CHARACTERIZATION OF NiO/YSZ ELECTRODE BY TEMPERATURE-PROGRAMMED REDUCTION

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ABSTRACT

Temperature-programmed reduction (TPR) was conducted for characterization of nickel oxide in NiO/YSZ electrode for SOFC. Nickel oxide in NiO/YSZ sintered at 1400°C was more reducible than that sintered at 1000°C. Electrical conductivity of the former was lower than that of the latter because of nickel aggregation. Consequently, reducibility of NiO measured by TPR was related with the ease of nickel aggregation and electrical conductivity of NiO/YSZ. This suggests that some interaction between NiO and YSZ and its extent related to the ease of nickel aggregation. In order to prevent nickel aggregation in Ni/YSZ cermet electrode, it is important that the interaction be increased, and TPR is one of the effective methods to evaluate the extent of the interaction.

1. INTRODUCTION

Fuel electrode materials for solid oxide fuel cells (SOFCs) require the following properties; (a) high electrical conductivity, (b) high catalytic activity to promote fuel and oxide ions to react, (c) physical and chemical stability under reducing atmosphere at high temperature, (d) thermal expansion match to yttria stabilized zirconia (YSZ) electrolyte to prevent flaking off the electrolyte. Ni/YSZ cerments have been generally used as fuel electrode materials because they have almost all required properties. However, activation overvoltage and concentration overvoltage of Ni/YSZ cermet electrode increase with decreasing three-phase boundary areas by the sintering of nickel because the operation temperature of SOFC is about 1000°C. This deterioration of the electrode properties is one of the main problems of SOFC. Thus, prevention of nickel aggregation and improvement of durability in SOFC are important subjects.

For evaluating the degree of nickel aggregation, there are well-known direct observation methods, i.e. scanning electron microscopy (SEM) and electron probe microanalyser (EPMA), and indirect methods, i.e. measurement of pore distribution and specific surface area. In this paper, in addition to these methods, temperature-programmed reduction (TPR) method, generally used in evaluation of catalysts, has been conducted for characterization of NiO/YSZ to observe reducibility into Ni/YSZ. The relationship between the reducibility of NiO and the ease of nickel aggregation are reported.
2. EXPERIMENTAL

Sample preparation

NiO/YSZ powder was prepared either by calcination of co-precipitated mixture of the hydroxides (wet process) or mixing of the primary oxide powders (dry process). In the wet process, Ni(NO₃)₂, ZrO(NO₃)₂ (Wako Pure Chemical), and Y(NO₃)₃ (Mitsuwa Chemical) were used as starting materials. X-ray diffraction powder analysis revealed that the powder thus prepared was the mixture of nickel oxide and 8mol% yttria doped zirconia. In the dry process, NiO powder (Wako Pure Chemical) and YSZ powder (Tosoh, TZ-8Y) were used.

NiO/YSZ powder was pressed into pellets of 20mm in diameter and 1.5mm in thickness under 11.7MPa and sintered in air between 1000°C and 1400°C for five hours. Samples for the measurement of electrical conductivity were obtained by cutting pellets into rectangular bars.

Characterization

Electrical conductivity was measured using the four or two probe dc techniques during heating at 500°C to 1000°C under atmosphere of H₂/N₂=3/7 mixed gases. The degree of aggregation of nickel was evaluated by observing the cross-section of sintered and reduced compacts with SEM and EPMA (Shimadzu, EPM-810Q).

TPR measurement

A schematic diagram of the TPR apparatus is shown in figure 1. The samples were held between two quartz wool plugs and packed in a quartz reactor in an oven. The powder sample was packed directly, but sintered compacts were ground to powder with an agate mortar before measurement. The sample was reduced with a reducing gas (H₂/Ar=3/7) at a constant heating rate of 10°C/min from room temperature to 1000°C, and kept at 1000°C for 30min. Hydrogen through a trap of molecular sieves for H₂O was detected by thermal conductivity detector (TCD), and H₂ consumption was monitored by recording TCD signals.

