Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 26 (2006) 593–597

www.elsevier.com/locate/jeurceramsoc

Preparation of SOFC anode composites by spray pyrolysis

Seiichi Suda [a,*], Mikio Itagaki [a], Eri Node [a], Seiji Takahashi [a], Mitsunobu Kawano [b], Hiroyuki Yoshida [b], Toru Inagaki [b]

[a] *Materials Research and Development Laboratory, Japan Fine Ceramics Center, Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan*

[b] *Energy Use R&D Center, The Kansai Electric Power Company Inc., Nakoji, Amagasaki, Hyogo 661-0974, Japan*

Available online 10 August 2005

Abstract

Lowering the SOFC working temperature would also be greatly attractive, but low temperature working SOFCs require high-performance anodes. The cermet SOFC anodes, which are composed of nickel and samarium doped ceria, were prepared by spray pyrolysis (SP), because SP produces spherical particles with small size distributions. SP-derived particles of NiO, SDC, and NiO/SDC composite had a round shape and comprised nanometer-sized primary grains. The cermet anodes were prepared by using SP-derived NiO/SDC composite particles or mixing SP-derived NiO and SDC particles. The anode prepared with the composite particles showed higher SOFC cell performance than that with the mixed ones. The composite particles had high surface areas and a capsule-type form. The outer shell would be composed of SDC and the inner core was NiO. The capsule-type composite particles would depress aggregation of Ni or NiO during reduction from NiO to Ni metals, and this depression would enhance SOFC anode performance.

Keywords: Powders-chemical preparation; Composites; Electrical properties; CeO_2; Fuel cells

1. Introduction

Solid oxide fuel cell (SOFC) is one of the most promising electric power conversion systems that have high conversion efficiency and low environmental load. SOFC generally works at 800–1000 °C to maintain high conversion efficiency and to utilize hydrocarbon fuels. Lowering the SOFC working temperature would also be greatly attractive because it extends durability of SOFC cells, expands applicable kinds of materials and elevates SOFC cost performance. Reducing thickness of solid electrolyte is one of the most effective strategies to keep low ohmic loss derived from an electrolyte at reducing temperatures. However, the performances of SOFC electrodes would be almost independent of their thickness, and then low-temperature working SOFCs require developments of higher-performance anodes. A high-performance anode needs a wealth of three phase boundaries (TPBs) where fuel gas and an oxygen ion can contact along electric conduction paths, because the conversion occur at TPBs inside an anode.

Cermets of nickel metal and samarium doped ceria (SDC) are used as anode materials because nickel is an excellent hydrogen oxidation catalyst as well as a highly electronic conductor and SDC has highly oxygen-ion conductivity depending on amount of doped samarium. The dispersion of Ni and SDC in an anode would much affect anode performance as well as homogeneity of anode microstructure. The Ni/SDC cermet anodes have been prepared by spray pyrolysis (SP),[1,2] because SP is a simple synthesis method to produce spherical particles with small size distributions[3–6] and high-performance anodes would be realized using homogeneous SP-derived particles. Three kinds of particles, nickel oxide (NiO), SDC and NiO/SDC composite particles, were then synthesized by SP. The cermet anodes were prepared by two processes; one was that NiO/SDC composite particles were directly synthesized by SP (NiO/SDC composite particles), and the other was that SP-derived NiO and SDC particles were mixed by ball milling (NiO/SDC mixed particles). Two types of SOFC single cells were fabricated with either of the NiO/SDC particles and the effects of composite on SOFC

* Corresponding author. Tel.: +81 52 871 3500; fax: +81 52 871 3599.
E-mail address: suda@jfcc.or.jp (S. Suda).

0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2005.07.038

anode performance were evaluated in order to develop high-performance anode for low-temperature working SOFC.

