

# Improved Cycle Capacity of Lithium-ion Battery by Structured Negative Electrode with PS-PVD Si:Sn Composite Nanoparticles

Makoto Kambara<sup>1</sup>, Tomoaki Tohara<sup>1</sup> and Ryoshi Ohta<sup>1</sup>

<sup>1</sup> Department of Materials Engineering, The University of Tokyo  
7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8654, Japan  
Phone: +81-3-5841-7099 E-mail: [mkambara@plasma.t.u-tokyo.ac.jp](mailto:mkambara@plasma.t.u-tokyo.ac.jp)

## Abstract

**The cycle capacity of lithium-ion batteries has been improved by the low temperature annealing of a anode film using the Si:Sn composite nanoparticles produced by plasma spraying physical vapor deposition (PS-PVD).**

## 1. Introduction

Si is a promising candidate for the negative electrode of the next generation high density lithium secondary batteries (LiB). This material is however inherently subject to huge volume change associated with de/lithiation reaction which causes eventually the fracture and thus the significant capacity drop in short cycles [1]. Extensive works on this issue for decades have revealed that the composite structure especially at the nanometer length scale can help in suppressing the fracture and thereby improving the capacity after long cycles [2-7]. From the production point of view, however, these structuring methods are not necessarily best fit for production at large quantity compatible to the industry [8]. In this aspect, plasma spray physical vapor deposition (PS-PVD), with which nanoparticles are produced at high throughputs using low-cost powder feedstock, can be recognized as an affordable approach [9]. Additional advantage of PS-PVD is that the composite structure can also be designed through co-condensation during PS-PVD of multi-component feedstock. In fact, Si nanoparticles produced by PS-PVD from metallurgical grade powders have exhibited a clear improvement in the cycle capacity. With Si-Cu powder mixture feedstock, furthermore, the composite Si nanoparticles on which Cu nanoparticles are directly attached are produced and they have demonstrated even further increased and stable capacity after longer cycles [10,11].

In the meantime, the network structure of the active material within the anode seems to be effective in maintaining high capacity [12], and attaining such composite structures by the slurry-based battery assembly approach are to be highly demanded for affordable production. With this as target, we have designed to use the characteristic PS-PVD composite nanoparticle as building block in the 3D Si network within the anode. That is, Sn is selected as the secondary element that is distributed uniformly within the anode and is expected to become ligament to connect Si nanoparticles during low temperature annealing in the standard anode assembly. With these as motivations, in this work, the PS-PVD Si:Sn composite nanoparticles are characterized especially as the potential building block in the anode network to improve the battery performance.

## 2. Experimental

Si:Sn nanoparticles have been produced by PS-PVD using the hybrid plasma spray system in which DC plasma jet is superimposed on the RF plasma flow. Advantage of this system is that the powder feedstock can be injected directly into the highest temperature zone without being trapped by the eddy so that powders are effectively heated for evaporation and subsequently cooled for condensation, which is a big difference from the conventional ICP and is a huge benefit for nanoparticle formation. Raw Si and Sn powders are first mixed in pot mill and are injected from the top of the plasma jet for complete evaporation. The high temperature Si+Sn vapor mixture is then immediately quenched in a water-cooled vessel placed underneath of the plasma jet, and nanoparticles so produced are collected from the wall of the vessel. The detailed can be found elsewhere [10].

The PS-PVD nanoparticles are sieved by a 45  $\mu\text{m}$  mesh and crushed by mortar and pestle under ambient. These particles are mixed with conducting carbon and polyimide binder to form slurry, which is applied onto Cu foil with 70  $\mu\text{m}$  thick. After being dried and roll-pressed (Normal dry), the electrode is loaded into tube furnace at around 230°C and annealed under Ar flow for a certain duration. These electrodes are assembled in a 2016 half-cells using Li metal as the counter electrode and 1M LiPF<sub>6</sub> in EC:DEC (1:1vol) as electrolyte. The cells are cycled at a constant current of 0.1 mA (0.02C) for 1-3 cycles and 0.5 mA (0.1C) for the following cycles with cut-off potentials of 0-1.5 V.

