

# Tin and Tin-Copper Composite Nanorod Anodes for Rechargeable Lithium Applications

B. D. Polat, O. Keles

**Abstract**—Physical vapor deposition under conditions of an obliquely incident flux results in a film formation with an inclined columnar structure. These columns will be oriented toward the vapor source because of the self-shadowing effect, and they are homogeneously distributed on the substrate surface because of the limited surface diffusion ability of ad-atoms when there is no additional substrate heating.

In this work, the oblique angle electron beam evaporation technique is used to fabricate thin films containing inclined nanorods. The results demonstrate that depending on the thin film composition, the morphology of the nanorods is changed as well. The galvanostatic analysis of these thin film anodes reveals that a composite CuSn nanorods having approximately  $900\text{mAhg}^{-1}$  of initial discharge capacity, performs higher electrochemical performance compared to pure Sn nanorods containing anode material. The long cycle life and the advanced electrochemical properties of the nanostructured composite electrode might be attributed to its improved mechanical tolerance and enhanced electrical conductivity depending on the Cu presence in the nanorods.

**Keywords**—Cu-Sn thin film, oblique angle deposition, lithium ion batteries, anode.

## I. INTRODUCTION

LITHIUM ion batteries are considered as one of the future source for energy storage. They are widely used in cell phone batteries, electrical vehicles and portable computers. In a Li ion battery, the anode is responsible for accommodation and release of lithium ions for reversible reactions (reaction 1) where A stands for an active material such as carbon, silicon, aluminum, tin, germanium, antimony or indium [1]-[8].



During the battery charging stage, Li ions generated from the lithium containing salts (such as  $\text{LiPF}_6$ ) or the cathode material, are electrically forced to be alloyed with the active metals (A) [1].

Recently, the lithium ion battery industry is continuously looking for materials with higher charge-discharge capacities. In this context, Sn is one of the best solution available thanks to its high theoretical capacity (up to about  $994\text{mAhg}^{-1}$ ). However, tin anodes, similar to other metallic materials, suffer from excessive volume changes, which occur during cycling.

O. Keles is with the Department of Metallurgical and Materials Engineering, Istanbul Technical University, Maslak, Istanbul, 34469 Turkey (phone: +90 212 285 3398; fax: +90 212 285 3427; e-mail: ozgulkeles@itu.edu.tr).

B. D. Polat is with the Department of Metallurgical and Materials Engineering, Istanbul Technical University, Maslak, Istanbul, 34469 Turkey.

Those changes lead eventually to the degradation of the anode and the loss of the electrical contact with the current collector [9]. In order to overcome this problem some researchers have suggested keeping a narrow cycling potential range to get lower lithium containing compounds like LiSn so that a weak mechanical stress would be expected in the electrode structure [10]. Another alternative solution is tailoring active materials into aligned nanostructures (nanorods) on current collectors. The interstitial space in-between the aligned nanorods could accommodate the volume changes and provide massive access sites for lithium ions. Hence distributing strain and stress gradually along the nanorods is expected to provide a solution for the retention of the initial high capacity. Different production methods have been used to produce these nanostructured Sn electrodes but among them, an electron beam deposition method becomes crucial since this method enables to control the material deposition kinetics, hence the thin film microstructure [11]-[13].

Added to these, to improve the cyclability of the electrodes, some other research groups focus on alloying Sn with different materials such as antimony, cobalt, nickel, titanium, iron or copper [14]-[19]. Among them, copper is mainly preferred because it has high conductivity and good solubility in tin, which promotes the formation of homogenous Cu-Sn composite nanorods resulting in a highly conductive and mechanically flexible electrode for Li ion batteries [19].

In this paper, we fabricate aligned Sn and Cu-Sn composite nanorod arrays on copper substrate using an oblique angle deposition method. Their electrochemical performances are compared when they test versus  $(\text{Li}/\text{Li}^+)$ , the counter electrode. The result shows that with the addition of Cu in the Sn nanorods, the cycle life of the battery can be improved up to 80<sup>th</sup> cycles, with 99% Coulombic efficiency.

## II. EXPERIMENTAL

Both the pure Sn and Cu-Sn composite nanorods were fabricated on copper discs (15.5mm diameter, 1.5mm thickness) by an oblique angle deposition (OAD) technique, where a graphite crucible containing Sn and Cu:Sn (1/1: wt/wt) pellets was used respectively to fabricate Sn and Cu-Sn films respectively.

