Short communication

# Sn/C non-woven film prepared by electrospinning as anode materials for lithium ion batteries

Lin Zou, Lin Gan, Feiyu Kang*, Mingxi Wang, Wanci Shen, Zhenghong Huang

*Key Laboratory of Advanced Materials of Ministry of Education, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

## ARTICLE INFO

## ABSTRACT

Sn/C non-woven film has been prepared by electrospinning and carbonization treatment. Investigation of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) indicate that the film is formed by non-woven fibers. The fibers consist of amorphous carbon and homogeneously dispersed tin particles, which are extremely tiny (around 1 nm). However, partial tin particles are oxidized when the film is kept in the air, which is confirmed by X-ray diffraction (XRD). The XRD measurement also suggests that the tin oxides completely decompose to pure tin after several electrochemical cycles. The reversible capacity of the film in the 20th cycle is 382 mAh g$^{-1}$, which is 96.7% of the capacity in the first cycle. Such Sn/C non-woven film could be a promising anode material in lithium ion batteries.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Lithium ion batteries have been widely used as power supply from cell phone to electric vehicles, which demands higher power density and higher energy density. New anode materials with higher capacity have attracted more interesting research because the theoretical capacity of graphite is only 372 mAh g$^{-1}$. Tin, of which the theoretical capacity is 993 mAh g$^{-1}$, has been considered as one of the most promising candidates of new anode materials for lithium ion batteries in the coming decades [1]. However, its large volumetric expansion during the charge/discharge process, which causes cracking of tin particles and rapid fading of capacity in cycles, has prevented pure tin from practical use.

One potential solution is to use nano-sized tin, tin alloy and tin based composite. Using nano-sized particles could not only release mechanical strains within particles [3–6] but also decrease the diffusion length of lithium ion, which could increase the performance of the electrode in high current situation. Nano-structured Sn–Co–C alloy anode has been commercially used in the Nexelion Hybrid Li-ion Battery [2] by Sony Co. Ltd. since 2005. Tin based anode materials, including nano-particles [3,4], nano-wire [5], thin film [6], etc. have been reported to possess good performance. In most case, nano-particles were loaded on a suitable substrate, such as graphite [7,8], porous carbon [9,10], hollow carbon sphere [11], carbon nanotube [12,13], and so on. Remarkably, Sn-graphite intercalation compound has been suggested to be a very good anode material

[14]. However, no authentically further progress was reported by far.

Recently, SnO$_2$ nano-wire has been prepared by electrospinning [15–17]. More attractively, the SnO$_2$ nano-wire could be porous structure and assembled by nano-particles around several tens of nanometers [17]. Considering its special structure, it might exhibit good cyclic properties as anode material if the PVA substrate was not removed but carbonized. Firstly, the carbonized PVA non-woven film would form a carbon fiber network, which would be binder free and enhance the conductivity of the electrode. Secondly, the tin or tin oxides contained in the carbon fiber would be nano-sized and carbon coated. In this work, we report the Sn/C non-woven film prepared by electrospinning and carbonization treatment using as anode materials in lithium ion battery with good cyclic performance.

## 2. Experimental/materials and methods

Firstly, polyvinyl alcohol (PVA, molecule weight = 80,000) and deionized water were mixed in the ratio of 10 g PVA/100 g deionized water. The mixture was stirred in water bath at 90 °C for 12 h to form a homogenous solution. Then 10 g SnCl$_2$·H$_2$O and 20 g deionized water were mixed and stirred until the SnCl$_2$ was completely dissolved. The SnCl$_2$ solution was added into the PVA solution and vigorously stirred in water bath at 90 °C for another 8 h to obtain the precursor for electrospinning.

