d}\right)^{1/2}\frac{V^{1/2}}{kT}. \tag{4}$$

In Fig. 5, the slopes calculated from Eq. (4) are displayed. The disagreement especially at 973 K indicates the existence of other factors as well as Schottky effect, which determines the applied voltage dependence of emission current.

3.4. The comparison of emission current between CeO_2 and other oxide

The emission current from CeO_2 with that from other solid oxide ionic conductors (YSZ and $12CaO·7Al_2O_3$ (C12A7)) are compared in Fig. 6 [2,11]. Because of the differences of the geometrical arrangement of the samples, it is difficult to compare the emission current precisely. However, CeO_2 showed obviously higher emission current than YSZ. Furthermore, in lower voltage region, it showed even higher emission current than C12A7, which is reported to show high emission current due to its particular cage structure with free oxygen radicals [11]. In higher voltage region, the emission current from CeO_2 was lower than that from C12A7.

3.5. The effects of donor and acceptor doping on emission current

Fig. 7 shows the effects of donor and acceptor doping on emission current at 1073 K when positive voltage of 450 V was applied. Donor-doped CeO_2, $Ce_{0.992}Nb_{0.008}O_2$, showed the highest emission current at initial 6 min after the positive voltage of 450 V was applied. However, it decreased rapidly, and after 6 min, the emission current from pure CeO_2 was the highest in these three cerium oxides. This result indicates the possibility that the emission current from an oxide is not affected solely by the change in its work function. Another possibility is that the electron state near the surface is different from that inside the bulk. Yashiro et al. [12] reported the results of oxygen isotope diffusion experiments of $Ce_{0.992}Nb_{0.008}O_2$, and pointed out that the composition of $Ce_{0.992}Nb_{0.008}O_2$ near the surface is different slightly from that inside the bulk. That is to say, there is a possibility that the work function of the surface is not as expected from the bulk composition.

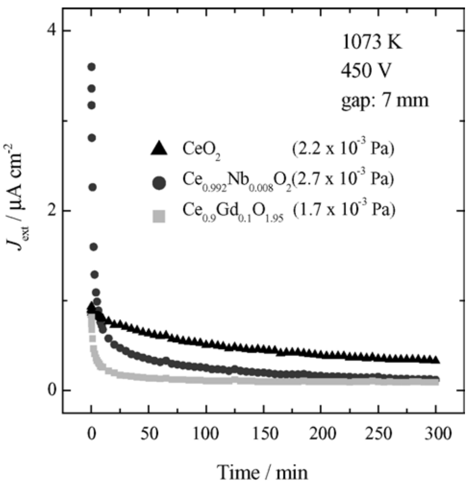

Fig. 7. Comparison of emission currents from donor-doped CeO_2, acceptor-doped CeO_2 and pure CeO_2.

4. Conclusion

Oxygen ion emission characteristics of CeO_2 were studied under electric field at elevated temperatures in vacuum. It was found that the emission current increases with temperature and decreases with the passage of time in analogy with the case of the negative and positive charge emission from YSZ and other oxides. The negative ions emitted from CeO_2 was assigned to negative oxygen ions (O^-) by mass spectrometry. However, the ratio of O^- ion to the total negative charges emitted from CeO_2 was not revealed because the mass spectrum of thermal electrons was not obtained in this work. It is necessary to measure the ratio of O^- ions to total negative ions and electrons emitted. It was also found that the emission current increases as applied voltage increases. The dependence of the emission current on the applied voltage did not follow Schottky effect model in some cases. The emission current from CeO_2 was higher than that from YSZ and C12A7 in low voltage region. The effect of donor and acceptor doping on emission characteristics of CeO_2 was also tested using $Ce_{0.992}Nb_{0.008}O_2$ and $Ce_{0.9}Gd_{0.1}O_{1.95}$. The enhancement of emission current was not observed except for the initial values obtained with $Ce_{0.992}Nb_{0.008}O_2$. This result indicates two possibilities; one is that emission current from oxides may be little affected by the change of work function, and another is that the work function near surface is not same as that of the bulk.

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