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Fabrication of High-performance Ni-GDC-nanocube Core-shell Anodes Prepared by a Chemical Reduction Method for Low-temperature Solid-oxide Fuel Cells[†]

YAMAMOTO Kazuhiro *, QIU Nan* and OHARA Satoshi**

Abstract

High-performance attractive SOFC anode material Ni-GDC-nanocube core-shell composites were successfully fabricated in a solution by chemical reduction method. The novel anode material was composed of a spherical metal Ni core and a covering GDC nanocube shell. 200 nm size of large Ni spheres provided great porous and Ni-Ni necking framework for current collection as macrostructure. On the surface of Ni spheres, 10 nm size of GDC nanocube particles covered with highly reactive {001} crystal facets acquired enlarged triple-phase boundary (TPB) as microstructure. In situ fabrication of Ni-Ni necking framework was achieved by crystal growth of Ni spheres during generation tests even at 500 °C operating. The non-sintered Ni-GDC-nanocube core-shell anode showed a higher power density compared with conventional Ni-GDC anodes sintered at 1300 °C. The designated macro- and microstructure of Ni-GDC-nanocube core-shell anodes were maintained after generation tests even at 700 °C operating.

KEY WORDS: (SOFCs), (anode), (sintering), (nanocubes), (nanoparticles)

1. Introduction

Solid-oxide fuel cells (SOFCs) have been receiving much attention as ideal next generation energy conversion devices for chemical energy into electricity owing to their high conversion efficiency. Many researchers devoted much effort to reduce the operating temperature below 800 °C, the main approaches were the use of thin solid electrolyte film, and modifying of electrode structure¹⁻³⁾. In conventional cell fabrication process, anode materials, for example NiO-GDC (gadolinium doped ceria), NiO-YSZ (yttrium doped zirconia), are sintered at high temperature as high as 1300 °C for any type of cell architecture (electrolyte, anode and cathode supported cell) to fabricate the necking structure of oxygen ionic conductor and current collector²⁻⁸⁾. However, the high temperature sintering inhibits insertion of fine nanostructures as a result of coarsening of anode material. Oxygen ionic conductivity is reduced with decreasing operating temperature⁹⁾, triple-phase boundary (TPB) as effective reaction sites in electrode are confined to near the electrolyte–anode interface. Therefore, conventional anode fabrication strategy is not suitable for low-temperature SOFCs operating at less than 600 °C. It is desirable that the

anode fabrication with fine microstructure for power generation and macrostructure for current collection are achieved by low temperature sintering or without any sintering.

In this paper, we demonstrate the novel fabrication process of a Ni-GDC-nanocube core-shell composite anode, which is prepared in solution by a chemical reduction method. The ideal macro- and microstructure are designed and given to the anode material. Ni-Ni framework as a macrostructure for fuel oxidation and current collection is promoted through the just a small crystal growth of metal Ni spheres during performance tests. Furthermore, GDC nanocube particles covered with highly reactive {001} crystal planes are deposited on the surface of Ni spheres as a microstructure for ionic conduction. This designated anode material enabled in-situ fabrication of good anode structure during generation tests, and showed higher power density than conventional NiO-GDC anodes sintered at 1300 °C. The designated anode macro- and microstructure were maintained even after 700 °C operating.

2. Experimental

Synthetic procedure of GDC (Ce_{0.9}Gd_{0.1}O_{1.95})

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nanocubes was described in our previous paper¹⁰. 4.6×10^{-2} g of GDC nanocubes was dispersed in 26.39 mL of ethylene glycol (EG) solvent. 0.444 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 1.8 mL of hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 98%) as a reducing agent were added into the dispersion. 5.45 mL of 1 M NaOH solution in EG solvent was added into the mixture, which was heated at 80 °C for 2 h. The volume ratio of Ni:GDC was adjusted to 65:35, and the molar ratios of $\text{Ni}^{2+}:\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}:\text{NaOH}$ were also adjusted to 1:20:3. After heating, aggregated black precipitate was collected with a neodymium magnet and then carefully washed with distilled water and ethanol. The sample powder was dried at 60 °C for 24 h and mixed with PEG#400 as a binder, and the resulting paste was used as an anode for single cell fabrication. The $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) cathode material prepared by co-precipitation method was also treated in the same manner. The resulting cathode paste was deposited on GDC as solid electrolyte (sintering temperature: 1500 °C, thickness: 400 μm ; diameter: 15 mm) by screen-printing and sintered at 850 °C for 2h. The anode paste was also deposited on the opposite side of the GDC disk without post-heat treatment. Power generation test at 600 °C was carried out, following the same procedures described in Ref. 10.

