Fabrication of tubular NiO/YSZ anode-support of solid oxide fuel cell by gelcasting

Dehua Dong, Jianfeng Gao, Xingqin Liu, Guangyao Meng *

Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

Abstract

A gelcasting process has been developed to fabricate tubular NiO/YSZ anode-support for solid oxide fuel cells (SOFCs) successfully. The rheological behaviors of the ceramic particle suspensions for gelcasting were investigated as a function of the process parameters, such as the amount of pore former, pH value, dispersant concentration, monomer concentration, ball-mill time and solid loading. The sintering shrinkage, microstructure, bending strength and electrical conductivity of the sintered specimens were examined. The tubular Ni/YSZ anode-support obtained under the optimized preparation conditions exhibited a porosity of 39.6%, mean pore size of below 0.9 μm, 482 s cm^{-1} in electrical conductivity at 700 °C, and the bending strength of 112.8 MPa, which can well meet the requirements for SOFCs.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Gelcasting; Solid oxide fuel cells; Tubular anode-support; Microstructure

1. Introduction

SOFCs are new electric power generation devices. Because of their high energy conversion efficiency, pollution-free and flexibility to various fuels and designs, they have attracted extensive attention. High temperature SOFCs have many problems, such as limited materials selection, high materials cost, etc. Thus, the intermediate temperature SOFC (IT-SOFC) is the current trend in SOFCs development. But the electrical resistance of the traditional electrolyte-supported SOFC is too high to achieve the high energy efficiency. In order to solve this problem, electrode supported modes with thin electrolyte become the research trend in recent years. There are two main configurations of SOFCs, i.e. the planar and the tubular. Compared to the planar, the tubular is easier to industrialize for the reason that it is convenient for sealing, making into stack, and easier to scaling up. Tubular ceramics are usually fabricated by extrusion, but it has a number of shortcomings, such as rough surface [1], high investment in equipment, long production cycle. Since invented by Janney and Omatete of Oak Ridge National Laboratory (ORNL) in 1991, gelcasting has been widely used as a new ceramic forming

process. It has many advantages over conventional forming processes, such as dry pressing, isostatic pressing, extrusion, and slurry casting. First of all, it can be made into near-net-shaped and complex-shaped body that is determined by the shape of mold. Secondly, green body has enough strength for machining. Third, ceramics made by gelcasting have homogeneous microstructure and high strength. Finally, it can be applied both in laboratory and industry scale [2].

Ni/YSZ cermet is a common anode material, which has high electrical conductivity, high electro-catalysis, and lower cost. In Ni/YSZ anode, metal Ni acts as electro-catalyst and current collector, and YSZ provides oxygen ionic conduction and body strength. In addition, pores in the anode microstructure provide the pathway for the fuel gas diffusion. And the interfaces of Ni with YSZ and the pores construct the so called three phase boundaries (TPBs) on which the electrochemical reactions occur. Thus anode-supports are requested to exhibit a homogeneous microstructure and fully dispersal of the ceramic particles.

Gelcasting is a wet-forming process, which may make NiO, YSZ, and pore former fully mixed. Commercial oxide powders always aggregate to some degree, so dispersant is needed to inhibit them from aggregating during ball-mill. Monomers make particles piled tightly when they polymerize, thus it can raise the strength and electrical conductivity of the specimens. The

---

* Corresponding author. Tel.: +86 551 3603234; fax: +86 551 3607627.
E-mail address: mgym@ustc.edu.cn (G. Meng).

amount of the pore former determines porosity, and the shape of pore former determines the pore structure and size. Based on the above considerations, anode-support with high porosity, electrical conductivity and strength could be prepared. Due to this virtue, many researchers used gelcasting to fabricate composite and doped materials with special functions as well as complex shapes in some cases [3–12]. Certainly, the anode-supports with complex-shape which may provide larger effective surface can be fabricated by gelcasting process. The tubular anode-supports with one end closed can be easily fabricated by appropriate mold, but it is impossible for extrusion. The uniform dimension of anode-supports makes them assemble into stacks more easily. So far, some researchers used gelcasting to synthesize key materials for SOFCs [10,12] and fabricate cathodes [5,6,11], but there is no report about tubular anode fabricated by gelcasting. In this study, a gel-casting process is developed to fabricate tubular NiO/YSZ anode-supports, and factors effecting on anode microstructure, bend strength, and electrical conductivity were investigated.

