

Short communication

Fabrication of ceramic films for solid oxide fuel cells via slurry spin coating technique

Rob Hui, Zhenwei Wang*, Sing Yick, Radenka Maric, Dave Ghosh

Institute for Fuel Cell Innovation, National Research Council Canada, 4250 Wesbrook Mall, Vancouver, BC V6T 1W5, Canada

Received 13 April 2007; received in revised form 12 May 2007; accepted 15 May 2007

Available online 29 May 2007

Abstract

Thin ceramic films of samaria-doped ceria (SDC) were deposited on green NiO–SDC substrate via a slurry spin coating technique followed by co-firing. The ceramic films as-prepared are homogenous and dense, without cracks and penetrating pinholes, as observed from cross-sectional SEM images. The thicknesses of the ceramic films for one coating run can be adjusted between 0.8 and 9 μm by altering the spin rate. The film thickness (h) is inversely proportional to the logarithm of the spin rate ($\text{Log}(f)$) in the range of 3000–10,000 rpm. The slurry spin coating procedure is largely a competition between the thinning and the drying. Half-cells with both 15 and 25 mm diameters were fabricated. In addition, YSZ electrolyte layer with a thickness of 15 μm was also deposited with a homogeneous and completely dense microstructure by two runs of slurry spin coating.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Slurry spin coating; Ceramic film; Ultra thin film; Solid oxide fuel cells

1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs, operated between 600 °C and 800 °C) and low temperature solid oxide fuel cells (LT-SOFCs, operated at temperatures lower than 600 °C) are attracting more attention due to their significant potential of improving long-term performance stability, widening the material selection, and allowing quick start-up [1–2]. Reduction of operating temperature, however, requires fabrication techniques that produce thin electrolyte (about 2–20 μm) [3–4] and even ultra thin electrolyte (thinner than 2 μm) in order to significantly lower the ohmic loss [5]. Most techniques currently adopted for the fabrication of thin ceramic film can be divided into three categories: vapour-phase deposition, particle deposition and liquid-phase deposition [6–7]. Vapour-phase processing, such as electrochemical vapour deposition (EVD) [8] and pulsed laser deposition (PLD) [9] can deposit gas-tight ceramic film as thin as 0.5–1 μm . Plasma spraying processing can also be used for the deposition of the electrolyte layer, but the film will be rather thick [10]. These techniques usually

require expensive equipment and/or costly procedures. In contrast, particle deposition processing, such as screen-printing [11] and slurry coating [12], are inexpensive, and therefore, widely adopted. However, the subsequent complex drying, baking and firing steps lower the productivity and the final yield. Moreover, it is difficult to fabricate ultra thin and gas-tight ceramic film using screen-printing or slurry coating routines. Liquid-phase deposition, mainly for precursor spin coating processing, can achieve compositional homogeneity at the molecular level by using precursor solution other than prefabricated powder. This processing favours the fabrication of ultra thin ceramic film [13–15], and is also relatively inexpensive in terms of equipment and procedure.

Recently, spin coating procedures using a slurry prepared from prefabricated powder as starting materials other than precursors, so-called slurry spin coating, have been successfully developed to fabricate 15 μm SDC electrolytes for anode-supported SOFCs [16–18]. In slurry spin coating, suitable organic additives are used to adjust the solid loading, viscosity and volatility of the solvent system. Combining the advantages of particle coating and slurry coating, this method is expected to fabricate ultra thin ceramic film in an inexpensive way. In this paper, ultra thin 20 mol.% samaria-doped ceria ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$, SDC) films were deposited by slurry spin

* Corresponding author. Tel.: +1 604 221 5604; fax: +1 604 221 3001.
E-mail address: Zhenwei.Wang@nrc-cnrc.gc.ca (Z. Wang).

coating on tape cast anode substrate in various thicknesses and on different cell sizes. Thin 8 mol.% yttria-stabilized zirconia (YSZ) film was also successfully fabricated in order to demonstrate the versatility of this technique.

