Performance of SnO_2/carbon nanotube composite electrode materials synthesised by the Pechini method

Rui Liu[1], *Wein-Duo Yang*[2], *Hsin-Yun Fang*[2]

[1]*Institute of Petroleum and Commodity, Harbin University of Commerce, Harbin 150076, People's Republic of China*
[2]*Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan*
E-mail: 57776806@qq.com

Published in Micro & Nano Letters; Received on 31st July 2015; Revised on 11th November 2015; Accepted on 12th November 2015

SnO_2/CNT (CNT: carbon nanotube) composite electrode materials have been successfully synthesised using the Pechini method. The crystal structures of SnO_2/CNTs were identified by X-ray diffraction. The surface morphology and internal structure, as revealed by scanning electron microscopy and transmission electron microscopy, indicated that SnO_2 nanoparticles were embedded in the CNT matrix or dispersed homogeneously on the outer walls of the CNTs. Furthermore, the charge–discharge properties of SnO_2/CNT composite electrode materials showed that the reversible discharge capacities of the SnO_2/CNT composite electrode materials were enhanced to 1062 mAh/g compared with that of pure SnO_2 nanoparticles, and the capacity retention remained at approximately 91% after the 12th cycle, improving the lifetime of the lithium batteries greatly.

1. Introduction: SnO_2, an n-pattern semiconductor material with broad band clearance, has been considered one of the most promising cathode materials for lithium (Li)-ion batteries due to excellent capacity [1–3]. However, pulverisation of the electrode material occurs easily due to dramatic volume expansion during the charging and discharging of the Li-ion battery, resulting in deteriorating cycle performance. This problem is a large obstacle to the wide use of SnO_2 in Li-ion batteries [4–6].

To overcome this disadvantage, many efforts have been undertaken to improve the lifetime of Li batteries with several types of modification methods. Composite tin oxide and other one-dimensional nanostructures can improve the circulation characteristics of tin materials [7–9]. Carbon nanotubes (CNTs) have a well-defined arrangement of atoms at the molecular level. These carbon nanomaterials can withstand high current and heat conduction due to stable mechanical and electrochemical properties. These properties in combination with a high specific capacity for Li storage can improve storage the performance and lifetime of Li batteries. Qiu *et al.* [10] prepared multi-wall CNTs deposited on zinc oxide by the chemical vapour deposition methodH to increase the specific surface area and electrical conductivity of the resulting material. Wu *et al.* [11] also fabricated an SnO_2 support surface for CNTs by the multi-step hydrothermal method, which can obviously improve the Li storage properties of SnO_2. Noerochim *et al.* [12] reported that a single-walled CNT/SnO_2 (SWCNT/SnO_2) composite was prepared by vacuum filtration of the SWCNT/SnO_2 material. The specific capacity of SWCNT/SnO_2 is much higher than that of CNT and SnO_2. Such capabilities demonstrate that this model holds great promise for applications requiring flexible and bendable Li-ion batteries. Obviously, the SnO_2/CNT composite materials solve the problems to a certain extent. However, process complexity and poor material uniformity become a new challenge in existing research.

In this Letter, we report the Pechini method [13] to synthesise the SnO_2/CNT composite materials. The crystallographic structure and microstructure of samples are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Furthermore, the electrochemical performance and battery performance of the SnO_2/CNT composite materials are also investigated.

2. Experimental: SnO_2/CNT composite materials were synthesised using the Pechini method. First, citric acid was dissolved in deionised water. Then, hydroxypropyl cellulose was added to obtain aqueous solution A. $SnCl_4$ was dissolved in anhydrous ethanol to obtain solution B. Solution A and solution B were mixed by stirring constantly for 2 h. The mixed solutions were heated under refluxing for 3 h. The resulting sample was dried at 120°C until it became a sol. Finally, the sample was calcined at 700°C for 4 h to obtain the SnO_2/CNT composite materials.

