Science of Sintering, **42** (2010) 153-159

doi: 10.2298/SOS1002153L

UDK 622.785:661.874

Preparation of Gradient Ni-SDC Anode by Tape Casting and Co-sintering

X. B. Li [1, *)], H. Y. Wang [2], H. X. Gu [1], J. Wang [1], W. J. Zhang [1], T. G. Wang [1]

[1] State Key Laboratory of Advanced Technology for Materials Synthesis & Processing, Wuhan University of Technology, Wuhan 430070, P. R. China
[2] Jiangxi Blue Sky University, Nanchang 330029, P. R. China

Abstract:

Gradient Ni-SDC anode and anode-supported SDC electrolyte were produced by tape casting method with laminating and co-sintering process. The best co-sintering temperature of gradient Ni-SDC anode and SDC electrolyte was 1300°C for 3 h. The open porosity of gradient Ni-SDC anode sintered at 1300°C was 36%, which offered sufficient open porosity of more than 30%. By adjusting the composition of Ni in gradient anode, the thermal expansion coefficient (TEC) of Ni-SDC anode could be adjusted close to that of SDC electrolyte, which improve the compatibility of anode and electrolyte. The bending strength of gradient Ni-SDC anode was 134 MPa. The electrical conductivity of gradient Ni-SDC anode was better than that of non-gradient Ni-SDC anode at 650 - 800°C.

Keywords: *Co-sintering, Tape casting, Gradient anode, Ni-SDC, SOFC*

Introduction

Solid oxide fuel cell (SOFC) is a green energy that can convert chemical energy directly to electrical energy. Reducing the operating temperature of SOFC can reduce the cost, thermal stresses and increase the system stability of SOFC. Ni-$Ce_{0.8}Sm_{0.2}O_{1.9}$ (Ni-SDC) cermet anode is a good candidate for intermediate temperature solid oxide fuel cells (IT-SOFC) operated at 600 - 800°C [1-3]. SOFC with a single layer anode shows a high degradation which can be ascribed to thermal expansion mismatch between anode and electrolyte and the agglomeration of Ni particles [3, 4]. Chen et al [5] investigated the Ni-SDC anode with yttria-stabled zirconia (YSZ) electrolyte and found that cracks were induced by the shrinkage mismatch between Ni-SDC and YSZ during the co-sintering stage and gradually disappear with increasing precalcination temperature. Xie et al [6] studied a porous Ni-YSZ substrate, a porous Ni-SDC anode and a dense SDC electrolyte fabricated by tape-casting, screen printing and co-firing techniques. The results indicated the multilayered structure had adequate mechanical strength and sufficient interface adhesion. Cheng et al [7] investigated gradient Ni-SDC anode with gradient Ni composition distribution and found that the gradient Ni-SDC anode had fine pore and grain structure and steady thermal expansion coefficients than the anode with homogeneous Ni composition distribution.

*) Corresponding author: lixibao2007@yahoo.cn

Tape casting is a cost-effective colloidal forming technique for producing thin, flat and large area ceramic plates of usually 10 - 1000 μm thickness. However, it has disadvantage such as low mechanical strength [8-10]. In this study, gradient Ni-SDC anode and anode-supported SDC electrolyte were fabricated by tape casting method with laminating and co-sintering process. The technological conditions of tape casting, laminating and co-sintering of gradient Ni-SDC anode with high mechanical and electric performance were optimized.

Experimental

Sample preparation. Commercial powders of NiO (A.R., Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), carbon black (A.R., Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and self-made SDC were used as raw materials. SDC powder was synthesized at 650 ^{o}C by spray pyrolysis technique [11]. The raw materials (55.0 wt.%) were firstly mixed and ball milled in solvent (distilled water, 34.0 wt.%) with 2.0 wt.% dispersant (TEA, A.R., Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) for 24 h. Secondly, 9.0 wt.% of binder (PVA, A.R., Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and plasticizer (glycerol, A.R., Tianjin Kermel Chemical Reagent Co., Ltd, Tianjin, China) were added to the slurry to ball milled for another 24 h. Prior to tape casting, slurries were sieved and vacuum pumped to remove air. Tape casting was performed on a tape casting machine (LYJ-150, Beijing Orient Sun-Tec Co. Ltd., China). After dried at 25 ^{o}C for 24 h, the green tape was detached.