2. Experimental

2.1. Substrates and slurries

NiO (Novamet Inc.) and SDC (Praxair Surface Technology) were used as received. Anode substrates of NiO–SDC (50:50 by weight ratio) were prepared by tape casting using solvent-based powder slurry mixed with appropriate organic binders with 7 wt.% carbon as pore former. A mixture of methyl *iso*-butyl ketone, toluene, and ethanol was adopted as solvent. Organic additives include a binder of polyvinyl butyral (Richard E. Mistler Corporation), a plasticizer of polyalkylene glycol (Richard E. Mistler Corporation) and butyl benzyl phthalate (Richard E. Mistler Corporation), and a dispersant of phosphate ester (AKZO NOBEL Surface Chemistry LLC). The total solvent to organic additives ratio is 2:1 by weight. The thickness of the green substrate was about 2 mm.

SDC slurry for spin coating was prepared through ball milling a mixture of SDC nanopowder (n Gimat Co. BET $122.38 \text{ m}^2 \text{ g}^{-1}$) and submicron powder (Praxair. TM. BET $46.109 \text{ m}^2 \text{ g}^{-1}$), together with the same mixed solvent and organic additives as those used in the tape casting. Total SDC powder in the slurry is 34 wt.%. The SDC slurry as-prepared showed a viscosity of 25.9 cP at room temperature. Similarly, YSZ slurry with a viscosity of 85.0 cP was prepared using YSZ powder (TZ8Y, TOSOH Corp.) as the raw material.

2.2. Spin coating procedure

Circular anode substrates were cut from the green substrate using a 19 mm diameter driller. The sample was then placed on a custom-made porous support, and both were held securely by vacuum through the center of a hollow shaft in the spin coater (Laurell Technologies Corporation, Model WS-400B-6NPP). A graduated syringe was inserted through the hole at the upper lid of the spin coater, as demonstrated in Fig. 1. Static dispensing with fixed spin rate was adopted for the spin coating. After the sample was accelerated to the specified rate, 0.1 ml of elec-

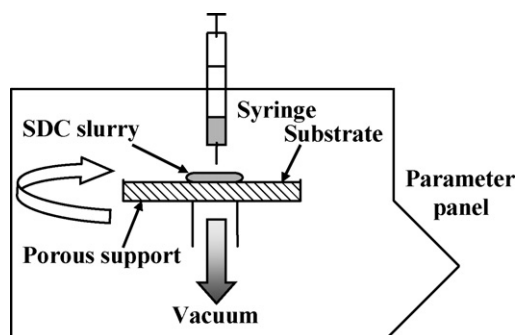


Fig. 1. Schematic diagram of spin coating.

trolyte slurry was injected onto the sample surface manually. The slurry spread across the whole sample surface within about 5 s, depending on the spin rate. The total rotation period was fixed for 30 s in order to thin, smooth and dry the electrolyte coating. After drying, the coated sample was co-fired at a temperature of 1400 °C for 5 h in air. Porosity of the fired anode substrates was 9 vol.%. The YSZ layer was coated at a spin rate of 6000 rpm for two coating-drying cycles, and then co-fired at 1400 °C. The surface and cross-section morphologies of the cells were observed using a scanning electron microscope (SEM, Hitachi S-3500N).

