Kinetic Studies on SOFC Air Electrode Prepared by Laser Ablation Method

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Introduction

In a recent trend, lower temperature operation of SOFC is attempted for solving various problems caused by high temperatures as 1000ºC. Since the reaction becomes more sluggish at lower temperatures, improving the electrode kinetics has more important meaning. Among all the internal cell resistances, the cathode overvoltage as oxygen molecules are reduced is significantly large. In order to decrease it, it is necessary to estimate the resistances at interfaces and bulks that oxygen species passes through, then to clarify the rate limiting step. Further, we need to know the controlling factor influencing these resistances from the viewpoint of materials property.

Interpretations of kinetic data need disintegration of the whole electrode reaction into successive single processes. However, discussion of individual each process is difficult, because of the complexity of real electrode that is porous and polycrystalline agglomerates of powders of different sizes. Electrodes are sometimes a mixture of several components. In these real electrodes, many reduction routes of oxygen molecules can be available and consequently correlating electrochemical behaviors and reaction model becomes difficult.

Simplifying and idealizing an electrode structure becomes a solution to these problems. A single crystal is apparently most appropriate in that sense, but not all the materials can be prepared in a single crystal. A thin film fabrication method, pulsed laser ablation, is a powerful tool to study the epitaxial growth of materials. If a single crystal is chosen as a substrate and the film growth rate is adjusted adequately low, the target material can grow epitaxially on the substrate. By using this method, we obtained highly oriented polycrystalline dense film which is close to a single crystal. When it is applied to electrode of SOFC cell, the route of oxygen molecule(O_2) in vapor phase transferred into oxide anion(O^{2-}) in the electrolyte can be described as follows; dissociative absorption onto electrode surface, insertion into electrode interior, diffusion inside the electrode bulk; passing the interface into the electrolyte.

In this way, we tried to apply such simple electrode prepared by ablation method. Single crystal YSZ plate was used as both deposition substrate and electrolyte. By combining this film and the impedance technique, the whole reduction process on the air electrode is tried to separate into basic processes. We discuss the effect of operating conditions such as oxygen partial pressure or temperature in order to specify each process. We also investigate the effect of difference in surface electrode structure controlled by epitaxial growth, as well as the effect of different kind of electrode materials.

Experimental

As the electrolyte of an electrochemical cell, 8mol%Y_2O_3 doped stabilized zirconia(8YSZ) was adopted. A single crystal flat plate of 8YSZ (10×10×0.5mm) which was commercially available, was cut and polished in order that three kind of crystal faces in miller indices as (100), (110), and (111), appear on the surface. This YSZ plate was used as the ablation substrate so that it can work as the electrolyte of a cell.

Two cathode materials, $La_{0.8}Sr_{0.2}MnO_3$(LSM) and $La_{0.8}Sr_{0.2}CoO_3$(LSC) have been deposited on different single crystalline 8YSZ substrates. The conditions of the laser ablation applied were as follows. The KrF excimer laser power was fixed at 300mJ and the pulse frequency was 10Hz. The substrate temperature was kept at 600ºC during the deposition. Oxygen gas was flowed into the chamber to show pressure of 0.025torr. The deposition was continued for 60 minutes. Two same films were always prepared at the same time, for one was provided for electrochemical analysis and another was used for structural characterization.

Result and Discussion

The characterizations of ablation films were done in terms of XRD and TEM observation. The out-of-plane diffraction patterns of LSC film electrodes deposited on YSZ(100), (110), and (111) substrates show one small peak, respectively. These peaks can be assigned to the LSC films and the single peak occurrence is considered as a result that each film has a special orientation.

A microstructure and film thickness of the ablation films was investigated by TEM. Figure 1 shows an example of the lattice images with the diffraction patterns of the LSC films. The pattern can be indexed by hexagonal unit cell and matches the thin film X-ray result. The film thickness was estimated to be about 30nm from the cross-sectional view. It is also described as a nonporous dense film, but grain boundaries are observed. The obtained film is concluded as an oriented pore-free polycrystalline film.

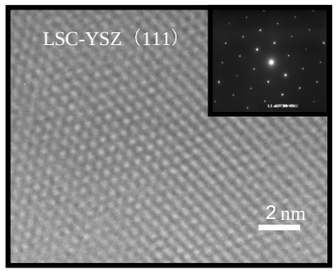

Fig. 1 TEM photo and electron diffraction pattern of the ablation film.

The impedance spectra were measured and fitted by the equivalent circuit model based on the reduction mechanism on our ablation film. Figure 2 is the data showing pO_2 dependency of the resistances in oxygen molecule adsorption process. The LSC electrodes show clear dependence on pO_2, while the LSM electrodes do not show much dependence on pO_2. The slope of the line connecting LSC resistance data is calculated to be about -1/2, which means that the rate determining step is the process from O_2 to $2O_{ad}$. On the other hand, the LSM lines showing little dependence on pO_2, are explained as charge transfer limiting. In both electrodes the film on YSZ(111) shows smaller resistance than (110). This may be attributed to the larger number of adsorbed oxygen molecules on the (111) electrode surface. More discussion will be given in the session.

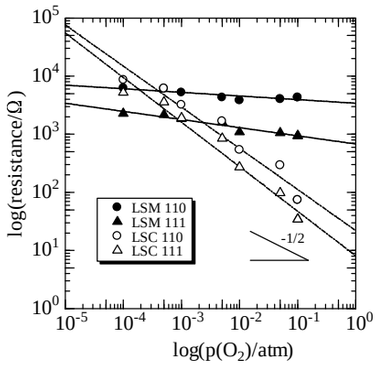

Fig. 2 pO_2 dependence of the resistances in surface reaction of LSM and LSC electrodes.