Both electrodes had continuous architectural assemblies of nanorods on non-porous thin films deposited on the copper discs. For each sample, first the non-porous thin film was deposited on a copper substrate with  $0^\circ$  an oblique angle to enhance the electronic contact and delay aggregation within the electrodes during electrochemical tests. Then, the nanorod arrays were formed on the flat nonporous thin film when the

deposition flux was hit onto the substrate surface's normal with an angle of  $80^\circ$ . Taking the advantage of shadowing effect during film growth, tilted nanorod arrays were formed, leading to form nanosized porosities within the thin film structure. The deposition flux was constant ( $4\text{\AA s}^{-1}$ ) during all process and the chamber pressure was  $10^{-6}$  Pa.

A pure silicon wafer ( $20 \times 10 \text{ mm}^2$ ) was also coated during the experiments, to make compositional analyses and measure the coating thickness accurately.

The composition of the film was determined by energy dispersive X-ray spectroscopy (EDS) analysis. The surface morphology as well as the thin film thicknesses was investigated by utilizing field-emission scanning electron microscopy (FE-SEM, JEOL JSM 7000F). The phases present in the coatings were determined using Philips PW3710 System with a  $2\theta$  range of  $20\text{--}90^\circ$  in steps of  $0.05^\circ$  (with  $\text{CuK}\alpha$  at 40 kV and 30 mA).

CR2032 coin cells were fabricated in order to test the electrochemical properties of thin film electrodes. The cells were assembled in a glove-box (MBRAUN Labmaster) under argon atmosphere. The testing cell is based on the following sequence: i) a working electrode, ii) a  $1\text{M LiPF}_6$  in ethylene carbonate-dimethyl carbonate, EC:DMC 1:1 (Merck Battery Grade) electrolyte solution, iii) separator (Celgrad2400), and iv) a lithium metal foil as a counter electrode.

The galvanic charge-discharge was carried out with a rate of  $50 \text{ mA g}^{-1}$  from  $0.05\text{V}$  to  $2.5\text{V}$  versus  $\text{Li/Li}^+$ , the counter electrode. Cyclic voltammetry (CV) was performed in the potential range of  $0.0\text{V}$ – $2.5\text{V}$  versus  $\text{Li/Li}^+$  with a rate of  $0.03 \text{ mV s}^{-1}$ .

### III. RESULTS AND DISCUSSION

#### A. Structural and Morphological Characterization

Introducing Cu atoms into the Sn thin film results in a variation in the thin film thickness and the morphology, which eventually affect the electrochemical performance of the anode material.

Surface views of the thin films are shown in Fig. 1. The pure nanostructured Sn electrode (sample1) has a remarkable pillar like structure and the thin film is fairly inhomogeneous in sizes (Fig. 1 (a)). Its cross sectional view demonstrates clearly that the pillars are not homogeneously deposited on the copper substrate, thus the thickness is around  $200\text{nm}$  (Fig. 1 (c)). On the other hand, the electrode made of Cu-Sn nanostructured composite thin film has well aligned nanorod arrays where the nanorods' diameters (less than  $100\text{nm}$ ) are very close to each other (Fig. 1 (b)). The cross sectional view displays that the resulting film thickness is around  $230 \pm 20 \text{ nm}$  and the interstitial space between the nanorods represents a homogeneously distributed nanosized porosities within the nanostructured composite thin film (Fig. 1 (d)).

XRD results show that the additional amount of copper enhances the formation of the copper rich  $\text{Cu}_{6.26}\text{Sn}_5$  crystallines instead of Sn nanocrystallines (Fig. 2). This structure is also justified by the EDS analysis, which indicates that the thin film has made of  $45\%\text{Sn}$  (%at) and  $55\%\text{Cu}$  (%at).

The difference between the source and the thin film composition might be related to the evaporation point differences of the metals at constant pressure and by the nature of the OAD method. In the OAD method, the deposition rate not only has a vertical component (with respect to the substrate surface), but also has a lateral component, which could result in a variation in thin film composition and thickness [20], as explained previously.