The as-prepared products were characterised by XRD (XRD, PANalytical, Cu Kα $\lambda = 1.5406$ Å), SEM (SEM, TFSEM-6330) and TEM (TEM, Hitachi Model HF-2000). Charge–discharge measurements (LAND CT2001A) were performed between 0.25 and 3.00 V against Li/Li^+. A three-electrode system was used (samples as the working electrode, an Ag/AgCl electrode as the reference electrode and a platinum electrode served as the counter electrode). Ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v) were used as the electrolytes.

3. Results and discussion: Fig. 1 shows XRD patterns of pure CNT, SnO_2 powders and SnO_2/CNT composite materials prepared in this work. The peaks with 2θ values of 26.6°, 33.9° and 51.0° for the SnO_2/CNT composite materials correspond to the (110), (101) and (211) lattice planes of SnO_2 (JPCDS 88-0287), respectively [14]. The diffraction peak at 44° of the SnO_2/CNT composite materials can be indexed to CNTs. The observed XRD patterns confirm that no structural changes took place during the composite process. Furthermore, the composite contains SnO_2 and CNT.

The typical SEM images and TEM images of SnO_2/CNT composite samples are shown in Fig. 2. As seen in Fig. 2*a*, clusters of SnO_2 particles are obviously embedded in the CNT matrix and dispersed homogeneously on the outer walls of the CNTs. The actual structure is more clearly seen in the TEM images (Fig. 2*b*), and we can see that SnO_2 uniformly appeared on the surface of the CNTs. Moreover, due to the presence of the CNTs, there is more space between the SnO_2 particles, which can improve the Li-storage capacity of this material.

Figs. 3 and 4 show the result of charge and discharge tests. A three-electrode system was used (samples as the working electrode,

doi: 10.1049/mnl.2015.0296

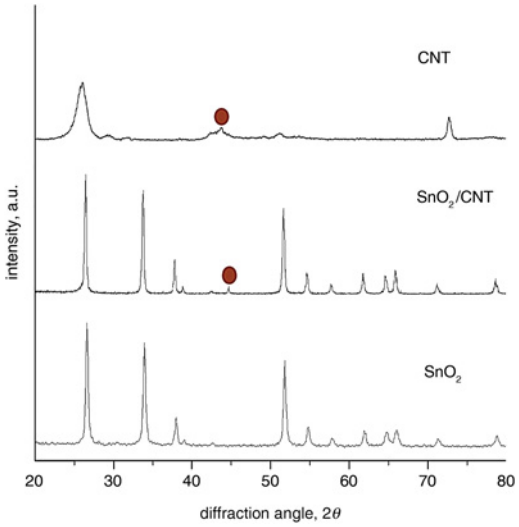

Fig. 1 *XRD patterns of SnO_2, CNT and SnO_2/CNT composite materials*

an Ag/AgCl electrode as the reference electrode and a platinum electrode served as the counter electrode). EC and DEC (1:1 v/v) were used as the electrolytes. The SnO_2/CNT composite materials demonstrate an increase in the first discharge capacity of 1062 mAh/g and a charge capacity of 298 mAh/g in the first cycle compared with those of pure SnO_2, as shown in Fig. 3. This enhanced