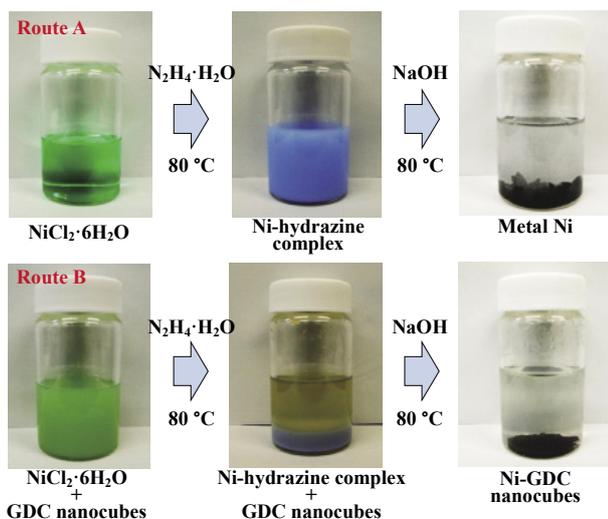


Figure 1 Images of fabrication process of spherical metal Ni particles (Route A) and Ni-GDC nanocubes B (Route B).

3. Results

Appearance of fabrication process of Ni-GDC-nanocube composite is shown in Figure 1. In route A (without GDC nanocubes), Ni^{2+} ions generate a light-blue complex $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ with excess $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and the complex precipitates. The complex color immediately changes to black by adding of NaOH solution, which means that the reduction reaction of $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ complex occurs just after adding of NaOH. This reduction mechanism of Ni^{2+} ion with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ is summarized as follow¹¹⁻¹³,



Fine metal Ni particles can easily aggregate owing to van der Waals forces and the magnetism. Such an agglomeration can lead to the crystal growth of metal Ni particles by Ostwald ripening.¹³ In route B (with GDC nanocubes), the $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ complex and GDC nanocubes were co-precipitated with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. During the agglomeration and Ostwald ripening, metal Ni gathered towards the interior as the core, and grew to a large particle. On the other hand, the GDC nanocubes were pushed towards the exterior and deposited on surface of the metal Ni particle.

The sample prepared by the chemical reduction method showed multiphase diffraction patterns composed of face-centered cubic (fcc) nickel metal and CeO_2 with a cubic fluorite structure (Figure 2(a)). In Figure 2(b), the sample morphology prepared in route A was confirmed 100 to 200 nm size of spherical particle. While, the sample morphology prepared in route B was also 200 to 300 nm size of spherical particle (Figure 2(c)). They had slightly larger diameters than metal Ni spherical particles, which indicated that GDC nanocube particles covered the surface of metal Ni spherical cores.

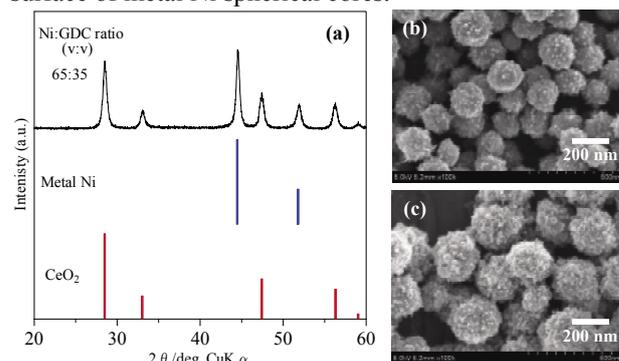


Figure 2 XRD pattern of the Ni-GDC nanocube composite prepared by chemical reduction method (a). SEM images of metal Ni spheres (b) and Ni-GDC nanocube core-shell anode ($v : v = 65 : 35$) (c).

After screen printing of the Ni-GDC-nanocube core-shell anodes (Ni:GDC = 65:35 (v:v)) paste, the single cell was directly examined to investigate the power generation property at 600 °C operating. The voltage-current ($V-I$) and power-current ($P-I$) curves are shown in Figure 3. Power generation occurred even at 500 °C, which indicated that the anode structures for power generation and current collection were successfully fabricated without any sintering of the anode material. Furthermore, higher power densities were obtained at higher operating temperatures. The maximum power density was 97 $\text{mW} \cdot \text{cm}^{-2}$ at 600 °C operating. The power generation performance was superior to NiO-GDC anodes prepared by an aerosol process and 1300 °C post-sintering.