2. Experimental procedure

Fig. 1 shows the illustration of SP instrument. SP consists of mainly three units: (1) atomization of starting solutions; (2) sequential firing of solution mists by flowing through various furnaces; and (3) collection of fired particles. The starting solution for NiO particles was prepared by dissolving nickel acetate in nitric acid and diluting with deionized water until NiO concentration was 0.1 mol dm^{-3}. The composition of SDC was determined to be $(SmO_{3/2})_{0.2}(CeO_2)_{0.8}$ previously.[7] The starting solution for SDC particles was prepared by dissolving samarium oxide in nitric acid, adding cerium nitrate, and finally diluting with deionized water until SDC concentration was 0.1 mol dm^{-3}. As for the NiO/SDC composite particles, NiO/SDC molar ratio was adjusted to be 5.6, and NiO/SDC concentration was set to be 0.1 mol dm^{-3}. A similar process to the preparation for NiO or SDC particles was applied to prepare the composite particles.

The starting solutions were atomized using an ultrasonic generator with an oscillation frequency of 1.7 MHz. Atomized mist was transferred to several furnaces by flowing air at the rate of 1.0 $dm^3\,min^{-1}$. The furnaces were arranged in a row to allow the mists to fire stepwise, and the temperatures of the furnaces were adjusted at 200, 400, 800, 1000 °C, respectively. The obtained composite particles were collected using a membrane filter with 0.2 μm pores. The NiO/SDC mixed particles were prepared by mixing NiO and SDC particles, which were, respectively, synthesized by SP, with a ball mill for 16 h. Both SP-derived composite particles and mixed particles were calcined at 1000 °C for 24 h in air. The morphologies of the particles were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The compositional distributions of the particles were also examined by energy dispersive X-ray spectroscopy (EDS). Specific surface areas of the particles were also measured with a BET specific surface analyzer.

Electrical properties of SOFC single cells were measured using the anodes obtained with the calcined particles. Disks of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM)[8,9] with a thickness of 0.2 mm and a diameter of 13 mm^{ϕ} were used as a solid electrolyte. The anode paste composed of the particles and polyethylene glycol (PEG) was screen-printed on an LSGM

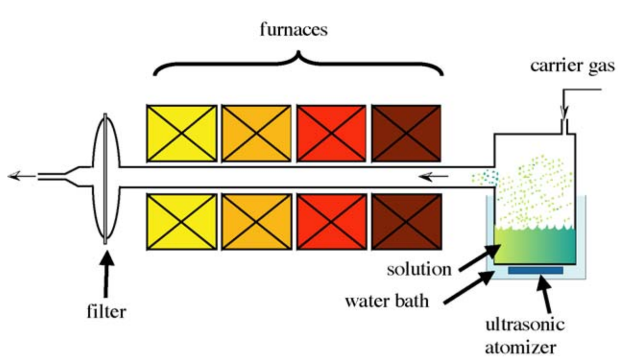

Fig. 1. Schematic illustration of spray pyrolysis equipment.

