Journal of Catalysis **209,** 256–259 (2002)
doi:10.1006/jcat.2002.3541

RESEARCH NOTE

Emissions of O⁻ Radical Anions and Electrons from Silver on a Solid Electrolyte

Yoshifumi Torimoto,*,[1] Masateru Nishioka,† and Masayoshi Sadakata†

Production and Engineering Department, Kao Company, 640 Wakayama, Japan; and †Department of Chemical System Engineering, Faculty of Engineering, The University of Tokyo, 113 Tokyo, Japan

Received June 21, 2001; revised October 24, 2001; accepted January 3, 2002

The emissions of O^- radical anions and electrons from a silver electrode on a solid electrolyte, yttria-stabilized zirconia (YSZ) or a quartz glass, have been observed using a quadrupole mass spectrometer. A simple experimental apparatus was designed to incorporate a gap between a silver electrode on a YSZ anode and a platinum space electrode. By applying a DC voltage across the gap, O^- radical anions and electrons were observed. The results of Arrhenius plots with respect to O^- show that the value of activation energy E_d for O^- dissociation from a silver electrode on YSZ is approximately 91.5–142.3 kJ/mol with respect to different electric fields. These values are considerably lower than the bonding energy between silver and oxygen atoms (4.2 eV). It is suggested that the change in the activation energy of O^- desorption with an electric field is due to the change of surface coverage of O^- on silver and O^- is correlated with backspillover oxygen. © 2002 Elsevier Science (USA)

Key Words: **solid electrolyte; YSZ; O^- anion radical; activation energy; electric field.**

1. INTRODUCTION

Earlier papers (2–4) have reported on a simple technique for extracting the oxygen anion radical (O^-) from a gold anode on Yttria-stabilized zirconia (YSZ) by applying a low electric field; this electric field might decrease the activation energy of O^- desorption from the YSZ anode. In the present work, silver is used for the anode of YSZ instead of gold because a wealth of literature exists on the silver–oxygen interaction.

Kondarides and Verykios (5) reported the existence of three adsorbed oxygen species on Ag catalysts using temperature-programmed desorption methods. A weakly adsorbed species is related to the 44.1 kJ/mol adsorption process, which is found to desorb below 150°C. An almost nonactivated process belonging to atomic oxygen is found at 285°C. The highly activated oxygen having 100.8 kJ/mol desorption energy is observed above 400°C. This species is suggested to be subsurface oxygen that is thought to play a role in ethylene epoxidation and combustion chemistry.

The role of subsurface oxygen in the oxidation of silver was confirmed by Schlogl and coworkers (6). It is found that the activation energy for oxidative coupling of methane over silver is 138 kJ/mol and the activation energy for oxygen diffusion in silver bulk is nearly 140 kJ/mol. This correlation suggests that oxidative coupling of methane is limited by the formation of subsurface oxygen via surface segregation of bulk dissolved oxygen.

The electronic structure calculation of atomic oxygen on Ag(110) and the subsequent reaction of this chemisorbed oxygen with ethylene have been performed by van den Hoek *et al.* (7). Their calculations show that the presence of subsurface oxygen reduces the bond energy between silver and adsorbed oxygen and causes the epoxidation reaction to occur easily.

In order to change the bond energy of subsurface oxygen and silver practically, Vayenas and coworkers (1, 8, 9) suggest that solid electrolytes can be used as active catalyst supports to alter the chemisorptive and catalytic properties of metals. They used a porous silver film on YSZ for investigation of methanol dehydrogenation and found that the reaction rate with the pumping of oxygen from YSZ was increased. They explained that the observed phenomena could be interpreted as being due to a decrease in the strength of chemisorptive bonds, because the work function was increased on the metal due to the formation of a double layer by oxygen ions which were transferred from YSZ to the metal electrode through three phase boundaries. They call these oxygen ions backspillover ions.

However there are numerous studies on activated oxygen, such as subsurface oxygen on silver; the role of oxygen has not been clearly understood because of complex reactions on the metal surface.