3. RESULTS AND DISCUSSION

Electrical conductivity

Electrical conductivity of NiO/YSZ=3/7 (weight ratio) bars obtained from the wet process powder sintered at different temperatures is shown in figure 2. The bars sintered at 1000°C and 1200°C had relatively high conductivity up to 700°C, but suddenly decreased over 800°C. On the contrary, the bar sintered at 1400°C had lower conductivity at 700°C, and exhibited a conduction like a semiconductor, that is, conductivity increased with increasing temperature. Thus the conductivity behavior was different, when the sintering temperature was different.
In order to investigate the cause of these results, we made SEM and EPMA analyses on the pellet sintered at 1000°C. Figure 3 shows the SEM images and the elemental distribution of nickel of the sample. The top photograph is of one of the NiO/YSZ pellets before reduction, the middle is of one of the Ni/YSZ pellets after reduction at 700°C at which temperature electrical conductivity was relatively high, and the bottom is of one of Ni/YSZ pellets after reduction at 1000°C at which temperature the conductivity became low. Aggregation of nickel was not observed in the pellet before reduction and some aggregates were observed when reduced at 700°C. However, it is shown that more aggregation of nickel occurred at 1000°C. Figure 4 shows the SEM image and the elemental distribution of nickel of the sintered pellet at 1400°C. The upper photograph is the one before reduction and the lower is after reduction at 1000°C. Aggregation of nickel was observed in pellets both before and after reduction. In these results, because precursor of nickel aggregates was not produced in the pellet sintered at 1000°C, the conductivity of the pellet was high at lower measurement temperature. On the contrary, since precursor of nickel aggregates was produced in the pellet sintered at 1000°C, the conductivity of this pellet was low at lower measurement temperature. In the pellet sintered at 1000°C, however, the conductivity seems to decrease with sintering over 800°C. It is well-known that metal atoms move and aggregate easily over the absolute temperature of about two thirds of its melting point. Therefore, the result that nickel aggregates over 800°C (1073K) is reasonable, because the melting point of nickel is 1455°C (1728K).

**TPR measurement**

In order to discuss the relation between conductivity and sintering temperature more carefully, reducibility of nickel oxide in the pellets sintered at different temperatures was evaluated by TPR.

Figure 5 shows TPR patterns of the powder obtained by the wet process and the crushed powder after sintering (NiO/YSZ=3/7). The vertical axis shows H2 consumption and the peak temperature shows the reduction temperature. From the figure, it is clear that the TPR patterns of each powder are different. Reducibility of NiO itself was also measured. The result is shown in figure 6. The NiO powder was reduced at ca. 300°C. These differences of the TPR patterns can be explained by so called "SMSI" (Strong Metal Support Interaction) effect in the field of catalysis (1). That is, the TPR peak of supported metal oxide is shifted to higher temperature than that of non-supported one because of an interaction between metal and support. Thus, it may be considered that the peak at about 300°C is the reduction peak of bulky nickel oxide without interaction, and that the peak above 350°C is the one with the interaction.

From these results of the electrical conductivity, SEM/EPMA, and TPR, our discussion follows. The TPR peak of nickel oxide in NiO/YSZ raw powder was shifted to higher temperature than pure NiO because of "SMSI". The peak was shifted to higher temperature by sintering at 1000°C because the interaction between NiO and YSZ became stronger. But by sintering at 1200°C, aggregation force of NiO became stronger, so bulky NiO was produced. Thus, the peak of 300°C appeared in this TPR pattern. Moreover, by sintering at 1400°C, aggregation force of NiO became stronger than the interaction, so the TPR pattern resembled that of the NiO powder. This reducibility, in other words, the degree of interaction between NiO and YSZ corresponds to the electrical conductivity.
Figure 7 shows TPR patterns of NiO/YSZ=5/5 (weight ratio) powder obtained by the wet process. It is clear that a similar relationship between reducibility and sintered temperature to the case of NiO/YSZ=3/7 powder was found. Figure 8 shows TPR patterns of NiO/YSZ=5/5 powder prepared by the dry process. The pattern was different from the one for the NiO powder. In this result, it is considered that the interaction occurs by simply mixing NiO with YSZ. It was reported that the extent of such interaction was determined by the kind of starting materials, the process, the calcining temperature, etc. (2). Therefore, it is suggested that the same may be said in the case of NiO/YSZ.

Consequently, an interaction between NiO and YSZ existed, and that its extent was related to the degree of the ease of nickel aggregation. Therefore, in order to prevent nickel in Ni/YSZ from sintering, it may be important that the interaction be increased. TPR is one of the effective methods to evaluate the extent of the interaction.

4. CONCLUSIONS

Temperature-programmed reduction (TPR) method was conducted for NiO/YSZ cermet electrode. Different sintering temperatures and different powder preparation methods gave different TPR patterns. These differences are dependent on the interaction between NiO and YSZ like that of catalyst metal and support oxide. It is considered that interaction should be increased to prevent nickel from sintering, and that TPR method is effective to evaluate the extent of the interaction.

ACKNOWLEDGMENTS

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Figure 1. Scheme of the TPR apparatus.

Figure 2. Electrical conductivity of NiO/YSZ=3/7 as a function of temperature (by 2 probe dc method).
Figure 3. SEM and Ni distribution of the cross-section of NiO/YSZ sintered at 1000°C (a) before reduction (b) after reduction at 700°C (c) after reduction at 1000°C
Figure 4. SEM and Ni distribution of the cross section of NiO/YSZ sintered at 1400°C (a) before reduction (b) after reduction at 1000°C
Figure 5. TPR patterns of NiO/YSZ=3/7 (weight ratio)

Figure 6. TPR pattern of NiO reagent
Figure 7. TPR patterns of NiO/YSZ=5/5 (weight ratio)

Figure 8. TPR patterns of NiO/YSZ=5/5 (weight ratio) powder by dry process.