



Short communication

Three-dimensional Li₂O–NiO–CoO composite thin-film anode with network structure for lithium-ion batteriesP. Zhang^a, Z.P. Guo^{a,b,*}, S.G. Kang^c, Y.J. Choi^c, C.J. Kim^c, K.W. Kim^c, H.K. Liu^a^a Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia^b School of Mechanical, Materials & Mechatronic Engineering, University of Wollongong, NSW 2522, Australia^c I-Cube Center, Gyeongsang National University, Gajwa-dong 900, Jinju, Kyungnam 660-701, South Korea

ARTICLE INFO

Article history:

Received 27 June 2008

Received in revised form 3 October 2008

Accepted 5 October 2008

Available online 5 November 2008

Keywords:

Li₂O–NiO–CoO composite

Thin-film

Network structure

Rate capability

Lithium-ion batteries

ABSTRACT

Three-dimensional Li₂O–NiO–CoO composite thin-film electrodes deposited on stainless steel substrates were synthesized by the electrostatic spray deposition (ESD) technique at 240 and 295 °C. The morphology of the composite was investigated by scanning electron microscopy. X-ray diffraction indicated that the as-deposited films are composites of Li₂O, NiO and CoO. The effects of the solvent used to dissolve the starting materials on the morphology and electrochemical performance of the thin-film electrodes were also investigated. It was found that the as-deposited thin-film electrodes exhibited a high reversible capacity (>800 mAh g⁻¹ when cycled between 0.01 and 3 V at a cycling rate of 0.5 C), good capacity retention, and outstanding rate capability. The superior electrochemical performance may have resulted from the combination of the very porous structure and the three-dimensional network of the as-deposited thin-film electrodes, which contributed to a high surface area, favoured lithium-ion diffusion, and formed a stable integral structure. The thin-film electrodes could be promising anodes for use in high power and high energy density lithium-ion batteries.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries are widely applied as the power source of choice for mobile devices and are required for applications in hybrid electric vehicles [1]. Anode materials currently used or under investigation include various kinds of carbon, novel alloys, transition metal oxides, nitrides, etc. [2–8]. It is essential to improve the rate capability (ability to deliver capacity at high current rates) and cyclic behavior of anode materials to meet the constantly increasing demand for high performance lithium-ion batteries. Transition metal oxides, such as CoO, NiO, Co₃O₄, and CuO, which exhibit reversible capacities about three times larger than those of graphite at a relatively low potential, are the most appealing and competitive materials for lithium-ion batteries [9]. However, the disadvantages of their high initial capacity loss and poor cycling performance restrict their application as anode materials for lithium-ion batteries [10]. To improve electrode capacity, cycling performance, and rate capability, some studies have proposed the synthesis of mate-

rials with a three-dimensional network structure that have high surface area and good ionic conductivity, as well as being free of binder and inert conductive agents [11–13].

Electrostatic spray deposition (ESD) is a unique method to create dense or porous films [11]. It has been used for the preparation of particles of metal oxides since the middle of the 1990s. It was reported that the morphology of the deposited layer can be influenced by the physical and chemical processes involved in the ESD [14–16]. Such processes include spray formation; droplet transport, evaporation, and disruption; preferential landing of droplets; discharge, droplet spreading, penetration of droplet solution, and drying; surface diffusion; and reactions [17]. Some unique films, such as with a reticular porous [11] structure, and nanofibers [18] can be obtained by the ESD method. It was found that thin-films of some synthesized compounds with these unique morphologies displayed significantly better electrochemical performance. The structures of as-prepared thin-films, and hence their electrochemical properties, can be easily controlled by varying the deposition conditions [19].

Recently, binary Ni–Co oxides have been developed as alternative electrode materials for supercapacitors, and their electrochemical properties in terms of the oxygen evolution reaction (OER) have also been widely studied in an alkaline medium [20]. Synergistic electrocatalytic behavior has been found and depends

* Corresponding author at: School of Mechanical, Materials & Mechatronic Engineering, University of Wollongong, NSW 2522, Australia. Tel.: +61 2 4221 5225; fax: +61 2 4221 5731.

E-mail address: zguo@uow.edu.au (Z.P. Guo).