3. Results and discussion

The microstructure of the SDC film, mainly characterized by thickness and homogeneity, depends on both the nature of the SDC slurry (viscosity, surface tension, volatility of solvent system, solid loading, slurry homogeneity, etc.) and the parameters chosen for the spin coating process (spin rate, rotation period, air turbulence, etc.). In this study, the properties of SDC slurry were fixed for all the samples. Thus, the spin parameters determined the coating microstructure. Fig. 2A shows the SEM photo of the cross section of the fractured cells with the thinnest SDC electrolyte. The spin rate for the functional layer and the electrolyte was 10,000 rpm and the cell was co-fired at 1400 °C for 5 h in

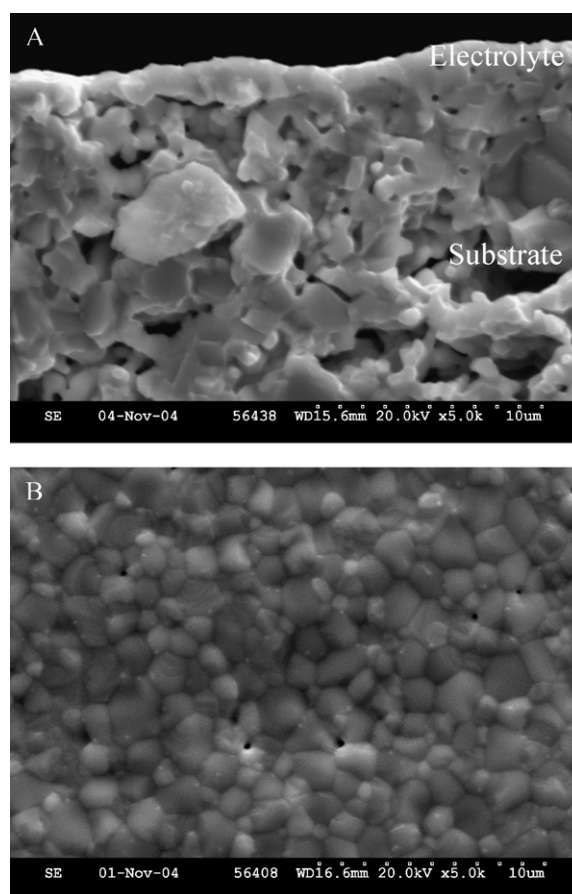


Fig. 2. Microstructure of the anode-supported cell with 0.8 μm SDC film. (A) Cross section; (B) surface.

air. The SDC film obtained shows a thickness of $0.8\ \mu\text{m}$ and a dense structure without penetrating cracks or pinholes. The film thickness varies slightly due to the surface roughness of the substrate in this scale. A small cove can hold more electrolyte slurry during spin, which grows into a thick segment after co-firing. Fig. 2B shows the surface morphology of the SDC film. The SDC layer is almost completely dense except for a few pinholes dispersed among the grain boundaries. Successfully fabricating an ultra thin and dense electrolyte layer in an inexpensive way is important for the reduction of ohmic resistance, especially for LT-SOFCs. However, conventional inexpensive techniques like screen-printing and slurry coating can only give a thick film, typically $5\text{--}20\ \mu\text{m}$ [12]. Thus, this slurry spin coating technique shows significant potential for inexpensively fabricating ultra thin ceramic film.

Ceramic films with different thicknesses have been fabricated through spin coating on NiO–SDC substrates. As shown in Fig. 3, all the SDC layers exhibit dense structures without obvious cracks and pinholes. The thicknesses of the electrolyte layers in Fig. 3A–D are 1, 2, 4 and $9\ \mu\text{m}$, obtained with corresponding spin rates of 9000, 8000, 6000, and 3000 rpm, respectively. Thicker films are obtained under lower spin rates and are more uniform. This suggests that slurry properties play a more important role than substrate topography under slow spinning.

During spin coating, fast rotation produces a centrifugal force that pushes the viscous slurry to the rim and flings excess slurry off. Meanwhile, spin rate can also affect the relative velocity between slurry and air, and in turn the characteristics of air turbulence near the coating surface. Both factors are important for the volatile speed of the solvent system and for the increase in coating viscosity. The slurry thinning procedure is thus largely a balance between thinning and drying. With the evaporation of the volatile species, viscosity increases drastically until the centrifugal force can no longer appreciably move the hardened resin toward the rim. After that, film thickness will not decrease significantly with further spinning. The subsequent drying, however, will further thin the resin.

