

Carbon paper as three-dimensional conducting substrate for tin anodes in lithium-ion batteries

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Received 28 July 2004; received in revised form 16 September 2004; accepted 27 September 2004

Available online 19 November 2004

Abstract

Tin on a carbon paper (CP) was investigated by repeated galvanostatic cycles with time-limited charges to insert different amounts of lithium per Sn atom, and tin electrodeposited on copper was also investigated for comparison of the cyclic stability. The results demonstrated that, unlike Sn electrodeposited on Cu foil, Sn on CP can undergo several tens of lithiation/delithiation cycles with Li/Sn atomic ratio ≤ 2 at high current density (0.70 mA cm^{-2}), thus confirming that carbon paper is a good current collector-substrate which is able to improve the cycling performance of tin by preserving the electric contact over cycling, in spite of the great volume changes during the lithium insertion/removal processes in tin.

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Keywords: Carbon paper; Current collector; Lithium-ion batteries; Tin anodes

1. Introduction

In lithium-ion battery field the search for anode materials alternative to graphite has led to the development of metal oxides [1,2] and metal alloys [3,4]. Li/metal alloys are very attractive for their specific capacity; however, the high volume change, which is related to the insertion/removal of lithium, causes the alloy pulverization and loss of electric contact that is responsible for the poor cycle life. The preparation of superfine and nanometric materials, intermetallic compounds and alloy/carbon composites are strategies that have been pursued to reduce this drawback [5–9], but only minor attention has been paid to the current collector nature and morphology, even if it was demonstrated [8,10] the effect of the surface roughness of copper foil on improving alloy's cyclability. After a study on the electrochemical stability of Cu_6Sn_5 on commercial carbon paper (CP) as a new current collector for this negative electrode [11] in which we demonstrated that the three-dimensional conducting matrix of CP

can host Cu_6Sn_5 and prevent the loss of electric contact during lithiation/delithiation we have extended our investigation to Sn on CP.

In the present study, electrodes of Sn on CP were tested under repeated lithiation/delithiation galvanostatic cycles with time-limited charges to insert different amounts of lithium, and their cyclability performance was compared with that of Sn on Cu.

2. Experimental

Sn was chemically prepared after Yang et al. [12] from degassed solutions of $0.062 \text{ M SnCl}_2 \cdot 2\text{H}_2\text{O}$ – $0.095 \text{ M Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and of 0.165 M NaBH_4 – 0.125 M NaOH with an home-made apparatus which allows the synthesis and all the phases of washing (with degassed water) and filtering to be performed in argon atmosphere. Ultrapure water (MilliQ— $18.6 \text{ M}\Omega \text{ cm}$, Simplicity Water System, Millipore Co.) was employed for all the solutions and rinsing. The chemical tin was used to prepare electrodes by perme-

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ation of a suspension of Sn (96 wt.%), polyvinylidene fluoride (4 wt.%) and acetone through carbon paper (Spectracorp 2050, 10 mil) sheets. These electrodes, with a Sn mass loading of $2.5\text{--}8.0\text{ mg cm}^{-2}$, were dried 1 h at $70\text{ }^{\circ}\text{C}$ under vacuum at room temperature before use. For comparison Sn was galvanostatically deposited on copper foils ($25\text{ }\mu\text{m}$ thick) from a $0.1\text{ M SnCl}_2\text{--}0.5\text{ M H}_2\text{SO}_4$ degassed solution at room temperature and -12 mA cm^{-2} (adhesive tape was used to limit the exposed area to 1 cm^2). As the efficiency of the electrodeposition was low, tin mass loading was evaluated by weighing and it was in the range $1.5\text{--}2.5\text{ mg cm}^{-2}$. The electrodes were dried under vacuum at $60\text{ }^{\circ}\text{C}$ before use.

The tin powder and the electrodes were characterized by X-ray diffraction (XRD) analysis with a Philips PW1050/81 diffractometer (Cu $K\alpha$ radiation, 40 mA, 40 kV). Scanning electron microscopy (SEM) analyses were performed with a Philips 515 scanning electron microscope.