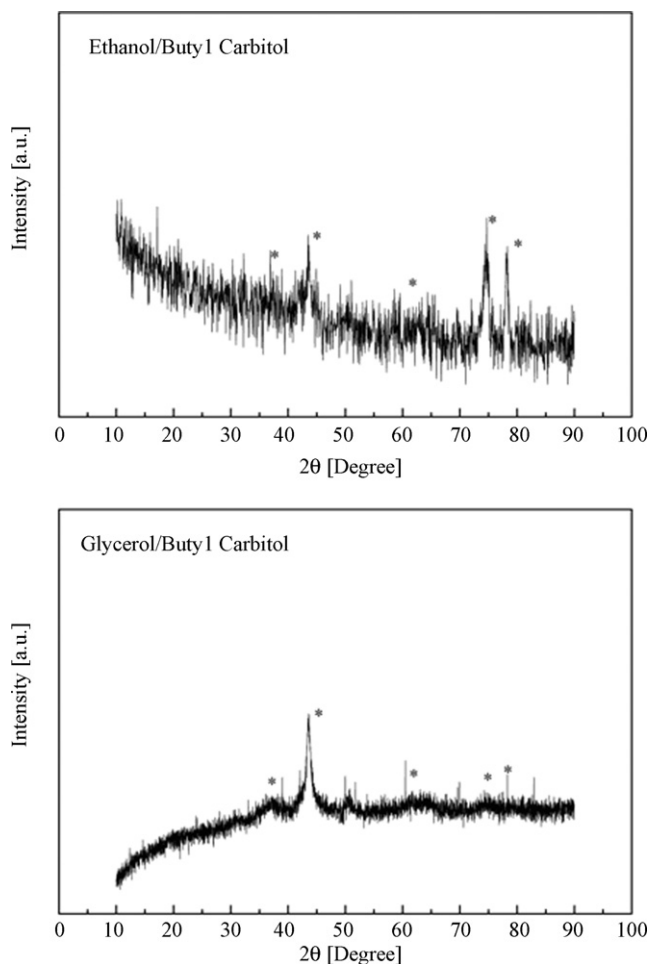


Fig. 1. XRD patterns of composite using ethanol/butyl carbitol (top) and glycerol/butyl carbitol (bottom) as solvent.

on the composition of the oxides [21]. However, only a few studies have been reported on their electrochemical properties as anode materials for lithium-ion batteries.

In this study, $\text{Li}_2\text{O-NiO-CoO}$ composite thin-films with a porous network structure were synthesized by the ESD technique. Li_2O was introduced here to suppress aggregation of the active materials [19]. The effects on the morphology and electrochemical performance of the as-prepared thin-films due to the solvent used for dissolving the starting materials were investigated. The initial capacity of the thin-films from the ethanol/butyl carbitol solution can be up to 1288 mAh g^{-1} , and the reversible capacity, was above 900 mAh g^{-1} after 25 cycles, after cycling between 0.01 and 3 V at a cycling rate of 0.5 C. The thin-films showed excellent capacity retention and rate capability.

2. Experimental

Preparation of precursor solutions: lithium acetate dihydrate (Sigma, Australia) was used as the lithium source. Nickel acetate tetrahydrate (Aldrich, Australia) and cobalt acetate tetrahydrate (Sigma-Aldrich, Australia) were used as the sources of nickel and cobalt. These materials were dissolved in a solvent composed of ethanol anhydrite (15 vol.%; Ajax Finechem), or glycerol (15 vol.%; Aldrich, Australia), combined with diethylene glycol butyl ether (85 vol.%; Dow Chemical Company) under stirring. The concentrations of Ni^{2+} and Co^{2+} were 0.005 mol L^{-1} . The concentration of Li^+ was 0.01 mol L^{-1} .

The equipment for the ESD has been described in many previous works [8]. The films were deposited on stainless steel substrates, which were heated to 240°C for ethanol/butyl carbitol and 295°C for glycerol/butyl carbitol, respectively. The precursor solution was pumped at the speed of 2 mL h^{-1} through a metal needle. A distance of 3.5 cm was maintained between the needle and the substrate. An 18 kV dc voltage was applied between the tip of the needle and the substrate to generate the spray of the precursor solution under ambient atmosphere. The weights of films were from 0.1 to 1.0 mg. The weight of the film depended on the duration of spray. The area of the thin-films is 0.8 cm^2 , which is controlled by putting a stainless steel sheet with a hole of 0.8 cm^2 on top of the substrate.

