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Emilie Perre, Pierre Louis Taberna, Driss Mazouzi, Philippe Poizot, Torbjörn Gustafsson, et al.. Electrodeposited Cu₂Sb as anode material for 3-dimensional Li-ion microbatteries. *Journal of Materials Research*, 2011, vol. 25 (n° 08), pp. 1485-1491. 10.1557/JMR.2010.0190 . hal-01168173

HAL Id: hal-01168173

<https://hal.science/hal-01168173>

Submitted on 25 Jun 2015

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Eprints ID : 8678

To link to this article : DOI:10.1557/JMR.2010.0190
URL : <http://dx.doi.org/10.1557/JMR.2010.0190>

To cite this version : Perre, Emilie and Taberna, Pierre Louis and Mazouzi, Driss and Poizot, Philippe and Gustafsson, Torbjörn and Edström, Kristina and Simon, Patrice *Electrodeposited Cu₂Sb as anode material for 3-dimensional Li-ion microbatteries*. (2011) Journal of Materials Research, vol. 25 (n° 08). pp. 1485-1491. ISSN 0884-2914

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Electrodeposited Cu_2Sb as anode material for 3-dimensional Li-ion microbatteries

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An increasing demand on high energy and power systems has arisen not only with the development of electric vehicle (EV), hybrid electric vehicle (HEV), telecom, and mobile technologies, but also for specific applications such as powering of microelectronic systems. To power those microdevices, an extra variable is added to the equation: a limited footprint area. Three-dimensional (3D) microbatteries are a solution to combine high-density energy and power. In this work, we present the formation of Cu_2Sb onto three-dimensionally architected arrays of Cu current collectors. Sb electrodeposition conditions and annealing post treatment are discussed in light of their influence on the morphology and battery performances. An increase of cycling stability was observed when Sb was fully alloyed with the Cu current collector. A subsequent separator layer was added to the 3D electrode when optimized. Equivalent capacity values are measured for at least 20 cycles. Work is currently devoted to the identification of the causes of capacity fading.

I. INTRODUCTION

The new powerful microelectronics need to be powered by high capacity and high rate battery systems. Today, to fulfill the needs, they are powered by oversized batteries thus restricting the potential use of these applications. Thin-film microbattery is one system that has been conceived to increase reaction kinetics. Low thickness of the electrode and electrolyte give shorter Li^+ diffusion lengths, thus enhancing the rate capability. However, as a consequence of their two-dimensional (2D) configuration (thin-films), they contain limited quantities of active material and they are unable to provide as much energy as conventional batteries. Designing three-dimensional (3D) microbatteries will increase the

content of active material that can be deposited onto the same footprint area. This can be achieved by increasing the surface area of the current collector rather than the electrode film thickness, leading to batteries able to provide both high specific energy output and high rate capabilities.¹

For microelectronic applications, manufacturing processes such as lithography have been developed and are now leading to high quality microfabrication. Using such processes, Min et al.² have synthesized 3D half-microbatteries consisting of alternated arrays of carbon rods (C-MEMS) and arrays of the same carbon rods coated by polypyrrol. They demonstrated better capacity per footprint area than for a conventional unpatterned battery. However, this kind of preparation includes a large amount of steps and it is costly. Soft chemistry preparation techniques such as electrodeposition, sol-gel synthesis, or electrophoresis have proved to be more

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DOI: 10.1557/JMR.2010.0190

adapted for battery preparation. Golodnitsky et al.³ have presented 3D Li-ion microbatteries consisting of successive layers of each of the battery components (current collector, electrode, electrolyte) deposited onto a 3D architected silicon substrate. The electrode material was directly electrodeposited onto the metallic current collector layer; thus, avoiding the electron percolating issue that could be encountered with thick electrodes. The cell obtained was able to sustain 100 cycles without showing considerable capacity losses.

Our approach is similar as we intend to deposit layers of the different battery components. However, in our case the three-dimensionally architected structure is the current collector itself, thus reducing the amount of nonactive material within the microbattery. We have selected the Cu current collector since it has proved possible to grow as freestanding and ordered arrays of Cu nanorods by simple electrodeposition into a template and then to plate them with the negative electrode material Fe_3O_4 .⁴ The diameter and distance between the obtained Cu columns is directly dependent on the template used and can be easily tuned and downscaled to a few hundreds of nanometers (nm), thus increasing the total available surface area.