The electrochemical characterization was carried out by galvanostatic charge/discharge cycles at $T = 30 \pm 1\text{ }^{\circ}\text{C}$ in a T-shaped cell sealed in dry-box (Mbraun Labmaster 130, O_2 and $\text{H}_2\text{O} < 1\text{ ppm}$). The working electrodes were cut with a hollow brass punch and the area was $0.70 \pm 0.01\text{ cm}^2$ for those on CP and $0.73 \pm 0.01\text{ cm}^2$ for those on Cu. The counter electrode was metallic Li in excess and the reference electrode for monitoring the electrode potentials was a Li foil. The separator, a Whatman GF/D glass fiber disk, was imbibed with the electrolyte solution ethylene carbonate:dimethylcarbonate (EC:DMC 2:1)— 1 M LiPF_6 (LP31 Merck, battery grade). The galvanostatic charge/discharge cycles were carried out at 0.500 mA , i.e. about 0.70 mA cm^{-2} . We intend with the terms charge and discharge, the lithiation and delithiation processes as the electrode was functioning in a lithium-ion cell. The discharges were potential-limited at different values (2.000 and 1.200 V); a potential of 0.800 V versus Li was applied for 20 min to the tin electrodes before starting the galvanostatic cycles with discharge cut off potential of 1.200 V . The charges were time-limited to insert defined amounts of lithium in tin. However, to avoid lithium deposition, a safe cut off potential of 0.005 V versus Li was set. This enabled the discharge process to start whenever the electrode potential reached the cut off of 5 mV before the set time elapsed and allowed the cycling tests to continue, still with a charge capacity lower than that set. Given that the coulombic efficiency (η) after 10–20 cycles was near 99% and maintained this value until the end of the cycling tests, the limitation of the charges by the reaching of the safe potential was the only responsible of the capacity decrease. The cells with electrodes having high tin mass loading were disassembled and reassembled to change the Li metal counterelectrode (and in some cases even the separator) after a certain number of cycles, when it seemed that Li metal deposition/dissolution at the counterelectrode interfered in Li_xSn cycling. The electrochemical deposition and characterization were carried out with a VMP multichannel potentiostat and a PAR 273 A potentiostat/galvanostat.

3. Results and discussion

The SEM image of Sn powder yielded by chemical reduction shows that the Sn aggregates are made of particle less than $1\text{ }\mu\text{m}$ in size (Fig. 1(a)) and the images of the chemical Sn on CP (Fig. 1(b)–(c)) show how the tin distribute in the carbon paper, with particles homogeneously covering the carbon fibers. The images of the electrochemical Sn on Cu (Fig. 2(a)–(b)) evidence different morphologies in different parts of the electrode, with particles and aggregates bigger than those of chemical tin. Fig. 3 displays that in the XRD patterns of the chemical Sn powder the tin oxides are almost absent, demonstrating that the chemical synthesis under Ar atmosphere is effective to prevent oxides formation.

Electrochemical tests on tin as negative electrode for lithium-ion batteries demonstrated that Sn acts as a catalyst for electrolyte decomposition until a thin passivation layer covers the catalytic surface, and that this layer makes the lithium diffusion more difficult with a resulting decrease of electrode capacity. Hence, the decrease of the potential discharge cut off was suggested to preserve a Li_xSn alloy, thus avoiding, at the end of each discharge, the formation of pure tin. It was also reported that if the lithiation rate is greater than the electrolyte catalytic decomposition rate, the Li_xSn alloy is rapidly formed and the catalytic action of pure tin probably ends [13].