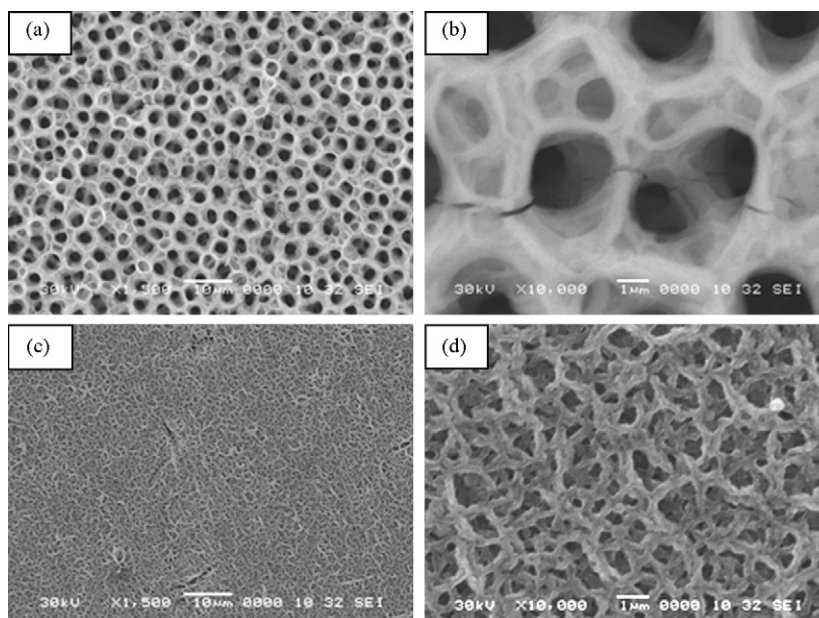


Fig. 2. SEM images of $\text{Li}_2\text{O-NiO-CoO}$ composite thin-film anode: (a and b) using glycerol/butyl carbitol as solvent; (c and d) using ethanol/butyl carbitol as solvent.

The morphology of the deposited films was investigated by scanning electron microscopy (SEM) (JEOL JSM-6460). X-ray diffraction (XRD) analysis was conducted on a Philips 1730 X-ray diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) with a 2θ range from 10° to 80° .

The electrochemical behavior of the test materials was examined via CR2032 coin cells with a lithium metal counter electrode, Celgard 2700 membrane separator and an electrolyte of 1 M LiPF $_6$, dissolved in a mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in weight ratio), were also used in the cells in this experiment. The cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany). Charge-discharge measurements were carried out at ambient temperature on a multi-channel battery cyler with a voltage cut-off of 0.01/3.0 V versus Li/Li $^+$.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the as-deposited Li $_2$ O–NiO–CoO thin-film electrodes, which could be identified as 3CoO.5NiO. The two diffraction patterns exhibit very broadened diffraction peaks, indicating that the thin-films are nanocrystalline or amorphous, which is an expected result from the low deposition temperatures (240°C for ethanol/butyl carbitol and 295°C for glycerol/butyl carbitol solution, respectively).

Fig. 2 shows SEM images of the Li $_2$ O–NiO–CoO thin-film electrodes synthesized from glycerol/butyl carbitol (Fig. 2(a and b)) and ethanol/butyl carbitol solution (Fig. 2(c and d)), respectively. Thin-films from glycerol/butyl carbitol solution show a three-dimensional network structure with uniformly monodispersed round pores. The size of the pores is in the range of 2–3 μm . From the SEM image at higher magnification, it can be observed that the “grids” consist of sub-walls, which are approximately 200 nm in thickness, and sub-holes, which are around one micrometer in diameter. For the thin-films from ethanol/butyl carbitol solution, the film texture is significantly different. A three-dimensional network structure with belt-like crossovers was formed. The holes are not uniform, and the belts are less than one micrometer in thickness. The combination of the very porous structure and the three-dimensional network structure of both thin-film electrodes would deliver a high surface area, favour ion diffusion during the reaction with lithium, and form a stable integral structure, which could deliver high capacity, good capacity retention, and excellent rate capability, as demonstrated by the discharge/charge results below.

