IMPROVEMENT OF ANODE PERFORMANCE
BY YSZ SURFACE MODIFICATION

H. Miyamoto, M. Sumi, K. Mori, and I. Koshiro
Takasago R & D Center, Mitsubishi Heavy Industries, Ltd.
2-1-1, Shinjima, Arai-cho, Takasago 676, Japan

F. Nanjo and M. Funatsu
Kobe Shipyard and Machinery Works, Mitsubishi Heavy Industries, Ltd.
1-1-1, Wadasaki, Hyogo-ku, Kobe 652, Japan

ABSTRACT

Yttria stabilized zirconia (YSZ) with a thin modified layer of a mixed ionic and electronic conductor on the anode side has been manufactured. Following modifiers were examined, 1) La0.25-Ce0.75, 2) Ce 3) Sm0.20-Ce0.80 4) Pr. We coated dense 8mol% YSZ with Ce or other solutions before manufacturing the anode. The coated YSZ was fired for 10 hours in air at 1400 or 1500°C. Ni/YSZ cermet electrode was manufactured by slurry coating method and fired again at elevated temperature.

All doped YSZ samples except Pr doped which had negative effects on the cell performance, showed remarkable decrease in IR drop, but polarization characteristics did not change. The doped cells also showed long term stability.

1. INTRODUCTION

SOFCs are attracting attention because of their high power density and energy efficiency. Long term stability of electrodes is essential for SOFC’s use. Ni/YSZ cermet anode sometimes has insufficient stability due to variation in microstructure at YSZ-anode interface. This causes deterioration of the anode.

The surface modified YSZs, which are expected to be mixed conductive, were manufactured to overcome the instability and to obtain better performance.

2. BACKGROUND

Several researchers (1,2,3) have reported that an addition of mixed conductors to anode can lead to better anode performance. Takahashi and Iwahara (1) made SOFC electrodes of (CeO2)0.6(LaO1.5)0.4 and (CeO2)0.6(YO1.5)0.4 on (ZrO2)0.85(CaO)0.15 or (ZrO2)0.82(YO1.5)0.18 electrolyte.

Kleitz et al. (2) used two kinds of CeO2-doped YSZ. A CeO2-YSZ composite was made by mixing CeO2 powder with the 9mol% YSZ powder before sintering. The other material, CeO2-covered YSZ, was made by spraying CeO2 slurry on porous YSZ. They applied these YSZ samples to the cathode in steam electrolysis to improve cathodic reaction. Isenberg et al. (3) made Ni/YSZ cermet cathode which
was impregnated with lanthanum-doped cerium oxide by thermal decomposition of nitrate salts. They found that the modified cathode was superior for the CO₂ reduction process in life support systems of space missions.

Recently, these surface modification techniques are attracting attention in the SOFC field because of their higher internal reforming potential.

3. SURFACE MODIFICATION FOR YSZ

We modified surface layer of YSZ to the mixed ionic and electronic conductive material by impregnating certain cations into YSZ. The distinctive feature of the treatment is that neither the bulk YSZ nor the bulk electrode is changed but only the surface of YSZ is modified.

The details of the treatment were as follows:
- Solid Electrolyte: 8mol% YSZ, 23mm in diameter, 250μm in thickness,
- Doping Materials: Saturated nitrate solutions of 1) La₀.₂₅ Ce₀.₇₅, 2) Ce, 3) Sm₀.₅ Ce₀.₅, 4) Pr,
- Sintering Temperature: 1400-1500°C, 10 hours or 24 hours.

Fig.1 shows SEM photograph of Ce-doped YSZ, where we can see slightly modified layer on the surface. Thin film X-ray diffraction patterns for non-doped YSZ, Ce-doped YSZ and CeO₂ powder are shown in Fig.2, Fig.3 and Fig.4 respectively.

Fig.5 shows an EPMA chart for Ce-doped YSZ, which shows Ce is doped over 10μm in depth. The modified YSZ was coated with NiO/YSZ cermet slurry and fired again to obtain anode. The effective area of the electrode was 10mm in diameter (0.785cm² in area).