Two types of samples as sample A and B were prepared. Sample A was composed of anode substrate (NiO : SDC weight ratio 60 : 40, abbreviated as 60Ni-SDC) and thin-film SDC electrolyte. Sample B was designed to add an anode interlayer (NiO : SDC weight ratio 40 : 60, abbreviated as 40Ni-SDC) between 60Ni-SDC anode substrate and SDC electrolyte to form a gradient Ni-SDC anode. Anode substrate was fabricated by laminating 20 sheets of anode tape with a thickness of 80 μm. After laminating the tapes, samples were warm pressed at 40 MPa and 90^{o}C for 30 min.

After laminating, warm pressing and binder burning-out, samples were co-sintered in the range of 1200 - 1350^{o}C in air for 3 h. To avoid the warpage problem, which generally occurs in the co-sintering process, samples were fired in a sandwich structure consisting of two porous zirconia plates. After co-sintering, samples were reduced by H_2 at 800^{o}C for 1 h in tubular furnace.

Characterization

DTA-TG was performed on the laminated green tape of NiO-SDC gradient anode with SDC electrolyte by a synchronous thermal analyzer (STA449c/3/G, NETZSCH, Germany) in order to determine the binder burning-out curve. The open porosity of Ni-SDC cermets and SDC ceramic was measured by the Archimedes method, in accordance with China standard No. GB/T 1966-1996. The thermal expansion from room temperature to 900^{o}C was conducted using rectangular Ni-SDC cermets and SDC ceramic upon heating at a heating rate of 5 ^{o}C/min in an Ar atmosphere by a dilatometer (DIL 402 PC, NETZSCH, Germany). Rectangular samples (3 × 3 × 40 mm) for bending strength testing were cut and polished from gradient and non-gradient Ni-SDC anode. The bending strength of samples was tested using MTS Ceramic Test System (MTS810, MTS Co. Ltd., USA) at room temperature. The electrical conductivity of gradient and non-gradient Ni-SDC anode was measured on rectangular samples (3 × 4 × 26 mm) by DC four-probe technique in temperature range from 500 to 800^{o}C. The microstructure of fracture surface of anode-supported SDC electrolyte sintered at 1300^{o}C for 3 h was observed by a scanning electron microscope (Model JSM-5610LV, JEOL Ltd., Japan).

Results and Discussion

Optimization of binder burning-out and co-sintering condition

Fig. 1 showed the DTA-TG analysis chart of laminated tape in which carbon black was the pore former. From Fig. 1, it can be seen that the polymer additives, such as dispersant, binder and plasticizer, and carbon black as the pore former were oxidized and decomposed at 200 - 600 ^{o}C and 1000 - 1200 ^{o}C, respectively, and were oxidized completely at 1200 ^{o}C. The volatilization of water was finished before 180^{o}C. The carbonization of glycerol and TEA was completed before 400^{o}C. The carbonization of PVA was completed before 600^{o}C. The oxidization of carbon black was finished before 1200^{o}C. And the firing of polymer additives should be carefully and slowly to avoid the cracking of green tapes. So the binder burning-out curve of laminated samples showed in Fig. 2 was determined according to the above analysis.

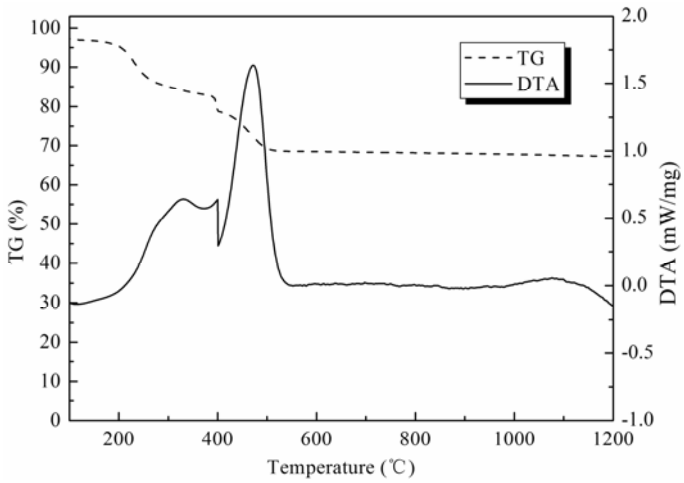

Fig. 1 DTA-TG analysis chart of laminated green tape of NiO-SDC gradient anode with SDC electrolyte