As-prepared precursor was delivered to a metal needle, of which the inner diameter is 1 mm, at a constant flow rate of 1.0 ml h$^{-1}$. The needle was connected to a high voltage DC power and horizontally clamped on an insulating glass stick. A piece of graphite paper was used as the collector. The height of the needle and the distance

* Corresponding author. Tel.: +86 10 62784872; fax: +86 10 62771160.
*E-mail address:* fykang@tsinghua.edu.cn (F. Kang).
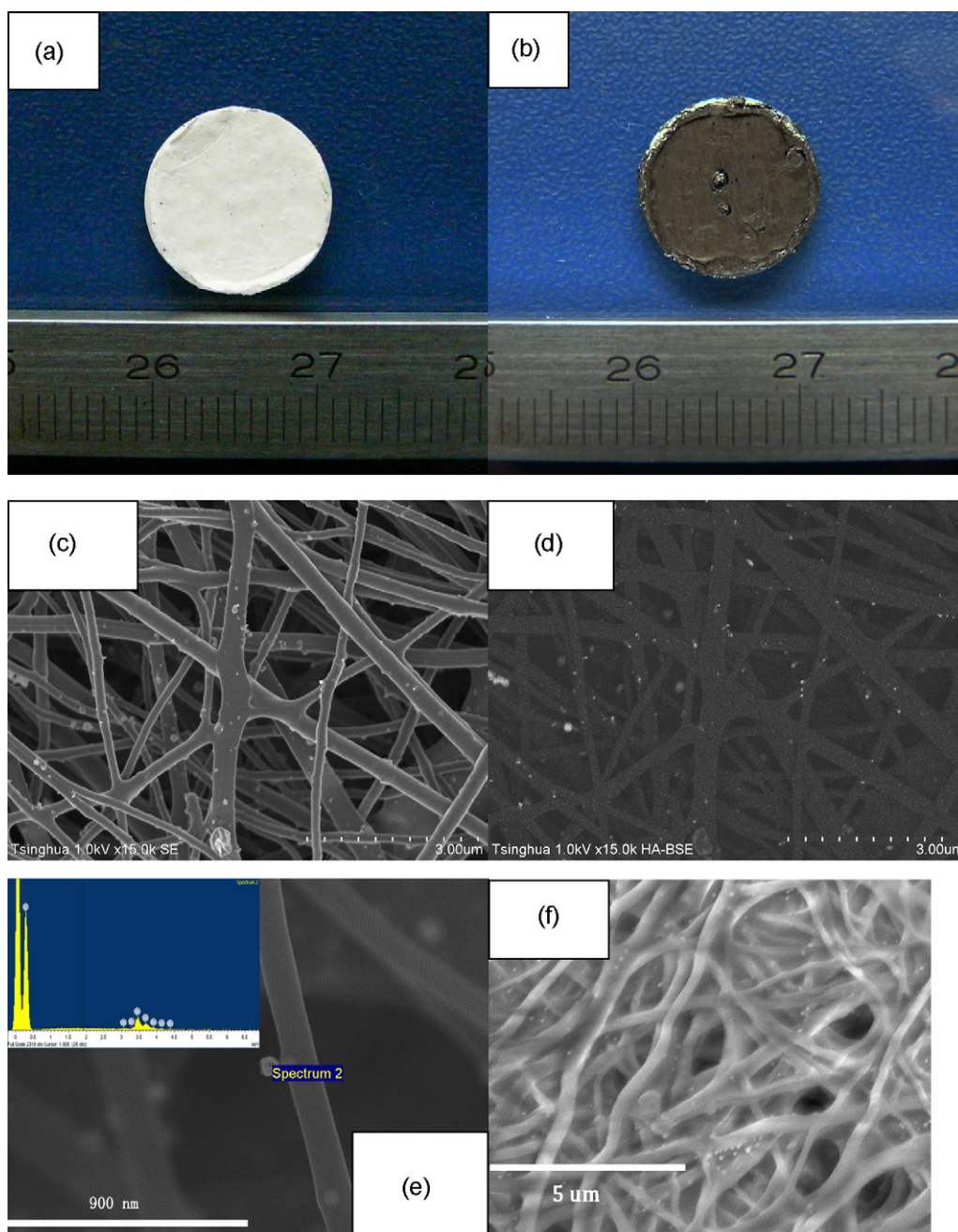
**Fig. 1.** (a and b) The photos of the raw NWF and the CNWF; (c) the SEM image of the CNWF; (d) the back-scattering electron image of CNWF; (e) the EDS pattern of tin particles loaded on the fiber of CNWF; (f) the SEM image of the CNWF after 10 cycles.