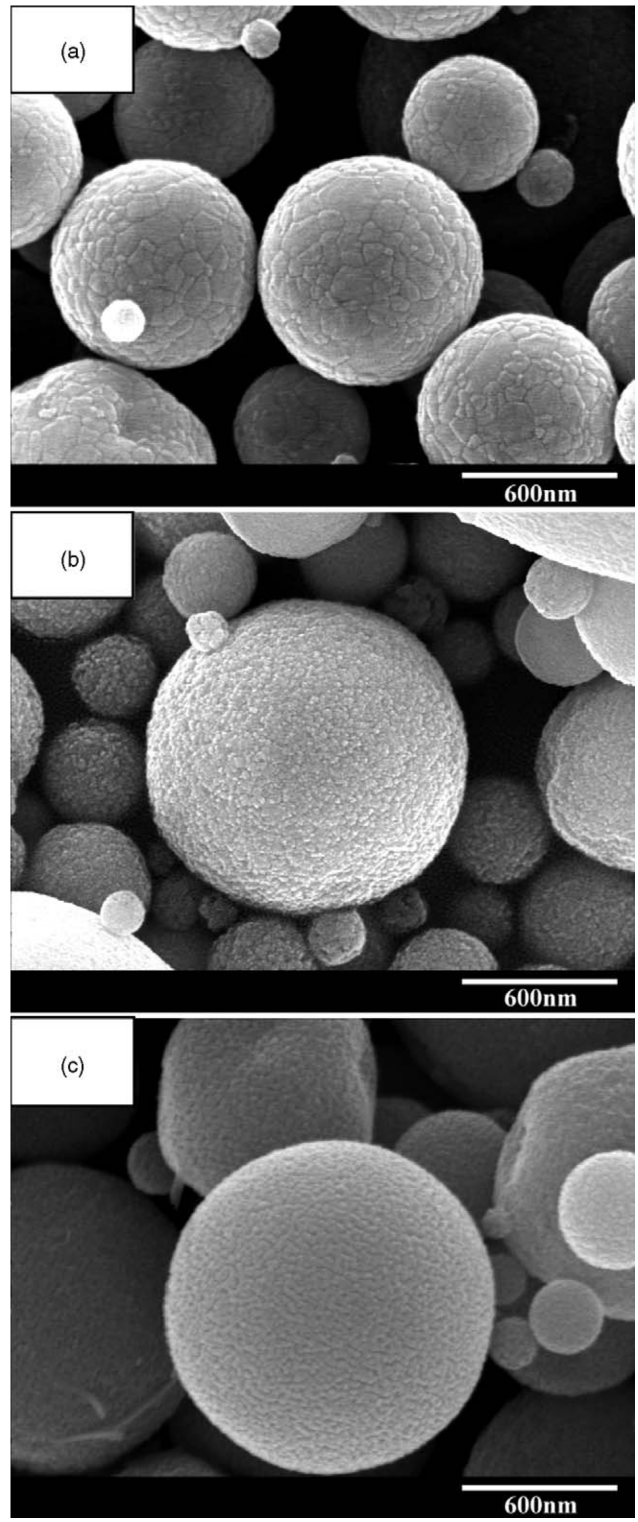

Fig. 2. SEM images of NiO (a), SDC (b), and NiO/SDC composite particles (c) synthesized by SP.

disk and fired at 1250 °C for 2 h in air. After the anode with 0.283 cm^2 was sintered to the LSGM disk, the cathode paste of $La_{0.2}Sr_{0.8}CoO_{3-\delta}$ (LSC) and PEG was also screen-printed on the other side of LSGM and fired at 1000 °C for 4 h in air. The electrical properties (power density and current density) of SOFC cells were measured at 700 °C using 3% humidified hydrogen and air. Platinum wire was wound around the electrolyte and fixed with platinum paste and electrode polarization was also measured by current interruption method.

3. Results and discussion

NiO, SDC and NiO/SDC composite particles were synthesized by SP, and morphologies of the particles were observed by SEM (Fig. 2). All of the particles prepared in this experiments had a round shape and comprised nanometer-sized primary grains. SP-derived NiO spherical particles had a particles size of 0.6–0.7 μm and comprised primary grains whose size was 30–150 nm. SDC spherical particles were also obtained by SP, but SDC spherical particles had a larger particle size (0.8–1.2 μm) and a smaller size of primary grains (10–30 nm) as compared with NiO particles. Nucleation of NiO and SDC crystallites occurred at almost the same temperature, and the difference in the grain size would be due to crystal growth rates of NiO or SDC. NiO/SDC composite particles had similar sizes to SDC. BET analysis revealed that the composite particles have high surface areas larger than 20 $m^2 g^{-1}$, and the primary grain sizes of the composite particles were about 10 times enhanced after the calcination at 1000 °C for 24 h in air.

