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Electrode Properties of Ni-YSZ Cermet Anode Using YSZ Powder Synthesized Through a Hydrothermal Process

by

Taku MITSUMORI[*1], Masahiro KINOSHITA[*1], Masashi YOSHINAGA[*2] and Kazuya SASAKI[*3]

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Abstract

Nanocrystalline yttria-stabilized zirconia (YSZ) for anode material of solid oxyed fuel cells (SOFCs) was synthesized by homogeneous precipitation through a hydrothermal process. YSZ specimens were calcined at 673 K, 873 K, 1073 K, 1273 K and 1473 K. X-ray diffraction (XRD) measurements revealed that crystalline sizes increased according to the increases of the calcining temperature. By scanning electron microscope (SEM) observations, primary particle sizes of the specimens were increased with the increase of the heating temperatures; on the contrary, secondary particle sizes were constant. NiO-YSZ anode was tested by electrochemical measurements at 973, 1073 and 1173 K. The maximum power density of 20.8 $mW \cdot cm^{-2}$ have been achieved at 1173 K, which was 5 times higher than that of the commercial products.

Keywords: YSZ, SOFCs, Secoundaly aggregation, Anode, Hydrothermal process, Homogeneous precipitation

1. Introduction

Nanocrystalline materials are expected as diversity materials of good electrochemical properties, high hardness and good sintering properties. For example, size of the crystal affects the electrochemistry and crystal growth rate.[1)] Advanced machines such as solid oxyed cuel cells (SOFCs), are fabricated low cost to use nanoclystalline materials. Nanocrystalline materials develop new areas such as the application of micro technology, such as so the SOFCs.[2,3)]

Interface is a reaction field and the reaction field is increased by the interface is widely.[4)] SOFCs is generated by reaction in anode triple phase boundaries (TPBs).

Yttria-stabilized zirconia (YSZ) is one of the materials used in SOFCs. It is used as an electrolyte mainly. YSZ has been synthesized in many methods.[5-7)] A precipitation is good method for synthesizing inorganic materials. The method to develop this method is homogeneous precipitation.[8-11)] Homogeneous precipitation is the method that can be made to proceed uniformly in the whole solution the precipitation reaction. By controlling the reaction time, this method can obtain a high purity and homogeneous powder sample.

Hydrothermal process is a method that the crystalline is grown and synthesized using high pressure and elevated temperature at constant volume.[12-15)] Hydrothermal process is expected as the method of synthesizing compounds that cannot be synthesized in the atmospheric pressure.

In this study, YSZ powder was synthesized by the through hydrothermal process. Nanocrystalline YSZ powder was synthesized at low temperature. Nanocrystalline YSZ powder is syntered well than conventional, wide TPBs. The electrode properties of anode used the synthesized YSZ powder and commercial YSZ powder were revealed by the electrochemical measurement.

2. Experimental

2.1. Nanocrystalline YSZ synthesis

8 mol% YSZ was synthesized by the homogeneous precipitation through hydrothermal process. Y_2O_3 (99.0%, Wako) was firstly dissolved into a certain amount of nitric acid (60.0%, Wako) at room temperature. $ZrOCl_2 \cdot 8H_2O$ (99.0%, Wako) was dissolved into deionized water and mixed with the yttrium nitrate solution. This mixed solution was added to urea (99.0%, Wako) and transferred to a teflon cup.

*1 Graduate Student, Course of Mechanical Engineering
*2 Assistant Professor, Department of Prime Mover Engineering
*3 Associate Professor, Department of Prime Mover Engineering

Then, teflon cup put into a stainless steel autoclave. The autoclave was heated for 48 hours at 393 K to generate hydrothermal condition. The precipitation was collected by centrifugation at 5000 rpm for 30 minutes and washed 5 times with deionized water and washed 2 times with ethanol (99.5%, Wako) to remove moisture. Gel YSZ was dryed by at 358 K in air and calcination at 673 K, 873 K, 1073 K, 1273 K or 1473 K for 2 hours.

2.2. Characteristic analysis

The crystalline structures were identified at room temperature by powder X-ray diffraction (Burker, D8 DISCOVER, operated at 40 kV, 40 mA), employing Cu Kα reaction (λ = *1.5418 Å*). The surfaces were observed by field emission scanning electron microscope (FE-SEM) (HITACHI, S-4800).