between the needle and the collector were adjustable. Typically, 25 kV high voltage was adopted and the distance between the needle and collector was 15 cm. After the electrospinning process, a non-woven film (NWF) in white color was obtained on the collector (Fig. 1a). The prepared sample was heated at 500 °C for 3 h in Ar/H$_2$ (95:5, v/v) atmosphere. The heating rate is 2 °C min$^{-1}$. Then a carbonized non-woven Sn/C film (CNWF) in black color was obtained (Fig. 1b). The film was carefully removed from the substrate for electrochemical investigation. The thickness of the film depends on the duration of electrospinning and the selected area on the graphite paper collector. According to our experiment, the raw film slightly shrunk after carbonization when it was relatively thicker, that we could remove the CNWF from the collector much easier.

The CNWF was characterized by thermogravimetry analysis (TGA), scanning electron microscopy (SEM), transmission electron

microscopy (TEM) and X-ray diffraction (XRD). The electrochemical performance was tested in a half-cell, in which lithium foil was used as the counter electrode and 1 M LiPF$_6$ was dissolved in a mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) as the electrolyte. The CNWF was used as working electrode directly after it was removed from the graphite substrate. No binder or conductive additive was used. The working and the counter electrodes were separated with Celgard 2400 separator. The cell was galvanostatically cycled between 0 and 2.00 V vs. Li/Li$^+$ under a current of 0.5 mA cm$^{-2}$.

## 3. Results and discussion

Thermogravimetry analysis (TGA) from room temperature to 1000 °C at oxygen atmosphere was adopt to investigate the

proportion of C and tin in the CNWF based on the equations below:

$$C + O_2 = CO_2 \tag{1}$$

$$Sn + O_2 = SnO_2 \tag{2}$$

$$2SnO + O_2 = 2SnO_2 \tag{3}$$

The component of CNWF could be presumed to be C and pure tin. The mass of pure tin is evaluated from the remnant mass after oxidation, which corresponds to the mass of $SnO_2$. Then the approximate proportion of C and tin could be calculated from the TGA result. The content of tin is ca. 37 wt.%.