According to spin coating theory [19–21], when the effect of evaporation during thinning can be neglected, film thickness is proportional to solid loading (volume percent) and inversely proportional to rotating speed, as described by

$$h \propto \alpha C \omega^{-1} \quad (1)$$

where h is the film thickness (μm), α the empirical constant, C the solid loading and ω is the angular speed (rad s^{-1}) ($1\ \text{rad s}^{-1} = 9.549\ \text{rpm}$).

However, when evaporation plays an important role, film thickness is inversely proportional to the square root of the

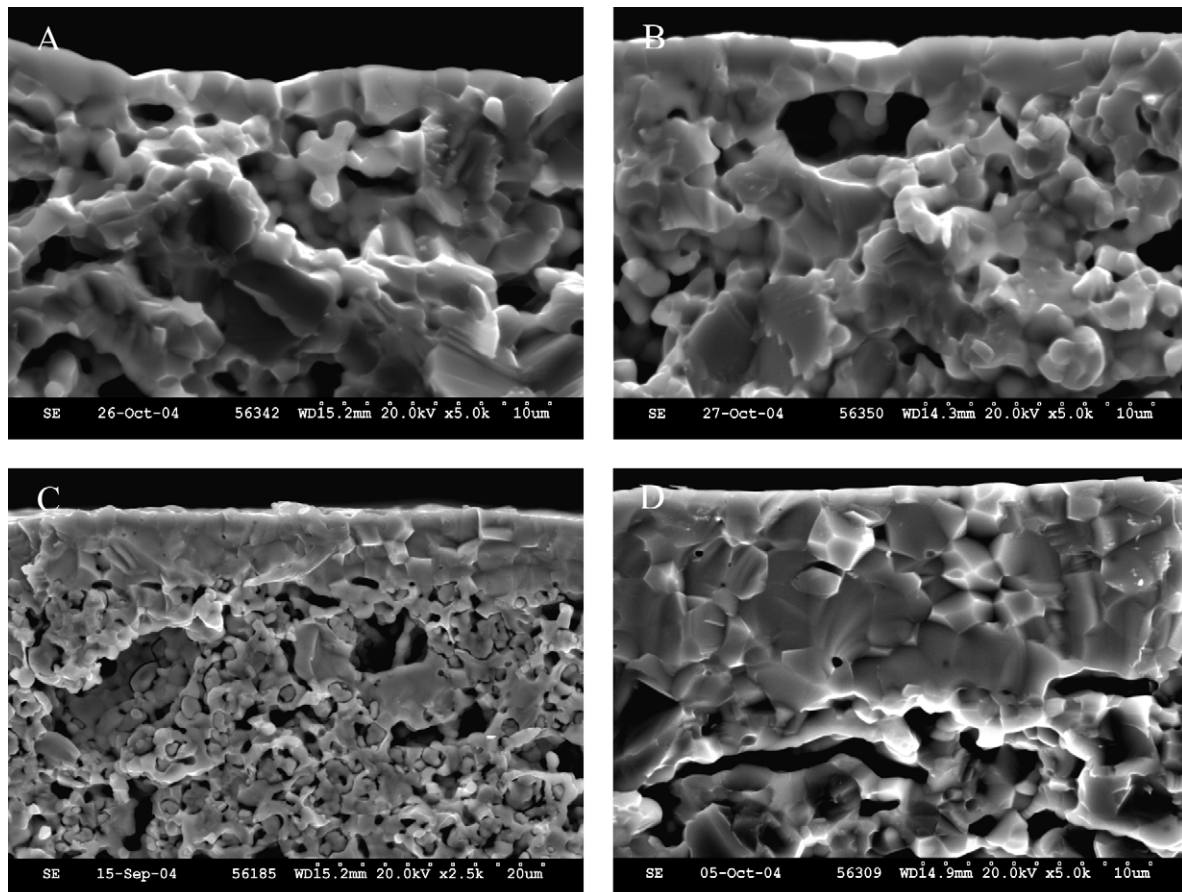


Fig. 3. Cross-section microstructure of the anode-supported cells with different film thicknesses. (A) $1\ \mu\text{m}$; (B) $2\ \mu\text{m}$; (C) $4\ \mu\text{m}$; (D) $9\ \mu\text{m}$.