In the present work, we attempt to dissociate activated oxygen from a silver surface by applying a low DC voltage in order to produce selectively activated oxygen in a gas

---

[1] To whom correspondence should be addressed. Fax: 0088-734-26-8979. E-mail: 127795@kastanet.kao.co.jp.

0021-9517/02 $35.00

phase. We found a continuous and selective emission of an oxygen radical anion (O$^-$) from the silver surface on a solid electrolyte just by incorporating a gap between the silver on the solid electrolyte and a space electrode and by applying a DC voltage.

2. EXPERIMENT

A simple experimental apparatus incorporating a gap between the silver anode on YSZ or a quartz glass and an external platinum electrode was designed and constructed. A DC electric source was provided with the positive terminal connected to the external electrode, and the silver anode was connected to the ground level so that a negatively charged species could be easily dissociated from the silver on the YSZ anode. The configuration of the experimental apparatus used to measure the negatively charged species from silver is shown in Fig. 1. The negatively charged species were identified using the MSQ-200, which is capable of measuring mass numbers up to 200. Ions with a particular mass were separated using the quadrupole mass filter and detected using a secondary electron multiplier (SEM, MURATA Seisakusho, CERATRON). The multiplication factor of SEM is 10^6–10^8. The ion pulse signals were introduced into an optical-fiber-coupled isolation amplifier (SONY Tektronix A69T06) so that the high positive voltage required for the SEM to measure the negatively charged species could be connected to the ground-level voltage. The pulses were sent to a digital oscilloscope (SONY Tektronix TDS744A) and a triggering system was used to distinguish the ion pulses from noise. The number of ion pulses were counted using a frequency counter (IWATSU SC7201) and the data of frequency with respect to mass number were saved in computer memory.

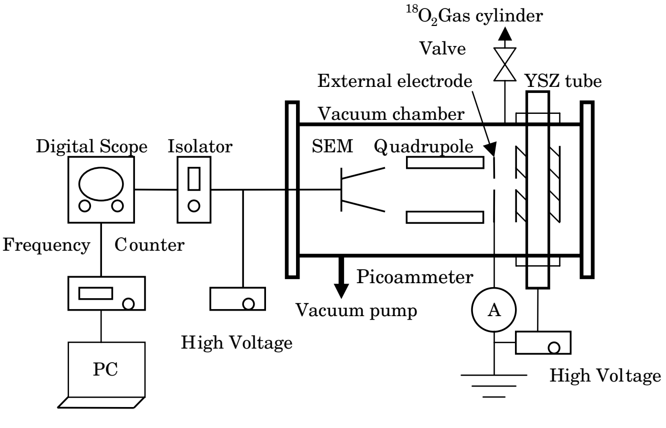

FIG. 1. The configuration of the experimental apparatus used to measure the negatively charged species from silver.

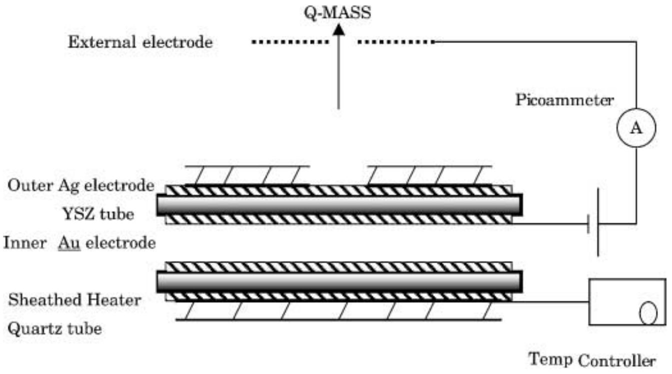

FIG. 2. The arrangement of applying voltage for collection of negatively charged species.