2.3. Single cell fabrication

Electrolyte disks for SOFCs cells were prepared the commercial YSZ powder (TOSOH, TZ-8YS). YSZ powder (3 g) was formed of 25 mm mold and pressed into pellet at 0.2 MPa. YSZ pellet was sintered for 6 h at 1673 K. A Pt paste was printed YSZ pellet by a screen printing method as a cathode. The Pt paste was painted on side of the YSZ pellet via reference electrode and burned at 1573 K for 2 hours. Conventional NiO-YSZ cermet anode was used as an anode of SOFC. NiO-YSZ was made by mixing commercial NiO product and the sintered YSZ at 1473 K in a volume ratio of Ni and YSZ to be 1:1 by a mortar. Mixed NiO-YSZ was mixed with 2-propanol, and attached to the YSZ pellet by the slurry coating method. NiO-YSZ was burned into YSZ pellet at 1473 K for 2 hours. YSZ pellet was attached to the SOFCs single cell evaluation device (CHINO, FC-400H SP ver.) with grass seal. The NiO-YSZ cermet anode was reduced in H_2 gas at 1273 K during the overnight hours. For comparison, SOFCs cell was fabricated by the commercial YSZ product by the same condition.

2.4. Electrochemical measurement

Power generation tests performed at 973 K, 1073 K and 1173 K and used potentiometer (IVIUM, Ivium Stat). Bubbled H_2 gas at room temperature was flowed into the anode at 30 ml/min and the cathode feed gas was dry pure O_2 gas at a flow rate of 30 ml/min.

3. Results and discussion

3.1. Crystalline of the synthesized YSZ

Figure 1 shows XRD patterns of (a) synthesized YSZ and (b) calcined at 673 K, (c) 873 K, (d) 1073 K, (e) 1273 K, (f) 1473 K, and (g) commercial YSZ powder. Figure 1 (a) shows synthesized YSZ before calcination and peak was not detected. Figure 1 (b) is calcined YSZ at 673 K and swelling was a broad and weak signal. Figure 1 (c) is calcined at 873 K and broad peak was detected. Figure 1 (d) is calcined YSZ at 1073 K and peaks were becoming sharp over this temperature. Synthesized YSZ powder crystallized calcination over 873 K. Difraction angle of synthesized YSZ powder at 30 °, 35 °, 50 °, 60 ° and 73 ° was agreement with cubic YSZ. All peaks obtained were cubic fluorite-type YSZ peaks. Acording to increasing the calcination temperature, the patterns became sharp and its intensity increased because of the growth of the crystalline.

Figure 2 shows crystalline size of synthesized YSZ. Crystalline size was calculated by the Scherrer equation (1).

$$D=\kappa\lambda/\beta\cos\theta \quad (1)$$

Here, D is the crystalline size, κ is the Scherrer constant (0.9), λ is the wavelength, β is the half-width. A peak of sround 30 ° was used for Scherrer eqation. The calculated crystalline sizes for the calcined temperature at 873, 1073, 1273 and

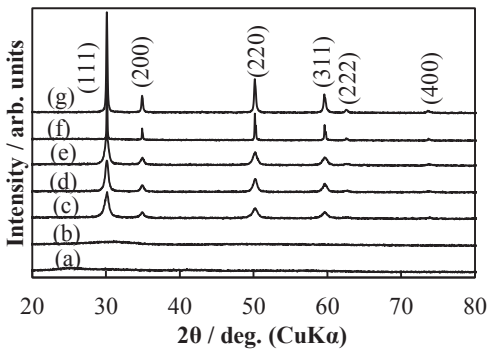

Fig. 1 XRD patterns of (a) synthesized YSZ and (b) calcined at 673 K, (c) 873 K, (d) 1073 K, (e) 1273 K, (f) 1473 K, and (g) commercial YSZ powder.

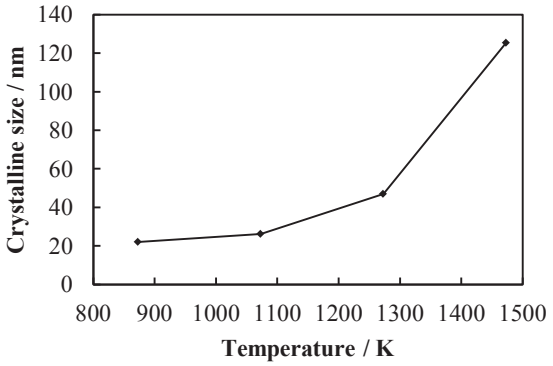

Fig. 2 Crystalline size of the synthesized YSZ.

