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XAFS study of local structure around metal atoms in solid electrolytes for solid oxide fuel cell prepared by spark plasma sintering

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Introduction

The 8 mol% yttria-stabilized zirconia (8YSZ) ceramics have been widely used as an electrolyte material for solid oxide fuel cells. We have studied aging effect of dense 8YSZ ceramics with different microstructures prepared by spark-plasma sintering (SPS) and conventional sintering (CS) using an electric furnace. The SPS ceramics consisting of submicrometer-grains showed relatively slow conductivity degradation with aging time compared with CS ceramics. Conductivity degradation was attributed to the increase in the bulk resistivity, which would be due to subtle structural changes in the 8YSZ unit cells. In this study we made XAFS analysis of the aged SPS and the CS 8YSZ ceramics.

Experimental

Local structures of the 8YSZ samples, which were aged at 1273 K in air up to 1000 hr, were examined by Zr K and Y K-XAFS analysis. Typically k^3-weighted EXAFS functions in the k-region of 2.5-15.0Å^{-1} for Zr K-EXAFS and 2.0-14.5Å^{-1} for Y K-EXAFS, respectively, were used for the calculation of radial structure functions.

Results and Discussion

Figs. 1 and 2 show the comparison of the radial structure functions obtained by Fourier transform of k^3-weighted Zr K and Y K-EXAFS for the 8YSZ raw material powder, the sintered 8YSZ by CS (broken line) and by SPS (solid line) and the samples after subsequent aging with different time, respectively.

Fig. 1 indicates that prominent broadening of the Zr-O peak is observed for both the CS and SPS samples after the sintering. And sudden sharpening of the Zr-O peak after aging is found for the CS sample, while significant change is not observed even after 1000hr aging for the SPS sample. This suggests that the local structure around the Zr atom at high temperature is 'frozen' by rapid cooling of the SPS process and that the local structure 'frozen' in a small domain does not change to thermally stable state so quickly because of kinetically restriction.

Fig. 2 indicates that prominent broadening of the Y-O peak is observed for both the CS and SPS samples after the sintering and that additional peak at around 2.6Å is observed for the CS sample. And significant sharpening of the Y-O peak is observed for both the CS and SPS samples with disappearance of the additional peak of the CS sample after aging. After 1000hr aging the Y-O peaks of the CS and SPS samples became very similar. This suggests that the phase separation would occur for the CS sample in high temperature sintering and the phase separation would disappear after long time aging. While the 'frozen' local structure by rapid cooling in the SPS process maintains after long time aging for the SPS sample as observed in the Zr-O local structure.

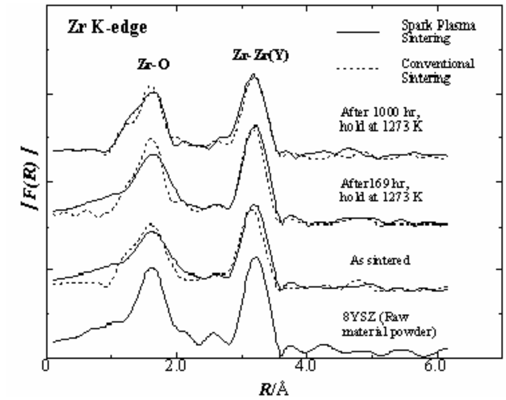

Fig. 1. The comparison of the radial structure functions derived from Zr K-EXAFS of the samples.

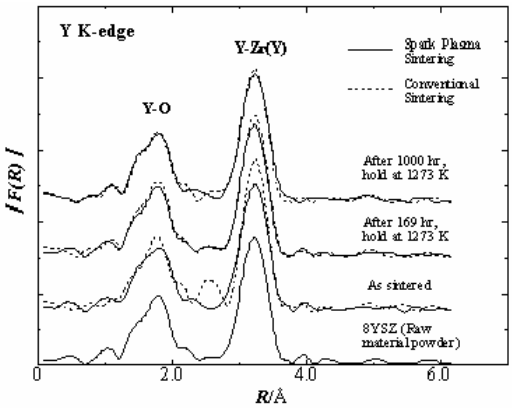

Fig. 2. The comparison of the radial structure functions derived from Y K-EXAFS of the samples.

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