The YSZ is a solid electrolyte in which O^{2-} can be formed by the dissociative chemisorption of O_2 at the cathode and transferred to the anode via the oxygen lattice defects in the YSZ. A cylindrical YSZ tube was used for the experiment because of the convenience of handling and it was inserted into a high vacuum chamber, which is sealed at two gage ports. The YSZ tube had an inner diameter of 13 mm, an outer diameter of 17 mm, and a length of 300 mm. Silver electrodes of 1-μm thickness were pasted on the outside of the YSZ tube (Ag electrode). The inside of the YSZ tube was coated with a gold electrode (Au electrode). The inner surface was exposed to air in order to supply O_2 to the inner electrode. The outer surface of the YSZ tube was used to generate a negatively charged species in the gas phase.

A platinum space electrode (Pt electrode) with a 5-mm-diameter hole at the center to allow the passage of negatively charged species was positioned at a distance of 15 mm from the anode surface of the YSZ tube. To heat the YSZ tube, a sheathed coil heater inside a quartz tube was used. A DC-regulated electric source was used to apply a DC voltage between the Pt electrode and the Au electrode on the inner surface of the YSZ tube. The electric current between the two electrodes was measured using a picoammeter (KEITHLEY 486). The arrangement for voltage application for the collection of negatively charged species is shown in Fig. 2.

Before increasing the temperature, the pressure in the system was reduced to 10^{-4} Pa. A voltage of 200 V was applied between the Au and Pt electrodes in order to determine the leakage current. No leakage current was observed.

After increasing the temperature of YSZ in the range of 748–798 K, a DC voltage varying from 200 to 300 V was again applied between the Au and Pt electrodes using the DC power source. A positive potential of 4 kV was applied to the SEM and the mass number was scanned. Thereafter, pulses generated from the SEM were observed using a pulse counting system consisting of a digital oscilloscope and a frequency counter.

In order to investigate the mechanism of desorption of negatively charged species, a quartz tube coated with silver only on the outside of tube was used instead of a YSZ tube.

A DC voltage was applied between the Ag electrode of the quartz tube and the Pt electrode. The measurement treatment of negative species from silver was the same as mentioned above.

According to the previous studies, two possible mechanisms are suggested for O^- formation from an oxygen molecule. The first one is the attachment of an electron to O_2 in the vacuum chamber and the other is the desorption from a low-work-function metal surface (11, 12). In order to examine the probabilities of the above two mechanisms, an O_2 isotope ($^{18}O_2$) was introduced into the vacuum chamber from a $^{18}O_2$ gas cylinder (Nippon Sanso Co.) using a leakage valve (shown in Fig. 1) where an electron and O^- from the YSZ–Ag system were observed. There were no signals related to the species of $^{18}O_2$ from the observation of the quadrupole mass spectrometer. This means that the observed negative species (an electron and O^-) in this experiment are emitted from the surface of the silver anode on YSZ.

3. RESULTS AND DISCUSSION

3.1. Measurement of Mass Number for Negatively Charged Species

The mass number of negatively charged species from a silver anode on YSZ and a quartz tube was measured using the above system. When the temperature exceeded 683 K, the production of negatively charged species increased significantly. The obtained mass spectrum from the YSZ system at 748 K on applying 200 V is shown in Fig. 3. In the figure, it should be noted that only the signals corresponding to mass numbers of electrons and O^- are observed. The signals from 1 to 5 are attributed to the electrons which could not be separated using a quadrupole mass filter because of their high velocity. The mass signals from 14 to 16 correspond to the oxygen radical anion (O^-). There are no signals for the superoxide (O_2^-) and O^{2-} ions. Using a quartz tube coated with a silver electrode exposed to air, a similar experimental treatment of the YSZ was implemented and the signals of electrons and O^- were observed continuously for several hours. After the signals were extinguished, the tube was exposed to air for several hours at room temperature and again the same experiments were implemented to observe the signals.