After calcinations at 1000 °C for 24 h in air, NiO/SDC mixed particles were used as an SOFC anode. SOFC cell performance was then investigated with the mixed particles. Fig. 3 shows cell voltage and power density plots against current density measured at 700 °C. Maximum power density of the cell synthesized with the mixed particles reached 308 mW cm^{-2} at 0.7 Acm^{-2}, and the short circuit density of the cell was 1.4 Acm^{-2}. Fig. 4 shows anodic polarization of the cell. The anodic overpotential was relatively large as compared with overpotential and ohmic loss of cathode. The effects of composite on SOFC anode performance were then investigated by comparing SOFC performances between the mixed and the composite particles. Fig. 5 shows cell voltage and power density plots for the cell fabricated with the composite particles. Maximum power density of the cell was 453 mWcm^{-2} at 1.0 Acm^{-2}, and the short circuit density of the cell was larger than 2.0 Acm^{-2}. Fig. 6 shows

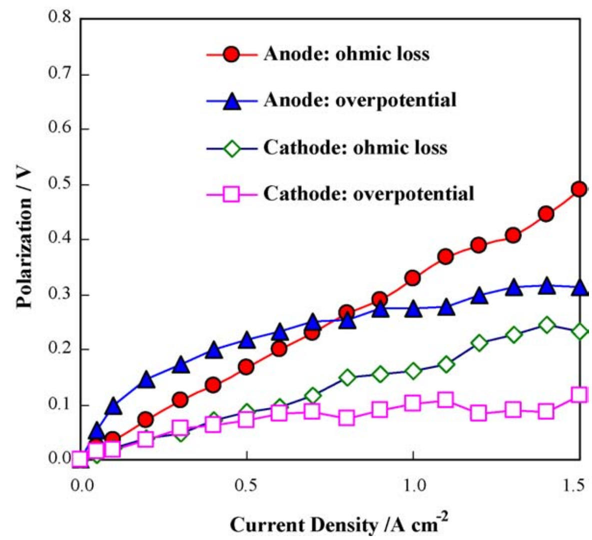

Fig. 4. Overpotential and ohmic loss of SOFC with Ni-SDC mixed anode.

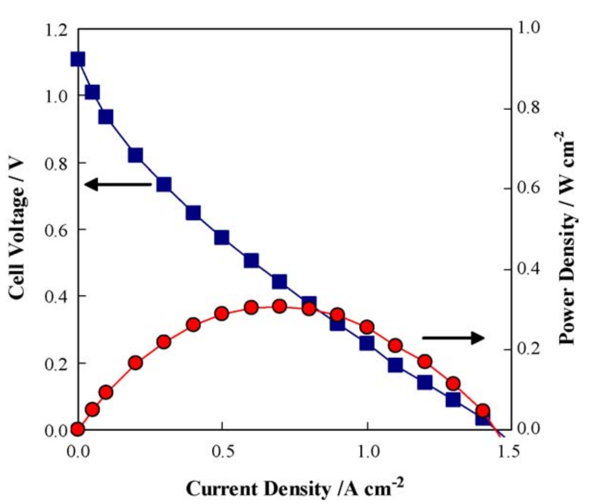

Fig. 3. Voltage-current density and power-current density plots of SOFC using Ni-SDC mixed anode. The test gases were air (50 $cm^3 min^{-1}$) and 3% humidified hydrogen (50 $cm^3 min^{-1}$). The cell temperature was 700 °C.