Fig. 1a and b shows the photos of the NWF and the CNWF on the graphite paper substrate. The color of the film changes from white to black due to the carbonization of the PVA. Some holes occur on the surface of the CNWF because of few liquid droplets of the pre-
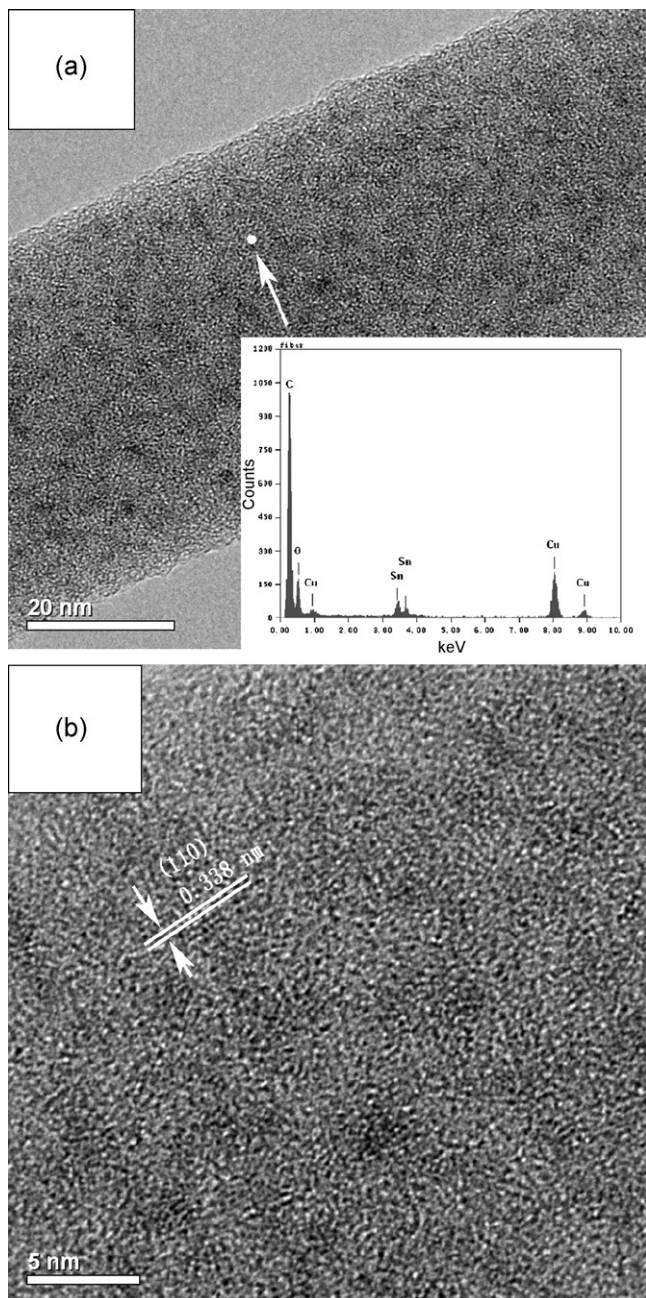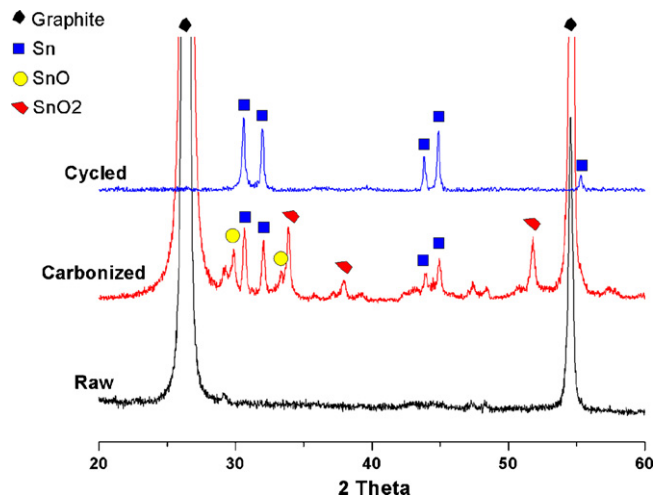


**Fig. 3.** XRD pattern of raw NWF, CNWF and the CNWF after 10 cycles.

cursor on the graphite substrate. Fig. 1c shows the SEM image of the CNWF. One can see the film is formed by non-woven fibers, of which the diameter is several tens to hundreds of nanometers. The surface of the fibers is smooth. However, some nano-particles are observed on the surface of the fibers. Based on the back-scattering electron (BSE) image (Fig. 1d), we find that such nano-particles contain more heavy element than the fibers, because the nano-particles are more bright than the fibers in the BSE image. The energy dispersive X-ray spectroscopy (EDS) pattern (Fig. 1e) indicates that such particle contains tin and carbon. As the raw fibers of the NWF is smooth (not shown here), the tin particles on the surface of the fibers may be formed during carbonization process. It could be explained that partial $Sn^{2+}$ was separated from the fibers firstly. Then it was reduced to Sn and grew up to tin particles in the Ar/$H_2$ atmosphere. This sample was observed by the SEM immediately after it was removed from the Ar/$H_2$ atmosphere, thus no oxygen was detected. In fact, in the XRD and TEM measurement, a mass of tin oxides are observed when the sample is kept in the air for some days. Fig. 1f shows the image of CNWF after 10 cycles. The sample remains the non-woven structure. However, the fibers are covered by the solid electrolyte interface (SEI) film, which also fill in the space between the fibers.