2. Experiment

2.1. Materials

In this study, commercial NiO and YSZ powders were used. NiO was pre-calcined at 700 °C for 2 h in order to reduce the high specific surface area, which made suspension with high viscosity. Polyacrylic acid (PAA) was used as dispersant. The pH value of suspension was adjusted by ammonia. Organic monomer (acrylamide, AM) and cross-linker (N,N'-methylenebisacrylamide, MBAM) were dissolved in deionized water at the ratio of AM:MBAM = 5:1 (wt) to prepare a premix solution. Ammonium persulfate ((NH_4)$_2S_2O_8$, APS) acted as an initiator. N,N,N',N'-tetramethylethylenediamine (TEMED) was a catalyst.

2.2. Preparation and characteristic of the suspensions

The procedure of the gelcasting process was similar to the previous study [13]. Oxide powders were mixed in ethanol at a ratio of m_{NiO}:m_{YSZ} = 6:4 by ball-milling for 24 h, then dried at 80 °C. The premixed solutions with the concentration of 10, 15, 20, 25, and 35% were prepared. The solutions were mixed with NiO/YSZ powders and ball-milled, and then suspensions with solid loading of 35, 37, 40, 45, and 50 vol.% were obtained. In order to enhance the dispersal of the particles, 1.5–6 wt% PAA was added, and pH value was adjusted to 10–11. 0–15 wt% starch as pore former was added into the suspensions. After being fully ball-milled, stable suspensions were attained. Suspensions viscosities were measured by a rotation rheometer (NXS-11).

2.3. Casting and characterization of the specimens

Before casting, APS and TEMED were added, and then the suspensions were ball-milled for 20 min and degassed for 10 min, and poured into a bar-molds (5 mm × 5 mm × 50 mm) and tube-molds (Ø10/6 mm). After monomers polymerized at 80 °C, green bodies were demolded and dried at room temperature under 90%RH for 48 h to avoid cracking and non-uniform shrinkage [3]. Green bodies were sintered at 1400 °C for 5 h, and sintered anodes were reduced at 750 °C in hydrogen for another 5 h. The porosity, pore size distribution, electrical conductivity, and bending strength were measured by Archimedes method, bubble-point method, four-probe method, and bending strength instrument (MTS-809Axial/torsionalTestSystem), respectively. The specimen microstructure was observed by SEM (a Hitachi X-650 Scanning Electronic Microscope).

3. Results and discussions

3.1. The rheological behaviors of the suspensions

The properties of Ni/YSZ anode depend on microstructure—the distribution of Ni, YSZ and pores, which is strongly influenced by the rheological behavior of suspension. Lower viscosity is in favor of particles dispersal, suspension homogeneity, degassing, casting, and defect-free. So, in order to attain high properties anode, we must take great efforts to study the rheological behavior of suspension. Many researchers found there were several factors affecting the rheological behavior of suspension, such as pH value, dispersant, monomer, and solid loading [3,4]. But all these factors differ from system to system. So this study will involve the following aspects.

3.1.1. The amount of starch

Gelcasting is generally employed to fabricate high-density ceramics, so pore former is needed to fabricate porous anode. Fig. 1 shows that starch not only increases viscosity, but also changes the rheological behavior of the suspension. The suspensions without starch show shear thinning behavior—suspension viscosities decrease with shear rate. On the contrary, the suspensions with 8% starch show shear thickening behavior—suspension viscosities increase with shear rate. It is the reason that the addition of starch greatly increased solid loading of the suspension, and the suspensions of high solid loading always show shear thickening behavior [14]. Fig. 2 can
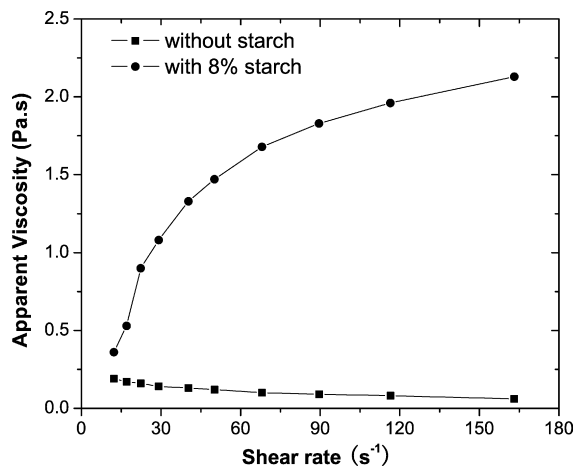