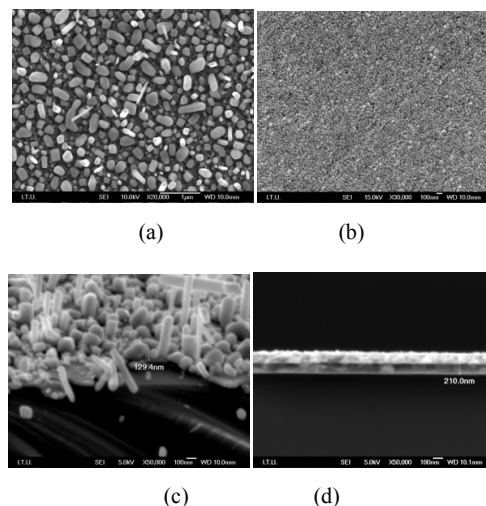


Fig. 1 FEG-SEM images of the nanostructured thin films' surface views a) The pure Sn thin film (Sample1), b) Cu containing Sn composite thin film (Sample 2); FEG-SEM images of nanostructured thin films' cross sectional views c) The pure Sn thin film (Sample1), d) Cu containing Sn composite thin film (Sample 2)

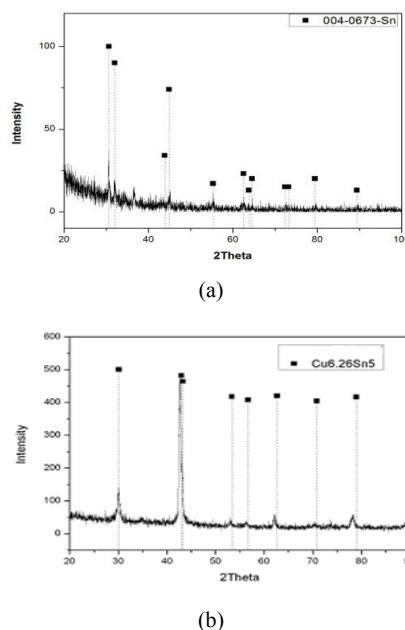


Fig. 2 XRD patterns of nano porous nanostructured a) Sn thin film (Sample1), b) Cu containing Sn thin film (Sample 2)

### B. Electrochemical Characterization

Cyclic voltammograms (CV) of Li/Sn and Li/Cu-Sn cells are shown in Fig. 3. The reduction peaks related to the formation of Li-Sn materials, and the anodic peaks corresponding to the lithium de-alloying reactions are detected on both samples. In Fig. 3a, irreversible reduction peak is observed around 0.7-1.0 V versus  $\text{Li/Li}^+$ , to show the electrolyte reduction reaction, in turn forms a solid electrolyte interface (SEI) layer on the anode surface [21], [22]. In addition, at 0.5V and 0.3 V some other reversible reduction peaks are detected due to the formation of Li-Sn alloys, with Li deficient and Li-rich phases respectively [23], [24].

In Fig. 3, a reduction peak around 0.1V indicates the formation of Li-Sn alloys, and the anodic peaks corresponding to the lithium de-alloying reactions from the active material. It is remarkable that since the area under the curves represents the exchanging charge quantity; Fig. 3 displays that the amount of the cathodic charge is not equal to that of the anodic charge, which reveals the occurrence of irreversible reactions during cycling.

The peaks revealed in Fig. 3 (b) justify that even copper has no reaction with lithium and only the Sn reacts with Li during the battery service life, the morphological changes result from the copper presence in the thin film, affect the electrochemical performance of the battery.

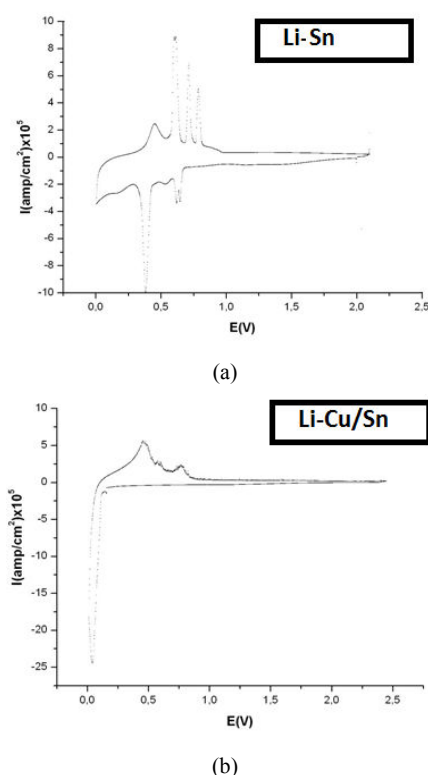


Fig. 3 Cyclic Voltammetry of nanostructured thin films a) pure Sn (Sample 1), b) Cu containing Sn composite (Sample 2)