To highlight how such parameters as amount of inserted lithium and discharge potential affect the cycling stability of Sn/CP electrodes, we performed repeated galvanostatic charge/discharge cycles at 0.70 mA cm^{-2} on chemical Sn/CP electrodes at different Li/Sn ratio and different discharge cut off potentials. The charge time and the discharge cut off potential of electrode A were set so as to insert 2.08 Li per Sn atom and to stop the discharge at 2.000 V , for electrode B the charge time was set to insert 1.08 Li atom per Sn still maintaining the discharge cut off potential at 2.000 V and for electrode C the charge time was increased to insert 1.84 Li per Sn atom but the discharge cut off potential was decreased to 1.200 V . These types of tests on different electrodes displayed good reproducibility. The coulombic efficiency of their first galvanostatic cycle ranged from 50% to 70%, being affected by irreversible capacity due to side-reactions at the electrode/electrolyte interface, and only after 20 cycles at least reached 99%. The behavior of these electrodes, shown in Fig. 4, is quite different. The electrode A, charged with high Li/Sn ratio and deeply discharged to 2.000 V , which shows a maximum specific capacity at the fifth cycle of 430 mA h g^{-1} ($\eta = 91\%$), rapidly lost capacity because it reached the potential of 5 mV before the charge was completed over the set time (after the 22nd cycle the counter electrode was changed, but this attempt to ameliorate the electrode performance was unfruitful) and after the 50th charge the electrode no longer could be discharged. However, it is worth noting that with the same Li/Sn setting it was possible to continue the cycling, after the first 10 cycles with discharge cut off at 2.000 V , when the cut off was decreased to 1.5 V or less. Great vol-

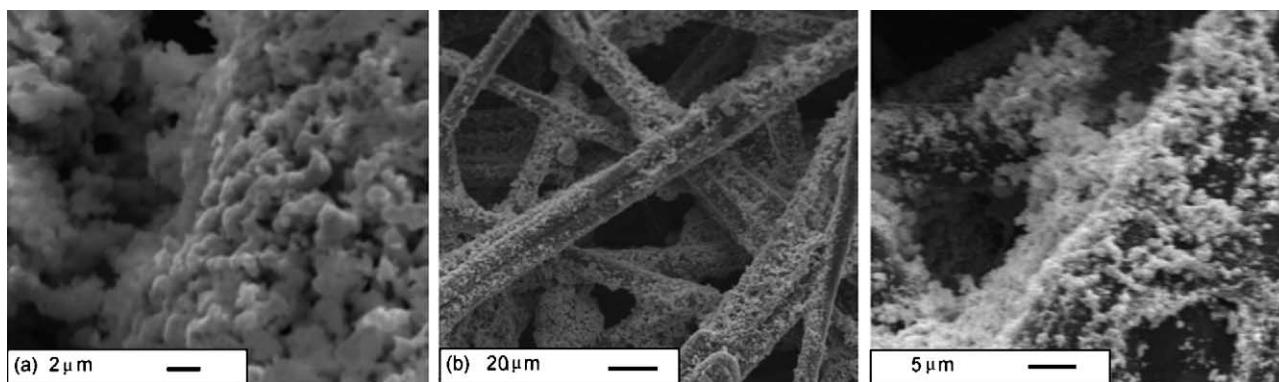


Fig. 1. SEM images of (a) chemical Sn powder and (b and c) chemical Sn/CP electrode.

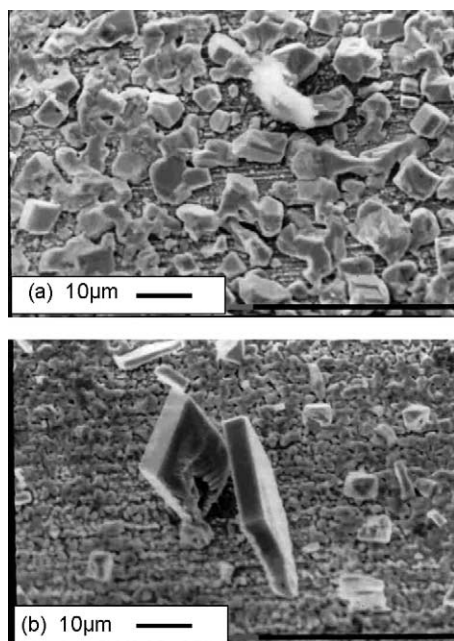


Fig. 2. SEM images of an electrochemical Sn/Cu electrode (different portions of the same electrode).