Regarding the active materials, metals alloying with lithium appeared to be attractive anodes as they exhibit high energy capacities but they undergo large volume variations during the alloying/dealloying processes.^{5,6} To circumvent these volume changes there are several different routes: it is common to prepare nano-sized particles, to disperse them in composite matrix and/or alloy them with compounds nonelectrochemically active toward lithium that will act as a mechanical buffer of the volume expansion (such as Cu_2Sb , Mn_2Sb , NiSn).⁷⁻¹⁰ We previously¹¹ have shown that Cu_2Sb can be obtained by electrodeposition of Sb onto a Cu flat substrate and that further heat treatment promotes alloying of Sb with Cu. The capacity retention of the electrode obtained was greatly improved when compared with pure Sb electrodes due to the ability of Cu to accommodate and buffer the volume variations of Sb.

In this work, we will show that Sb also can be uniformly electrodeposited onto arrays of three-dimensionally ordered Cu current collectors. The thin films thus obtained showed capacity values close to the theoretical ones and greatly increased cycle life. Direct alloying of Sb with the current collector can be profitable since the interface between the current collector and the electrode material is improved. Furthermore, it will not be necessary with the addition of extra inactive material to buffer the volume changes during cycling, which would greatly affect the overall battery performance, especially for a 3D microbattery configuration. The cycling performances of different deposits are presented and their electrochemical behavior discussed.

The next step for designing a microbattery is the preparation of a thin and conformal separator layer. Nathan et al.¹² reported the deposition of a gel polymer in the pores of a microstructured electrode to function as separator and electrolyte for a 3D Li-ion microbattery. They selected an electrolyte composed of a commercially available poly(vinylidene fluoride) (PVDF)-based copolymer in which SiO_2 particles were added. Such electrolytes are sufficiently mechanically stable to prevent the use of a separator and present relatively high ionic conductivity ($1.10\text{--}4 \text{ S}\cdot\text{cm}^{-1}$).¹³ Thus we selected a similar electrolyte to be used in our nanostructured 3D architecture.

Our first attempts are presented in Sec. II.

II. EXPERIMENTAL

Here, Cu nanorods have been used both as current collector and a part of the electrode itself for battery testing. The synthesis of Cu nanorods has been previously described in detail by Taberna et al.⁴

Prior to Sb electrodeposition, the substrate was immersed for a few minutes in an aqueous solution of 0.5 M $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ and 1 M H_2SO_4 (Acros Organics, Geel, Belgium) to remove oxide traces onto the copper surface.

Cu_2Sb has been obtained in a two steps process. Antimony has first been electrodeposited onto the Cu substrate using an Autolab PGSTAT30 potentiostat-galvanostat (Metrohm Autolab, Bromma, Sweden). The electrodeposition electrolyte consisted of a mixture of antimony tartrate and sodium tartrate (Fluka, Stockholm, Sweden) dissolved in distilled water. Sb concentration was fixed to 0.15 M and the tartrate concentration to 0.45 M. To favor the electrodeposition of Sb instead of the precipitation of Sb_2O_3 , the pH of the solution was decreased to 1 by addition of sulfuric acid. Current pulsed electrodeposition has been selected instead of a constant current method to increase the homogeneity and conformity of the deposit. The electrodeposition conditions were fixed as follows: a current pulse was applied for a short duration (t_{dep}) to electrodeposit Sb, a 0 mA rest period (t_{rest}) was then applied to allow diffusion of the electroactive species to the Cu surface. The applied pulse intensities and their durations have been varied to obtain a conform deposit of Sb onto the Cu surface. Unless stated otherwise, the overall deposition process was maintained for 2 h.

The samples were then heat-treated for various time lengths at 120 °C in a vacuum furnace with the aim of completing the alloying process.

The hybrid polymer separator was composed of 1 g of GlycioxyPropyl triMethoxySilane, 0.2 g of Poly(Vinylidene Fluoride-co-HexaFluoroPropene), 30 mg of distilled water, 5 g of acetone, and 28 mg of dibutyl phthalate-DiButyl Phthalate (Aldrich, Lyon, France). The solution was sprayed onto the nanostructure and heat-treated at

120 °C under vacuum for 1 h to promote polycondensation. DiButyl Phthalate was finally extracted with diethyl ether.