In Fig. 4, the Li/Sn and Li/Cu-Sn cells' galvanic charge-discharge test results are given. The Li/Sn nanorod cell

demonstrates an initial discharge capacity around  $1000 \text{ mAhg}^{-1}$ , which is almost equal to the theoretical capacity of Sn (Fig. 4 (a)). However, the Li/Cu-Sn nanorod cell performs around  $900 \text{ mAhg}^{-1}$  capacity in the first discharge (Fig. 4 (b)), which is less than the first sample. The capacity of this  $\text{Cu}_{6.26}\text{Sn}_5$  thin film having composite nanorods exceeds the theoretical capacity of the flat  $\text{Cu}_{6.26}\text{Sn}_5$  thin film. This might be explained by the formation of the solid electrolyte interface layer (SEI), which is formed once the anode material reacts with Li from the electrolyte.

Herein it is worth to note that the difference in the initial capacity of both samples might be explained considering the amount of active material (Sn) present in the thin films, which is less in the Cu-Sn nanostructured composite thin film (Sample 2) compared to the pure Sn nanostructured thin film (Sample 1).

In Fig. 4 (a), the change in the capacity value of the pure Sn nanostructured thin film electrode versus cycle numbers is given. After the first discharge, the capacity diminishes gradually in the following 20 cycles (Fig. 4 (a)). Once the discharge capacity has  $450 \text{ mAhg}^{-1}$ , a steady state regime starts and re-ins up to 45<sup>th</sup> cycles (Fig. 4 (a)) with 95% Coulombic efficiency, then the sample is failed. It is possible to explain this performance by the restricted tolerance of the Sn thin film to the volumetric change during the cycling, leading to the delamination of the thin film after 45<sup>th</sup> cycles. Moreover, knowing that (Fig. 1 (a)) the nanostructure pure Sn thin film has inhomogeneously distributed pillar like tin particles in the thin film, the reaction of the thin film with Li is expected to be inhomogeneous as well. During the charge/discharge reactions, an electrochemical agglomeration may occur within these tiny particles, which makes larger particles more sensitive to cracking - crumbling due to their greater absolute volume change resulting in a short cycle life.

For the Cu-Sn composite thin films having homogeneously distributed nanorod arrays, a decrease in the capacity occurred at the very beginning of the cycling and once the capacity goes down to  $450 \text{ mAhg}^{-1}$ , it becomes almost stable to 80<sup>th</sup> cycle (Fig. 4 (b)). This decrease in capacity (with a very low Coulombic efficiency) may be attributed to the reduction of the electrolyte and the subsequent SEI formation on the composite anode surface. Then, once a stable SEI layer forms on the anode, the decay in the capacity disappears and a steady state regime of charge-discharge capacity is attained (see Fig. 4 (b)).

Fig. 4a and b reveal that even the initial discharge capacity value is smaller for  $\text{Cu}_{6.26}\text{Sn}_5$  compared to that of the Sn, the composite thin film with well aligned nanorods performs a high Coulombic efficiency and long service life up to 80<sup>th</sup> cycle (Fig. 4 (b)). Fig. 4 (b) proves that this particular result might be explained considering the morphology and the composition of the thin film. The presence of the homogenous structured, well-aligned nanorods forms nano-sized porosities among them, which facilitate the  $\text{Li}^+$  movement within the electrode and shorten the  $\text{Li}^+$  diffusion distances. Added to this, its large surface area reduces the local current density and decreases the polarization. Moreover, the additional amount of copper

having buffering effect enhances the tolerance of the thin film against the drastic volume change occurred in the thin film, when  $\text{Li}^+$  entered into the homogenously distributed nanorod arrays of Cu-Sn composite thin film. Thus, it is found that the long cycle life can be sustained by the addition of copper in the nanostructured Sn anodes having homogenously distributed nanoporosities. Cracking and pulverization of the film, hence the loss of electrical contact would be prevented in this way.