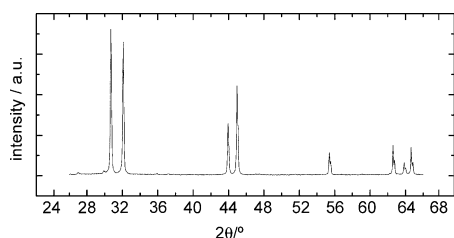


Fig. 3. XRD patterns of chemical Sn powder.

ume changes that produce alloy pulverization and continuous growing of a passivation layer on the fresh surface (the coulombic efficiency in electrode A was 97% and 98% at the 10th and 15th cycles and reached 99% only after 35 cycles) may explain this behavior.

Differently, the insertion of only 1.08 Li per Sn in electrode B provides more stability, even if the discharge cut off

voltage is 2.000 V, and the capacity goes from a maximum of 240 mA h g^{-1} ($\eta = 99\%$) to an almost constant value of 170 mA h g^{-1} ($\eta = 99\%$) after more than 150 cycles. In this case it is clear that the minor amount of inserted lithium produces minor volume changes and, in turn, minor fresh tin surface exposed to the electrolyte. Thus, the presence of the thin passivation layer built up during the first cycles may act as protection shield without being detrimental for lithium diffusion. The electrode C, whose charge time was set to insert 1.84 Li per Sn and discharge was stopped at 1.200 V, displays a decrease in charge and discharge capacity very similar to that of electrode A for the first forty cycles ($\eta = 97\%$ and 98% at the 10th and 15th cycles, and $\geq 99\%$ after the 20th cycle) and, after 80 cycles, an anomalous increase of the capacity up to recovering the maximum initial capacity. We can explain this behavior by considering that a passivation layer is formed, probably different in nature than that on electrode A because tin is never produced at the end of discharges limited to 1.200 V, and that it may detach from the Li_xSn as consequence of great volume changes, thus restoring the initial surface and capacity. In addition, possible Li_xSn cracks ex-

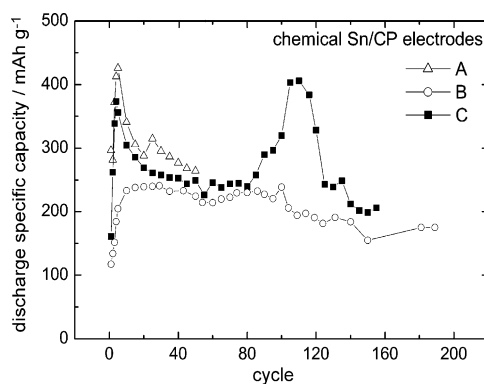


Fig. 4. Discharge capacity from galvanostatic charge/discharge cycles at 0.70 mA cm^{-2} of chemical Sn/CP electrodes at different amounts of lithium inserted and different discharge cut off voltages. For each electrode, the mass, the set Li/Sn atomic ratio, the set charge time and the discharge cut off voltage, respectively, are: electrode A, 6.0 mg cm^{-2} , 2.09 Li/Sn, 3 h 58 min, 2.0 V; electrode B, 6.9 mg cm^{-2} , 1.08 Li/Sn, 2 h 20 min, 2.0 V; electrode C, 6.3 mg cm^{-2} , 1.84 Li/Sn, 3 h 40 min, 1.2 V.

pose fresh surface and offer easier paths for lithiation, still being maintained the electric contact by the carbon fibers into which tin is hosted.

Fig. 5 shows the voltage profiles of the Sn/CP electrodes of Fig. 4 compared to those of the bare carbon paper whose charge time was set to 2 h, very near to the initial charge time set for the electrode B (2 h 20 min). The charge times set for electrodes A and C were almost comparable (near 4 h). The voltage profiles of the first cycles of Sn/CP are different from those of the bare CP and the voltage values are more positive. Fig. 4 showed that the discharge capacity of both Sn/CP electrodes A and C (set to insert 2.09 and 1.84 Li/Sn, respectively) decreased sharply after the first cycles. From the voltage profiles, we can see that the cut off of 5 mV was reached after very few cycles and, consequently, the charge capacity decreased more and more. While the electrode A could be delithiated no more after the 50th cycle, the electrode C seemed to regain a good contact after 80 cycles as shows the dotted voltage profiles of the 110th cycle in Fig. 5, and this supports our hypothesis that the passivation layer may detach from the electrode surface restoring the initial capacity. The comparison of the electrode B (set to insert 1.08 Li/Sn) and the bare CP charged over comparable times, evidenced a sharper decrease of the charge time of CP (1 h 51 min and 47 min for Sn/CP and CP, respectively, at the 140th cycle) indicating that CP is unable to sustain long cycling with high amount of lithium inserted (increased stability of CP was, however, observed with lower amount of lithium inserted but with scarce reproducibility). The evolution of the voltage pro-