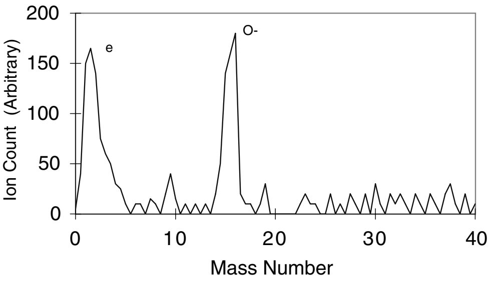

FIG. 3. The obtained mass spectrum at 748 K with application of 200 V.

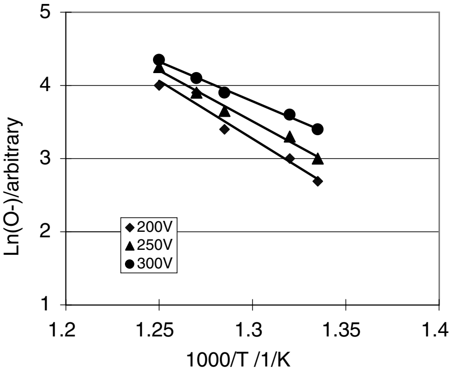

FIG. 4. The Arrhenius plot of Ag–YSZ with respect to each electric field.

3.2. Effect of Temperature and Electric Field on O^- Emission

The effects of temperature and electric field on O^- ion pulses for YSZ and a quartz system were examined. Ion pulses of O^- were measured for different temperatures and different electric fields. The temperature was varied over the range 735–798 K and the applied voltage was 200, 250, and 300 V for each temperature. The O^- ion pulses were counted by a frequency counter and the results showing the Arrhenius plot of YSZ and a quartz system with respect to each electric field are illustrated in Figs. 4 and 5, respectively. The least-squares line through the data plot of the YSZ system at each electric field leads to the values of activation energy E_d of 142.3, 121.3, and 91.5 kJ/mol. In contrast to the YSZ results, the activation energy for a quartz tube coated with silver is constant at 100 kJ/mol under different electric fields. These results reveal that the activation energy for O^- desorption (91.5–142.3 kJ/mol for the Ag–YSZ system and 100 kJ/mol for Ag–Quartz) is significantly lower than

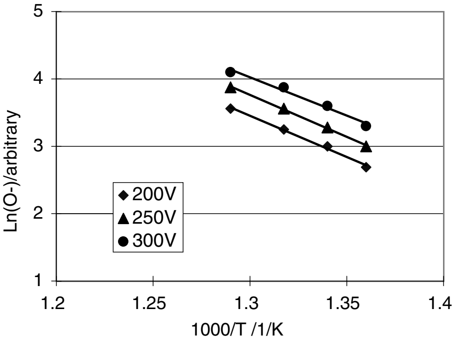

FIG. 5. The Arrhenius plot of the Ag–Quartz tube with respect to each electric field.

the work function of silver (4.3 eV) as well as the bonding energy between silver and oxygen (4.1 eV reported by van den Hoek and Baerends (10)). There are two possibilities for O$^-$ emission from a solid surface with low activation energy: subsurface oxygen and backspillover oxygen, as previously mentioned. The first is an oxygen atom under a metal surface. An adsorbed oxygen atom on the surface is diffused into the subsurface of metal at high temperature. There are several groups that report the existence of subsurface oxygen (5, 6, 10). The second is a migrated oxygen anion from a solid electrolyte, which is proposed by Vayenas and coworkers (1, 8, 9). This backspillover oxygen spreads over the catalytically active surface with pumping of oxygen from YSZ, which can be controlled by voltage between the Ag and gold (Au) electrodes, and alters its work function and catalytic properties.

Therefore it could be suggested that the O$^-$ from the quartz–Ag system might be subsurface oxygen because there is no solid electrolyte in this system. On the other hand O$^-$ from the YSZ–Ag system might be related to backspillover oxygen because it can be influenced by V/d, as Fig. 4 shows, while the subsurface oxygen can not be influenced by V/d, as Fig. 5 shows.