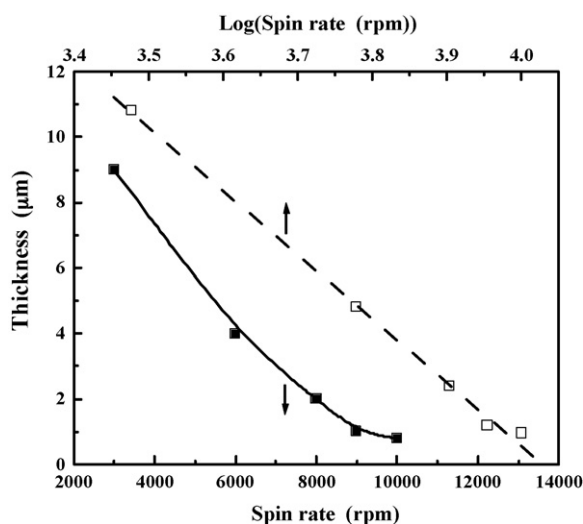


Fig. 4. Relationship between spin rate (f) and film thickness (h).

rotating speed, as described by

$$h \propto \alpha C \omega^{-0.5} \quad (2)$$

It should be indicated that the thicknesses of the SDC layer from SEM observation in this study are different from the original values before sintering. Immediately after spin coating, the drying of the electrolyte coating under room temperature, constrained by the predry substrate, is mainly one-dimension shrinkage in the Z-direction. During co-firing, the radial shrinkage of the electrolyte can also take place, with shrinkage of about 20%. Meanwhile, densification under high temperature is accompanied by free shrinkage in the Z-direction, with the partial shrinkage depending on coating thickness. Therefore, the thickness of the SDC layer from SEM observation is determined not only by the coating step but also by the co-firing process. Fig. 4 gives the relationship between spin rate and film thickness. In our study, the film thickness, h , by SEM observation, follows a linear relationship with $\text{Log}(f)$. This can be empirically described by

$$h \propto \text{Log}(f) \quad (3)$$

where f is the spin rate (rpm). This empirical relationship is different from the traditional spin coating theories that focus on thin layer coating without post-treatment.

Spin coating technique is mainly used to deposit ultra thin ceramic film on the surface of small substrates. To fabricate a thick film (thicker than $10 \mu\text{m}$) or to enlarge the sample size would be difficult because of the limitations brought by different centrifugal forces. A large sample would enhance the difference of radial centrifugal force and in turn result in inhomogeneous distribution of the electrolyte slurry, especially in the outer part. However, when the spin rate is not too high, the slurry properties play a more important role during shear distribution and coating formation. By carefully controlling the processing parameters, larger cells with a thin electrolyte can also be fabricated. Fig. 5 shows the macro-photos of the cells with 15 and 25 mm diameter. The electrolyte layer was coated at a spin rate of 6000 rpm, and

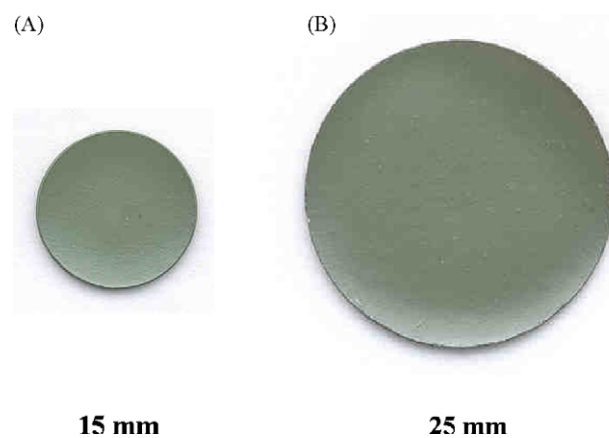


Fig. 5. Macrophotos of the SDC cells with different size. (A) 15 mm; (B) 25 mm.

both cells show complete electrolyte coverage. Adjusting slurry properties and lowering the spin rate would further improve the film microstructure. However, this size is still not big enough for scale-up and the technical obstacles would drastically increase during scale-up.