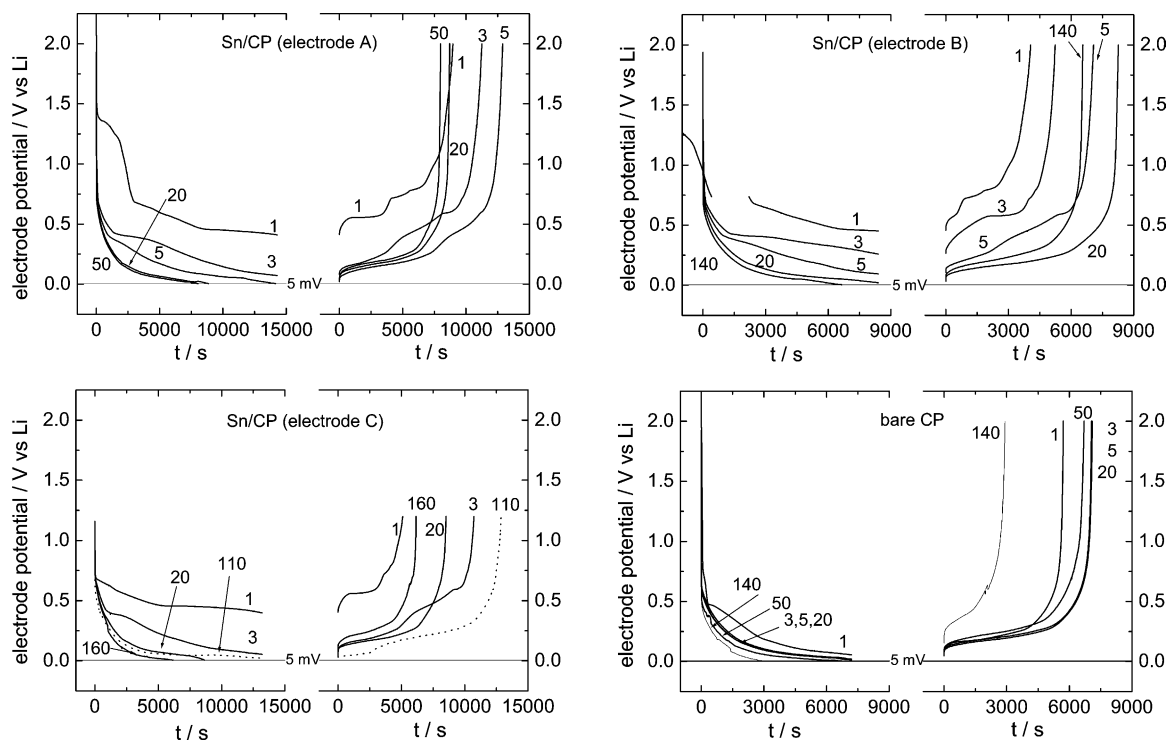


Fig. 5. Voltage profiles of galvanostatic charge/discharge cycles at 0.70 mA cm^{-2} of chemical Sn/CP electrodes A–C, and of bare CP (10.3 mg cm^{-2}). The initial charge times were 3 h 58 min, 2 h 20 min, 3 h 40 min and 2 h for the Sn/CP electrodes and for CP, respectively.