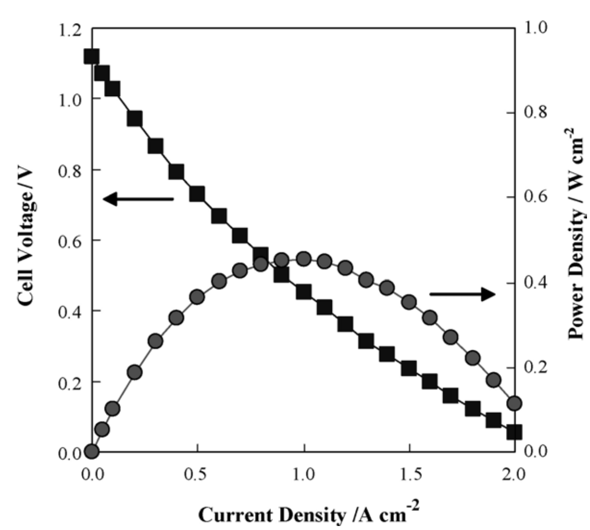

Fig. 5. Voltage–current density and power–current density plots of SOFC using Ni/SDC composite anode. The test gases were air (50 $cm^3 min^{-1}$) and 3% humidified hydrogen (50 $cm^3 min^{-1}$). The cell temperature was 700 °C.

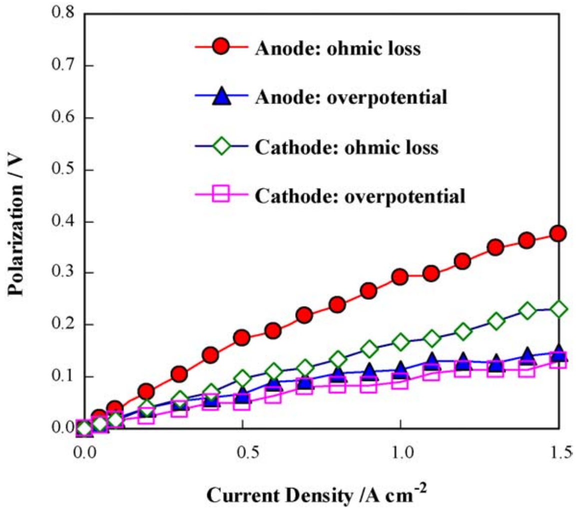

Fig. 6. Overpotential and ohmic loss of SOFC with Ni/SDC composite anode.

anodic and cathodic polarizations of the cell derived from the composite particles. Cathodic overpotential and ohmic loss of the cell derived from the composite particles were comparable to those from the mixed ones. Ohmic losses of the anodes derived from the composite particles and the mixed ones showed almost the same voltage loss. A notable difference was revealed in anodic overpotential. The composite reduced anodic overpotential to about one-third of its value obtained using the mixed particles, and improved power density. The composite would depress aggregation of Ni or NiO during heating cell and enhance the concentration of TPBs.

Cross section of the composite particles was observed by TEM to clarify morphologies of the particles formed by the composition (Fig. 7). SP led encapsulated particles, and EDS analysis revealed that the outer capsule would be composed of SDC and the inner core was NiO. Fig. 8 shows the interfaces between LSGM electrolyte and Ni/SDC cermet anode after reduction from NiO to Ni metal. Both the interfaces had tight connections between dense electrolyte and porous anode, but the anode derived form the composite particles was more porous than that from the mixed ones.

The capsule-type particles resulted in high-performance anode. The formation mechanism of high-performance anode from the capsule-type particles is still vague, but we suppose that the behavior at a high temperature between the composite particles and the mixed ones would differ from one another as Fig. 9. Nickel metal is sintered at a lower temperature than SDC.[10] Isolated NiO particles tend to aggregate during the reduction from NiO to Ni and would result in less porous anode. NiO in the capsule-type particles was enclosed with SDC and the SDC capsule would depress NiO aggregation and the depression led to form porous anodes with a wealth of TPBs.

