

Available online at www.sciencedirect.com



Electrochimica Acta 51 (2006) 3385-3390

Acta

**ELECTROCHIMIC** 

www.elsevier.com/locate/electacta

# Electrochemical lithiation of new graphite–nanosized tin particle materials obtained by SnCl<sub>2</sub> reduction in organic medium

L. Balan<sup>a</sup>, R. Schneider<sup>b</sup>, J. Ghanbaja<sup>a</sup>, P. Willmann<sup>c</sup>, D. Billaud<sup>a,\*</sup>

<sup>a</sup> LCSM, UMR CNRS 7555, UHP Nancy I, BP 239, 54506 Vandoeuvre-les-Nancy Cedex, France
<sup>b</sup> LSOR, UMR CNRS 7565, UHP Nancy I, BP 239, 54506 Vandoeuvre-les-Nancy Cedex, France
<sup>c</sup> CNES, 18 Avenue E. Belin, 31055 Toulouse Cedex, France

Received 9 May 2005; received in revised form 29 September 2005; accepted 29 September 2005 Available online 21 November 2005

## Abstract

 $SnCl_2$  was reduced in the presence of graphite by *t*-BuONa-activated NaH. The resulting (tin/graphite)-based system was composed of nanosized tin particles deposited on the graphite surface and of free tin aggregates. Lithium electrochemical insertion occurs in graphite and in tin. A reversible specific charge of 500 mAh/g is found stable upon cycling.

This value is lower than the maximum theoretical one (650 mAh/g) assuming a Sn/12C molar composition and the formation of the highest lithium content alloy  $Li_{22}Sn_5$ . It is suggested that the part of tin responsible for the stable reversible capacity is the one bound to graphite. To the contrary, free tin aggregates could contribute to a capacity which decreases upon cycling in connection with the volume changes accompanying lithium insertion/extraction in/out of these aggregates.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Lithium-ion battery; Graphite; Tin; Anodic material; Chemical reduction

## 1. Introduction

Carbonaceous materials are commonly used as negative electrodes in commercial lithium-ion batteries [1]. With graphitebased anodes, the maximum theoretical specific charge of 372 mAh/g corresponds to the formation of the stage I LiC<sub>6</sub> graphite intercalation compound. Lithium intercalation occurs at a low voltage, typically lower that 0.3 V versus Li<sup>+</sup>/Li and the volume change accompanying Li intercalation/deintercalation, as low as 10%, allows the electrode to maintain its integrity upon cycling. The demand to further increase both electrode specific charges and long life cycling has stimulated the research for new storage electrode materials [2-4]. Among them, metals able to alloy lithium have been proposed as alternative electrodes which can display large theoretical storage capacities. However, they suffer from poor long-term cycling stability due to the large volume changes occurring during lithium insertion and extraction. It has been demonstrated that these drawbacks can be partly overcome by reducing the metal particle size and by using

0013-4686/\$ - see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2005.09.045

multi-phase systems or alloys [5-12]. An alternative way for improving the electrode consists in associating to carbonaceous materials lithium storage metals of high specific charge [13-17].

In recent papers, we showed that the reduction of some metal chlorides (SbCl<sub>5</sub>, BiCl<sub>3</sub>, SnCl<sub>2</sub>) by the first stage KC<sub>8</sub> graphite intercalation compound in THF medium led to the formation of Sb, Bi and Sn-based graphite materials able to insert lithium reversibly [18,19].

The evolution of their electrochemical performances upon cycling was discussed in terms of particle size, crystalline or amorphous character of the lithium storage element and more likely of their ability to form bonds with graphite [18,20].

Bi and Sb/graphite composites were also obtained by reduction in the presence of graphite of BiCl<sub>3</sub> and SbCl<sub>5</sub> with alkoxide-activated NaH in organic media [16,17,20]. In that case, graphite-supported nanosized metal particles are embedded in an organic matrix constituted of the alkoxide. The graphite/Sb system exhibits an improved and stable reversible capacity upon cycling.