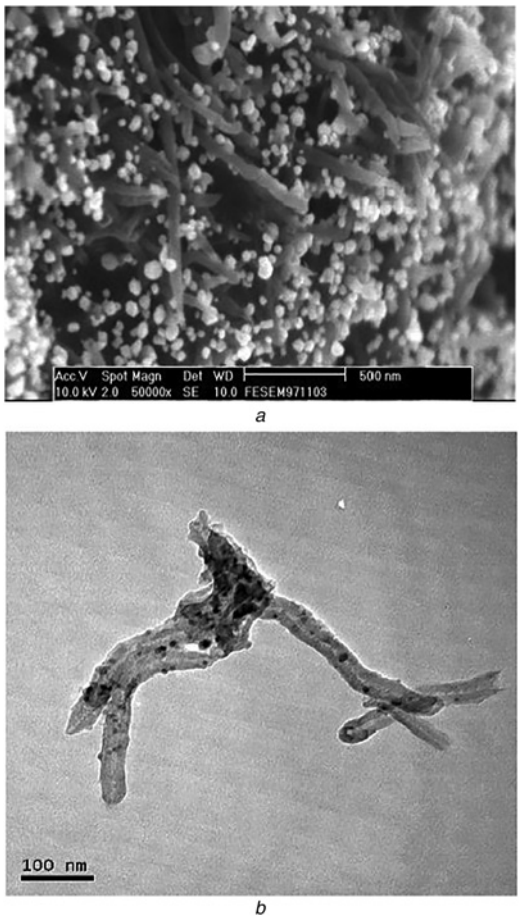

Fig. 2 *Typical SEM images and TEM images of SnO_2/CNT composite samples*
a SEM images of SnO_2/CNT composite materials
b TEM images of SnO_2/CNT composite materials

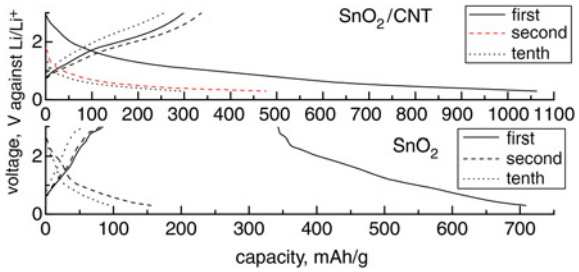

Fig. 3 *Charge/discharge capacity of pure SnO_2 and SnO_2/CNT composite materials*

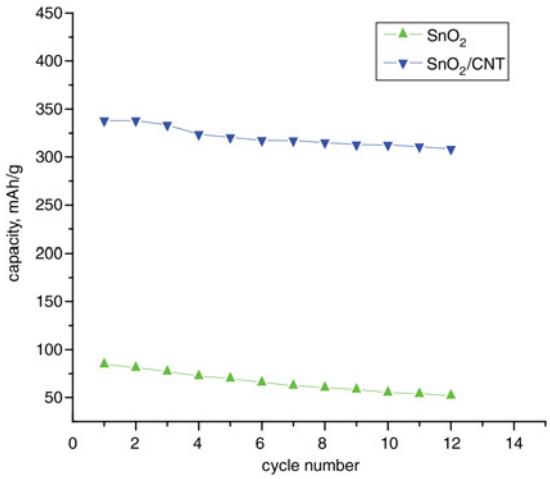

Fig. 4 *Electrochemical properties of pure SnO_2 and SnO_2/CNT composite materials during the 12th cycles*

charge capacity could be attributed to the formation of more space, in favour of the electrolyte and Li-ion diffusion. On the other hand, that enhanced charge capacity could also be attributed to the formation of solid electrolyte interface on the surface of the electrode [15].

In Fig. 4, the performance of SnO_2/CNT composite materials and pure SnO_2 particles is shown for the first 12 cycles. On the second charge/discharge cycle, the SnO_2/CNT composite materials exhibited reversible capacity with 99% capacity retention. Even at the 12th charge/discharge cycle, the reversible capacity still retains 91% capacity, which can greatly improve the Li battery life. Moreover, the capacity of the SnO_2/CNT composite material is also much greater than that of SnO_2. In addition to better diffusion as mentioned above, this result may indicate that CNTs not only work as a buffering and conductive matrix, but also perform as a host matrix for Li, increasing the overall capacity of the composite.

4. Conclusions: In summary, the SnO_2/CNT composite materials have been synthesised by the Pechini method. Composite phases of SnO_2/CNT were identified by XRD. SnO_2 nanoparticles are deposited on the outer walls of the CNT or embedded in the CNT. Compared with pure SnO_2, the discharge capacity of SnO_2/CNT composite was enhanced to 1062 mAh/g and a charge capacity of 298 mAh/g. The capacitance retention of SnO_2/CNT is more than 91% at 12th cycles, which can improve the cycle life of HLi-HionH batteries. Moreover, the capacity of the SnO_2/CNT composite material is much greater than that of pure SnO_2 particles.