The morphology, homogeneity, and composition of the coatings were characterized by scanning electron microscopy (SEM; JEOL JEM200CX, Tokyo, Japan and LEO1550, Cambridge, UK), and x-ray diffraction (XRD; Siemens D5000, Toulouse, France). To evaluate their electrochemical performances, samples were cycled versus lithium in a coin cell configuration. The electrolyte used was a mixture of Ethylene Carbonate:DiMethyl Carbonate with a molar ratio 1:1 containing 1 M LiPF₆ salt. The current applied for electrochemical characterization was calculated by considering a 100% faradic efficient electrodeposition of Sb. The cycling performances, rate capabilities, and impedance of the cells were studied using VMP3 Bio-logic equipment (Claix, France).

III. RESULTS AND DISCUSSION

A. Sb-coated Cu 3D electrode arrays

Pulsed current electrodeposition rather than galvanostatic deposition was selected to promote good diffusion of the species to be deposited into the narrow 3D structure. Pulse parameters such as deposition current and pulse time lengths were varied. Whatever the duration and current of the pulses, the occurrence of a deposit on the copper rods was clearly observed with SEM [Fig. 1(a) versus Figs. 1(b)–1(d)]. However, the morphology and coverage of the deposited material were directly related to the electrodeposition conditions.

Even though full coverage of the Cu arrays by Sb was successfully obtained when applying 2-mA pulses [Fig. 1(b)], an inhomogeneous deposit morphology was observed due to diffusion limitations. The Sb deposit agglomerated on the nanorod tips, while large crystallites were formed at the bottom between the pillars.

When using equivalent time steps, $t_{\text{dep}} = t_{\text{rest}} = 50$ ms and lower applied current (1 mA) during the deposition step, the Sb deposit appeared more homogeneous [Fig. 1(c)]. When the deposition time was lower than the rest period, $t_{\text{dep}} = 10$ ms $<$ $t_{\text{rest}} = 50$ ms [Fig. 1(d)], the deposit appeared very homogeneous and smooth. Smaller particles were deposited than when the deposition and rest periods were equivalent.

The deposit was characterized by XRD and shown to be a mixture of Sb and Cu₂Sb. Alloying of Sb with Cu happened spontaneously at room temperature, as already reported by Bryngelsson et al.¹¹

The different samples were subsequently cycled versus lithium to study the influence of the different deposition parameters on their battery performances: reversibility, capacity, and cycling capability. For each electrode, the applied cycling current was determined based on the expected deposited weight of Sb considering a 100% faradic efficiency Sb electrodeposition. The first cycles and the capacity retention of the cycled samples are presented in Fig. 2.

Galvanostatic curves obtained versus lithium confirmed the spontaneous formation of the alloy Cu₂Sb. The profile of the obtained cyclings [Figs. 2(a), 2(c),