In this communication, we studied the reduction of  $SnCl_2$  by *t*-BuONa-activated NaH with the aim to obtain graphite/Snbased composites of high specific charge for their use as negative electrode materials of Li-ion batteries. Both structure and mor-

<sup>\*</sup> Corresponding author. Tel.: +33 3 83 68 46 22; fax: +33 3 83 68 46 23. *E-mail address:* billaud@lcsm.uhp-nancy.fr (D. Billaud).

phology of these materials were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Their suitability as anodes materials in Li-ion batteries was evaluated by classical galvanostatic and voltammetry techniques.

## 2. Experimental

Anhydrous tin(II) chloride (Aldrich) was used without purification. THF was distilled from sodium benzophenone adduct and stored over Na wires. *Tert*-butyl alcohol (*t*-BuOH) was distilled over Na. Sodium hydride (65%, NaH Fluka) in mineral oil was used after two washings with THF.

The synthesis was handled under standard airless techniques in a nitrogen atmosphere according to a procedure described in a previous paper [21]. In a Schlenk tube, *t*-BuONa-activated NaH and graphite (UF4 Carbone Lorraine, surface area of  $10 \text{ m}^2/\text{g}$ ) were stirred in anhydrous THF for 5 min. SnCl<sub>2</sub> is then added to the reaction medium in one portion. The Schlenk contents were further stirred at 65 °C for 15 min. After completion of the reaction, the solution was rotary evaporated under air to remove volatile organic, which led to the obtention of a grey powder of *t*-BuONa-stabilized Sn(0) particles and graphite. Afterward, all handling were performed under nitrogen atmosphere.

The reduction products were characterized by X-ray diffraction (XRD) using the Mo K $\alpha$  radiation of an automated powder diffractometer (Rotaflex Ru-200B, Rigaku generator and CPS 120 INEL detector transmission assembly). Electron microscopy studies (imaging, selected area electron diffraction (SAED)) were carried out by using a Philips CM20 microscope operated at 200 kV. Elemental analysis was performed by energy dispersive X-ray spectrometry (EDXS) using an EDAX spectrometer.

For TEM characterizations, the samples were previously dispersed in THF by sonication. A drop of the obtained suspension was deposited on a carbon observation grid which was further introduced into the microscope column.

Electrochemical insertion of lithium was performed in half cells. A lithium ribbon was used both as reference and auxiliary electrode. The electrolyte was a LiClO<sub>4</sub> (1.5 mol/kg)-ethylene carbonate (EC) solution. A 1-methyl-2-pyrrolidinone slurry of the graphite/Sn-based composite (95 wt.%) and of the polyvinylidene fluoride (PVDF) binder (5 wt.%) was used to coat a copper current collector. A Mac Pile II system operating either in galvanostatic or voltammetry modes was used. In the voltammetry mode, the current was monitored when the voltage was scanned by steps at a low rate (2.5 mV/2 min) between 0 and 2.5 V versus Li<sup>+</sup>/Li. In the galvanostatic mode, the output voltage was recorded for a specific current cell of 7  $\mu$ A/mg applied for 6 min followed by a 10 s relaxation period.

## 3. Results and discussion

#### 3.1. Elaboration of the graphite/tin-based material

We have recently reported a low temperature method for the synthesis of nanoscale tin(0) particles which uses *t*-BuONa-

activated NaH as the reducing agent [21]. The chemical reaction that we employed for the preparation of the graphite/tin-based material can be formulated as:

$$SnCl_2 + 2t$$
-BuOH + 4NaH + graphite  
 $\frac{THF}{65 \circ C}Sn(0)/2t$ -BuONa/graphite + 2NaCl + 2H<sub>2</sub>  $\uparrow$ 

A slight excess of NaH is added to the reaction medium to insure the complete reduction of SnCl<sub>2</sub>. The C/Sn atomic ratio is equal to 12.

Our technique to synthesize Sn(0) nanoparticles takes advantage of the weak coordinating properties of *t*-BuONa which acts as a stabilizer and avoids aggregation of the particles generated in the course of the reduction.