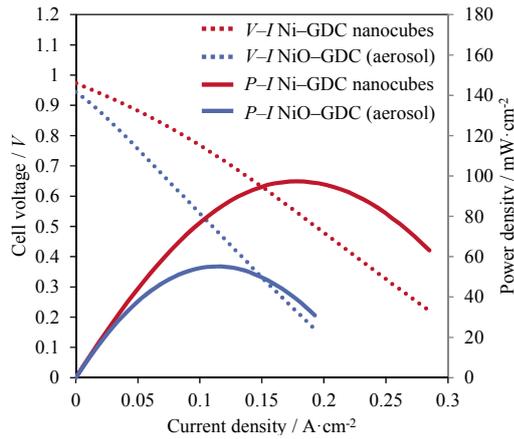


Figure 3 V-I and P-I curves of single cells. The cell-performance tests were performed at 600 °C.

Cross sectional SEM images of the Ni-GDC nanocube core-shell anode after power generation test at 700 °C operating are shown in Figure 4(a), (b). It was confirmed that the macrostructure of the Ni-GDC-nanocube core-shell anode as an electrode, remained unchanged even after the test at 700 °C. Meanwhile, the needle-like structures on the surface of the metal Ni spheres disappeared after the power generation test. The surface morphology changed to very smooth (Figure 4(b), which meant that in situ fabrication of Ni-Ni framework for current collection was provided as a result of insubstantial crystal growth of the metal Ni spheres at the operating temperature (over 500 °C). Furthermore, the core-shell like morphology did not change even after operating at 700 °C. It seems that this high stability of novel anode material is contributed by the large particle size of Ni spheres and GDC nanocube particles on the surface of Ni spheres. Especially, GDC nanocube particles inhibit the excessive crystal growth and migration of Ni spheres. After power generation tests, the anode material was crushed and its micro-structure was closely examined. HR-TEM observation revealed that the initial particle size of GDC nanocubes and the {001} crystal facets did not change even after the power generation test at 700 °C (Figure 4(c)). It is suggesting that the anode microstructure as reaction sites produced during the power generation test could be preserved. It should be noted that the macro- and microstructure of the anode fabricated without high temperature sintering showed good power generation performance and exhibited very high stability during the generation test.

The fine GDC nanocube particles deposited on the metal Ni spheres provided many contact points between Ni spheres and GDC nanocubes, and the resulting enlarged TPB can be regarded as a reason for high power density at 600 °C operating. Furthermore, it is suggested that the Ni-GDC-nanocube core-shell anode could introduce many ultra-fine contacts to the electrolyte-anode interface similar to the anode functional layer^{14, 15}. Schematic images for anode fabrication process are

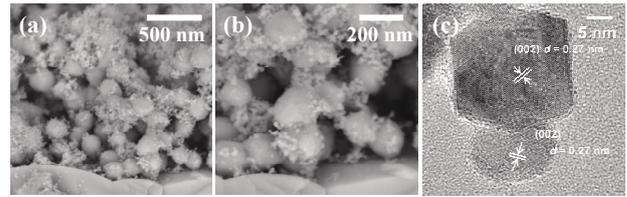


Figure 4 Cross sectional SEM images of Ni-GDC nanocube core-shell anode after 700 °C operating; (a) low-magnification and (b) high-magnification. HR-TEM image of GDC nanocube particles after 700 °C operating (c).

shown in Figure 5. In conventional fabrication process, nanostructured anode material is sintered at high temperature as high as 1300 °C, and then the nanostructure disappears by coarsening of NiO and GDC particles. This can provide good connection and long pathway for current collection and oxygen ion migration. However, such coarsened NiO and GDC particles can provide only the small TPB. On the other hand, designed Ni-GDC-nanocube core-shell anode gives good Ni-Ni connection for current collection through the crystal growth of Ni spheres at over 500 °C operating. In this time, large metal Ni spherical morphology does not change, while fine and many contact structures between Ni spheres and GDC nanocubes are maintained and provide enlarged TPB. However, in Figure 4(a) - (c), crystal growth of GDC nanocubes was not confirmed, which indicated that oxygen ionic pathway in the anode was very short, and effective anode thickness was limited near the electrolyte-anode interface. The anode can provide long current collection pathway and enlarged TPB, though it was suggested that we could utilize just a small fraction of the enlarged TPB near the electrolyte-anode interface.