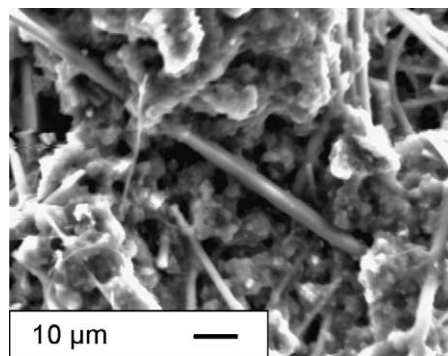


Fig. 6. SEM image of chemical Sn/CP (electrode B of Fig. 4 after 190 cycles).

files of Sn/CP electrodes over cycling is difficult to explain. While in the case of Cu_6Sn_5 [11] we were able to attribute, with the support of XRD analysis, the progressive smoothing of the voltage profiles to a deterioration of the material without important consequence on cycle life, in this case we had no evidences of a deterioration in the Li_xSn (the XRD patterns before and after cycling were almost identical) and we could only see, by the SEM image of Sn/CP electrode B after 190 cycles reported in Fig. 6, a morphological modification by agglomeration of Sn particles when compared to the images of Fig. 1(b) and (c).

Having in mind that Sn/CP electrodes with high mass loading (ca. 7 mg cm^{-2} for the electrodes A–C) may have more difficulties to maintain the electric contact of all the

material with CP, we prepared Sn/CP electrodes with low Sn mass loading ($2.5\text{--}4\text{ mg cm}^{-2}$) and we compared their charge/discharge processes with those of bare CP as well as those of Sn/Cu electrodes ($1.5\text{--}2.5\text{ mg cm}^{-2}$), also to evidence the benefit in the use of CP instead of Cu foil as current collector. Fig. 7 reports the discharge capacity data over galvanostatic charge/discharge cycles of four Sn/Cu electrodes (D–G) at different extents of inserted lithium ($0.92\text{--}1.5\text{ Li/Sn}$) and with different discharge cut off potentials. Fig. 7 also displays capacity data of two Sn/CP electrodes (H and I) cycled under the same conditions of electrodes F and G (0.92 and 1.5 Sn/Li , 0.005 and 1.200 V versus Li). These experiments performed on several electrodes displayed good reproducibility. For the Sn/Cu electrodes D and E it was clear that deep discharges up to 2.000 V were detrimental (after 10 cycles, η increased from 91% to 98%) even with a very low amount of inserted lithium, contrarily to what happened for low lithium insertion in Sn/CP electrode B. When the discharges are stopped to 1.200 V , the amount of inserted lithium could reach 1.5 atom per Sn with “cycling stability” for no more than 30 cycles, with η decreasing from 99% (fifth cycle) to 95% (100th cycle). Unlike the Sn/Cu electrodes, the Sn/CP electrodes H and I showed stable discharge capacity over more than 100 cycles ($94\% < \eta < 99\%$ with η increasing over cycling), demonstrating the advantage in the use of CP as substrate/current collector. The loss of capacity of Sn/Cu electrodes over cycling was due to the loss of electric contact during lithiation/delithiation which caused delamination from the Cu current collector as the wide crack in Fig. 8 demonstrates (electrode D after 100 cycles). These results are a further confirmation that the use of a CP substrate more pliant than a metal foil is successful to improve cycle life of tin anodes. Fig. 9 shows the voltage profiles of the cycles 1, 5, 30 and 50 of electrodes Sn/CP and Sn/Cu of compar-