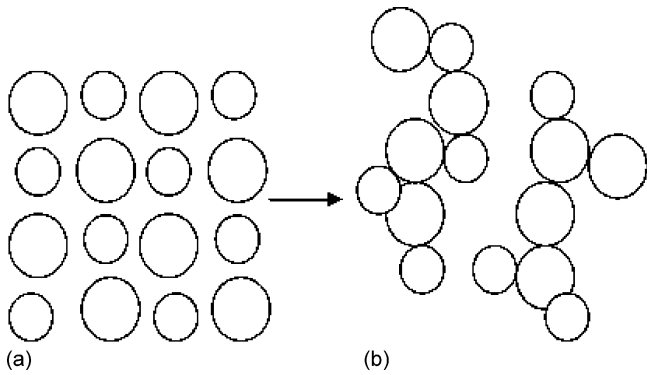Fig. 1. Rheological behaviors of the suspensions with 8% or without starch.

Fig. 2. Simulating picture of particles arrange of high solid loading at (a) low shear rate and (b) high shear rate.

explain the phenomenon of shear thickening behavior in high solid loading suspensions. In Fig. 2a, particles arrange regularly at lower shear rate, and seldom collide, so shear force is small. At higher shear rate, particles arrange irregularly and more collide (see Fig. 2b), as increases shear force. Fig. 3 shows viscosity increases slowly as the amount of starch increases from 0 to 10%, but there is a drastically increase above 10%. Therefore, the amount of starch should be less then 10%.

3.1.2. Dispersant concentration

The dispersant can prevent the particles from aggregating by absorbing on the particles surface, which reduce the suspension viscosity and improve the strength of green body made by gel-casting. In this work, PAA was employed as the dispersant. PAA is a polyelectrolyte and can impart electrostatic and steric stabilization. However, as a polymer, it also increases the suspension viscosity to some degree. As shown in Fig. 4, at the lower PAA concentration, the dispersal of PAA was dominated, and the suspension viscosity decreased as PAA concentration increased. When the PAA concentration was larger than 3%, the particles had been fully dispersed, and excess PAA would increase viscosity. So the suspension viscosity increased with PAA concentration. Moreover, excess PAA hindered the polymerization
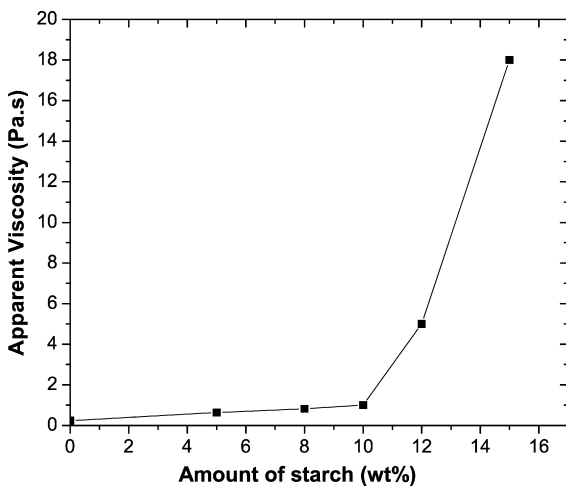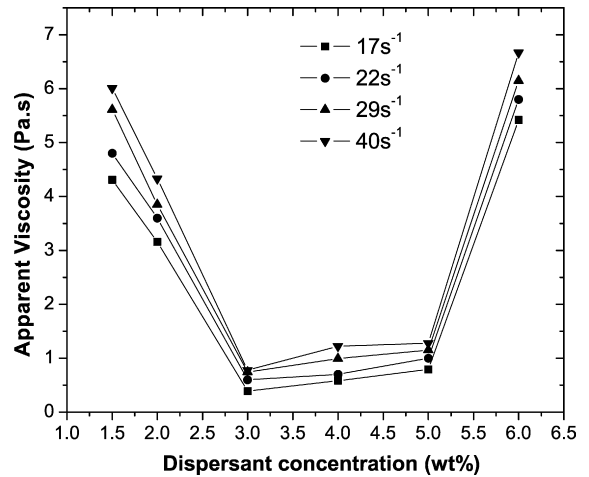

Fig. 4. Rheological behaviors of the suspensions with concentration of dispersal.

of monomers and reduced strength of the green bodies. So the optimum PAA concentration was about 3%.