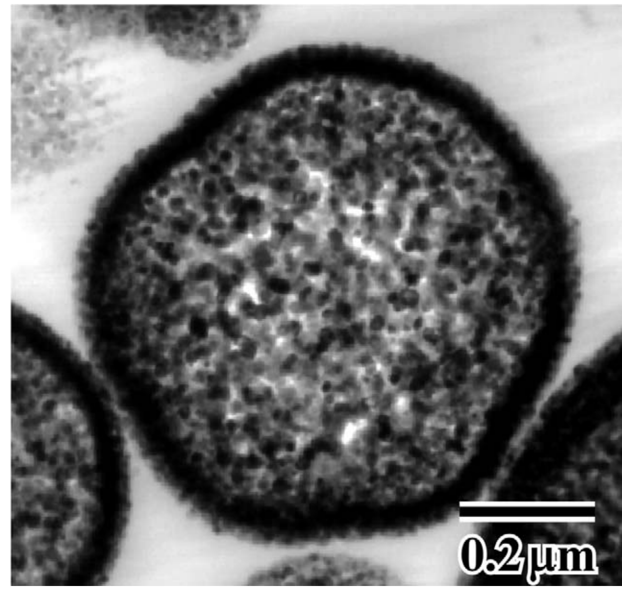

Fig. 7. TEM image of cross section of NiO/SDC composite particles.

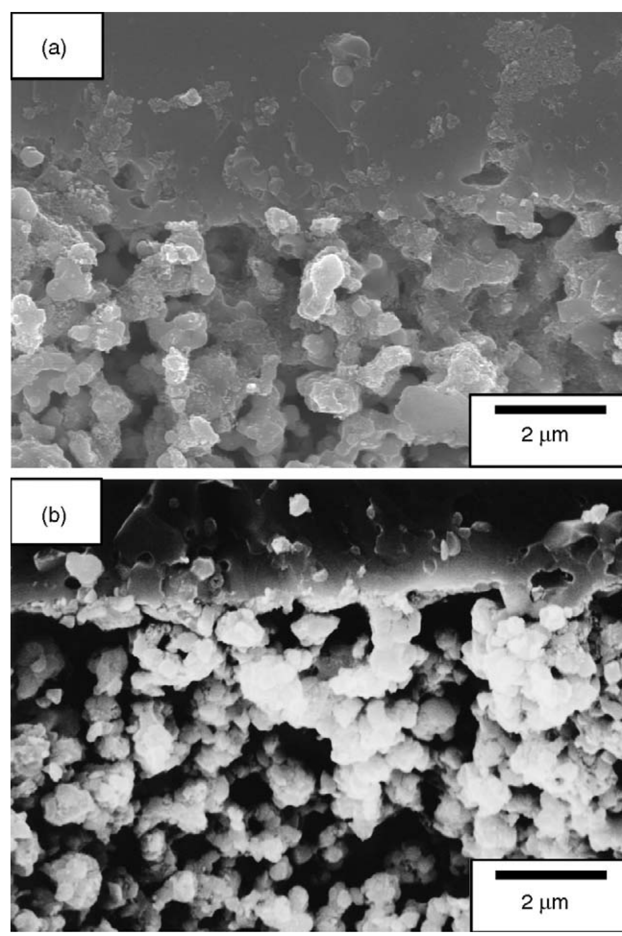

Fig. 8. SEM images of interfaces between YSZ electrolyte and Ni-SDC mixed anode (a) or Ni/SDC composite anode (b).