## VI. CONCLUSION

In this work, nanostructured pure Sn thin film and homogenously distributed nanorod arrays of  $\text{Cu}_{6.26}\text{Sn}_5$  composite thin films are produced via an oblique angle deposition technique. The study shows that the  $\text{Cu}_{6.26}\text{Sn}_5$  nanorods containing composite thin film had a long cycle life and a high Coulombic efficiency. The experimental results indicate that adding Cu into the Sn nanorods provides the mechanical flexibility and reduces the brittleness of tin, in turn makes the structure more stable. Consequently, changing the composition and the structure of the nanostructured Sn leads to form an anode material of high performance used in lithium ion batteries.

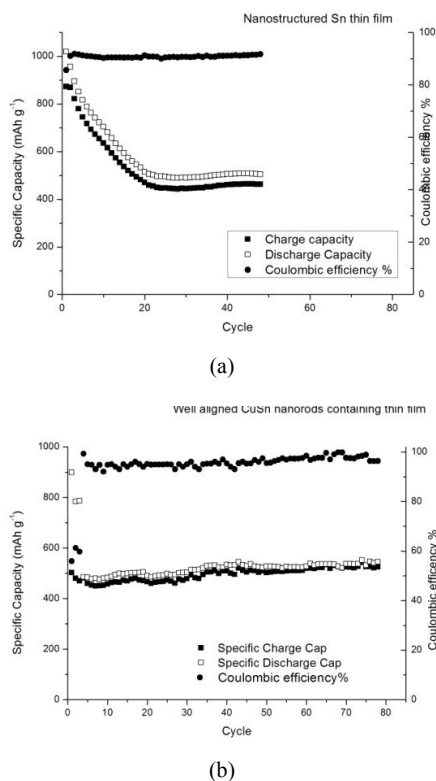


Fig. 4 Cycle-Capacity graphs of (a) The pure Sn nanostructured thin film (Sample1), (b) Cu containing Sn nanostructured thin film with nanorod arrays (Sample 2)

## ACKNOWLEDGMENT

This work is a part of the research project 110M148 approved by The Scientific and Technological Research Council of Turkey (TUBİTAK).