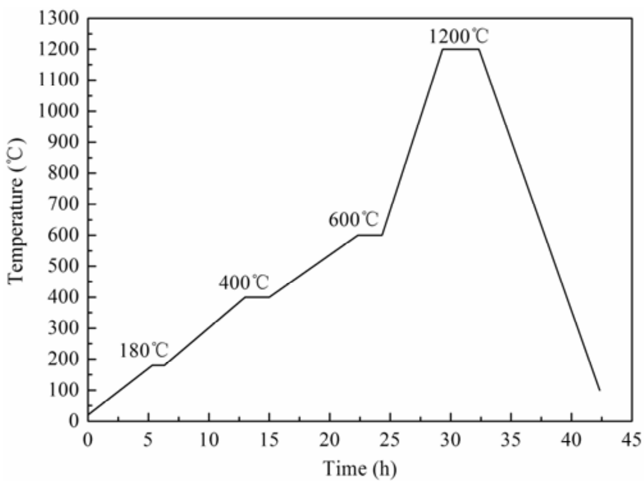

Fig. 2 Binder burning-out curve of NiO-SDC gradient anode with SDC electrolyte

To further optimize the co-sintering temperature, Ni-SDC anode substrate, Ni-SDC anode interlayer, gradient Ni-SDC anode and SDC electrolyte were sintered at 1250, 1300 and 1350^{o}C for 3 h respectively after binder burning-out. Fig. 3 showed the open porosity of anode and electrolyte as a function of sintering temperature. It can be seen that the temperatures of 1300 and 1350^{o}C were appropriate to obtain almost dense electrolyte. The open porosity of gradient Ni-SDC anode sintered at 1300^{o}C was around 36%. Regarding an open porosity of 30% as a criterion for gas transport inside the anode [12], the open porosity of anode sintered at 1350^{o}C was too low, which was not suitable for SOFC anode. Therefore, the best co-sintering temperature of 1300^{o}C was selected.

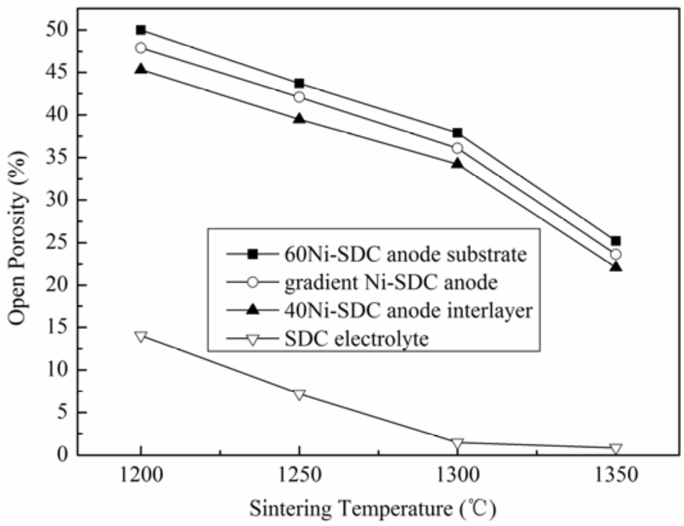

Fig. 3 Influence of sintering temperature on the open porosity for anode and electrolyte

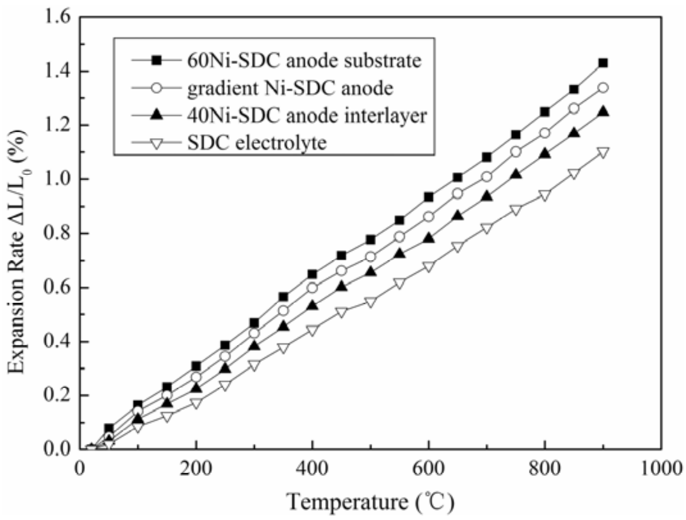

Fig. 4 Temperature dependence of thermal expansion rates for anode and electrolyte

Thermal expansion

To improve anode/electrolyte thermal expansion matching, anode interlayer (40Ni-SDC) was introduced. Fig. 4 showed the temperature dependence of thermal expansion rates for anode substrate, anode interlayer, gradient Ni-SDC anode and electrolyte. It can be seen that the thermal expansion rates of anode interlayer and gradient Ni-SDC anode are between anode substrate and SDC electrolyte. The average TEC values were calculated in the temperature range of 100 - 900°C. The SDC electrolyte and gradient Ni-SDC anode showed an average TEC of 12.8×10^{-6} /K and 15.0×10^{-6} /K, respectively. The TEC value difference between gradient Ni-SDC anode and SDC electrolyte was within the limits acceptable to thermodynamic compatibility of 15 - 20% [13]. Therefore, anode/electrolyte thermal expansion mismatch was reduced by the gradient Ni-SDC anode.