3.1.3. pH value

At above pH 7, PAA can release anions and impart electrostatic stabilization. The isoelectric points of pH for YSZ and NiO are 7.3 and 9.6, respectively [15]. The anions released from PAA absorb on particles surface and make isoelectric points of them lower than 7 [15,16]. So a stable suspension with lower viscosity was attained when pH value was adjusted to 10–11 by ammonia.

3.1.4. Concentration of monomer

Organic monomers on the particles surface are polymerized by an initiator and form large linear molecules. Cross-linker makes linear molecules cross-link under the conditions of catalyst existence or heating up to some temperature or both, which leads to particles immobilization and consolidation. The monomer concentration greatly influences the suspensions viscosity, as can be seen from Fig. 5. Just like PAA, on the one hand, organic monomers play a role of steric stabilization; on the other
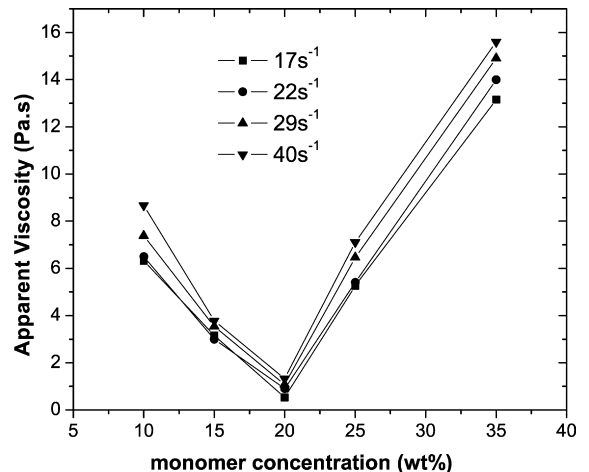

Fig. 3. Rheological behaviors of the suspensions with different amount of starch.
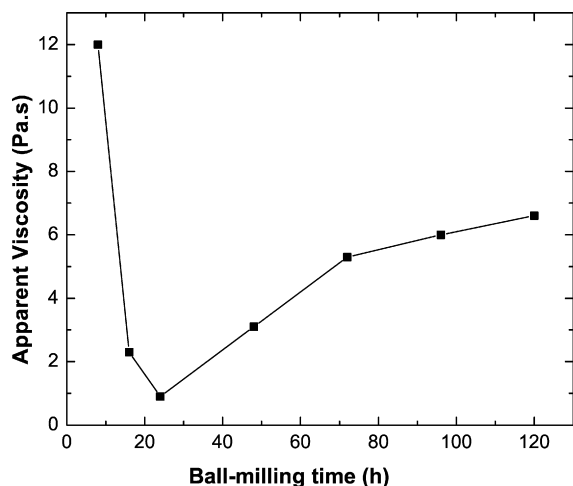

Fig. 5. Rheological behaviors of the suspensions with concentration of monomer.

Fig. 6. Effect of ball-milling time on viscosity of suspension.

Fig. 7. Effect of solid loading on the shrinkage of NiO/YSZ anode sintered at 1400 °C.

hand, it increases viscosity. After particles are fully dispersed, excess monomers raise viscosity rapidly. Result in Fig. 5 indicates that 20% is the optimum monomer concentration in order to obtain a lower viscosity suspension.

3.1.5. Ball-milling time

During ball-milling, the shear force produced by the roll of balls breaks up the agglomerated particles, and the dispersant molecules absorb on the particle surface to prevent them from aggregating again. Thus ball-milling process can decrease suspension viscosity. But as shown in Fig. 6, the suspension viscosity actually increases gradually with time during ball-milling. That was probably due to the dissolution of some starch because of friction heat produced by ball-milling. So the optimum ball-milling time was 24 h.

