ABSTRACT

The reaction mechanism of oxygen electrode has been studied by impedance spectroscopy in order to improve the performance of a solid oxide fuel cell. Reproducible impedance spectra was confirmed by using the improved cell, consisting of a thin YSZ disk and sintered platinum electrodes. The spectra measured for an O₂ / O₂ cell at 1173 K were composed of three depressed arcs at least. The partial pressure of oxygen influenced the impedance values. For two large semi-circles at frequencies less than 100k Hz, the time constants evaluated by complex nonlinear least squares fitting are independent of the partial pressure of oxygen. These results suggest no influence of the oxygen content on the reaction mechanism of oxygen reduction. Since the resistance of the semi-circle at frequencies between 300 and 100k Hz, however, increases with reducing the oxygen content, this arc corresponds to the charge transfer of an adsorbed oxygen atom.

INTRODUCTION

A ceramic fuel cell has been studied by many groups to improve the cell performance. One of the most important subject is to produce the stable electrode material. For this purpose we have to obtain the standard materials, even if those cannot be used for the practical cell. Moreover, the reaction mechanism should be analyzed for the oxygen reduction and the hydrogen oxidation.

In this study, we tried to improve the life time of the cell by using platinum electrodes and a thin YSZ disk, in which the reproducible electrochemical signals could be measured for a long time. The reaction mechanism of the oxygen reduction has been studied by impedance spectroscopy.

EXPERIMENTAL

The solid electrolyte used was a thin disk of 8 mol% yttria-stabilized zirconia (8YSZ), which was prepared by extraction method (1) from fine YSZ powder (Toso Company Ltd., TZ-8Y). The thickness of this disk was 0.25 mm. The thin 8YSZ disk of 25 mm diameter was supported by thick ring of 3 mol% YSZ, as
shown in Fig.1. An anode and a cathode were prepared by painting a fluxless platinum paste (Fukuda Foil Company). These electrodes were sintered at 1273 K for two hours under hydrogen atmosphere. The reference electrode was platinum wire attached on 3YSZ.

This monolithic type cell with current collector of platinum gauze (200 mesh) was pressed between two alumina tubes as shown in Fig.2. The platinum wire lead and the current collector supported by quartz tube was attached to each sintered platinum electrode by SUS spring. Gas tight sealing was provided by two Pyrex glass rings. The composition of gases was regulated by a mixing instrument (Kojima Seisakusho, GM-3A). The oxygen, argon and hydrogen gases used in this study were of high purity grade. To vary the partial pressure of oxygen in the cathode gas, the 4% oxygen gas diluted with argon was also used.

Impedance spectra were measured by galvanostatic method within the frequency range from 0.1 to 1 MHz by using a Solartron Instruments Model 1260 impedance/ gain-phase analyzer, a Model 1287 potentiostat, and a Toyo Technica CAP-1 electrochemical software. The impedance data were recorded and analyzed with a NEC Model PC-9801 personal computer. The amplitude of the sinusoidal signal was 10 μA for the most measurements. The dc bias current used in this study was less than 0.1 mA. The electrochemical signals were usually measured at temperatures between 973 K and 1173 K.

RESULTS AND DISCUSSION

Impedance Spectra of a H2/O2 Cell

A well-defined impedance spectrum could be measured with a H2/O2 cell. Figure 3 depicts typical spectra without dc bias measured at 973, 1073 and 1173 K. It was quite difficult to obtain the stable impedance spectra at 1273 K, because of the sintering of the platinum electrode. At temperatures lower than 1173 K, however, similar spectra were observed for several decades of hours, although the cell resistance gradually increased as shown in Fig.4. The increase in the impedance suggests that the platinum electrode is improper for the practical cell, but we can confirm that the life time of this electrode is long enough for the analysis of the electrode reactions.

Impedance Spectra of an O2/O2 Cell

In order to analyzes the reaction mechanism of the oxygen electrode, the impedance of an O2/O2 cell was studied. The typical impedance spectra without dc bias measured in this type cell are shown in Fig.5. The Nyquist plots indicate that our cell can be used to analyze the mechanism of the oxygen electrode, since the impedance varied little within several hours even at 1173 K. Comparing with the impedance spectra measured in the H2/O2 cell, our platinum electrode is quite stable at the cathode. That is, the increase of the impedance in Fig.4 was mainly caused by the degradation of the platinum electrode at the hydrogen anode.