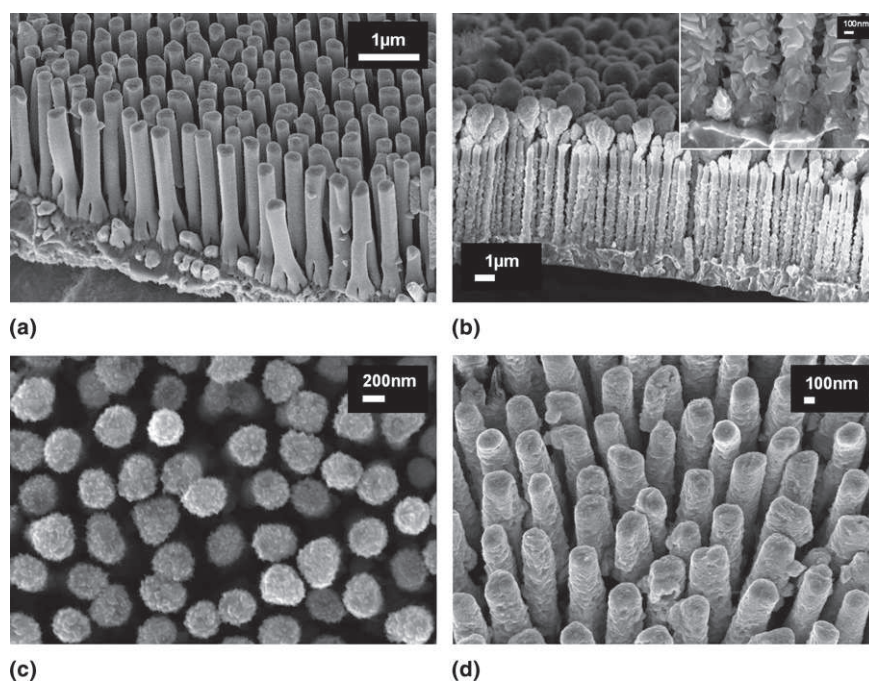


FIG. 1. (a) SEM micrograph of a raw Cu nanorods array and Sb electrodeposited onto arrays of Cu nanorods using different pulse conditions. (b) -2 mA for 100 ms and rest for 50 ms steps applied for 2 h, inset: zoom on the bottom part of the 3D nanostructure, (c) -1.3 mA for 50 ms and rest for 50 ms steps applied for 2 h, (d) -1.3 mA for 10 ms and rest for 50 ms steps applied for 2 h.

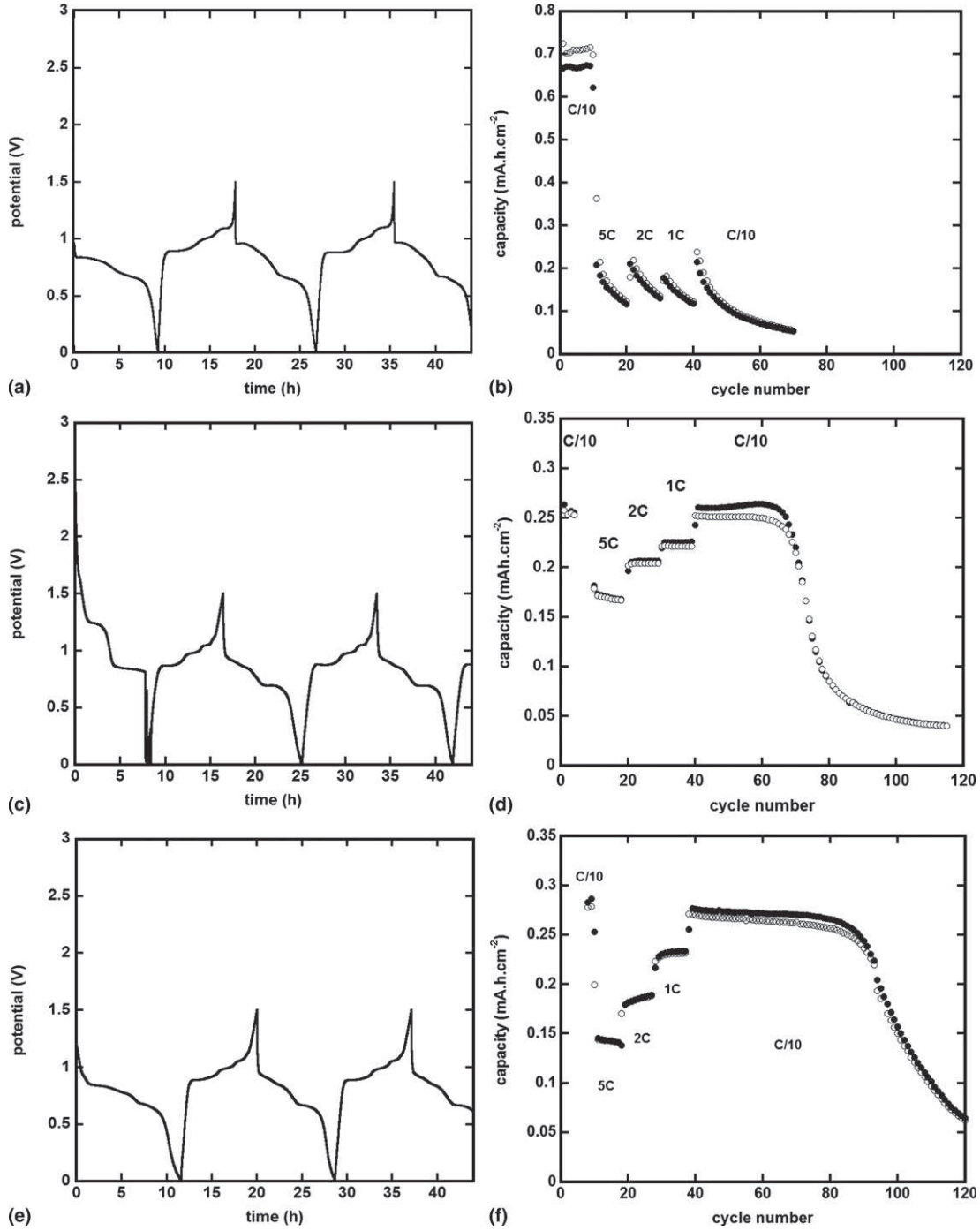
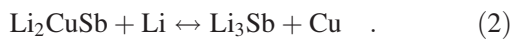