Mechanical strength

The bending strength of gradient and non-gradient Ni-SDC anode was 134 MPa and 150 MPa, respectively, both were good enough to satisfy the requirement of the mechanical properties for anode-supported SOFC [6, 14, 15]. Non-gradient Ni-SDC anode had a little higher bending strength than gradient Ni-SDC anode. This was in the range of error.

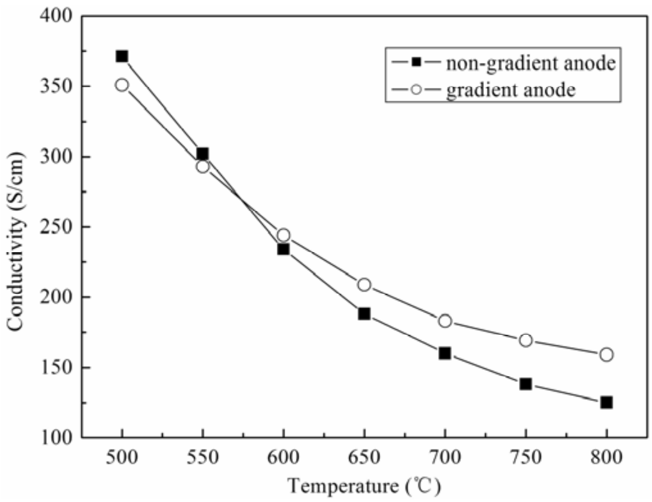

Fig. 5 Dependence of electrical conductivity on temperature for gradient and non-gradient Ni-SDC anode

Electrical conductivity

Fig. 5 showed the electrical conductivity of gradient and non-gradient Ni-SDC anode as a function of temperature. The conductivity decreased with the increase of temperature. This was due to the reason that the oxidation of Ni increased with the increase of temperature and the conductivity of NiO was lower than Ni. The conductivity of non-gradient Ni-SDC anode decreased faster than gradient Ni-SDC anode. At the temperature between 650 and 800°C, the conductivity of gradient Ni-SDC anode was higher than non-gradient Ni-SDC anode. This indicated that gradient Ni-SDC anode formed a continuous and well developed network and a good contact between particles, which improved the conductivity of anode.

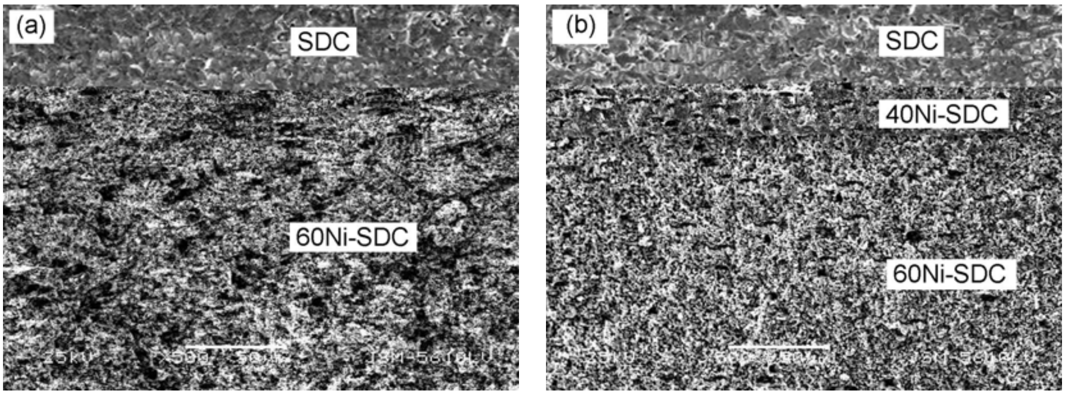

Fig. 6 SEM micrographs of cross section of anodes with electrolyte (a) non-gradient Ni-SDC anode, (b) gradient Ni-SDC anode

Microstructure

Fig. 6 showed the SEM micrographs of fracture surface of gradient and non-gradient Ni-SDC anode with SDC electrolyte sintered at 1300^{o}C for 3 h. It can be seen that the dense SDC electrolyte layer adhered well to the porous 60Ni-SDC anode layer and 40Ni-SDC interlayer. The 40Ni-SDC interlayer combined with 60Ni-SDC anode layer formed a gradient Ni-SDC anode, by which the anode/electrolyte thermal expansion mismatch was reduced.