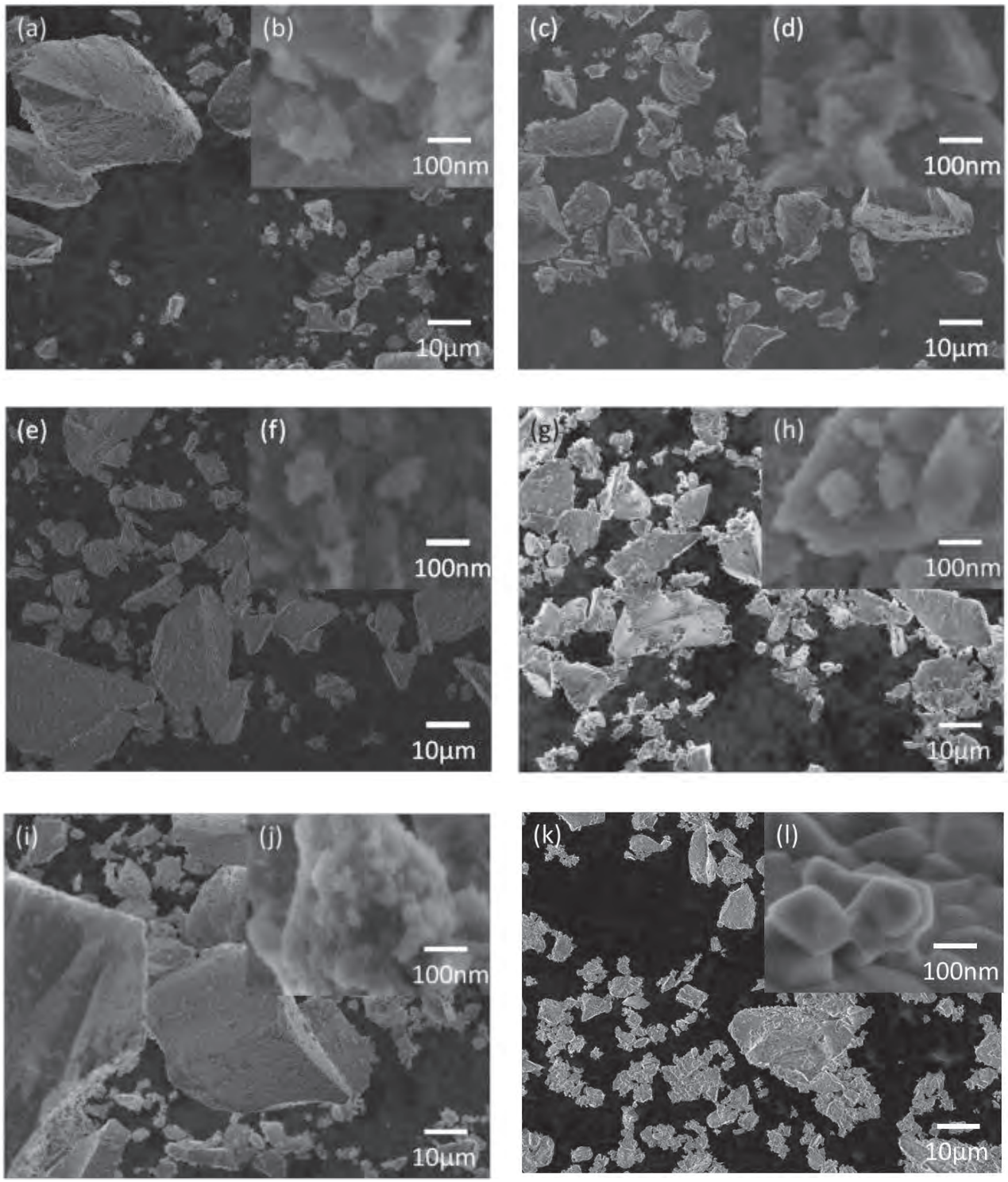

Fig. 3 SEM images for (a) synthesized YSZ and (c) calcined one at 673 K, (e) at 873 K, (g) at 1073 K, (i) at 1273 K and (k) at 1473 K, and (b), (d), (f), (h), (j) and (l) present for the magnified images.

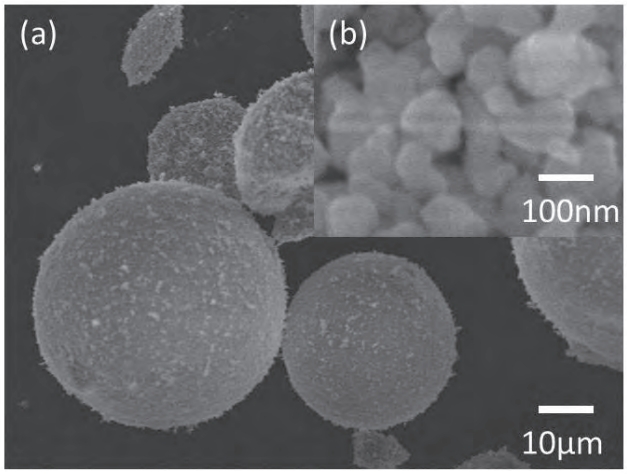

Fig. 4 SEM images for the mixed anode powder; (a) the commercial YSZ product and (b) its magnified image.

