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Slip casting combined with colloidal spray coating in fabrication of tubular anode-supported solid oxide fuel cells

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Abstract

A simple and cost-effective slip casting technique was successfully developed to fabricate NiO–YSZ anode substrates for tubular anode-supported single SOFCs. An YSZ electrolyte film was coated on the anode substrates by colloidal spray coating technique. A single cell, NiO–YSZ/YSZ (20 μm)/LSM–YSZ, using the tubular anode supports with YSZ coating, was assembled and tested to demonstrate the feasibility of the techniques applied. Using humidified hydrogen (75 ml/min) as fuel and ambient air as oxidant, the maximum power densities of the cell were 760 mW/cm^2 and 907 mW/cm^2 at 800 °C and 850 °C, respectively. The observed OCV was closed to the theoretical value and the SEM results revealed that the microstructure of the anode fabricated by slip casting is porous while the electrolyte film coated by colloidal spray coating is dense.

Keywords: Solid oxide fuel cell; Anode-supported; Tubular; Slip casting; Colloidal spray coating

1. Introduction

Solid oxide fuel cells (SOFCs) have been recognized as one of the most promising technologies for converting chemical energy of fuels to electrical power because of its high conversion efficiency, low emission pollution and practical fuel flexibility.[1–7] There are two major designs of SOFCs: planar and tubular types. Although the planar design is easier to stack so as to increase the efficiency of the system, the tubular design has many desirable characteristics over their planar counter-parts, including high mechanical and thermal stability, simple seal requirements, rapid startup capability, good thermal shock resistance and excellent power cycling.[8–13]

Using an anode support with a thin-coated electrolyte is an effective approach to reduce the thickness of electrolyte and lower the operation temperature of SOFCs while to retain high performance. Fabrication of the anode substrate and the electrolyte coating is one of the key steps. To date, a few techniques for making tubular anode supports, especially the extrusion processes, have been revealed, but there is lack of information and literatures about slip casting technique used in fabricating anode-supported tubular SOFCs.[14–18] Slip casting technique is a traditional ceramic technique. It is handy, cost-effective and is suitable for making thin wall products with various complex shapes.[1,19] Meanwhile, many techniques have been developed to fabricate yttria-stabilized zirconia (YSZ) electrolyte film on porous anode substrates. Colloidal spray coating is a simple and economic technique to fabricate thin electrolyte films. This technique sprays the colloidal suspension to the substrates directly using air brush or spray gun. It can produce very thin, dense and stable electrolyte coatings on the substrates. Moreover, colloidal spray coating is very suitable for tubular substrates because this technique is not limited by the shape of anode substrates. It is also suitable for mass production. In principle, by combining slip casting with colloidal spray coating techniques, anode-supported SOFCs with any shape can be fabricated conveniently in a low-cost way.

Slip casting combined with colloidal spray coating techniques have been used to fabricate tubular anode-supported SOFCs. The fabricating process was described in detail in this paper. To demonstrate the feasibility of the techniques, a single cell composing of the tubular anode substrate with YSZ coating was assembled and characterized. The microstructure of the anode substrate and the YSZ coating was examined by SEM analysis.

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2. Experimental

2.1. Preparation of Ni–YSZ tubular anode substrates by slip casting

A plaster slurry was made by mixing plaster powder (Guangzhou Plaster Plant, Guangzhou, China) with water in the weight ratio of 1:1. The slurry was immediately poured into a container. A glass test tube was inserted into the slurry vertically without attaching the bottom of the container. The plaster slurry was solidified after a while and the glass test tube was removed. The plaster was dried below 60 °C and then a plaster mould was ready.