FIG. 2. Capacity retention and cycling curves (first cycles) of Sb electrodeposited onto Cu nanorod arrays at different conditions: (a, b) -1.3 mA for 50 ms and rest for 50 ms steps applied for 2 h, (c, d) -1.3 mA for 10 ms and rest for 50 ms steps applied for 2 h, (e, f) -1.3 mA for 10 ms and rest for 50 ms steps applied for 2 h, then heat-treated at 120 °C for 1 h.

and 2(d)] corresponds to the reactions previously described by Fransson et al.¹⁴ where lithium alloys with Cu_2Sb according to the following reactions.

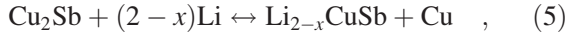


Reaction (1) can be divided into two steps that have been expressed differently by Morcrette et al.¹⁵ [see reactions (3) and (4)] and Matsuno et al.¹⁶ [see reactions (5) and (6)]. The variation concerned the amount of Cu extruded during those two reactions.





or



The 3-step process observed on cycling was less visible during the first discharge; probably due to the formation of a solid-electrolyte interphase (SEI) layer thus masking the lithiation processes.¹¹ During the next cycles, the curve profile was characteristic for Cu_2Sb cycling versus lithium for all the half-cells tested where the 3-step reaction is clearly seen during the delithiation process.¹² The potential values observed for each step were independent of the synthesis conditions and corresponded to the potential values reported by Bryngelsson et al.¹¹

However, the capacity retention of the obtained arrays of electrodes obtained was found to be dependent on the electrodeposition conditions. Better capacity retention was observed for deposits made under the following pulsed conditions: -1.3 mA for 10 ms and a resting period of 50 ms at 0 mA [Fig. 2(f)]. An increase of the current density during the Sb deposition step led to poor capacity retention independent of the applied cycling rate [Fig. 2(b)]. This behavior was linked to the deposit morphology characterized, in that case, by bigger particles and nonconformal deposit of Sb onto the Cu rods [Fig. 1(b)]. A decrease of the deposition-step time versus the rest-step time (10 ms versus 50 ms) led to better capacity retention [Fig. 2(d)], probably due to the enhanced homogeneity of the coating, especially at the bottom of the Cu rod arrays. The capacity decay observed after 60 cycles can be ascribed to the presence of pure Sb. Because Sb endures a large volume expansion during lithiation, the appearance of cracks and loss of contact in some parts of the coating is then more likely.

To promote full alloying of Sb with Cu, a heat treatment was performed after a 1 h Sb electrodeposition. The obtained electrode was tested versus lithium. The first cycles and capacity as a function of the number of cycles were plotted in Figs. 2(e) and 2(f). The charge–discharge profile curve was similar to the curve previously presented. Nevertheless, while maintaining the same capacity values, the capacity retention was greatly enhanced. The reason for such an increase was attributed to an increase of the mechanical buffering capacity of the Cu matrix around the Sb.

As the heat-treatment time was increased, the capacity retention was enhanced (Fig. 3). The formation of the Cu_9Sb_2 alloy previously reported by Bryngelsson¹¹ was not electrochemically observed even after a 12 h heat treatment. The temperature was probably not high enough to favor the structural formation of Cu_9Sb_2 after 12 h.