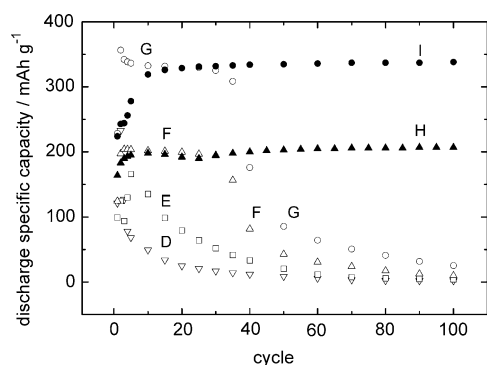


Fig. 7. Discharge capacity from galvanostatic charge/discharge cycles at 0.70 mA cm^{-2} of electrochemical Sn/Cu (D–G) and Sn/CP (H and I) electrodes at different amounts of lithium inserted and different discharge cut off voltages. For each electrode, the mass, the set Li/Sn atomic ratio, the set charge time and the discharge cut off voltage, respectively, are: electrode D, 1.8 mg cm^{-2} , 1.08 Li/Sn , 38 min, 2.0 V ; electrode E, 2.3 mg cm^{-2} , 0.92 Li/Sn , 42 min 30 s, 2.0 V ; electrode F, 1.6 mg cm^{-2} , 0.92 Li/Sn , 30 min, 1.2 V ; electrode G, 2.3 mg cm^{-2} , 1.50 Li/Sn , 1 h 9 min, 1.2 V ; electrode H, 2.9 mg cm^{-2} , 0.92 Li/Sn , 50 min, 1.2 V ; electrode I, 4.0 mg cm^{-2} , 1.5 Li/Sn , 1 h 54 min, 1.2 V .

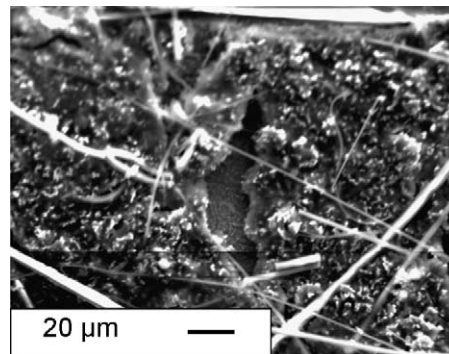


Fig. 8. SEM image of electrochemical Sn/Cu (electrode D of Fig. 7 after 100 cycles).

ble low Sn loading and amount of inserted Li, and of bare CP, with charge times set at 50, 30 and 50 min, respectively. Unlike the voltage profiles of Sn/Cu which displayed the almost total loss of electric contact at the 50th cycle, those of Sn/CP electrodes displayed the step of lithium insertion at ca. 0.4 V up to the 50th cycle. The profiles of heavier electrodes, reported in Fig. 5, lost this step after ca. 20 cycles, probably because in heavier Sn/CP electrodes the agglomeration process is more important and more evident. It is worth noting that in the case of heavy $\text{Cu}_6\text{Sn}_5/\text{CP}$ [11] electrodes the smoothing of the profiles took place after a greater number of cycles probably because the presence of Cu buffers the Sn volume changes and prevents the Sn agglomeration. These latter results are an evidence that the capacity of Sn/CP electrodes is mainly due to Li_xSn . It has to be considered, too, that the CP whose voltage profiles were reported in Fig. 9 was a particularly stable electrode, the best we had. Generally CP was unable to sustain charge process as long as Li_xSn did and to maintain constant performance for a high number of cycles at the same high current density (as Fig. 5 showed for longer charge time).

All these results demonstrate that the better strategy to ameliorate the performance of tin-based electrodes remains to use intermetallic compounds such as Cu_6Sn_5 hosted in CP which displayed, for electrode loading of 7.5 mg cm^{-2} , a stable capacity of 2.1 mAh cm^{-2} for more than 150 cycles [11]. The use of the three-dimension CP substrate seems to be an interesting strategy to be pursued also with other intermetallic compounds. On the other hand, the use of different type of carbon such as carbonaceous mesophase spherules [14] and nanotubes [15] to ameliorate the performance of tin or intermetallic compounds has been pursued and very recently the approach of preparing anode with tin nanoparticles confined within the micropores of the activated carbon structure gave interesting results [16]. In the same direction, attention has been paid also to binder, which is of critical importance in maintain cohesion between particles and current collector, especially when the alloy volume changes are significantly high [17].