Nickel oxide (NiO) powder was prepared by glycine–nitrate process (GNP).[20] Glycine (analytical reagent, A.R.) and Ni $(NO_3)_2{\cdot}6H_2O$ (A.R.) with a weight ratio of 1:1 were heated on a hot plate with a suitable amount of distilled water until they auto-ignite, producing metal oxide 'ash'. The NiO and 8 mol% yttria-stabilized zirconia (YSZ, Building Material Academy of China) powders were mixed in a weight ratio of 1:1. In addition, 10 wt% Arabic resin (balata) was firstly dissolved in the distilled water and added in the NiO–YSZ powders as pore former to get sufficient porosity. After ball-milled with a proper amount of water for several minutes, the anode slurry was poured into the dry plaster mould. Water in the slurry was absorbed by the plaster mould and a solid layer of NiO–YSZ was formed on the wall. The slurry was provided continuously to keep the top surface of the liquid in the plaster mould at a constant level, until a required wall thickness was achieved. The surplus slurry was decanted. The NiO–YSZ layer on the wall shrank during drying in the air and separated from the mould. The NiO–YSZ tubular anode substrates was removed from the mould, dried completely and pre-fired at 1000 °C for 4 h with a heating rate of 2 °C min^{-1}. The wall thickness of the tubular anode can be controlled by the amount of the slurry used. After that, a NiO–YSZ layer which was called the anode functional layer was deposited onto the outside of the sintered anode tubes using dip coating technique in order to form a homogeneous surface for colloidal spray coating. The slurry for the anode function layer is composed of NiO (synthesized by glycine–nitrate process), YSZ (TZ-8Y, Tosoh Corporation, Tokyo, Japan), ethylcellulose (A.R., Dongfeng Chemical Reagents Plant, Wenzhou, China), terpineol (A.R., Tianjin Kermel Chemical Reagents Development Centre, Tianjin, China), oil and ethanol. The detailed slurry composition for anode function layer was listed in Table 1. The thickness of the tubular anode is 0.08 cm and the out-diameter of the tubular anode substrates is about 0.572 cm after pre-calcination at 1000 °C for 4 h, while it becomes 0.478 cm after co-sintered with the YSZ electrolyte at 1400 °C for 4 h. The schematic diagram of slip casting technique was shown in Fig. 1. The picture of the as-made tubular anode substrates by Slip casting technique and the whole cell was shown in Fig. 2.

Table 1
Composition of the NiO–YSZ anode function layer slurry

Composition	Weight (g)	Function
NiO	5	Anode composition
YSZ	5	Anode composition
Terpineol	2.35	Plasticizer
Ethylcellulose	0.15	Binder
Ethanol	100	Solvent
Oil	0.1	Disperser

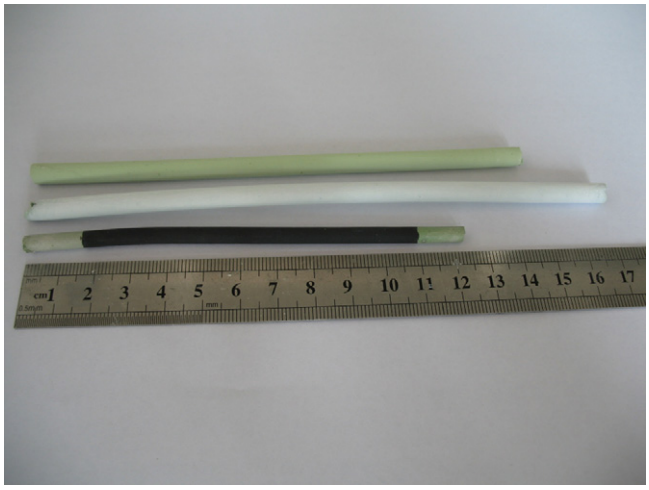

Fig. 2. Photograph of contrast among the anode substrate, thin electrolyte-coated anode substrate and the whole tubular cell.

2.2. Preparation of YSZ electrolyte film on the tubular anode substrate

YSZ powder with an average particle size of 0.2 μm bought from Tosoh Corporation (TZ-8Y, Tosoh Corporation, Tokyo, Japan) was chosen to make thin electrolyte films in this study. YSZ powder was firstly ball-milled with ethanol media by planetary ball mill for more than 30 h using an agate jar (70 cm^3) and zirconia ball media (1 cm in diameter) to ensure thorough mixing. A rotation speed of 200 rpm was used during ball milling.