The voltage profiles of the electrochemical cells containing Li $_2$ O–NiO–CoO/Li are shown in Fig. 3. The first discharge delivered a specific capacity of 1070 and 1288 mAh g $^{-1}$, respectively, for the thin-films from glycerol/butyl carbitol and ethanol/butyl carbitol solutions. Both values are significantly higher than the theoretical capacity, if only the 3CoO.5NiO component is active. The extra capacity is likely related to the reversible formation and decomposition of a polymeric gel-like film formed on the surface of the CoO–NiO during discharge/charge cycling [22,23]. The existence of the Li $_2$ O component in the thin-film electrodes may prohibit the growth of both CoO and NiO [19], thus creating a high surface area for the active materials, which contributes to the high specific capacities of the thin-film electrodes. The discharge capacity of the composite thin-film electrodes at a 0.5 C cycling rate exhibits no obvious capacity drop during the first 25 discharge/charge cycles, although there is capacity fluctuation (Fig. 4), which may be caused by the testing instruments. In contrast to what has been observed in other work [12,19], there is also no obvious capacity increase during discharge/charge cycling. The thin-films from ethanol/butyl carbitol solution show a higher specific capacity compared to those deposited from glycerol/butyl carbitol. The morphology of the thin-

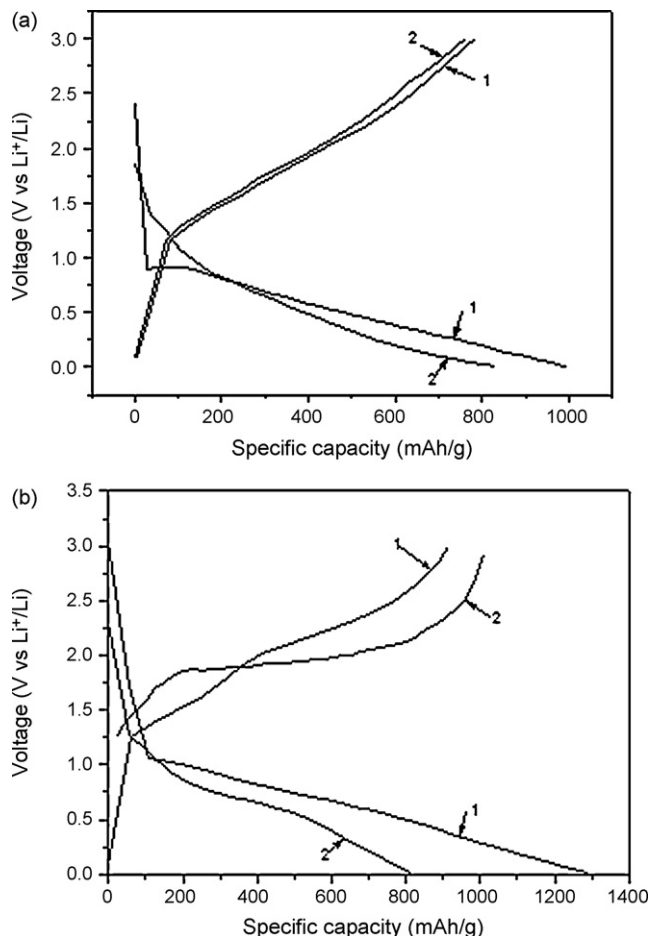


Fig. 3. Discharge/charge curves of the Li $_2$ O–NiO–CoO composite thin-film electrodes cycled between 0.01 and 3 V versus Li $^+$ /Li at a cycling rate of 0.5 C: (a) using glycerol/butyl carbitol as solvent; (b) using ethanol/butyl carbitol as solvent.

films after 25 discharge/charge cycles was also investigated using SEM (Fig. 5), and it was found that the three-dimensional network structures were maintained for both thin-film electrodes. However, by comparison with those SEM images before cycling, little cracks can be found on the films, some texture structures

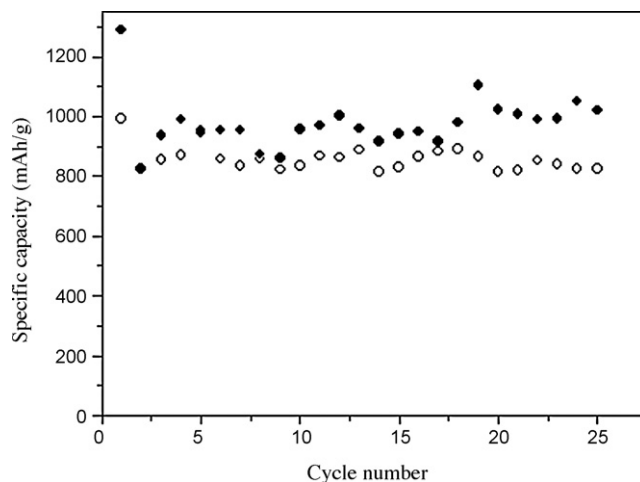


Fig. 4. Cycling behavior of the Li $_2$ O–NiO–CoO composite thin-film electrodes cycled between 0.01 and 3 V versus Li $^+$ /Li at a cycling rate of 0.5 C: (○) using glycerol/butyl carbitol as solvent; (●) using ethanol/butyl carbitol as solvent.