## 3. Results and discussion

From the X-ray diffraction patterns of the PS-PVD Si:Sn nanoparticles, the strong peaks associated with the crystalline Si are observed as the major phase. Compared to Si, quite small peaks from Sn(200) and Sn(211) are also observed, suggesting that the crystalline metallic Sn is present in the particles. No peaks indexed to SnO<sub>x</sub> is detected.

HR-TEM observation of these particles confirms that the Si particle size is ranging from 40 to 60 nm, which is in good agreement with the size estimated by the Rietveld analysis of the XRD pattern of 49.9 nm on average. Furthermore, from the HR-TEM observation with EDS elemental analysis, Sn nanoparticles with approximately 10 nm in size is confirmed at the surface of Si nanoparticle. EDS analysis also confirmed the presence of Sn at the edge of the Si particles with a few nm thickness. Since a certain amount of oxygen is also detected at the surface of Si nanoparticle,

SnO<sub>x</sub> is expected to form to coat the Si nanoparticle along with the heterogeneously attached Sn nanoparticle.

In fact, from x-ray photoelectron spectroscopy (XPS) of the as processed powders, the spectra for Sn 3d<sub>5/2</sub>, is clearly seen to shift to the higher energy region. The peak separation quantitative analysis indicates 94% of Sn<sup>4+</sup> and 6% of Sn<sup>0</sup>, confirming the formation of SnO<sub>2</sub> coating. However, once these particles are included in anode and exposed first for normal drying, the top surface of the anode film is slightly reduced to form 4.4% of Sn<sup>2+</sup>, i.e. SnO, and 26.5% of Sn<sup>0</sup>. With further annealing in Ar flow at 230°C, the surface of the anode again is found composed of 91.8% of SnO<sub>2</sub> and 8.2% of Sn<sup>0</sup>, that is, the surface of anode is covered primarily by SnO<sub>2</sub>. In contrast, however, XPS analysis after deep Ar etching shows that the peaks of Sn 3d<sub>5/2</sub> is not changed significantly with the normal drying or with annealing, allowing the Sn<sup>2+</sup> phase of 13-17% as shown in Fig.1. That is, metallic Sn still resides in the interior of the anode.

The capacities of the cell using these PS-PVD powders are compared in Fig. 2. Addition of Sn to Si seems to be effective in increasing the capacity. This is plausibly by the increased electric conductivity due to the presence of metallic Sn that is reported by Zhong et al. [13]. More interestingly, it is clearly seen that the half cell with Si + 1 at% Sn anode after 230°C for 5min has maintained much greater capacity than the one without Sn or without annealing. Since the melting point of Sn is 230°C, Sn is supposed to deform and connect as ligament between Si particles upon heating to 230°C. As SnO is decomposed to molten Sn and Sn<sub>3</sub>O<sub>4</sub> at 270°C, it would also partly work as ligament, considering

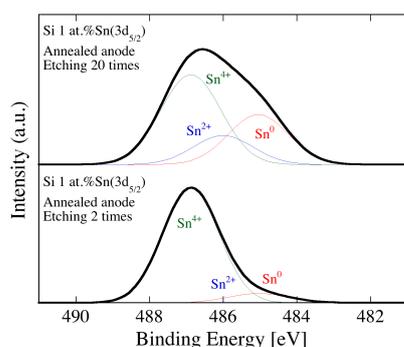


Fig. 1 XPS spectra for Si:Sn anode after annealing.