5 g of YSZ ultrasonically suspended in ethanol for 30 min by mixing with 1 wt% ethyl–cellulose (A.R., Dongfeng Chemical

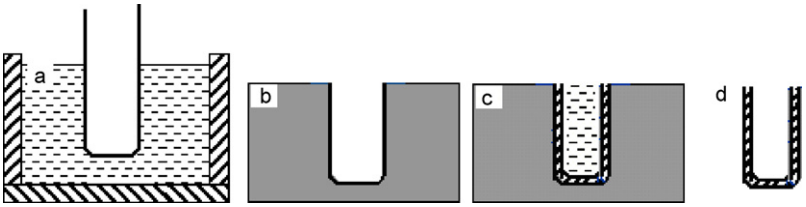

Fig. 1. Schematic diagram of slip casting technique: (a) a container with a glass test tube in the center; (b) a dry tubular plaster mould; (c) a plaster mould filled with NiO–YSZ slurry; (d) a tubular anode substrate.

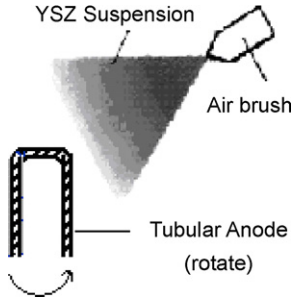

Fig. 3. Schematic diagram of colloidal spray coating technique.

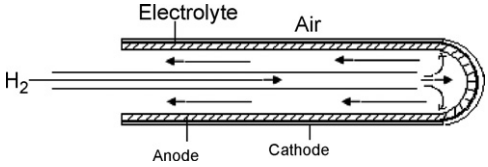

Fig. 4. Schematic diagram of single tubular SOFC.

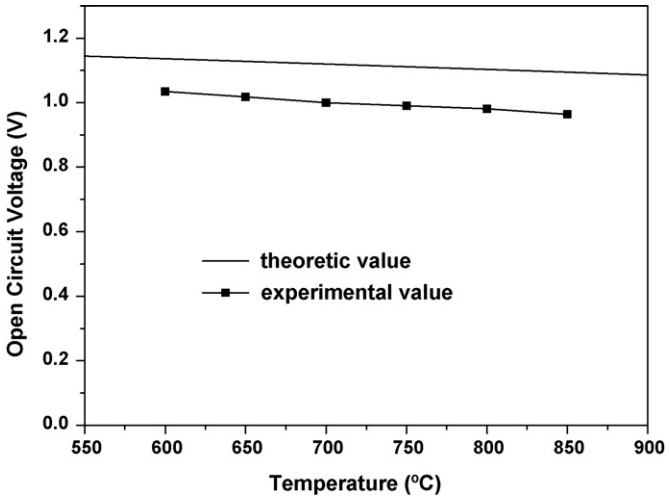

Fig. 6. Comparison of experimental and theoretical open-circuit voltages at different testing temperatures.

Reagents Plant, Wenzhou, China) and 3 wt% polyvinyl butyral (PVB, Guangda Bingfeng Chemical Plant, Tianjin, China) are used as binder. The addition of the binder can increase the strength of the film, making the electrolyte films free from possible cracks during drying and sintering. The colloidal suspension was ready. An air brush was used to spray the YSZ colloidal suspension onto the NiO–YSZ tubular anode substrate to get a thin film. Finally the tubular anode-supported thin film was sintered at 1400 °C for 4 h with a heating rate of 1 °C min^{-1} to increase the density of YSZ film. The schematic diagram of colloidal spray coating technique was shown in Fig. 3.

2.3. Cell assembling and testing

Cathode powder $La_{0.7}Sr_{0.3}MnO_3$ (LSM) was synthesized by citric–nitrate process. LSM and YSZ (TZ-8Y, Tosoh Corporation, Tokyo, Japan) powders were mixed in a weight ratio of 6:4. And then the mixed powders were ground with polyvinyl butyral to get the stable composite cathode ink. After that, the LSM–YSZ composite cathode ink was applied on YSZ electrolyte film and sintered at 1200 °C for 2 h with a heating rate of 2 °C min^{-1}. The effective cathode area was 0.143 cm^2.

Silver paste (Shanghai Research Institute of Synthetic Resins, Shanghai, China) was used as the current collector for both anode and cathode. A four-probe set-up was adopted to eliminate the ohmic loss in the silver wires. The single tubular SOFC was attached to one end of an alumina tube with the anode inside by using silver paste as sealing and jointing material.

