Preparation of SOFC Electrode Powders by the Aerosol Flow Pyrolysis method and Characteristics of the Electrodes

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1. Abstract

The aerosol flow pyrolysis (AFP) method has recently been applied to the research of various materials such as catalyst and superconductor because of the fine powders, narrow particle size distribution and high dispersibility. SOFC electrode powders were also prepared by the aerosol flow pyrolysis method in this study. Using this method, fine powders with smaller than 1 μm in mean particle size and narrow particle size distribution were obtained. The cathode (La(Sr)MnO₃/YSZ) formed by the AFP-powder showed excellent properties in cell performance. In a single cell test using these electrodes, 0.3 W/cm² power density was measured in an electrolyte of 1 mm thickness. In the anode (Ni/YSZ), the desirable morphology, that one Ni grain was surrounded with YSZ (8mol% Y₂O₃ stabilized ZrO₂) grains, for long term stability and high efficiency was obtained.

2. Introduction

In general, the cell voltage decreases with increasing the current in fuel cell. The voltage decrement contributes to (1) the ohmic resistance of cell constructive materials such as electrolyte, the electrodes and interconnector etc., and (2) the overvoltage occurred by electrochemical reactions in the electrodes. Therefore, it is necessary to decrease the ohmic resistance for cell materials and the overvoltage of the electrode.

The ohmic resistance of electrodes may depend on the inherent resistance of electrodes, the morphology, the homogeneity, and the contact resistance between electrode and interconnector. The overvoltage of electrode is related with electrochemical reaction that consists of the immigration of feed gas and product, and the exchange of charge on the three phase boundary. In general, the immigration of feed gas and product depend on the electrode morphology, and the exchange of charge depends on the length of the three phase boundary and the activity of the electrode materials. Therefore, the overall efficiency of SOFC is greatly controlled by the morphology of the electrode.
As SOFC is usually operated around 1000°C, the self-diffusion and inter-diffusion of each element of the cell materials are promoted exponentially with increasing temperature resulting in the morphology change of the electrode and deterioration of cell efficiency with operating time. For the purpose of long term stability, it is necessary to stabilize the morphology of the electrode by suppressing the diffusion of elements or by applying steric hindrance using dispersed particles.

In controlling of morphology of the electrodes, the properties of starting electrode powder are very important i.e. suitable particle size, narrow particle size distribution and uniform composition.

As powders prepared by the AFP-method have these excellent properties, it was applied to prepare SOFC electrode powders.

3. Aerosol Flow Pyrolysis Apparatus

Powder preparation technique using the AFP-method possesses the following potential advantages: (1) Chemical homogeneity is enhanced relative to the solid state reaction. (2) The obtained particles have a spherical shape of sub-micron and narrow particle size distribution. (3) The well-dispersed particles are also obtained for mixture systems.

The AFP-apparatus used in this study is shown in Fig. 1. The system consists of ultrasonic nebulizers, a reaction furnace with four-zones and a powder collector. In the AFP-apparatus, the solution is atomized into a reactor. In a reactor, the water in the aerosol droplets evaporates. Then, the aerosol droplets is condensed. The precipitated particles are to form micro particles by thermolysis over 400°C.

4. Materials

La(Sr)MnO₃/YSZ (LSM/YSZ) was applied to cathode materials. Until now, LSM/YSZ prepared by the drop-pyrolysis method (DP-method) have been developed in our laboratory. The cathode (LSM/YSZ) by DP-method has good long-term stability. However, as the electrode resistance is comparatively high, the cell performance was not excellent. The high resistance was caused by the presence of coarse LSM particles. The coarse particles may be formed by steep pyrolysis condition in DP-method. The AFP-method was applied to the preparation of LSM/YSZ powder in order to get a mild pyrolysis condition.

Ni/YSZ was applied to anode material. It is well accepted as SOFC anode
Westinghouse Corp. has demonstrated a Ni/YSZ anode with high cell performance and long term stability. The morphology of the anode showed that one Ni grain was surrounded by some YSZ grains. The morphology may increase the length of three phase boundary and the steric hindrance (for the Ni diffusion). Therefore, in order to get the similar morphology, AFP-method was applied to the preparation of Ni/YSZ powder.

5. Powder Preparation by AFP-method

5-1. LSM/YSZ

SEM micrographs of LSM/YSZ powder prepared by AFP- and DP-method are shown in Fig.2. Results of particle size distribution measured by a laser diffraction and scattering is shown in Fig.3. Mean particle size of the powder prepared by AFP-method is about 1 \mu m and the particle size distribution is narrow. As shown in Fig.2, the particles were solid and each particle consisted of the primary particles smaller than 60 nm. The AFP powder had a crystal structure of both LaMnO$_3$ and 8 mol% YSZ from the result of X-ray diffraction pattern. These results suggest that LSM and 8 mol% YSZ particles are well dispersed.

5-2. Ni/YSZ

SEM micrographs of NiO/YSZ powder prepared by DP- and AFP-method are shown in Fig.4. NiO/YSZ powder prepared by the DP-method has large NiO particles. The powder prepared by AFP-method does not have large NiO particles, and the one particle is the mixture of YSZ and NiO particles partially surrounded by YSZ particles. Result of particle size distribution is the same as LSM/YSZ.