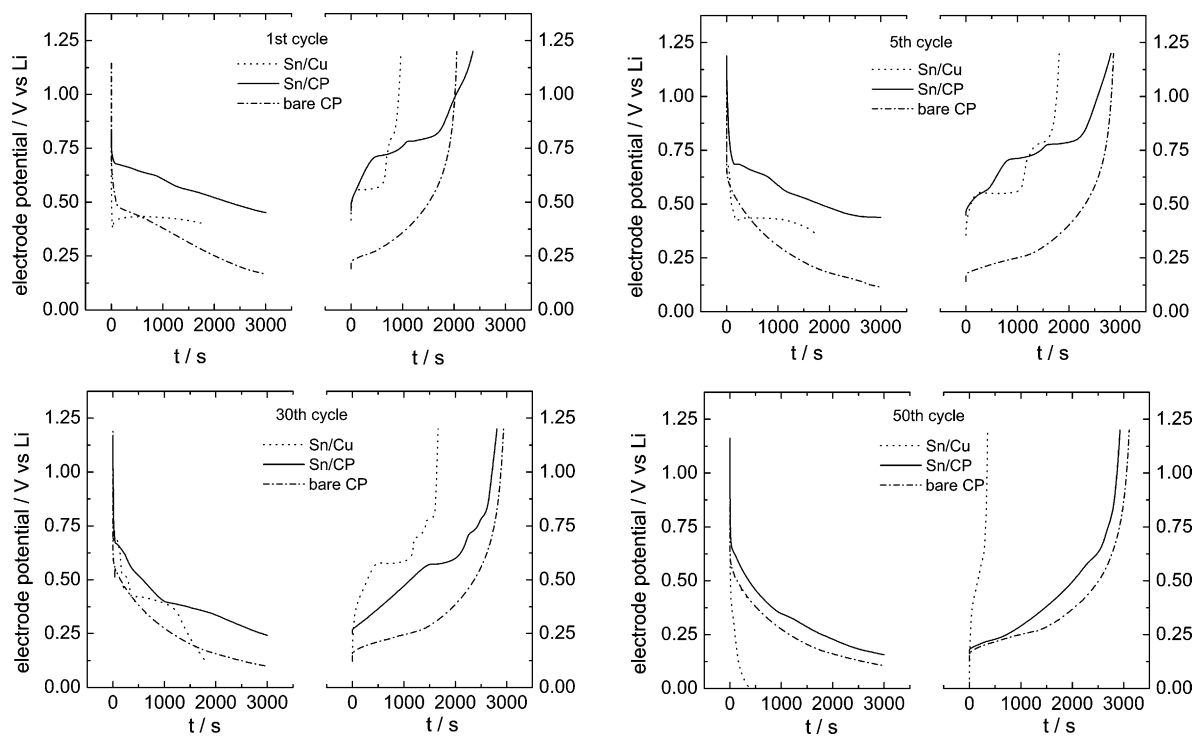


Fig. 9. Voltage profiles of galvanostatic charge/discharge cycles between 0.005 and 1.200 V at 0.70 mA cm^{-2} of chemical Sn/CP (electrode H), electrochemical Sn/Cu (electrode F) and bare CP electrodes. For each electrode, the mass, the set Li/Sn atomic ratio and the set charge time, respectively, are: electrode H, 2.9 mg cm^{-2} , 0.92 Li/Sn, 50 min; electrode F, 1.6 mg cm^{-2} , 0.92 Li/Sn, 30 min; bare CP electrode, 10.0 mg cm^{-2} , 50 min.

4. Conclusions

The results of this study on Sn/CP electrodes confirm that a suitable conducting substrate-current collector is of paramount importance in the design of electrodes for lithium-ion batteries. The carbon paper, due to its three-dimension morphology and to its electronic conductivity, meets the requirements of good substrate and current collector, being a lightweight, three-dimension matrix with micrometric, interconnected carbon fibers that can host Sn without addition of conducting agent. These characteristics make it more compliant than Cu foil to the volume stresses of the hosted tin. We demonstrate that carbon paper improves the cyclability performance of tin at high charge/discharge rate when compared with tin on copper, and this is a significant result to test the reliability of carbon paper. However, the use of tin instead of tin-based intermetallic compounds is still unfavorable due to the high volume changes of tin during lithiation/delithiation processes and a buffering system closely interconnected with tin lattice such as Cu in Cu_6Sn_5 is more effective for high performing tin-based anodes.

Acknowledgements

Research funded by COFIN2002 (Nanostructured alloys as anodes for Li-ion batteries). The authors thank Dr. R. Berti

(Department of Physics, University of Bologna) for the useful suggestions in SEM.

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