Ultra thin electrolyte can significantly reduce the ohmic resistance, but the anode-supported structure can suffer seriously from the decrease in mechanical strength, especially

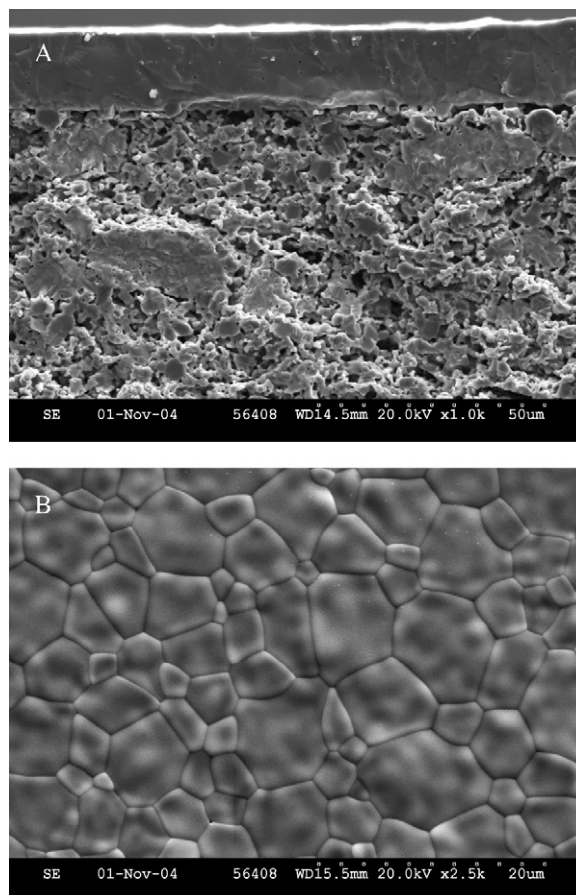


Fig. 6. Microstructure of the cross section (A) and the surface (B) of the cell with $15 \mu\text{m}$ YSZ film supported on NiO–SDC substrate.

for ceria-based electrolyte films operated under the reduction by hydrogen. Consequently, state-of-the-art electrolyte films thicker than 10 μm are still widely used in IT-SOFCs [4]. Through one coating run, it is not easy to deposit thick films due to the tendency for crack formation, especially around the perimeter. Besides, the large difference in the centrifugal force and the shrinkage stress that resulted from the fast solvent evaporation during high speed rotation also contributed to the cracks. In order to obtain thick film, repeated spin coating cycles are usually performed, with each coating run producing a thin but complete layer. Furthermore, subsequent coatings cannot only increase the film coating thickness but can also partially repair the defects caused by the previous run. Fig. 6 shows SEM photos of the cross section (Fig. 6A) and YSZ surface microstructure (Fig. 6B) of the cell. The cell has an electrolyte layer of 15 μm thickness from two coating runs at 6000 rpm followed by co-firing. The electrolyte layer is homogenous in thickness and completely dense. Prior to this work, such microstructure was obtained only via slurry coating [4] or screen printing [11].