According to Vayenas' theory, the use of an external electrode and the increase in the electric field can increase the surface of a double layer formed by the backspillover oxygen, consequently increasing work function and as a result weakening the chemisorptive bond between O$^-$ and the metal, which decreases the activation energy in the case of the YSZ–Ag system. The decrease of activation energy due to the increase in the electric field can be explained more clearly by the following equations.

If the desorption rate of O$^-$ can be expressed by an Elovich-type equation, then

$$[\mathrm{O}^-] = a \times \exp(-E/\mathrm{RT}) \times \exp(\beta\theta). \qquad [1]$$

If the surface coverage can be proportional to the electric field V/d and can be in inverse proportion to temperature, the surface coverage can be expressed as $\theta = \beta \times V/d \times (1/T)$. Then,

$$[\mathrm{O}^-] = a \times \exp(-(E - bV/d)/\mathrm{RT}), \qquad [2]$$

where a and b are constants, V/d is the electric field, E is the activation energy, θ is surface coverage, and $[\mathrm{O}^-]$ is the number of O$^-$ ion pulses. Equation [2] is consistent with the equation obtained experimentally in the previous paper (3).

4. CONCLUSION

In the present work, the emission of O$^-$ and electrons from a silver electrode on the YSZ anode or a quartz glass have been observed using a quadrupole mass spectrometer. A simple experimental apparatus was designed to incorporate a gap between a silver electrode on a YSZ anode or quartz glass and a platinum space electrode. By applying a DC voltage across the gap, O$^-$ radical anions and electrons were observed. The results of the Arrhenius plot reveal that the values of activation energy E_d for O$^-$ dissociation from silver on YSZ are significantly lower than the work function of silver and also the bonding energy between silver and oxygen. These phenomena can be interpreted based on the following hypothesis. It can be assumed that the use of an external electrode can increase the work function and weaken the chemisorptive bond and also that the surface coverage can be increased by supplying oxygen from YSZ so as to decrease the activation energy. The observed O$^-$ emitted from the silver electrode on YSZ could be identical to the backspillover oxygen reported by Vayenas *et al.* The most interesting finding is that not only a high selectivity of O$^-$ and electrons from silver on a YSZ anode but also a low discharge voltage can be used to produce electrons and oxygen radical anions.

This is also a new finding because there are no reports, to our knowledge, concerning the desorption of O$^-$ from silver on a YSZ anode under a low electric field.

ACKNOWLEDGMENT

Financial support from the Japan Science and Technology Corporation is gratefully acknowledged.

REFERENCES

1. Vaynenas, C. G., Bebelis, S., Yentekakis, I. V., and Lintz, H. G., *Catal. Today* **11**, 3 (1992).
2. Torimoto, Y., Harano, A., Suda, T., and Sadakata, M., *Jpn. J. Appl. Phys.* **36**, L238 (1997).
3. Torimoto, Y., Shimada, K., Nishioka, M., and Sadakata, M., *J. Chem. Eng. Jpn.* **33**, 557 (2000).
4. Torimoto, Y., Shimada, K., Nishioka, T., and Sadakata, M., *J. Chem. Eng. Jpn.* **33**, 914 (2000).
5. Kondarides, D. I., and Verykios, X. E., *J. Catal.* **143**, 481 (1993).
6. Nagy, A. J., Mestl, G., and Schogl, R., *J. Catal.* **188**, 48 (1999).
7. van den Hoek, P. J., Baerends, E. J., and van Santen, R. A., *J. Phys. Chem.* **93**, 6469 (1989).
8. Stoukides, M., and Vayenas, C. G., *J. Catal.* **70**, 137 (1981).
9. Bebelis, S., and Vayenas, C. G., *J. Catal.* **138**, 570 (1992).
10. van den Hoek, P. J., and Baerends, E. J., *Surf. Sci.* **221**, L791 (1989).
11. Greber, T., *Chem. Phys. Lett.* **222**, 292 (1994).
12. Greber, T., Grobecker, R., Mongante, A., Boettcher, A., and Ertl, G., *Phys. Rev. Lett.* **70**, 1331 (1993).