The microstructure of the fibers was investigated by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). Fig. 2a shows TEM image and EDS pattern of the CNWF fibers. We can see that the fiber is a composite of amorphous carbon, tin and tin oxides. The tin and tin oxides locate to the saturated area of the fiber according to the EDS measurement. The diameter of the particles of the tin and tin oxides is extremely tiny, around 1 nm. We can see that such particles homogeneously disperse in the fiber. Such extremely tiny particles suggest that it may show good cycle performance using as anode material of lithium ion batteries. As shown in Fig. 2b, a few crystals could be observed by the HRTEM. The layer distance of one of the crystals in the HRTEM image is 0.338 nm, which is the $d_{110}$ value of $SnO_2$. However, we can also see that many tin or tin oxides are not well crystallized, which suggests that the heating temperature and the duration may need to be adjusted. Although the fresh sample is a composite of carbon and pure tin according to SEM analysis, the TEM and HRTEM investigation reveals that partial tin particles are oxidized when the sample is kept in air.

Fig. 3 shows XRD pattern of the raw NWF, CNWF and CNWF after 10 cycles. The raw NWF and CNWF are investigated with the graphite substrate together. Two strongest peaks at 26.5° and 54.6°



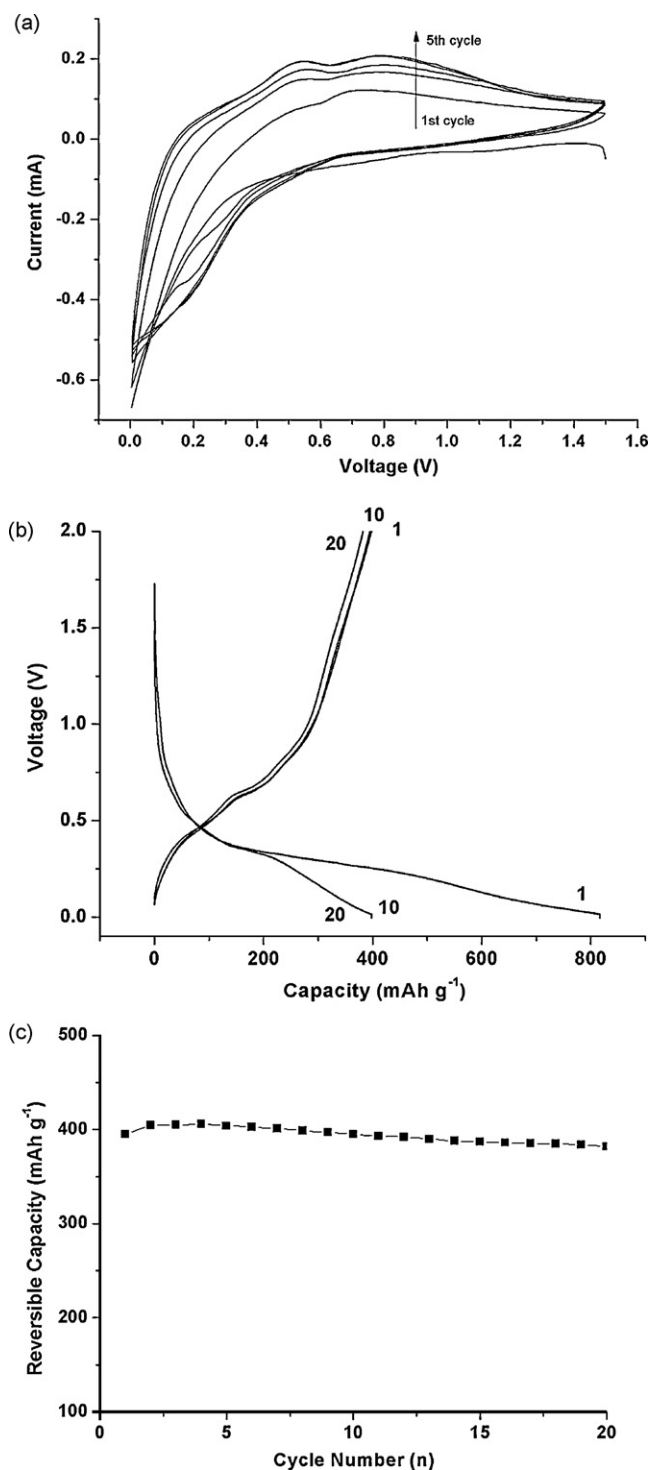**Fig. 2.** TEM image (a) and HRTEM image (b) of the fibers of the CNWF.