3.1.6. Solid loading

The higher solid loading in the suspension may lead to the higher suspension viscosity and the higher density of the resulted ceramic. So many researchers devoted to fabricate high-density materials by casting high solid loading suspensions [3,4]. However, SOFCs anodes should be porous, so it is not necessary to pursue extensively the high solid loading. Fig. 7 shows how the solid loading affects sintering shrinkage rate, which should be considered for the afterwards co-sintering process with electrolyte layer. Generally, the shrinkage rate of the anode-support is required to be equal to or a little higher than that of the electrolyte layer in order to obtain a fully dense electrolyte layer. Bao et al. [17] found that the shrinkage rate of YSZ sintered at 1400 °C for 5 h was 20.5%. After sintered at 1400 °C, the shrinkage rate of anode made by gelcasting with solid loading of 45% was 21.6% in this study. So the proper solid loading should not be over 45%.

There are some other factors affecting the rheological properties of suspensions, such as particle size, temperature, and kinds of monomer, which are not investigated in this study. According to above, the optimum amount of starch, dispersant, PH value, monomer, ball-milling time, and solid loading were <10%, 3%, 10–11, 20%, 24 h, and <45%, respectively. Under
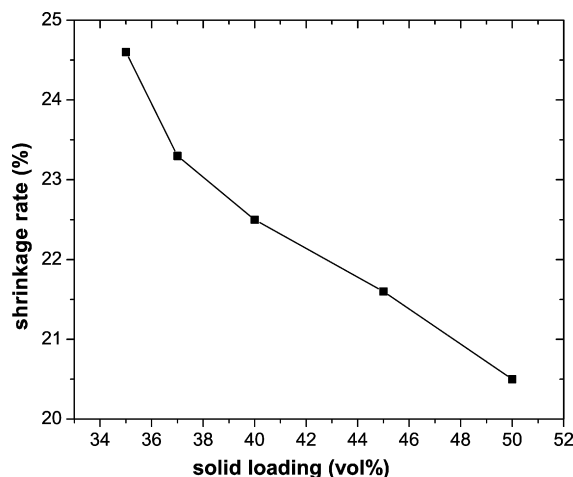
these conditions, the suspension viscosity was 0.53 Pa s (at shear rate of $17\,s^{-1}$), which was suitable for casting [4,14]. Fig. 8 shows a tubular green body of NiO/YSZ cermets anode made by gelcasting.

3.2. The control of pore structure

Pore structure is very important for anode. The electrochemical reaction on SOFC anode side is expressed as follows:

$$H_2 + O^{2-} \rightarrow H_2O + 2e$$

$$\text{or} \quad CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e$$
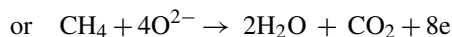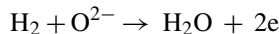
As a support, anode is much thicker than other components. So anode should provide enough open pores for transporting

Fig. 8. Photograph of green body of NiO/YSZ anode tube made by gelcasting.

fuels and reactive products so that electrochemical reaction can be lasted. Otherwise, great concentration polarization loss will make cell power decrease rapidly. There are two kinds of pores: open pores and close pores. Close pore is ineffective, so the shape and size of pore former is very important. Pore characterizations involve porosity, pore size distribution and gas penetration, but the status of measuring gas penetration cannot really represent the working condition in anode microstructure. Higher porosity may reduce close pore, and also reduce its strength and electrical conductivity. According to the theory of seepage flow, more than 33% porosity is needed to form most open pores, so anode porosity should be controlled between 30% and 40%. For the same porosity, the anode with larger pores would have less TPBs. Du and Sammes [18] used capillary flow porometry technique to have revealed that the largest open pore size was 0.152 μm and the mean flow pore size was 0.052 μm. It is difficult to fabricate small pore size ceramics with high porosity. Fortunately, the pore size of gelcasting body could be much smaller than that of cold-pressed body [6].