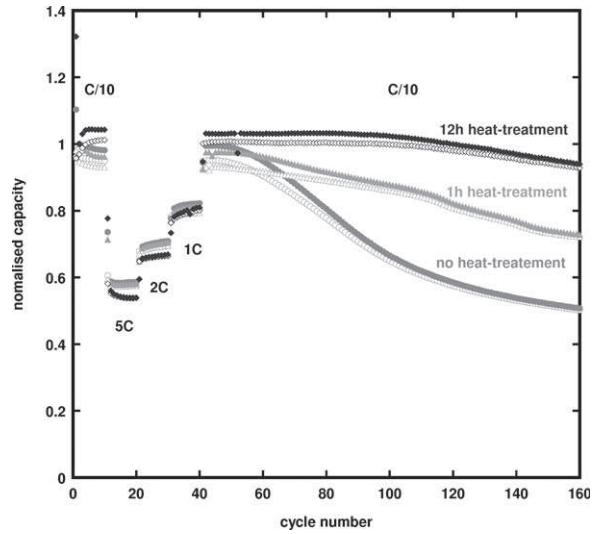


FIG. 3. Capacity retention of Sb electrodeposited onto arrays of Cu nanorods at -1.3 mA for 10 ms and rest for 50 ms steps applied for 1 h, followed by a heat treatment at 120 °C.

Cycling rate has been varied on cycling for the different Cu_2Sb arrays to monitor the efficiency of the deposits as battery material. All samples synthesized with an electrodeposition step of -1.3 mA were able to recover their initial C/10 capacity after a series of 10 cycles at 5, 2, and 1 C. The high cycling rate stability confirms the great power capability of these kinds of 3D electrodes.

B. Hybrid polymer separator

The next critical step in the synthesis of 3D micro-batteries was the preparation of a thin, conformal and pine-hole-free layer of separator. The separator synthesis was studied using Cu_2Sb 3D arrays obtained after a 2 h pulsed electrodeposition of Sb (-1.3 mA for 10 ms—rest for 50 ms) followed by a 12 h heat treatment at 120 °C under vacuum.

The separator synthesis and insertion into the 3D electrode was realized in three steps (Fig. 4): The monomer and additives were dissolved in acetone, the obtained solution was sprayed onto the 3D electrode, which was then heat-treated at 120 °C for 1 h under vacuum to favor polycondensation. The spray and polycondensation steps were repeated up to 3 times to vary the separator thickness.

A top view of the obtained deposit is presented in Fig. 5. The roughness observed corresponded to distinct groups of nanorods being separated by the thickest layer of polymer. The presence of a separator along all the rods and deep down in the arrays could not be confirmed.

To demonstrate the ability of the coating to be an ionic conductor but electronically insulating, the obtained electrodes were electrochemically tested versus lithium without any additional porous separator. Accordingly,

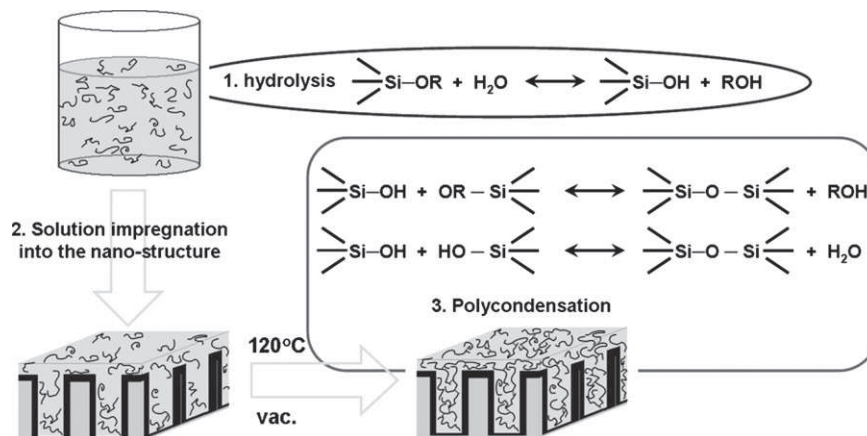


FIG. 4. Schematic diagram of separator preparation and impregnation in the Cu_2Sb 3D electrode.

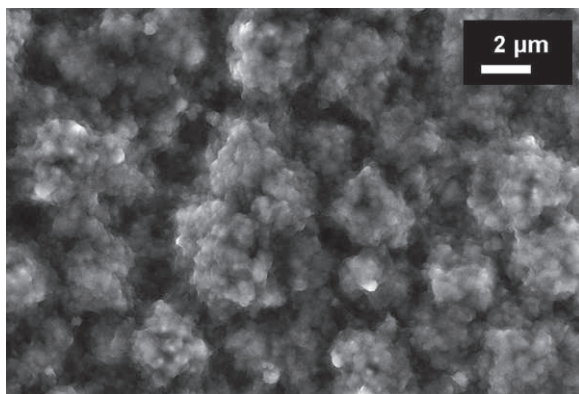


FIG. 5. SEM micrograph of Cu_2Sb covered by one sprayed layer of polymer separator.

the lithium anode was directly plated onto the separator coating.