6. Electrode Performance

6-1. Experimental method of electrode performance measurement

The electrode powders were printed on YSZ pellets (TOSOH TZ-8Y, 13 mm \phi, 1 mmt, effective electrode area: 0.28 cm$^2$). After sintering these samples between 1200°C to 1400°C in air, a reference electrode was wound around the pellet with Pt-wire and Pt-paste. The electrode performance was evaluated by means of polarization characteristic in the cell test. The electrode polarizations, which consist of electrochemical overvoltage (\eta) and ohmic resistance (IR), were measured by current interruption technique at 1000°C using a Rigaku ion transport number measurement apparatus. Results from AFP-method were compared with those of formed by the DP-method.
6-2. Cathode

Polarization characteristics of cathode (LSM/YSZ) are shown in Fig. 5. Polarization of the cathode formed by AFP-powder, compared with that by the DP-powder, was improved, so that the polarization (\( \eta \) and \( IR \)) was 20 mV at 200 mA/cm\(^2\), which is about a quarter of that by the DP-powder.

SEM micrographs of the electrodes after cell test are shown in Fig. 6. In the cathode (LSM/YSZ) morphology formed by the DP-powder, coarse LSM grains were observed. But in the cathode (LSM/YSZ) morphology formed by the AFP-powder, the coarse LSM grains were not observed. The cathode (LSM/YSZ) morphology by AFP-powder was more uniform than that by the DP-powder. Furthermore a good connection between each grains were observed.

The microstructure observations indicate that (1) mild pyrolysis condition prevents the growth of LSM particles in the powder and (2) sintering of LSM grains is prevented due to high dispersibility of YSZ and LSM.

The microstructure observations and the electrode performance indicate (1) that a high dispersibility of YSZ and LSM contributes to the increase of the length of three phase boundary and (2) that a good connection between grains contributes to the decrease of the ohmic resistance.

Power density curve as a function of current density is shown in Fig. 7. Power density using a cathode formed by the DP-powder was maximum 0.24 W/cm\(^2\) at 500 mA/cm\(^2\). Using a cathode formed by the AFP-powder, 0.3 W/cm\(^2\) was obtained at the same current density and the power density showed a tendency to increase further.

6-3. Anode

Polarization characteristics of an anode (Ni/YSZ) is shown in Fig. 8. \( \eta \) of an anode formed by the AFP-powder was improved in comparison with that formed by the DP-powder. SEM micrographs of the anode after cell test is shown in Fig. 9. One Ni grain is surrounded by YSZ grains. Furthermore, coarse Ni grains, which were observed in the anode formed by the DP-powder, were not observed in the anode formed by the AFP-powder.

6-4 A Long Term Stability (anode)

Time dependence of the anode (Ni/YSZ) polarization are shown in Fig. 10. The anode (Ni/YSZ) formed by AFP-powder, compared with the anode (Ni/YSZ) formed
by DP-powder, has good long term stability. The good stability of AFP-Ni/YSZ may be attributed to the morphology that one Ni grain is surrounded by YSZ grains.

7. Conclusions

_Cathode: La(Sr)MnO₃/YSZ_

(1) Spherical secondary particle containing dispersed fine primary particles of La(Sr)MnO₃ and YSZ (smaller than 60 nm) was obtained by AFP-method.

(2) The cathode polarization (γ and IR) were improved by high dispersibility of La(Sr)MnO₃ and YSZ and by good connection between each grains.

_Anode: Ni/YSZ_

(1) The anode (Ni/YSZ) formed by the AFP-powder has the morphology that one Ni grain is surrounded with YSZ grains. The anode is excellent in long term stability.

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Fig. 1 AFP-apparatus used in this study

Fig. 2 SEM micrographs of LSM/YSZ powders prepared by the AFP- and the DP-method
(a) DP-method (b)(c) AFP-method
Fig. 3  Particle size distribution of powders prepared by DP and AFP

Fig. 4 SEM micrographs of NiO/YSZ powder prepared by DP and AFP
Fig. 5  Polarization characteristic of LSM/YSZ by DP and AFP

at 200mA/cm²

Fig. 6  SEM micrographs LSM/YSZ by DP and AFP after cell test

(Cell Test Conditions: cell temperature: 1000°C  time: 4hr atmosphere: H₂+3%H₂O, air)
Fig. 7 Power density curve as a function of current density

**cathode:** LSM/YSZ (DP and AFP)  
**anode:** Ni/YSZ  
*(Cell Test Conditions: cell temperature: 1000°C time: 4hr atmosphere: H₂+3%H₂O, air)*

Fig. 8 Polarization characteristic of Ni/YSZ by DP and AFP
Fig. 9 SEM micrographs of Ni/YSZ by DP and AFP after cell test

(Cell Test Conditions: cell temperature: 1000°C time: 4hr atmosphere: H₂+3%H₂O, air)

Fig. 10 Time dependence of anode polarization