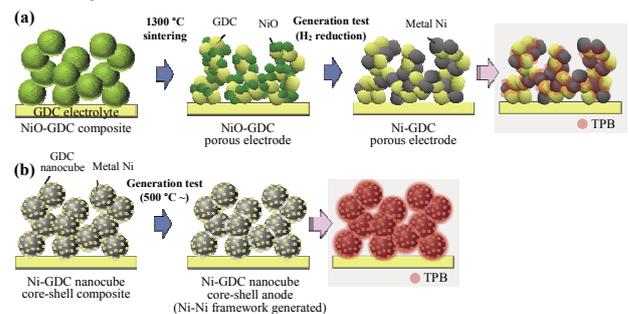


Figure 5 Schematic images of conventional anode fabrication by high temperature sintering process (a) and novel anode fabrication process without any sintering (b).

4. Conclusion

A novel fabrication process of high-performance Ni-GDC-nanocube core-shell anode for low-temperature SOFCs, using only a solution-based chemical reaction was successfully achieved. The anode material had a unique core-shell structure, and the metal Ni spherical core was covered with highly reactive GDC nanocubes. The characteristic composite structure could provide a

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much longer current collection pathway without any sintering. The effective metal Ni-Ni framework was formed by means of crystal growth of metal Ni spheres during the power generation test at a temperature as low as 500 °C. Meanwhile, the non-sintering fabrication process introduced an enlarged TPB with 10 nm size of GDC nanocube particles near the interface between the electrolyte and the anode. Such micro- and macrostructures of the anode contributed the great stability after the power generation test at 700 °C. We conclude that the Ni-GDC-nanocube core-shell anode is a suitable anode material for next-generation low-temperature SOFCs.

Acknowledgements

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References

- 1) E.D. Wachsman, and K. T. Lee, *Science*, **18**, (2011) 935.
- 2) K.T. Lee, N.J. Vito, H.S. Yoon, and E.D. Wachsman, *J. Electrochem. Soc.*, **159**, (2012) F187.
- 3) K. Hamamoto, T. Suzuki, B. Liang, T. Yamaguchi, H. Sumi, Y. Fujishiro, B. Ingram, A.J. Kropf, and J.D. Carter, *J. Power Sources*, **222**, (2013) 15.
- 4) T. Yamaguchi, S. Shimazu, T. Suzuki, Y. Fujishiro, and M. Awano, *Electrochem. Comm.*, **10**, (2008) 1381.
- 5) G. Chen, H.X. You, Y. Kasai, H. Sato, and A. Abudula, *J. Alloy. Compd.*, **509**, (2009) 5159.
- 6) T. Yamaguchi, S. Shimizu, T. Suzuki, Y. Fujishiro, and M. Awano, *Electrochim. Acta*, **54**, (2009) 1478.
- 7) R. Maric, S. Ohara, T. Fukui, H. Yoshida, M. Nishimura, T. Inagaki, and K. Miura, *J. Electrochem. Soc.*, **146**, (1999) 2006.
- 8) S. Ohara, R. Maric, X. Zhang, K. Mukai, T. Fukui, H. Yoshida, T. Inagaki, and K. Miura, *J. Power Sources*, **86**, (2000) 455.
- 9) B.C.H. Steele, *Solid State Ionics*, **129**, (2000) 95.
- 10) K. Yamamoto, T. Hashishin, M. Matsuda, N. Qiu, Z. Tan, and S. Ohara, *Nano Energy*, **6**, (2014) 103.
- 11) J.Y. Choi, Y.K. Lee, S.M. Yoon, H.C. Lee, B.K. Kim, and J.M. Kim, *J. Am. Ceram. Soc.*, **88**, (2005) 3020.
- 12) R. Eluri, and B. Paul, *J. Nanopart. Res.* (2012) 14:800.
- 13) N. R. Nik Rosalina, A. Azizan, and Z. Lockman, *Sains Malaysian*, **41**, (2012) 1037.
- 14) D. Yoon, J.J. Lee, H.G. Park, and S.H. Hyun, *J. Electrochem. Soc.*, **157**, (2010) B455.
- 15) K.T. Lee, H.S. Yoon, J.S. Ahn, and E.D. Wachsman, *J. Mater. Chem.*, **22**, (2012) 17113.