4. Conclusions

In this paper, slurry spin coating technique has been developed in order to fabricate both ultra thin ceramic films (as thin as 0.5 μm) and thicker films (as thick as 15 μm). The ceramic films obtained are crack-free and almost completely dense. The thickness of ceramic films (h) can be adjusted by controlling the spin rate and the number of repeat cycles, and it is inversely proportional to the logarithm of the spin rate ($\text{Log}(f)$) in the 3000–10,000 rpm range. The spin coating procedure is largely a competition between thinning and drying. By repeating the coating-drying cycles, film thickness can be increased. Compared to traditional spin coating, the thickness range of the coating is noticeably larger and therefore more practical. Since slurry spin coating is an inexpensive technique, it offers a promising way to fabricate thin ceramic film for solid oxide fuel cells.

Acknowledgements

Thanks to the National Fuel Cell and Hydrogen Program of the National Research Council of Canada for the financial support of this work.

References

- [1] Z. Shao, S.M. Haile, *Nature* 431 (2004) 170–173.
- [2] S.R. Hui, D. Yang, Z. Wang, S. Yick, C. Decès-Petit, W. Qu, A. Tuck, R. Maric, D. Ghosh, J. Power Sources, in press.
- [3] J. Yan, H. Matsumoto, M. Enoki, T. Ishihara, *Electrochem. Solid-State Lett.* 8 (2005) A389–A391.
- [4] Z. Wang, M. Cheng, Y. Dong, M. Zhang, H. Zhang, J. Power Sources 156 (2006) 306–310.
- [5] N. Ito, M. Iijima, K. Kimura, S. Iguchi, J. Power Sources 152 (2005) 200–203.
- [6] J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perdnis, L.J. Gauckler, *Solid State Ionics* 131 (2000) 79–96.
- [7] Y.-Y. Chen, W.-C.J. Wei, *Solid Oxide Ionics* 177 (2006) 351–357.
- [8] U.B. Pal, S.C. Singhal, *J. Electrochem. Soc.* 137 (1990) 2937–2941.
- [9] D. Yang, X. Zhang, S. Nikumb, C. Decès-Petit, R. Hui, R. Maric, D. Ghosh, *J. Power Sources* 164 (2007) 182–188.
- [10] R. Hui, Z. Wang, O. Kesler, L. Rose, J. Jankovic, S. Yick, R. Maric, D. Ghosh, *J. Power Sources*, in press.
- [11] X. Zhang, M. Robertson, S. Yick, C. Decès-Petit, E. Styles, W. Qu, Y. Xie, R. Hui, J. Roller, O. Kesler, R. Maric, D. Ghosh, *J. Power Sources* 160 (2006) 1211–1216.
- [12] Z. Wang, M. Cheng, Y. Dong, M. Zhang, H. Zhang, *Solid State Ionics* 176 (2005) 2555–2561.
- [13] Y. Pan, J.H. Zhu, M.Z. Hu, E.A. Payzant, *Surf. Coat. Technol.* 200 (2005) 1242–1247.
- [14] S.G. Kim, S.P. Yoon, S.W. Nam, S.H. Hyun, S.A. Hong, *J. Power Sources* 110 (2002) 222–228.
- [15] Y.Y. Chen, W.-C.J. Wei, *Solid State Ionics* 177 (2006) 351–357.
- [16] K. Chen, Z. Lü, N. Ai, X. Huang, Y. Zhang, X. Xin, R. Zhu, W. Su, *J. Power Sources* 160 (2006) 436–438.
- [17] J. Wang, Z. Lü, X. Huang, K. Chen, N. Ai, J. Hu, W. Su, *J. Power Sources* 163 (2007) 957–959.
- [18] J. Wang, Z. Lü, K. Chen, X. Huang, N. Ai, J. Hu, Y. Zhang, W. Su, *J. Power Sources* 164 (2007) 17–23.
- [19] A.G. Emslie, F.T. Bonner, L.G. Peck, *J. Appl. Phys.* 29 (1958) 858–862.
- [20] D. Meyerhofer, *J. Appl. Phys.* 49 (1978) 3993–3997.
- [21] K.-S. Chou, K.-C. Huang, H.-H. Lee, *Nanotechnology* 16 (2005) 779–784.