**Fig. 4.** Cyclic voltammetry measurement (a), charge/discharge profile (b) and cyclic performance (c) of the CNWF.

are (0 0 2) and (0 0 4) peaks of the graphite substrate. There are also some unknown peaks in XRD patterns of the raw NWF and CNWF. However, these peaks are not observed in the pattern of the CNWF after 10 cycles, which means that these peaks are probably reflected to the impurity of the graphite substrate or more complicated tin oxides. For the raw NWF, no clear peaks except for graphite exist in XRD pattern. After carbonization, a mass of Sn, SnO and $SnO_2$ could be observed because of the decomposition and reduction of the $SnCl_2$ and then the oxidation of tin. After 10 cycles, only pure tin is observed. The peaks of SnO and $SnO_2$ disappeared due to the

irreversible decomposition of tin oxides into $Li_2O$ and Sn in cycles [7].

Electrochemical behavior of the CNWF is well illustrated by the cyclic voltammetry (CV). Fig. 4a shows the 1st–5th cycles of the CNWF at a scanning rate of $0.1\,mV\,s^{-1}$. In the first cycle, the hump above 1 V in the reduction process could be attributed to the decomposition of tin oxides [7,8]. In the oxidation process of later cycles, the two hump from 0.4 to 0.9 V could be related to the de-alloying of $SnLi_x$ [7]. We can see that these two humps become stronger in cycles, which may be explained that the tin particles, which are covered by amorphous carbon in the fibers, gradually make contribution to the capacity. Superposition of these humps occurs in the 4th and 5th cycle, which means that tin has been fully charged/discharged. Fig. 4b indicates that the discharge capacity of the CNWF in the 1st cycle is $816\,mAh\,g^{-1}$ and the charge capacity is $395\,mAh\,g^{-1}$. The irreversible capacity of the CNWF in the first cycle is $421\,mAh\,g^{-1}$, which should be the result of the decomposition of electrolyte, formation of SEI [18,19] and decomposition of tin oxides [7,8]. Judging from the profile of discharge above 1 V, which attributes to the decomposition of tin oxides, the difference between the 1st and 10th cycle is not notably distinguishing, thus the decomposition of electrolyte and formation of SEI should be the primary reason for the large irreversible capacity in the first cycle. The reversible charge capacity of the CNWF in the 1st, 10th and 20th cycle is 395, 392 and $382\,mAh\,g^{-1}$, respectively. Both carbon fiber network [18,19], tin and tin oxides [3–6] contribute to the reversible capacity of the anode electrode. According to our further experiments (not shown here), the reversible capacity of the electrode could be improved by increasing the portion of the mass of tin. As shown in Fig. 4c, the cyclic property of the CNWF is stable. The reversible capacity remains 96.7% after 20 cycles. The improvement of cycle performance of CNWF attributes to several reasons. Firstly, the cycle performance of the carbon fiber network itself generated by electrospinning and carbonization treatment is good, which has been demonstrated by several previous works [18,19]. Secondly, the tin and tin oxides particles are nano-sized and homogeneous dispersed in the carbon substrate. It could release mechanical strains within particles and prevent the particles from cracking during cycles, thus the cyclic stability of tin could be greatly improved. Thirdly, the carbon fiber network could supply good electric conductivity for tin and tin oxides particles. These advantages make the CNWF attractive for the fabrication of anode materials.