#### 3.2. X-ray characterization

Fig. 1 presents the XRD patterns of the crude material resulting from the reduction of SnCl<sub>2</sub> by t-BuONa-activated NaH, in the presence of graphite (a), after ethanol washing (b) and after ethanol and water washings (c). The SnCl<sub>2</sub> reduction is effective since reflections of both Sn(0) and NaCl are present while those of SnCl<sub>2</sub> are no more visible. The excess of NaH was removed by ethanol washing (Fig. 1b) while NaCl can be eliminated by further washing with water (Fig. 1c). Low intensity reflections of Na<sub>2</sub>SnO<sub>2</sub>·3H<sub>2</sub>O are present in Fig. 1c indicating the presence of small amounts of this oxidized product after washing with water. Graphite reflections can also been seen. The graphite 002 reflection at 336 pm indicates that graphite is not modified during the reduction process. The coherence length along the c-axis of graphite, L<sub>c</sub>, was estimated from the value of the full width at half height of the 002 reflection, according to the Scherrer formula  $(L_c = 0.9\lambda/\beta \cos\theta)$ . A  $L_c$  value of 20 nm was found. Tin reflections can be indexed in the tetragonal structure of tin. The average size of the tin crystalline domains is equal to 10 nm. Subsequent ethanol and water washings



Fig. 1. XRD patterns of the Sn/graphite-based system (a) as-synthesized, (b) after EtOH washing and (c) after  $H_2O$  washing.



Fig. 2. TEM studies of the as-prepared graphite/Sn material: (a) bright field micrograph and (b) EDXS analysis.

do not modify the structural parameters of both graphite and tin.

#### 3.3. TEM characterization

Fig. 2a shows the bright field micrograph of the crude material obtained after reduction of  $SnCl_2$  by *t*-BuONa-activated NaH and deposited on the TEM observation grid after its dispersion in THF by sonication. Therefore, it must be pointed out that the TEM micrographies cannot represent exactly the texture and organization. They give however an idea of the nature and the size of the observed particles. The average diameter of tin particles is 10.0 nm. Examination of the organic phase by EDXS confirms the presence of carbon, oxygen, sodium and tin in the material in agreement with the presence of the likely excess NaH, NaCl and *t*-BuONa (Fig. 2b). Washing the crude material with ethanol results in an aggregation of tin particles. The average diameter of these aggregates is close to 16 nm as shown in

the micrograph presented in Fig. 3a. Further washing with water causes a strong agglomeration of tin particles due to the complete removal of the organic matrix surrounding Sn(0) particles (Fig. 3b). The average size of these tin aggregates is close to 50 nm. The corresponding SAED pattern insert of Fig. 3b displays dotted rings characteristic of the tetragonal structure of tin (space group: *I*41/*amd*).

## 3.4. Electrochemical study

Fig. 4 presents selected current versus potential curves obtained for the Sn/graphite-based system, at a rate of 2.5 mV/2 min, after ethanol and water washings. The working electrode was prepared by dispersing the material (95 wt.%) and the polyvinylidene fluoride (PVDF) binder (5 wt.%) in 1-methyl-2-pyrrolidinone. The negative current observed between 2.5 and 1 V versus Li<sup>+</sup>/Li during the first reduction can be attributed to the irreversible reduction of tin oxides formed



Fig. 3. TEM micrographs of the graphite/Sn material after washing with EtOH (a) and with H<sub>2</sub>O (b). The inset shows the related SAED pattern.



Fig. 4. Selected current vs. potential curves of the graphite/Sn-based system obtained after washing with EtOH and H2O.

during the reduction and washing processes according to the following reactions:

$$\text{SnO}_2 + 2\text{Li}^+ + 2e^- \rightarrow \text{SnO} + \text{Li}_2\text{O}$$

 $SnO + 2Li^+ + 2e^- \rightarrow Sn + Li_2O$ 

In the literature, the reductions of  $\text{SnO}_2$  and SnO occur at 1.88 and 1.58 V, respectively [22,23]. Below 1.0 V, the negative currents can first be related to the likely formation of the solid electrolyte interphase (SEI) on graphite and Sn surfaces [5,24], then to the Li<sub>x</sub>Sn alloys formation [22,25–27] and finally to lithium intercalation into graphite [28].