Hydrogen saturated with water at room temperature (3% water) was used as fuel at the anode side at a flow rate of 75 ml/min and ambient air was used as oxidant at the cathode side. The flow rate of fuel gas was controlled by a mass flow controller. The single cell, NiO–YSZ/YSZ/LSM–YSZ, was tested in the temperature range of 600–850 °C. The cell performance and electrochemical impedance spectroscopy were measured using CHI604B (Shanghai Chenhua Instruments Ltd., China). The current–voltage (*I–V*) curves were tested by linear sweep voltammetry at a scanning rate of 5 mV s^{-1}. The impedances

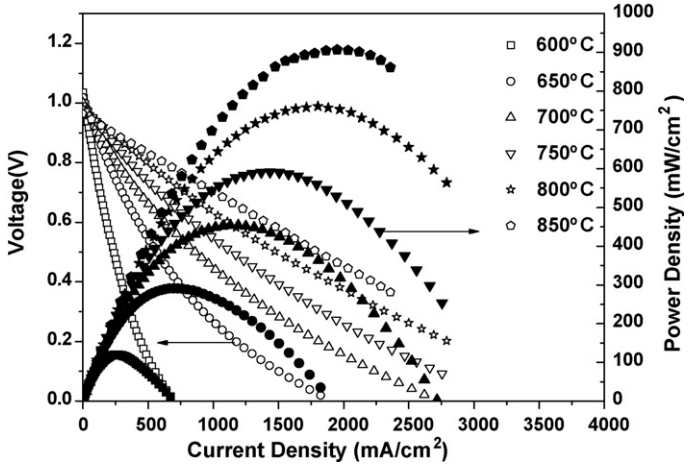

Fig. 5. Voltage and power density versus current density of a tubular SOFC operated on humidified hydrogen (3% water).

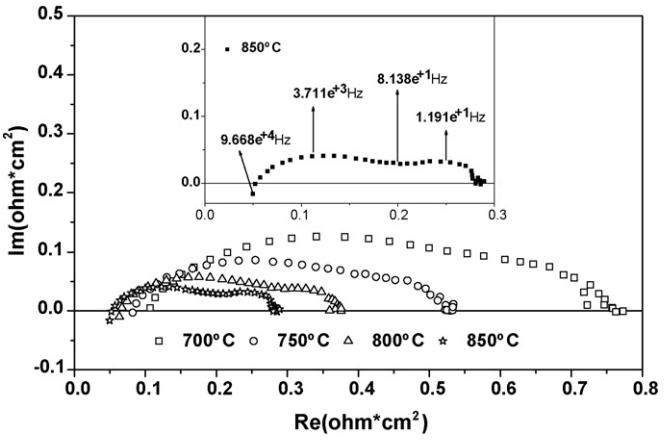

Fig. 7. Electrochemical impedance spectra measured from 600 °C to 850 °C.

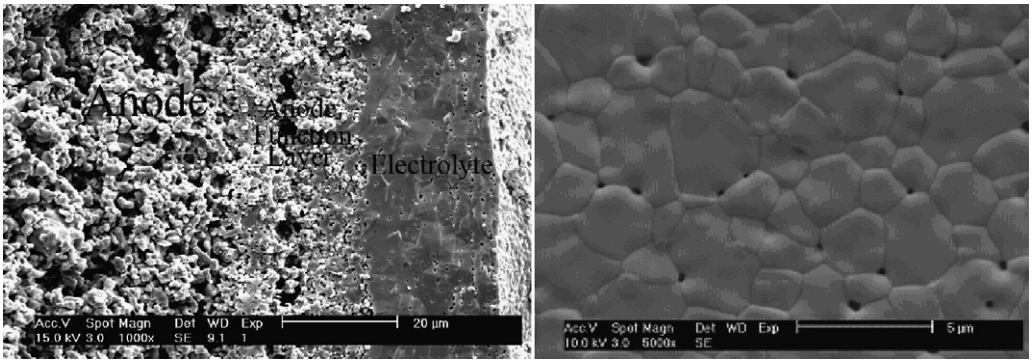

Fig. 8. SEM micrographs of (left) cross-section of a SOFC single cell after testing and (right) surface of film after sintering.

were measured in the frequency range of 100 kHz–0.1 Hz with a signal amplitude of 5 mV under open-circuit condition. After electrochemical test, the cell was fractured and examined using a scanning electron microscope (SEM). The single tubular SOFC was schematically illustrated in Fig. 4.