## 4. Conclusion

Sn/C non-woven film has been prepared by electrospinning and carbonization process. The CNWF consists of Sn/C fibers. Images of SEM, TEM and HRTEM indicate that the fresh fiber is a composite of amorphous carbon and nano-sized tin particles, which is around 1 nm. However, partial tin particles in the CNWF are oxidized when the sample is kept in air. The existence of the tin oxides is confirmed by XRD measurement, which also shows that the tin oxides completely decompose to pure tin after several cycles. The reversible capacity of CNWF in the 20th cycle is $382\,mAh\,g^{-1}$, which is 96.7% of the capacity in the first cycle. Such CNWF could be a promising anode material in lithium ion batteries.

# References

[1] M. Armand, J.-M. Tarascon, Nature. 451 (2008) 652–657.
[2] http://www.sony.net/SonyInfo/News/Press/200502/05-006E/.
[3] S.-I. Lee, S. Yoon, C.-M. Park, J.-M. Lee, H. Kim, D.M. Im, S.-G. Doo, H.-J. Sohn, Electrochim. Acta. 54 (2008) 364–369.
[4] L. Simonin, U. Lafont, E.M. Kelder, J. Power Sources 180 (2008) 859–863.
[5] J.-H. Kim, S. Khanal, M. Islam, A. Khatri, D. Choi, Electrochem. Commun. 10 (2008) 1688–1690.
[6] M. Marcinek, L.J. Hardwick, T.J. Richardson, X. Song, R. Kosterchi, J. Power Sources 173 (2007) 965–971.
[7] L. Balan, R. Schneider, J. Ghanbaja, P. Willmann, D. Billaud, Electrochim. Acta 51 (2006) 3385–3390.
[8] Y. Wang, J.Y. Lee, T.C. Deivaraj, J. Electrochem. Soc. 151 (2004) A1804–1809.
[9] B.K. Guo, J. Shu, K. Tang, Y. Bai, Z.X. Wang, L.Q. Chen, J. Power Sources 177 (2008) 205–210.
[10] Z.Y. Wang, M.A. Fierke, A. Stein, J. Electrochem. Soc. 155 (2008) A658–A663.
[11] W.M. Zhang, J.S. Hu, Y.G. Guo, S.F. Zheng, L.S. Zhong, W.G. Song, L.J. Wan, Adv. Mater. 20 (2008) 1160–1165.
[12] Y. Wang, J.Y. Lee, Angew. Chem. Int. Ed. 45 (2006) 7039–7042.
[13] T.P. Kumar, R. Ramesh, Y.Y. Lin, G.T-K. Fey, Electrochem. Commun. 6 (2004) 520–525.
[14] J.S. Pena, T. Brousse, D.M. Schleich, Solid State Ionics 135 (2000) 87–93.
[15] Y. Wang, M. Aponte, N. Leon, I. Ramos, R. Furlan, N. Pinto, J. Am. Ceram. Soc. 88 (2005) 2059–2063.
[16] Y. Wang, I. Ramos, J.J.S. Aviles, Nanotechnology 18 (2007) 1–7.
[17] A. Yang, F X.M. Tao, J. Am. Ceram. Soc. 91 (2008) 257–262.
[18] C. Kim, K.S. Yang, M. Kojima, K. Yoshida, Y.J. Kim, Y.A. Kim, M. Endo, Adv. Funct. Mater. 16 (2006) 2393–2397.
[19] L.W. Ji, X.W. Zhang, Nanotechnology 20 (2009) 1–7.