4. ANODE PERFORMANCE

Polarization characteristics of these samples under SOFC conditions were measured in 100% hydrogen and air system at 1000°C. Fig.6 shows anodic polarization characteristics for Ni/YSZ anode on La-Ce-doped YSZ, while Fig.7 shows that of non-doped YSZ. Polarizations of three samples, La-Ce, Sm-Ce and Ce, showed only small changes compared with non-doped YSZ. But these three samples showed remarkable decrease in IR drop. On the contrary, Pr doped YSZ showed significant increase in IR drop.

Fig.8 shows AC impedance measurement results for Ni/YSZ anode on the La-Ce doped YSZ and non-doped YSZ. The measurement conditions were 1000°C, 4% hydrogen and 12% steam balanced with nitrogen. La-Ce-doped YSZ showed smaller arc compared with non-doped YSZ.

Fig.9 illustrates polarization and IR drop for La-Ce doped YSZ for 11 days.
There were no significant changes in polarization and IR drop.

5. DISCUSSION

As already mentioned, several researchers have reported on the addition of mixed conductors to anode or YSZ. In these cases, there is a possibility of an increase in IR drop. We made an attempt to modify only the surface of YSZ to prevent the increase in IR drop. From experimental results on Ce based dopants, we found decreases in IR drop. On the contrary, polarizations were not changed. Fig. 10 illustrates a hypothetical reaction model. Non-doped YSZ, the left-hand figure, allows the anodic reaction only at the 3 phase areas which are limited to the electrode particles-YSZ interface, while doped YSZs, the right-hand figure, allow reaction over the surface which decreases IR drop and activation polarization because of the increase in the effective area. The concentration polarization is not changed because the bulk Ni/YSZ cermet electrode morphology is not altered. Further experimental studies, including changes in gas concentration and porosity of Ni/YSZ electrode, are required to verify this hypothesis.

La-Ce, Sm-Ce and Ce gave almost the same effect, while Pr gave negative effect both on the electrode performance and on the endurance. The reason is not clear at the moment. Finally, we assume that Ce doped YSZs owe their stability to the solid solution of dopants in YSZ.

ACKNOWLEDGMENTS

The authors wish to gratefully acknowledge Prof. H. Iwahara of Nagoya Univ., for discussions and useful advice on this research.

REFERENCES

1. T. Takahashi and H. Iwahara, DENKI KAGAKU, 38, 509 (1970).
2. S. A. Hammou and M. Kleitz, “Advances in Ceramics,” 24, 819, Science and Technology of Zirconia III, The American Ceramic Society, Inc. (1988).
3. A. O. Isenberg and R. J. Cusick, “Carbon Dioxide Electrolysis with Solid Oxide Electrolyte Cells for Oxygen Recovery in Life Support Systems,” 18th Intersociety Conference on Environmental Systems (1988).
Fig. 1 Cross-sectional fracture surface of Ce-doped YSZ (doped at 1500°C, 24 hours)

Fig. 2 Thin film XRD pattern for YSZ

2θ

Co-Kα

CPS

5.00 10.00 20.00 30.00 40.00 50.00 60.00 70.00 80.00 85.00
Fig. 3 Thin film XRD pattern for Ce-doped YSZ (doped at 1500°C, 24 hours)

Fig. 4 XRD pattern for CeO₂
Fig. 5  EPMA for Ce-doped YSZ
(doped at 1500°C, 24 hours)
Fig. 6 Polarization and IR drop of Ni/YSZ anode on La-Ce-doped YSZ

Fig. 7 Polarization and IR drop of Ni/YSZ anode on non-doped YSZ
Fig. 8 AC impedance measurements for La-Ce-doped and non-doped YSZ

Fig. 9 Variations of polarization and IR drop for Ni/YSZ anode on La-Ce-doped YSZ
Non-doped YSZ

Surface modified YSZ

Fig. 10 Hypothetical reaction model at the anode