In this study, we found small amount of PAA has a little effect on porosity. Fig. 9 shows the effect of starch on porosity and sintering shrinkage rate. Porosity increases with the amount of starch, but shrinkage rate reduces slowly. It is the reason that starch is also a binder and can make particles piled tightly during forming. According to the demanding of porosity, the reasonable amount of starch is 2.5–5%. Figs. 10 and 11 show how monomer concentration affected shrinkage rate, porosity, and pore size distribution. Just like starch, monomer polymerization made particles piled tightly and reduced the shrinkage rate. Nevertheless, porosity decreased as the amount of monomer increased. It was the reason that the amount of monomer added was too small to affect the porosity as starch. Fig. 11 also shows that the pore size of the specimen made from lower monomer concentration was bigger than the one from higher monomer concentration. As more monomer was added, polymerization made particles piled tightly, and pores became smaller. As pores became smaller, the small pores formed by exiting of organic compounds broadened the pore size distribution. The broadened pore size distribution is beneficial to gas flowing and diffusing.
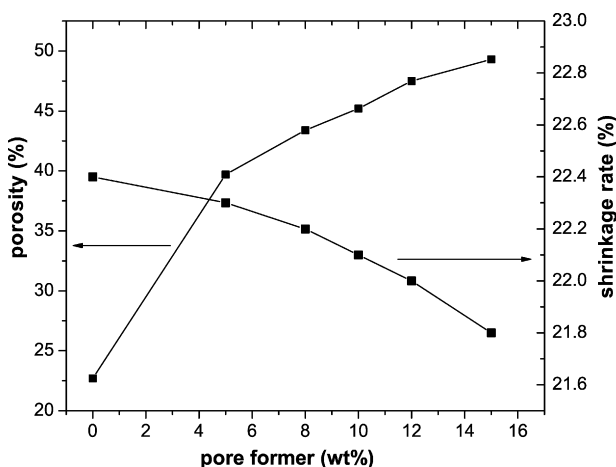
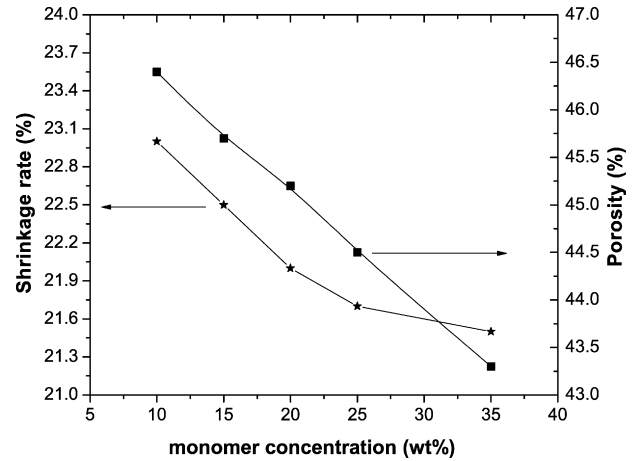

Fig. 10. Effect of monomer concentration on shrinkage rate and porosity.

When monomer concentration was more than 15%, mean pore size was below 0.9 μm, and few pores were larger than 1 μm, which was very suitable for coating electrolyte thin film.

3.3. Mechanical strength

As the supports of SOFCs, it should have enough strength to meet the need of fabricating other parts of SOFCs (such as electrolyte, cathode, and inter-connector) and assembling them into stacks. More monomers polymerization make particles piled much tightly, and bend strength of anode increased, as can be seen in Fig. 12. Bend strength increased rapidly at 20% of monomer concentration, which was due to the lowest viscosity of suspension and the best dispersal of particles. There was a strength loss of 20 MPa after reducing. With 20% monomer and 8% starch, anode had bend strength of 100 MPa and porosity of 43.4%. If the amount of starch reduced to 5%, porosity would reduce to 39.6%, and bend strength rose to 112.8 MPa. Du and Sammes [18] fabricated tubular Ni/YSZ anode by extrusion, which had bend strength of 130 MPa and porosity of 28%. So gelcasting is a good form method of fabricating high strength and

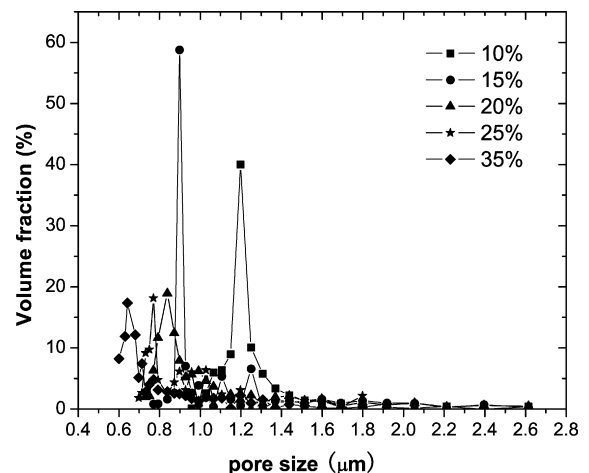Fig. 9. Effect of starch on sintering shrinkage rate and porosity.