5. Acknowledgment: The generous financial support by the Ministry of Science and Technology of Taiwan (grant no: MOST

103-2221-E-151-055) and by the Ph.D. program of Harbin University of Commerce of China (grant no: 14LG13) was gratefully acknowledged.

6 References

[1] Zhang H.K., Song H.H., Chen X.H.: 'Preparation and electrochemical performance of SnO_2@carbon nanotube core–shell structure composites as anode material for lithium-ion batteries', *Electrochim. Acta*, 2012, **59**, pp. 160–167

[2] Jia T.K., Chen J., Deng Z., *ET AL.*: 'Facile synthesis of Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures and their application in lithium storage', *Mater. Sci. Eng. B*, 2014, **189**, pp. 32–37

[3] Dirican M., Yanilmaz M., Fu K., *ET AL.*: 'Carbon-enhanced electrodeposited SnO_2/carbon nanofiber composites as anode for lithium-ion batteries HJ', *Power Sources*, 2014, **264**, (15), pp. 240–247

[4] Kamali A.R., Fray D.J.: 'Tin-based materials as advanced anode materials for lithium ion batteries: a review', *Rev. Adv. Mater. Sci.*, 2011, **27**, pp. 14–24

[5] Wang J.Z., Du N., Zhang H.: 'Large-scale synthesis of SnO_2 nanotube arrays as high-performance anode materials of Li-ion batteries', *J. Phys. Chem. C*, 2011, **115**, (22), pp. 11302–11305

[6] Jensen K.M.Ø., Christensen M.P.J.: 'Revealing the mechanisms behind SnO_2 nanoparticle formation and growth during hydrothermal synthesis: an in situ total scattering study', *J. Am. Chem. Soc.*, 2012, **134**, (15), pp. 6785–6792

[7] Murayama N., Izu N., Shin W.: 'Preparation of SnO_2 nanosized powder by precipitation method with nano-mixing of carbon powder', *J. Ceram. Soc. Jpn.*, 2005, **113**, pp. 330–332

[8] Liang Y., Fan J., Xia X.H.: 'Synthesis and characterisation of SnO_2 nano-single crystals as anode materials for lithium-ion batteries', *Mater. Lett.*, 2007, **61**, (22), pp. 4370–4373

[9] Sharma Y., Sharma N., Rao G.V.S.: 'Studies on nano-Cao.SnO_2 and nano-$CaSnO_3$ as anode for Li-ion batteries', *Chem. Mater.*, 2008, **20**, (21), pp. 6829–6839

[10] Wang C.F., Xie S.Y., Lin S.C.: 'Glow discharge growth of SnO_2 nano-needles from SnH_4', *Chem. Commun.*, 2004, **15**, pp. 1766–1767

[11] Wu P., Du N., Zhang H.: 'CNTs@SnO_2@C coaxial nanocables with highly reversible lithium storage', *J. Phys. Chem. C*, 2010, **114**, (51), pp. 22535–22538

[12] Noerochim L., Wang J.Z., Chou S.L., *ET AL.*: 'Free-standing single-walled carbon nanotube/SnO_2 anode paper for flexible lithium-ion batteries', *Carbon*, 2012, **50**, (3), pp. 1289–1297

[13] Zhang R., Lee J.Y., Liu Z.L.: 'Pechini process-derived tin oxide and tin oxide-graphite composites for lithium-ion batteries', *J. Power Sources*, 2002, **112**, pp. 596–605

[14] Bonino C.A., Ji L., Lin Z., *ET AL.*: 'Electrospun carbon-tin oxide composite nanofibers for use as lithium ion battery anodes', *ACS Appl. Mater. Interact.*, 2011, **3**, (7), pp. 2534–2542

[15] Jung Y.S., Lee K.T., Ryu J.H.: 'Sn-carbon core-shell powder for anode in lithium secondary batteries', *J. Electrochem. Soc.*, 2005, **152**, (7), pp. A1452–A1457

doi: 10.1049/mnl.2015.0296