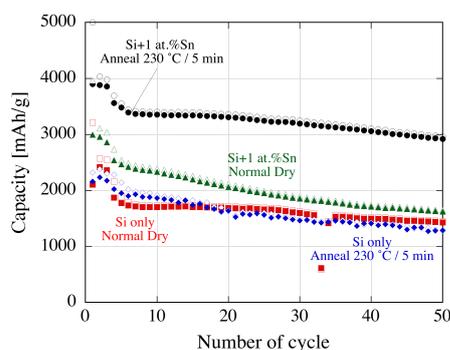


Fig. 2 Comparison of the cycle capacity between the cells using Si:Sn-NP as anode annealed for different conditions.

the Gibbs-Thomson effect. In addition, as SnO<sub>2</sub> is apparently observed at the surface of the anode, the presence of small SnO<sub>2</sub> particulate coating itself [14] and/or formation of stable SEI such as Li<sub>2</sub>O after lithiation of SnO<sub>2</sub> especially at the region of high Li concentration, as is observed for carbon coating on the anode surface [15], would be the possible reasons for this improvement. Further analysis such as EIS is however necessary to confirm the characteristics role of the Sn addition.

#### 4. Conclusion

We have found that the addition of Sn to Si nanoparticle formation by PS-PVD and the subsequent low temperature annealing during anode synthesis is effective in improving the capacity retention characteristics significantly. Although further detailed analysis is necessary, the preliminary analysis has shown that the co-condensed Sn and its monoxides are expected to act as ligament to form active-material network. Also, the SnO<sub>2</sub> coating especially at the surface of anode would be beneficial to maintain high capacity.

#### Acknowledgement

This work is partly supported by the Grant-in Aid for Scientific Research (B) 15H04152 and also by the Tanikawa Fund.

#### References

- [1] J. Graetz, C. C. Ahn, R. Yazami and B. Fultz, *Electrochem. Solid-State Lett.* **6**, A194 (2003)
- [2] A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, G. Yushin, *Nature Mater.* **9**, 353 (2010).
- [3] S. H. Ng, J. Wang, D. Wexler, S. Y. Chew, H. K. Liu, *J. Phys. Chem.* **C111** 11131 (2007).
- [4] X.H. Liu, L. Zhong, S. Huang, S.X. Mao, T. Zhu, J. Y. Huang, *ACS Nano* **6** 1522 (2012).
- [5] X. Li, M. Gu, S. Hu, R. Kennard, P. Yan, X. Chen, C. Wang, M. J. Sailor, J. G. Zhang and J. Liu, *Nat. Commun.* **5**, 4105 (2014)
- [6] N. Liu, Z. Lu, J. Zhao, M. T. McDowell, H. W. Lee, W. Zhao and Y. Cui, *Nat. Nanotechnol.* **9**, 187 (2014)
- [7] I. H. Son, J. H. Park, S. Kwon, S. Park, M. H. Rummeli, A. Bachmatiuk, H. J. Song, J. Ku, J. W. Choi, J. Choi, S.-G. Doo and H. Chang, *Nat. Commun.* **6**, 7393 (2015).
- [8] C. Martin, *Nat. Nanotechnol.* **9**, 327 (2014).
- [9] M. Kambara, A. Kitayama, K. Homma, T. Hideshima, M. Kaga, K.-Y. Sheem, S. Ishida and T. Yoshida, *J. Appl. Phys.* **115**, 143302 (2014)
- [10] R. Ohta, K. Fukada, T. Tashiro, M. Dougakiuchi, M. Kambara, *J. Phys. D: Appl. Phys.* **51**, 105501 (2018).
- [11] M. Kambara, T. Hideshima, M. Kaga, T. Yoshida, *Encyclopedia Plasma Technol.*, 1176 (2017).
- [12] T. Wada, T. Ichitsubo, K. Yubuta, H. Segawa, H. Yoshida, H. Kato, *Nano Lett.* **14**, 4505 (2014).
- [13] L. Zhong, C. Beaudette, J. Guo, K. Bozhilov, L. Mangolini, *Sci. Rep.* **6**, 30952 (2016)
- [14] C. Kim, M. Noh, M. Choi, J. Cho, B. Park, *Chem. Mater.* **17**, 3297-3301 (2005)
- [15] L. Liu, P. Guan, C. Liu, *J. Electrochem. Soc.* **164**, A3163 (2017).