Conclusions

Gradient Ni-SDC anode with high mechanical and electric performance had been prepared by tape casting method with laminating and co-sintering process. Samples were binder burnt-out from room temperature to 1200^{o}C and co-sintered in the range of 1200 - 1350^{o}C in air. The best co-sintering temperature of gradient NiO-SDC anode and SDC electrolyte was 1300^{o}C for 3 h, in which sufficient open porosity of around 36% was obtained. NiO-SDC samples were reduced to Ni-SDC anodes by H_2 at 800^{o}C for 1 h in tubular furnace. The TEC of gradient Ni-SDC anode had been adjusted close to that of SDC electrolyte, which improve the compatibility of anode and electrolyte. Gradient Ni-SDC anode and non-gradient Ni-SDC anode both had excellent bending strength of 134 MPa and 150 MPa, respectively. The electrical conductivity of gradient Ni-SDC anode was superior to that of non-gradient Ni-SDC anode at 650 - 800^{o}C. The gradient structure was the key to adjust the thermal expansion mismatch between anode and electrolyte.

References

1. M. Kawano, T. Matsui, R. Kikuchi, H. Yoshidu, T. Inagaki, K. Eguchi, J. Power Sources, 182 (2008) 496.
2. T. Misono, K. Murata, T. Fukui, J. Chaichanawong, K. Sato, H. Abe, M. Naito, J. Power Sources, 157 (2006) 754.
3. X. E. Zhang, S. Ohara, R. Maric, H. Okawa, T. Fukui, H. Yoshida, T. Inagaki, K. Miura, J. Power Sources, 83 (1999) 170.
4. W. Z. Zhu, S. C. Deevi, Mater. Sci. Eng. A, 362 (2003) 228.
5. M. Chen, B. H. Kim, Q. Xu, B. G. Ahn, J. Membrane Sci., 334 (2009) 138.

6. Y. S. Xie, X. E. Zhang, M. Robertson, R. Maric, D. Ghosh, Mater. Sci. Forum, 539 (2007) 1421.
7. J. G. Cheng, H. B. Li, X. Q. Liu, G. Y. Meng, Mater. Sci. Forum, 423-425 (2003) 449.
8. M. Ni, M. K. H. Leung, D. Y. C. Leung, Chem. Eng. Technol., 30 (2007) 587.
9. M. Chen, T. L. We, Z. Huang, J. Inorg. Mater., 14 (1999) 745.
10. C. Y. Huang, Z. L. Tang, Z. T. Zhang, J. Mater. Eng., 7 (2000) 13.
11. X. B. Li, G. Q. Shao, T. G. Wang, J. Wuhan Uni. Technol., 32 (2010) 9.
12. Y. H. Yin, W. Y. Zhu, C. R. Xia, G. Meng, J. Power Sources, 132 (2004) 36.
13. Q. Xu, D. P. Huang, F. Zhang, W. Chen, M. Chen, H. X. Liu, J. Alloy. Compd., 454 (2008) 460.
14. M. Chen, B. H. Kim, Q. Xu, O. J. nam, J. H. Ko, J. Eur. Ceram. Soc., 28 (2008) 2947.
15. M. Radovic, E. Lara-Curzio, Acta Mater., 52 (2004) 5747.

Садржај: *Методом ливења трака са процесом ламинирања и косинтеровања произведена је градијентна Ni-SDC анода и анодно подржан SDC електролит. Најбоља температура косинтеровања градијентне Ni-SDC аноде и SDC електролита била је 1300^{o}C за 3 часа. Отворена порозност градијентне Ni-SDC аноде синтероване на 1300^{o}C била је 36% која је нудила довољну отворену порозност изнад 30%. Подешавањем састава Ni у градијентној аноди могао су се подесити термички коефицијент ширења (TEC) Ni-SDC аноде близу вредности за SDC електролита што је побољшало компатибилност аноде и електролита. Јачина на савијање градијентне Ni-SDC аноде била је 134 MPa. Електрична проводност градијентне Ni-SDC аноде је боља од неградијентне Ni-SDC аноде на 650-800^{o}C.*

Кључне речи: *Косинтеровање, ливење трака, градијентна анода, Ni-SDC, SOFC.*