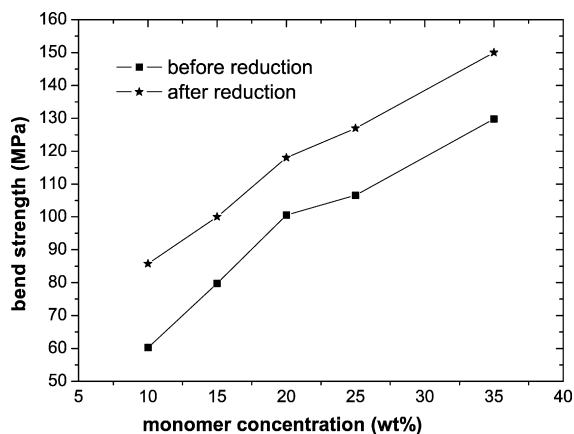Fig. 11. Effect of monomer concentration on distribution of pore size.

Fig. 12. Effect of monomer concentration on bend strength.

high porosity anode, and it would make anode-support become thinner.

3.4. Electrical conductivity

Fig. 13 shows the effect of monomer concentration on electrical conductivity. Just as suspension viscosity, at monomer concentration of 20%, suspension reached the lowest viscosity, and particles in suspension got the most fully dispersal, which brought about the highest electrical conductivity. According to Figs. 5 and 13, the viscosity of 25% and 35% monomer suspension are larger than those of 10% and 15%, but the electrical conductivity of 25% and 35% monomer suspension are little higher than those of 10% and 15%. It indicates that the monomer polymerization increases electrical conductivity in some degree by making particles compact. The highest electrical conductivity was $482\,s\,cm^{-1}$, which is higher than that of the anode made from materials synthesized by wet-chemical method [19], which has a well dispersal of NiO and YSZ. The fracture surface of Ni/YSZ anode is shown in Fig. 14, and metal Ni (bright) is well dispersed in the YSZ framework (dark). The irregular and slice-shape of Ni implies well connection each other. All of these prove particles were fully dispersed in gelcasting suspension.
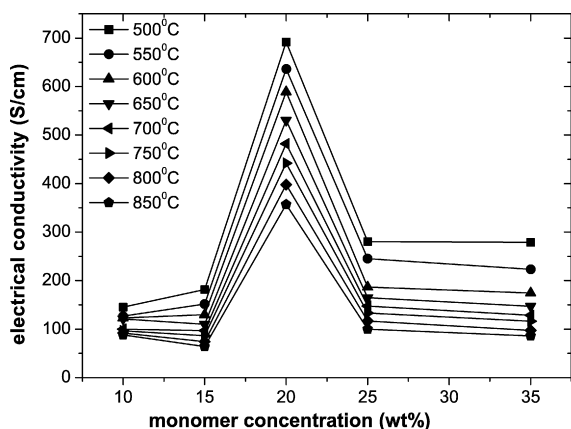

Fig. 13. Effect of monomer concentration on electrical conductivity at different temperature.
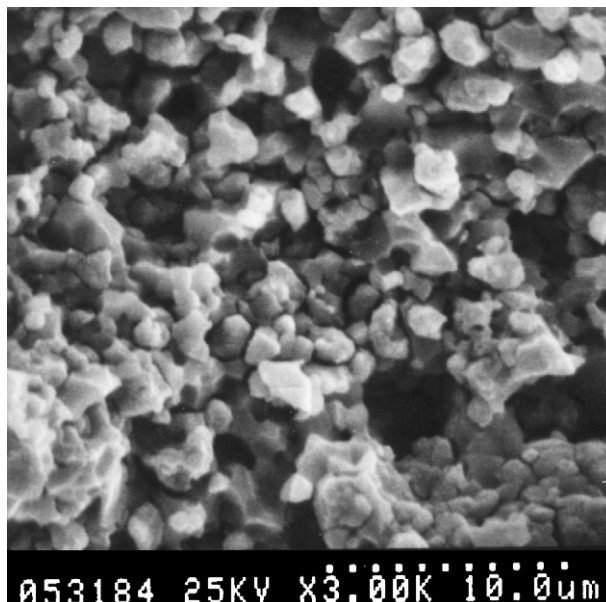