According to previous data, lithium tin alloys ( $Li_2Sn_5$ , LiSn,  $Li_7Sn_3$ ,  $Li_5Sn_2$ ,  $Li_{13}Sn_5$  and  $Li_{22}Sn_5$ ) are formed in a 0.76–0.38 V potential range in agreement with our experimental data. Peaks are also present in the oxidation process. Between 0.4 and 0.8 V, they correspond to the reversible lithium dealloying. Around 0.2 V, they are related to lithium deintercalation out of graphite. Profiles of the first voltammograms and the following ones differ significantly. Tin oxide reduction which occurs during the first reduction leads to the formation of the insulating  $Li_2O$  that likely influences the kinetics of lithium insertion in tin and graphite.

Upon cycling, the intensity of the peaks related to lithium insertion into tin decreases before being stable. As previously discussed in a previous paper, the presence of tin aggregates not bound to graphite could contribute to the decrease of the reversible capacity of tin [19]. In such conditions, the large volume variations accompanying the alloying/dealloying processes, are likely responsible for the pulverization of these aggregates in smaller particles which are electrically disconnected with consequently a decay of the electrode activity.

Fig. 5 shows selected charge/discharge curves of an electrode containing the active Sn/graphite-based composite (95 wt.%) washed with ethanol and water and the PVDF binder (5 wt.%). A specific current of 20  $\mu$ A/mg is applied in a 0–2.4 V potential range. The potential plateaux correspond to the peaks observed on the related voltammograms. The C/Sn atomic ratio is equal to 12, according to the quantities of reactants and to elemental analysis results.

The expected theoretical maximum capacity of the active 12C/Sn system is equal to 650 mAh/g, assuming the formation of the highest lithium content alloy,  $\text{Li}_{22}\text{Sn}_5$ . During the first reduction, a capacity of 993 mAh/g is found, in which about 345 mAh/g are connected to irreversible reactions related to the SEI formation and to tin oxide reduction. This irreversible capacity decreases with the cycle number.

The reversible capacity decreases from 650 mAh/g (1st cycle) to a stabilized value of 500 mAh/g (10th cycle) as shown in Fig. 6.

The decrease of the irreversible capacity with the cycle number observed in the galvanostatic curves is related to a shortening of the reversible capacity in the 0.5-0.2 V potential range in which lithium tin alloy formation occurs. As discussed in our previous papers, the decrease of the reversible capacity could be due to lithium insertion into free tin particles and aggregates not



Fig. 5. Selected charge and discharge curves of graphite/Sn composite washed with ethanol and water.



Fig. 6. Evolution of the reversible capacity upon cycling of the graphite/Sn composite.

bound to graphite [21]. As a matter of fact, lithium insertion in such free aggregates leads to dramatic volume expansions generating cracks and crumbling of the electrode with consequently the electrical insulation of tin particles leading to the electrode capacity fade. The stable experimental reversible capacity of 500 mAh/g can therefore be related to graphite and to the part of tin bound to graphite.

# 4. Conclusion

SnCl<sub>2</sub> can be reduced in Sn(0) by sodium *tert*-butyl alkoxideactivated NaH in THF at 65 °C. When the reduction is carried out in the presence of graphite, the resulting material is composed of Sn(0) particles, graphite, an organic matrix and NaCl. Tin crystallized in the expected tetragonal structure is present either as nanosized particles dispersed on the graphite surface or as large free aggregates.

Electrochemical lithium insertion in such tin–graphite systems gives evidence for lithium intercalation into graphite and for lithium–tin alloys formation. A stable reversible capacity of ca. 500 mAh/g was found. This value is lower than the maximum theoretical capacity of 650 mAh/g assuming the formation of the highest lithium content alloy,  $Li_{22}Sn_5$ . It appears that only a part of tin is involved in the insertion/deinsertion reversible process. It is hypothesized that this reversible alloying/dealloying is related to the fraction of tin bound to graphite. The other part of free tin aggregates is supposed to behave as massive tin in which lithium insertion generates cracks and pulverization of the electrode with consequently a loss of electrical contact between tin particles and a capacity decay upon cycling.