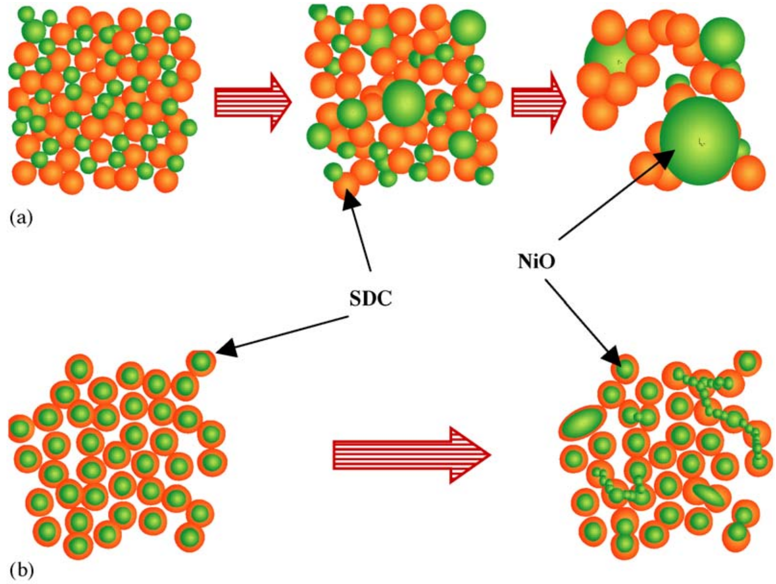

Fig. 9. Schematic of a possible NiO aggregation of mixed particles with NiO and SDC (a) or NiO/SDC composite particles (b) during heating.

4. Conclusions

The Ni/SDC cermet anodes were synthesized using SP-derived particles, and the effects of the composite on SOFC anode performances were investigated to develop high-performance anodes for low-temperature working SOFCs. SP-derived particles of NiO, SDC, and NiO/SDC composite had a round shape and comprised nanometer-sized primary grains. The cermet anode was prepared with the NiO/SDC composite or the NiO/SDC mixed particles. The anode prepared with the composite particles showed one-third lower anodic overpotential and higher power density than that with the mixed ones. The composite particles had high surface areas and a capsule-type form. The outer capsule was composed of SDC and the inner core was NiO. Isolated NiO particles tend to aggregate during the reduction. The SDC capsule would depress NiO aggregation and the depression would lead to form porous anodes with a wealth of TPBs.

References

1. Ohara, S., Maric, R., Zhang, X., Mukai, K., Fukui, T., Yoshida, H. *et al.*, High performance electrodes for reduced temperature solid oxide fuel cells with doped lanthanum gallate electrolyte I. Ni-SDC cermet anode. *J. Power Sources*, 2000, **86**, 455–458.
2. Fukui, T., Ohara, S., Murata, K., Yoshida, H., Miura, K. and Inagaki, T., Performance of intermediate temperature solid oxide fuel cells with La(Sr)Ga(Mg)O_3 electrolyte film. *J. Power Sources*, 2002, **106**, 142–145.
3. Ishizaki, H., Sakurai, O., Mizutani, N. and Kato, M., Homogeneous Y_2O_3-stabilized ZrO_2 powder by spray pyrolysis method. *Am. Ceram. Soc. Bull.*, 1986, **65**, 1399–1404.
4. Choi, K. H., Korai, Y. and Mochida, I., Preparation of CO_2 absorbent by spray pyrolysis. *Chem. Lett.*, 2003, **32**, 924–925.
5. Itatani, K. and Aizawa, M., Fabrication of multi-functional ceramics by the utilization of spray-pyrolysis technique. *J. Soc. Inorg. Mater. Japan*, 2003, **10**, 285–292.
6. Xia, B., Lenggoro, I. W. and Okuyama, K., Novel route to nanoparticle synthesis by salt-assisted aerosol decomposition. *Adv. Mater.*, 2001, **13**, 1579–1582.
7. Abrantes, J. C. C., Coll, D. P., Nunez, P. and Frande, J. R., Electronic transport in $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ ceramics under reducing conditions. *Electrochim. Acta*, 2003, **48**, 2761–2766.
8. Slater, R. P., Irvine, J. T. S., Ishihara, T. and Takita, Y., The structure of the oxide ion conductor $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ by powder neutron diffraction. *Solid State Ionics*, 1998, **107**, 319–323.
9. Ishihara, T., Matsuda, H. and Takita, Y., Doped $LaGaO_3$ perovskite type oxide as a new oxide ionic conductor. *J. Am. Chem. Soc.*, 1994, **116**, 3801–3803.
10. Berkel, F. P. F., Heuveln, F. H. and Huijsmans, J. P. P., Characterization of solid oxide fuel cell electrodes by impedance spectroscopy and I–V characteristics. *Solid State Ionics*, 1994, **72**, 240–247.