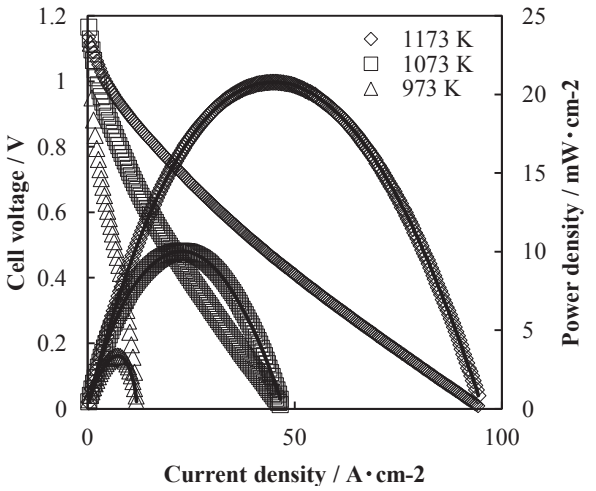

Fig. 5 Current-voltage and current-power characteristic for the cell with the 1473 K calcined YSZ anode at 973, 1073 and 1173 K.

1473 K were 22.1, 26.2, 47.0 and 125 nm, respectively. Crystalline size grew with the rise of temperature.

Figure 3 shows SEM images for (a) synthesized YSZ and (c) calcined one at 673 K, (e) at 873 K, (g) at 1073 K, (i) at 1273 K and (k) at 1473 K, and (b), (d), (f), (h), (j) and (l) present for the magnified images. The secondary particles of figure 3 (a) were about 100 μm. The secondary particles size didn't change due to the increase of calcined temperature. The primary particles of YSZ before calcined were about 100 nm. The primary particles of YSZ calcined at 673 K was about 200 nm, at 873 K was about 500 nm, at 1073 K was 1 μm, at 1273 K was about 1.2 μm and at 1473 K was 2 μm. Primary particles changed due to the increase of calcined temperature. The growth by calcining of primary particles was good agreement to the crystalline sizes. Increase of the crystalline sizes with increasing heating temperatures this was clearly in agreement with the other report.[16)]

Figure 4 shows SEM images for the anode powder as prepared; (a) The commercial YSZ and (b) its magnified image. Synthesized YSZ powder calcinated at 1473 K was used for SOFCs cell because primary particle was about same, and secoundaly particle size was difflent. Both of the YSZ powders were mixed uniformly with NiO powder for SOFCs cells.

3.2. Characteristic of electrode

Figure 5 shows current-voltage and current-power characteristic for the 1473 K calcined YSZ anode at the temperature of 973, 1073 and 1173 K. The power per unit area used synthesized YSZ was shown 20.8 mW・cm^{-2}.

Figure 6 shows current-voltage and current-power characteristic for the cell with the commercial YSZ powder anode at 973, 1073 and 1173 K.

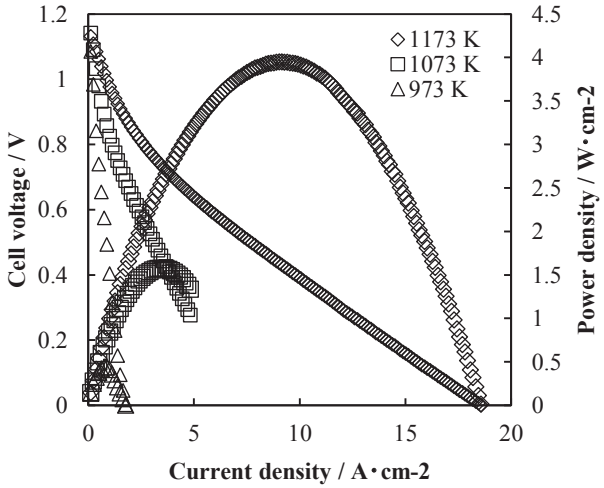

Fig. 6 Current-voltage and current-power characteristic for the cell with the commercial YSZ product anode at 973, 1073 and 1173 K.

The power per unit area used the commercial YSZ powder was shown 4.0 mW・m^{-2}. The pellet using synthesized YSZ was 5 times power densities than that for the commercial YSZ powder. Difference between synthesized YSZ powder and comarcial YSZ powder is the strength of the collection of secondary particle size by fig. 3 (k) and fig. 4(a). A power generation charastaristic of YSZ powder with long TPBs of weak secoundary aggregation was higher than short TPBs of strong secoundary aggregation.

4. Conclusions

Electrode characteristic of synthesized YSZ was better than the commercial YSZ powder. The method of hydrothermal process through homogenious precipitation could synthesis weak secondary aggregation YSZ powder.

Using this YSZ powder, anode performance was improved.

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