Modification of the experimental conditions of SnCl<sub>2</sub> reduction affects the tin particle size, the larger one being obtained by increasing the reduction duration [19]. Thus, a better contact between graphite and well dispersed tin particles of optimum size would contribute to obtain a reversible capacity closer to the theoretical value. The determination of free and graphite bound tin could be obtained by using suitable characterization techniques like Mössbauer and electron energy loss spectrocopies. Such studies are being currently in progress to support the hypothesis that the improvement of the cycling performances of the Sn/graphite system are related to the formation of bonds, likely covalent, between graphite and tin. Although their large and stable reversible capacities, the use of such materials as negative electrodes of Li-ion battery is strongly dependent on the possibility to reduce their large irreversible capacities.

## References

- [1] T. Nagaura, K. Tazawa, Prog. Batteries Solar Cells 9 (1990) 209.
- [2] J. Yang, Y. Takeda, N. Imanishi, J.Y. Xie, O. Yamamoto, Solid State Ionics 96 (2000) 277.
- [3] J.O. Besenhard, J. Yang, M. Winter, J. Power Sources 68 (1) (1997) 87.
- [4] O. Crosnier, T. Brousse, X. Devaux, P. Fragnaud, D.M. Schleich, J. Power Sources 94 (2001) 169.
- [5] M. Winter, J.O. Besenhard, Electrochim. Acta 45 (1999) 31.
- [6] T. Brousse, R. Retoux, U. Herterich, D.M. Schleich, J. Electrochem. Soc. 145 (1) (1998) 1.
- [7] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2045.
- [8] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2943.
- [9] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novak, Adv. Mater. 10 (10) (1998) 725.
- [10] J.O. Besenhard, M. Hess, P. Komenda, Solid State Ionics 40–41 (1990) 525.
- [11] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, Science 276 (1997) 1395.

- [12] P.E. Lippens, J. Olivier-Fourcade, J.C. Jumas, Hyperfine Interact. 126 (2000) 137.
- [13] J.Y. Lee, R. Zhang, Z. Liu, J. Power Sources 90 (2000) 70.
- [14] J. Santos-Pena, T. Brousse, D.M. Schleich, Solid State Ionics 135 (2000) 87.
- [15] J. Read, D. Foster, J. Wolfenstine, W. Behl, J. Power Sources 96 (2001) 277.
- [16] A. Dailly, P. Willmann, D. Billaud, Electrochim. Acta 48 (2002) 271.
- [17] A. Dailly, J. Ghanbaja, P. Willmann, D. Billaud, J. Power Sources 136 (2004) 281.
- [18] A. Dailly, L. Balan, J. Ghanbaja, P. Willmann, D. Billaud, Carbon 43 (2005) 1001.
- [19] L. Balan, J. Ghanbaja, P. Willmann, D. Billaud, Carbon 43 (2005) 2311.
- [20] A. Dailly, J. Ghanbaja, P. Willmann, D. Billaud, Electrochim. Acta 48 (2003) 977.
- [21] L. Balan, R. Schneider, D. Billaud, J. Ghanbaja, Mater. Lett. 59 (2005) 1080.
- [22] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2045.
- [23] R.A. Huggins, Solid State Ionics 113-115 (1998) 57.
- [24] A. Naji, J. Ghanbaja, B. Humbert, P. Willmann, D. Billaud, J. Power Sources 63 (1996) 33.
- [25] J. Wang, I.D. Raistrick, R.A. Huggins, J. Electrochem. Soc. 133 (1986) 457.
- [26] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2943.
- [27] W. Liu, X. Huang, Z. Wang, H. Li, L. Chen, J. Electrochem. Soc. 145 (1998) 59.
- [28] D. Guérard, A. Hérold, Carbon 13 (1975) 337.