No drastic change in the cycling behavior was observed as a function of the separator thickness (Fig. 6). In both cases, no short-circuit of the electrodes was observed and cycling curves showed plateaus corresponding to the same Cu_2Sb lithium alloying/dealloying reactions. However, when compared to the Cu_2Sb electrodes tested previously, the capacity values ($0.22 \text{ mAh}\cdot\text{cm}^{-2}$ instead of $0.26 \text{ mAh}\cdot\text{cm}^{-2}$) and cell stability were decreased on cycling (20 cycles instead of 120). The cause for capacity fading could be attributed to various phenomena such as chemical or electrochemical degradation of the separator, existence of water linked in the hybrid polymer structure or an incomplete polycondensation step leading to loss of mechanical strength. Preliminary infrared (IR) and thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) results did not, however, confirm the presence of water in the structure. The irreversible capacity measured on first cycle is larger than the values measured for the arrays of $\text{Cu}/\text{Cu}_2\text{Sb}$ only, thus suggesting

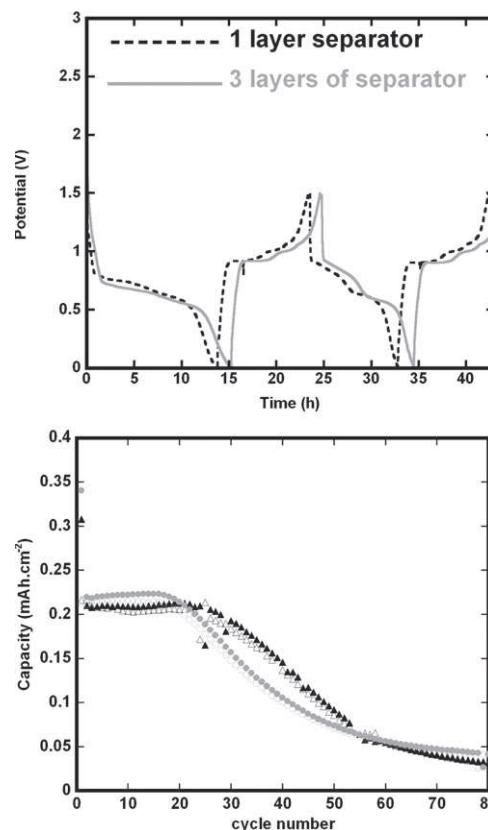


FIG. 6. The capacity retention for Cu_2Sb arrays covered by one or three sprayed layers of polymer separator. The inset shows the first two cycles.

a possible reaction of the separator with the electrode/electrolyte interface.

IV. CONCLUSION

We showed that it is possible to electrodeposit antimony onto a complex 3D structure of Cu current collectors and form Cu_2Sb by annealing of the structure. The

process presents several advantages. Electrodeposition is a versatile and soft synthesis technique. No addition of extra copper for alloying or carbon black/binder used in the standard electrode slurry was required. Thus, the number of parameters that influence the electrode cycling behavior are reduced. The amount of nonelectrochemically active material is also reduced, which in the case of microbatteries is an essential parameter. The behavior, when cycling of the so-obtained composite current-collector/electrode nanorods, is in accordance with the results presented by Bryngelsson et al.¹¹ Moreover, the capacity per footprint area when compared to a thin film 2D electrode is increased as previously demonstrated by Taberna et al.⁴

Deposition of a hybrid polymer separator layer by spray deposition did not lead to the formation of a thin and conformal layer onto the arrays of electrode. However, we showed that the thin layer deposited on the complex architecture was sufficient enough to avoid short circuiting of the cell. Even though the causes of capacity fading on cycling are not yet identified, the first results obtained so far are promising. Currently, work is being done to go toward a better understanding of the reactions occurring. Thus, it would be possible to improve polymer separator characteristics and cycling performances.

ACKNOWLEDGMENTS

This work was supported by the Alistore European Research Institute (ERI), the Swedish Research Council (VR), SUPERLION within EU-FP7 under the Grant Agreement No. 214832-2. We also acknowledge the French Ministry of Research for the Ph.D. grant of Emilie Perre.

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