## REFERENCES

- [1] R. Hu, M. Zhu, H. Wang, J. Liu and O. Liuzhang, J. Zou, "Sn buffered by shape memory effect of NiTi alloys as high-performance anodes for lithium ion batteries." *Acta Materialia*, vol. 60, 2012, pp. 4695.
- [2] Q. Wang, H. Li, L. Chen and X. Huang, "Novel spherical microporous carbon as anode material for Li-ion batteries", *Solid State Ionics*, vol. 152, 2002, pp. 43.
- [3] J.C. Arrebola, A. Caballero, J. L. G. Camer, L. Hernen, J. Morales and L. Sanchez, "Combining 5 V  $\text{LiNi}_0.5\text{Mn}_{1.5}\text{O}_4$  spinel and Si nanoparticles for advanced Li-ion batteries." *Electrochem. Commun.*, vol. 11, 2009, pp. 1061.
- [4] M. J. Lindsay, G. X. Wang and H. K. Li, "Al-based anode materials for Li-ion batteries." *J. Power Sources*, vol. 119, 2003, pp. 84.
- [5] M. Wachtler, J. O. Besenhard and M. Winter, "Tin and tin-based intermetallics as new anode materials for lithium-ion cells." *J. Power Sources*, vol. 94, 2001, pp. 189.
- [6] C. K. Chen, X. F. Zhang and Y. Cui, "High Capacity Li Ion Battery Anodes Using Ge Nanowires." *Nano Letters*, vol. 8, 2008, pp. 307.
- [7] A. R. Kamali and D. J. Fray, "Tin-based materials as advanced anode materials for lithium ion batteries." *Re. Adv. Mater. Sci.*, vol. 27, 2011, pp. 14.
- [8] K. -H. Lee, Ph.D Thesis, "Synthesis of Si nanowires for an anode material of Li batteries.", Pohang University of Science and Technology, Korea, 2007.
- [9] J. O. Besenhard, J. Yang and M. Winter, "Will advanced lithium-alloy anodes have a chance in lithium-ion batteries." *J. Power Sources*, vol. 68, 1997, pp. 87.
- [10] H. Nara, T. Yokoshima, T. Momma and T. Osaka, "Highly durable SiOC composite anode prepared by electrodeposition for lithium secondary batteries." *Energy and Environmental Science*, vol. 5, 2012, pp. 6500.
- [11] J. Hassoun, G. Derrien, S. Panero and B. Scrosati, "A SnSb-C nanocomposite as high performance electrode for lithium ion batteries." *Electrochim. Acta*, vol. 54, 2009, pp. 4441.
- [12] S. Gopukumar, D. H. Gregory, H. -S. Kim and D. Shu, "Lithium-Ion Batteries: Recent Advances and New Horizons." *Inter. J. Electrochem.*, Article ID: 878416, 2012.
- [13] Y. L. Kim, S. J. Lee, H. K. Baik and S. M. Lee, "Sn-Zr-Ag Alloy Thin-Film Anodes." *J. Power Sources*, vol. 119, 2003, pp. 106.
- [14] H. Yan, S. Sokolov, J. C. Lytle, A. Stein, F. Zhang and W. H. Smyrl, "Colloidal-crystal-templated synthesis of ordered macroporous electrode materials for lithium secondary batteries" *J. Electrochem. Soc.*, vol. 150A, 2003, pp. 1102.
- [15] Y. Du, J. Yan, Q. Meng, J. Wang and H. Dai, "Fabrication and excellent conductive performance of antimony-doped tin oxide-coated diatomite with porous structure" *Materials Chemistry and Physics*, vol. 133, 2012, pp. 907.
- [16] G. Ferrara, C. Arbizzani, L. Damen, M. Guidotti, M. Lazzari, F. G. Vergottini, R. Inguanta, S. Piazza, C. Sunseri and M. Mastragostino, "High-performing Sn-Co nanowire electrodes as anodes for lithium-ion batteries." *J. Power Sources*, 211, 103 (2012).
- [17] D. Wang, Z. Yang, F. Li, D. Liu, X. Wang, H. Yan and D. He, "Improved performance for lithium-ion batteries with nickel nanocone-arrays supported germanium anode." *Materials Letters*, vol. 65, 2011, pp. 1542.
- [18] J. Yi, X. Li, S. Hu, W. Li, R. Zeng, Z. Fu and L. Chen, "TiO<sub>2</sub>-coated SnO<sub>2</sub> hollow spheres as anode materials for lithium ion batteries." *Rare Metals*, 30, 589 (2011).
- [19] U. G. Nwokeke, R. Alcantara, J. L. Tirado, R. Stoyanova and E. Zhecheva, "The electrochemical behavior of low-temperature synthesized  $\text{FeSn}_2$  nanoparticles as anode materials for Li-ion batteries." *J. Power Sources*, vol. 196, 2011, pp. 6768.

- [20] Y. -S. Lin, J. -G. Duh and H. -S. Sheu, "The phase transformations and cycling performance of copper–tin alloy anode materials synthesized by sputtering." *J. Alloys and Compounds*, vol. 509, 2011, pp. 123.
- [21] K. Robbie, J. C. Sit, and M. J. Brett, "advanced techniques for glancing angle deposition." *J. Vac. Sci. Technol.*, 115, B16, (1998).
- [22] R. Z. Hu, M. Q. Zeng and M. Zhu, "Cyclic durable high-capacity Sn/Cu<sub>6</sub>Sn<sub>5</sub> composite thin film anodes for lithium ion batteries prepared by electron-beam evaporation deposition." *Electrochimica Acta*, vol. 54, 2009, pp. 2843.
- [23] M. Winter, W. K. Appel, B. Evers, T. Hodal, K. C. Möler, I. Schneider, M. Wachtler, M. R. Wagner, G. H. Wroding and J. O. Besenhard, "Studies on the Anode/Electrolyte Interface in Lithium Ion Batteries." *Monatshefte für Chemie*, vol. 132, 2001, pp. 473.
- [24] M. Winter and J. O. Besenhard, "Electrochemical lithiation of tin and tin-based intermetallics and composites." *Electrochim. Acta*, vol. 45, 1999, pp. 31.