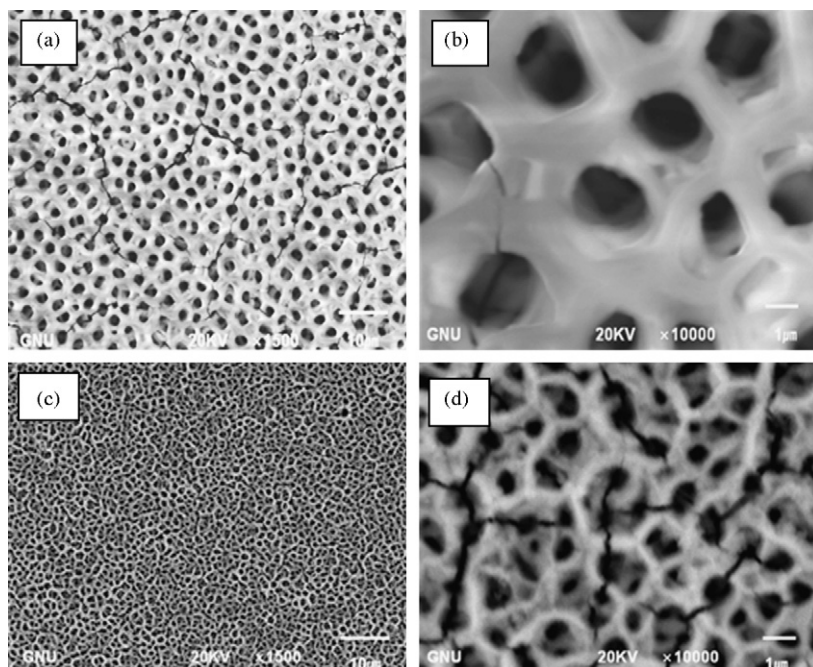


Fig. 5. SEM images of $\text{Li}_2\text{O-NiO-CoO}$ composite thin-film anode after 25 discharge/charge cycles: (a and b) using glycerol/butyl carbitol as solvent; (c and d) using ethanol/butyl carbitol as solvent.

on the grids disappear, and the grids become smoother. These phenomena may be the reason for the different electrochemical behavior when compared to the published results from Chen's group [12,19].

Fig. 6 shows the reversible capacity of the $\text{Li}_2\text{O-NiO-CoO}$ composite thin-film electrodes as a function of the cycling rate (0.1–5 C). Both thin-film electrodes also show excellent rate capability. The specific capacity reached 482 and 612 mAh g^{-1} for the thin-film electrodes from glycerol/butyl carbitol and ethanol/butyl carbitol solutions, respectively, when discharged/charged at a 5 C rate (Fig. 5). The difference in the rate capabilities for the two kinds of thin-film electrodes originates from the difference in their morphology, which induces different surface area and impedance [19]. The high capacity, the good cycling performance, and the excellent rate capability indicates that these thin-film electrodes are promis-

ing candidate anodes for lithium-ion batteries for high-power applications such as electric vehicles or hybrid electric vehicles.

4. Conclusion

Herein, we report a feasible synthesis of thin-film electrodes with three-dimensional network structures by a convenient ESD method. SEM measurements showed that porous network structures with different film textures could be obtained by using different solvents. The as-deposited thin-film electrodes show a high reversible capacity, good capacity retention, and outstanding rate capability. The specific capacity reached 612 mAh g^{-1} for the thin-film electrodes from ethanol/butyl carbitol solution when discharged/charged at a 5 C rate.

Acknowledgements

Financial support from the Australian Research Council through an ARC Discovery project (DP0878611) and the second stage of the BK21 project, Korea, is gratefully acknowledged. Moreover, the authors would like to thank Dr. Tania Silver at the University of Wollongong for critical reading of the manuscript.