3. Results and discussion

3.1. Electrochemical performance of the single tubular SOFC

Fig. 5 shows the performance of the single tubular SOFC from 600 °C to 850 °C, using humidified hydrogen (75 ml/min) as fuel and ambient air as oxidant. The performance of the cell is encouraging, showing maximum power densities of the cell were 760 mW/cm^2 and 907 mW/cm^2 at 800 °C and 850 °C, respectively.

Fig. 6 presents the comparison of experimental and theoretical open-circuit voltages at different testing temperatures. The theoretical OCVs values were calculated based on the Nernst equation by assuming that the oxygen partial pressure at the cathode side was 0.21 and that the hydrogen and vapor partial pressure at anode side was 0.97 and 0.03, respectively. As shown in Fig. 6, at all testing temperatures, the experimental OCV values are a little lower than the theoretical values. As can be seen from Fig. 8, the YSZ electrolyte film is quite dense and crack-free in cross-section. So, the gas leakage through the YSZ film is insignificant. The difference between experimental OCV values and theoretical ones may come from the gas leakage across the Ag paste sealing or the test setup leakage.

The impedance spectra of the single tubular SOFC under the open-circuit condition tested at different temperatures were shown in Fig. 7. For the whole cell impedance, the intercepts on the real axis at high-frequency corresponded to the cell ohmic resistance while the arcs at low-frequency were the overall electrodes polarization resistance including both anode and cathode polarization resistance. Impedance spectra show that the ohmic resistance is small and the polarization resistance dominates in the overall resistance. Therefore, further improvement of electrode activity and electrode/electrolyte interface for anode-supported YSZ SOFCs is very necessary in future study.

3.2. Micrograph of cross-section of a single cell and the surface of YSZ film

The micrograph of (left) cross-section and (right) the surface of YSZ film of the tubular anode-supported single cell after testing were shown in Fig. 8. It is clear that the microstructure of the anode fabricated by slip casting is porous while the electrolyte film coated by colloidal spray coating is dense. The anode function layer adjacent to the electrolyte made by dip coating is less porous than the anode fabricated by slip casting. As Fig. 8 shows, further improvement of the microstructure of the anode will be necessary in the future. The thickness of the spray-coated YSZ electrolyte film was about 20 μm. The resistivity of YSZ thin film at 800 °C is about 24 Ω cm [21,22] according to the literature. Using this value, we can calculate the ASR (area specific resistance) of the 20 μm thick YSZ film as $24\,\Omega\,\text{cm} \times 20\,\mu\text{m} \times 10^{-4} = 0.048\,\Omega\,\text{cm}^2$.

This also shows that the polarization resistance is dominant while the YSZ electrolyte resistance was negligible. Combining Fig. 8 with Fig. 6 demonstrates that the YSZ film coated by colloidal spray coating is quite dense and crack-free.

4. Conclusions

In this paper simple and cost-effective slip casting technique was developed to fabricate the tubular anode-supported single SOFCs successfully. And an YSZ electrolyte film was successfully fabricated on NiO–YSZ tubular anode substrates by colloidal spray coating technique. The single cell, NiO–YSZ/YSZ (20 μm)/LSM–YSZ, exhibited good performance in the intermediate temperature. The observed OCV implies that the YSZ electrolyte film is reasonably dense. The results of impedance spectra showed that the fuel cell performance was limited by the electrode polarization resistance while the YSZ electrolyte resistance was negligible. SEM results revealed that the microstructure of the anode is good and the YSZ film was quite dense. All the factors above indicate that it is practical to introduce slip casting technique and colloidal spray coating technique to fabricate the tubular anode-supported SOFCs. Slip casting technique may be promising for tubular anode substrate fabrication though further investigation is nec-

essary. And colloidal spray coating is also a good technique for the fabrication of YSZ electrolyte films used in SOFCs.