The impedance spectrum of the oxygen electrode consists of three semi-circles at least. Since the impedance of a semi-circle measured with frequencies higher than 100 kHz is too small to analyze, we will discuss the other two arcs; the
depressed semi-circle measured at frequency range between 300 and 100kHz (arc-A) and the warped one (arc-B) at low frequencies less than 300Hz.

Reaction Mechanism of an Oxygen Electrode

To analyze the above two semi-circles, the effects of the partial pressure of oxygen were analyzed. As shown in Fig.6, the decrease in the oxygen pressure $P(O_2)$ induces the higher resistance, although the shape of the Nyquist plots varies little. To analyze the reaction mechanism, an equivalent circuit as shown in Fig.7 was assumed for the oxygen electrode. This consists of five components: the resistance of YSZ, the charge transfer and the mass transfer steps at both electrodes. The depressed arcs suggest that the constant-phase element (CPE) should be considered for the electrode reaction. The CPE is an empirical impedance function of the type,

$$Z_{PE} = A(j\omega)^{-\alpha}$$  \[1\]

which has proved of considerable value in data fitting. Here $A$ is a constant. The fractional parameter $\alpha$ varies from -1 to +1.

The impedance of each component was estimated by complex nonlinear least squares (CNLS) fitting (2). As shown in Fig.8, the curves obtained by CNLS fitting are in good agreement with measured impedance at all frequencies. From these curves, the resistance and time constant for each arc were evaluated as shown in Table 1. These parameters for the arc-B are independent of the oxygen content in the cathode gas. On the other hand, the resistance of arc-A observed at higher frequencies increases with reducing the oxygen content, whereas its time constant remains unchanged. From these results, the following mechanism could be assumed. The arc-A corresponds to the charge transfer reaction at the active site,

$$O(\text{active-site}) + 2e^- \rightarrow O_2$$  \[2\]

whereas the arc-B observed at lower frequencies corresponds to the mass transfer step of the adsorbed oxygen atom,

$$O_{\text{ad}} \rightarrow O(\text{active-site})$$  \[3\]

Further results are required to confirm the above mechanism. We are now studying the oxygen reaction by using another electrode material such as ruthenium as well as by different electrochemical measurements.

CONCLUSION

Reproducible impedance spectra could be obtained by improving the procedure of the cell components. The analysis of the impedance measured in the $O_2/O_2$ cell suggests that the reduction of oxygen occurs by three steps. Two of them correspond to the charge transfer step at the active site and one corresponds to the mass transfer of adsorbed oxygen atom.
REFERENCES

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2. J. R. Macdonald, Impedance Spectroscopy, pp.16-20, pp.180-182, John Wiley & Sons, New York (1987)

Table 1 Resistance and times constant for arc-A and arc-B by CNLS fitting.

| $P(\text{O}_2)$ / atm | arc-A $R/S^1$ | $\tau/s$ | arc-B $R/S^1$ | $\tau/s$ |
|-----------------------|---------------|----------|---------------|----------|
| 1.0                   | 155           | $1.1 \times 10^5$ | 243           | $2.3 \times 10^2$ |
| 0.45                  | 169           | $1.3 \times 10^5$ | 231           | $2.0 \times 10^2$ |
| 0.31                  | 199           | $2.5 \times 10^5$ | 241           | $2.8 \times 10^2$ |

Fig. 1 Monolithic solid-oxide fuel cell components
Fig. 2 Schematic representation of an experimental cell

Fig. 3 Typical Nyquist plots measured for a H$_2$ / O$_2$ cell
Fig. 4 Variation of the impedance spectra of a H₂/O₂ cell with elapsed time

Fig. 5 Impedance spectra measured for an O₂/O₂ cell at 1173 K
Fig. 6 Effects of oxygen partial pressure on the impedance of an O₂/O₂ cell at 1173 K

Fig. 7 Equivalent circuit considered for an O₂/O₂ cell

R_{YSZ}: resistance of YSZ,
R_{ct}: resistance for charge transfer
R_{mt}: resistance for mass transfer

Fig. 8 Impedance curves by CNLS fitting.