References

- [1] B. Scrosati, *Nature* 373 (1995) 557–558.
- [2] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novak, *Adv. Mater.* 10 (1998) 725–763.
- [3] S.H. Ng, J. Wang, D. Wexler, K. Konstantinov, Z.P. Guo, H.K. Liu, *Angew. Chem.* 118 (2006) 7050–7053.
- [4] Z.P. Guo, J.Z. Wang, H.K. Liu, S.X. Dou, *J. Power Sources* 146 (2005) 448.
- [5] Z.P. Guo, Z.W. Zhao, H.K. Liu, S.X. Dou, *Carbon* 43 (2005) 1392.
- [6] L. Yuan, Z.P. Guo, K. Konstantinov, P. Munroe, H.K. Liu, *Electrochem. Solid-State Lett.* 9 (2006) A524.
- [7] G. Binotto, D. Larcher, A.S. Prakash, R.H. Urbina, M.S. Hegde, J.-M. Tarascon, *Chem. Mater.* 19 (2007) 3032–3040.
- [8] J.B. Ducros, S. Bach, J.P. Pereira-Ramos, P. Willmann, *J. Power Sources* 175 (2008) 517–525.
- [9] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, *Nature* 407 (2000) 496–499.
- [10] Y. Yu, Y. Shi, C. Chen, *Nanotechnology* 18 (2007) 055706.
- [11] J.L. Shui, Y. Yu, C.H. Chen, *Appl. Surf. Sci.* 253 (2006) 2379–2385.

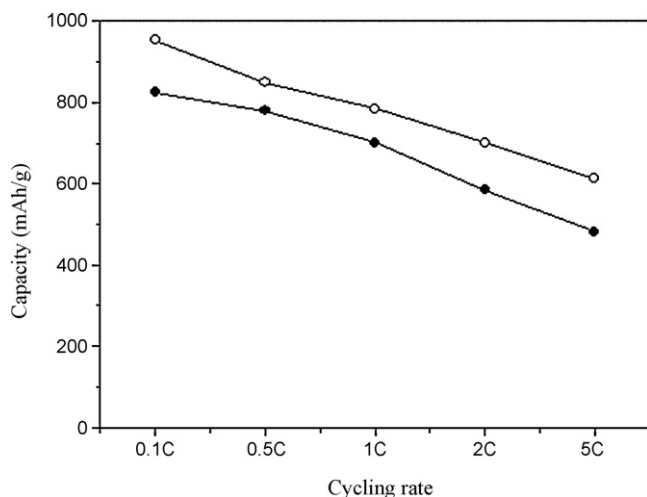


Fig. 6. The reversible capacity of the $\text{Li}_2\text{O-NiO-CoO}$ composite thin-film electrodes as a function of the cycling rate (0.1–5 C): (●) thin-film using glycerol/butyl carbitol as solvent; (○) thin-film using ethanol/butyl carbitol as solvent.

- [12] Y. Yu, C.H. Chen, Y. Shi, *Adv. Mater.* 19 (2007) 993–997.
- [13] Y. Yu, J.L. Shui, S. Xie, C.H. Chen, *Aerosol Sci. Technol.* 39 (2005) 276–281.
- [14] H. Huang, X. Yao, X.Q. Wu, M.Q. Wang, L.Y. Zhang, *Thin Solid Films* 458 (2004) 71–76.
- [15] S.C.G. Leeuwenburgh, J.G.C. Wolke, J. Schoonman, J.A. Jansen, *Thin Solid Films* 472 (2005) 105–113.
- [16] D. Perednis, O. Wilhelm, S.E. Pratsinis, L.J. Gauckler, *Thin Solid Films* 474 (2005) 84–95.
- [17] C. Chen, E.M. Kelder, P.J.J.M. van der Put, J. Schoonman, *J. Mater. Chem.* 6 (1996) 765–771.
- [18] J.S. Im, S.-J. Park, T.J. Kim, Y.H. Kim, Y.-S. Lee, *J. Colloid Interf. Sci.* 318 (2008) 42–49.
- [19] Y. Yu, C.H. Chen, J.L. Shui, S. Xie, *Angew. Chem.* 117 (2005) 7247–7251.
- [20] K.W. Nam, E.S. Lee, J.H. Kim, Y.H. Lee, K.B. Kim, *J. Electrochem. Soc.* 152 (2005) A2123.
- [21] C.C. Hu, Y.S. Lee, T.C. Wen, *Mater. Chem. Phys.* 48 (1997) 246.
- [22] S. Grugeon, S. Laruelle, L. Dupont, J.M. Tarascon, *Solid State Sci.* 5 (2003) 895–904.
- [23] R. Dedryvere, S. Laruelle, S. Grugeon, P. Poizat, D. Gonbeau, J.M. Tarascon, *Chem. Mater.* 16 (2004) 1056–1061.