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References

1. Minh, N. Q., Ceramic fuel cells. *J. Am. Ceram. Soc.*, 1993, **76**(3), 563–588.
2. Zhang, Y., Zha, S. and Liu, M., Dual-scale porous electrodes for solid oxide fuel cells from polymer foams. *Adv. Mater.*, 2005, **17**, 487–491.
3. Steele, B. C. H., Fuel-cell technology: Running on natural gas. *Nature*, 1999, **400**, 619–621.
4. Tompsett, G. A., Finnerty, C., Kendall, K., Alston, T. and Sammes, N. M., Novel applications for micro-SOFCs. *J. Power Sources*, 2000, **86**, 376–382.
5. Singhal, S. C., Advances in solid oxide fuel cell technology. *Solid State Ionics*, 2000, **135**, 305–313.
6. Doriya, M., SOFC system and technology. *Solid State Ionics*, 2002, **152/153**, 383–392.
7. Tu, H. and Stimming, U., Advances aging mechanisms and lifetime in solid-oxide fuel cells. *J. Power Sources*, 2004, **127**, 284–293.
8. Kendall, K. and Palin, M., A small solid oxide fuel cell demonstrator for microelectronic applications. *J. Power Sources*, 1998, **71**(1–2), 268–270.
9. Heinzel, A., Hebling, C., Muller, M., Zedda, M. and Muller, C., Fuel cells for low power applications. *J. Power Sources*, 2002, **105**(2), 250–255.
10. Saunders, G. J. and Kendall, K., Reactions of hydrocarbons in small tubular SOFCs. *J. Power Sources*, 2002, **106**(1–2), 258–263.
11. Du, Y., Sammes, N. M., Tompsett, G. A., Zhang, D., Swan, J. and Bowden, M., Extruded tubular strontium- and magnesium-doped lanthanum gallate, Gadolinium-doped ceria and yttria-stabilized zirconia electrolytes, Mechanical and thermal properties. *J. Electrochem. Soc.*, 2003, **150**(1), A74–A78.
12. Kilbride, I. P., Preparation and properties of small diameter tubular solid oxide fuel cells for rapid start-up. *J. Power Sources*, 1996, **61**, 167–671.
13. VanHerle, J., Ihringer, R., Sammes, N. M., Tompsett, G., Kendall, K., Yamada, K., Wen, C., Kawada, T., Ihara, M. and Mizusaki, J., Concept and technology of SOFC for electric vehicles. *Solid State Ionics*, 2000, **132**, 333–342.
14. Borglum, B. P., US patent 6,217,822 B1, United States Patent and Trademark Office, 2001.
15. Sun, J. J., Koh, Y. H., Choi, W. Y. and Kim, H. E., Fabrication and characterization of thin and dense electrolyte-coated anode tube using thermoplastic coextrusion. *J. Am. Ceram. Soc.*, 2006, **89**(5), 1713–1716.
16. Lee, B. T., EsfakurRahman, A. H. M. and Kim, J. H., Novel design of microchanneled tubular solid oxide fuel cells and synthesis using a multipass extrusion process. *J. Am. Ceram. Soc.*, 2007, **90**(6), 1921–1925.
17. Sammes, N. M. and Du, Y. H., Fabrication and characterization of tubular solid oxide fuel cells. *Int. J. Appl. Ceram. Technol.*, 2007, **4**(2), 89–102.
18. Sarkar, P., Yamarte, L., Rho, H. and Johanson, L., Anode-supported tubular micro-solid oxide fuel cell. *Int. J. Appl. Ceram. Technol.*, 2007, **4**(2), 103–108.
19. Liu, J., Direct-hydrocarbon solid oxide fuel cells. *Prog. Chem.*, 2006, **18**, 1026–1033.
20. Chick, L. A., Pederson, L. R., Maupin, G. D., Bates, J. L., Thomas, L. E. and Exarhos, G. J., Glycine-nitrate combustion synthesis of oxide ceramic powders. *Mater. Lett.*, 1990, **10**, 6–12.
21. Zhao, F. and Virkar, A. V., Dependence of polarization in anode-supported solid oxide fuel cells on various cell parameters. *J. Power Sources*, 2005, **141**, 79–95.
22. Lü, Z., Wang, J. M., Chen, K. F., Huang, X. Q., Ai, N., Zhu, R. B. and Su, W. H., Study on the ohmic resistance of solid oxide fuel cell based on YSZ membrane fabricated by slurry spin coating. Tenth international symposium on solid oxide fuel cells (SOFC-X). *Electrochem. Soc. Trans.*, 2007, **7**(1), 2155–2160.