Fig. 14. SEM photograph of fracture surface of Ni/YSZ anode.

4. Conclusions

Gelcasting is a good method to fabricate tubular Ni/YSZ anode-support of SOFC. The rheological behavior of suspension directly influenced casting and production, so the optimum conditions of gelcasting suspension were investigated. Under these conditions, a suspension with the viscosity of 0.53 Pa s (at shear rate of $17\,s^{-1}$) was attained, which was suitable for gelcasting. The results of characterizing anode suggested monomer concentration greatly affected anode properties, especially bend strength and electroconductivity, which related to the dispersal of particles. Therefore, the sufficient dispersal is not only the key of gelcasting, but also the virtue of gelcasting. The tubular Ni/YSZ anode made by gelcasting process with 39.6% in porosity, 112.8 MPa in bending strength, and $482\,s\,cm^{-1}$ at $700\,°C$ in electroconductivity met well the requirements for SOFCs.

References

[1] S.D. Kim, S.H. Hyun, J. Moon, J.-H. Kim, R.H. Song, J. Power Sources 139 (2005) 67–72.
[2] O.O. Omatete, M.A. Janney, S.D. Nunn, J. Eur. Ceram. Soc. 17 (1997) 407–413.
[3] K. Niihara, B.-S. Kim, T. Nakayama, T. Kusunose, T. Nomoto, A. Hikasa, T. Sekino, J. Eur. Ceram. Soc 24 (2004) 3419–3425.
[4] X. Liu, Y. Huang, J. Yang, Ceram. Int. 28 (2002) 159–164.
[5] X. Liu, J. Gao, Y. Liu, R. Peng, D. Peng, G. Meng, Solid State Ionics 152–153 (2002) 531–536.
[6] G.-J. Li, R.-M. Ren, Z. Wu, Mater. Lett. 58 (2004) 2583–2585.
[7] L. Ma, J. Yang, L. Zhao, Y. Huang, J. Eur. Ceram. Soc. 22 (2002) 2291–2296.
[8] Y.-F. Liu, X.-Q. Liu, H. Wei, G.-Y. Meng, Ceram. Int. 27 (2001) 1–7.

[9] D. Guo, K. Cai, Y. Huang, L. Li, Z. Gui, Mater. Res. Bull. 38 (2003) 807–816.

[10] S. Zha, C. Xia, X. Fang, H. Wang, D. Peng, Ceram. Int. 27 (2001) 649–654.

[11] G. Meng, H. Wang, W. Zheng, X. Liu, Mater. Lett. 45 (2000) 224–227.

[12] Y. Yin, W. Zhu, C. Xia, G. Meng, J. Power Sources 132 (2004) 36–41.

[13] Y. Gu, X. Liu, G. Meng, D. Peng, Ceram. Int. 25 (1999) 705–709.

[14] C.-G. Ha, Y.-G. Jung, J.-W. Kim, C.-Y. Jo, U. Paik, Mater. Sci. Eng. A 337 (2002) 212–221.

[15] Y. Sunagawa, K. Yamamoto, A. Muramatsu, J. Phys. Chem. B 110 (2006) 6224–6228.

[16] Y. Zhang, J. Gao, D. Peng, M. Guangyao, X. Liu, Ceram. Int. 30 (2004) 1049–1053.

[17] W. Bao, Q. Chang, G. Meng, J. Membr. Sci. 259 (2005) 103–109.

[18] Y. Du, N.M. Sammes, J. Power Sources 136 (2004) 66–71.

[19] F.C. Fonseca, D.Z. de Florio, V. Esposito, J. Electrochem. Soc. 153 (2) (2006) A354–A360.