

# High-Energy Micro-grain Silicon Anodes for Lithium-Ion Technology

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**Abstract**— As more and more applications require high energy density electrochemical storage systems that deliver more than 200 Wh/kg, Lithium-ion batteries with silicon-based anodes provide promising electrochemical properties especially high specific capacity. In this paper, we present a micro-grain structured silicon deposited by DC sputtering on special copper foil that serves as current collector. It is demonstrated that high-density silicon anodes are obtained with more than 2000 mAh g<sup>-1</sup> and 2.0 mAh cm<sup>-2</sup> which can be considered as a commercial value. Finally, it is found that with such anodes the irreversible capacity during the first galvanostatic cycle can be lower than 20%.

**Keywords**—silicon, anode, DC-sputtering, lithium ion battery

## I. INTRODUCTION

It is well known that silicon presents one of the most important anode materials for the improvement of lithium-ion cells in terms of energy density. Indeed, silicon's high theoretical specific capacity to lithium (more than 3800 mAh/g at room temperature), environmental friendliness, low potential compared to lithium and material abundance turns silicon to a strong candidate for the replacement of carbon-based anodes [1]. However, one of the main drawbacks of silicon's application to the lithium-ion technology is its poor electrochemical cycling stability over several galvanostatic cycles, mainly due to silicon's huge volume change (around 300%) during lithiation and delithiation that lead to high internal mechanical stress [2]. Many alternatives have been proposed that alleviate this mechanical expansion through the use of nanostructured silicon sometimes combined with carbon-based materials [3]. However, most of proposed solutions are technically and financially demanding at least for production. In this presentation, we investigate the physical and the electrochemical properties of micro-grain structured silicon deposited on special copper with nodular grains.

## II. EXPERIMENTAL

Silicon material was grown on special copper foil in a DC magnetron sputtering system. High purity argon was introduced into the chamber before the plasma ignition with a pressure of 7 mTorr. The substrate was maintained at room temperature at 10 cm distance from the n-doped high purity silicon target (Mateck GmbH, Germany) and the deposition was performed using DC power of 160 W with deposition rate

of around 16 nm min<sup>-1</sup>. Samples with various silicon mass loadings ranging from 0.25 to 1.0 mg cm<sup>-2</sup> were developed. As substrate and current collector, special roughened copper foil was used. Electrodes were analyzed by Scanning Electron Microscopy (SEM) in order to obtain information on the structure and the texturing of deposited materials.

To evaluate the electrochemical properties of the Si-based anodes, half-cells with testing electrode and lithium foil as counter electrode were assembled in a glove box filled with pure Ar. The electrolyte used in the experiments was 1 M LiPF<sub>6</sub> in a 1:1 (v/v) mixture solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) with 2 wt.% Vinylene Carbonate (VC) additive. A BaSyTec (CTS) multichannel battery tester was used for the deep galvanostatic charge-discharge cycling of the two-electrode cells in the potential range of 0.05-0.7 V at 25°C. The electrodes were charged / discharged with constant current until cut-off voltage. For the calculation of the specific capacity (mAh g<sup>-1</sup>) the silicon mass was estimated by weighing the electrode before and after the deposition via the aid of a high accuracy balance.

## III. RESULTS - DISCUSSION

SEM pictures of silicon anode on top of special copper foil for mass loading of 0.5 mg cm<sup>-2</sup> are illustrated in Fig. 1. Top view picture demonstrates that silicon is deposited on top of the substrate in small granular structure with an average size in the order of μm. Depending on the deposition time (i.e. silicon mass), amorphous silicon is organized in micro-grains that become larger as growth time further increases (not shown here). In addition to the SEM analysis, adhesion tests with Kapton® tape were carried out and demonstrated that all samples, independently of the growth condition and mass loading, are highly resistive to silicon's delamination and can potentially withstand severe mechanical stress between the current collector and the silicon. It has to be investigated whether the electrochemical properties would, as well, be improved during galvanostatic cycling.

Fig. 2 shows the voltage-capacity profiles during charging and discharging procedure. During the first lithiation galvanostatic cycle, voltage decreases sharply down to 0.2 V where a plateau is present until 700 mAh g<sup>-1</sup> followed by a smooth sloped decrease down to 0.05 V. The existence of a plateau at 0.2 V has been widely observed in the literature and has been attributed to the Li intercalation to amorphous silicon

by the creation of alloys of the form  $\text{Li}_x\text{Si}$  [4, 5]. In the next galvanostatic cycles, after Solid Electrolyte Interface (SEI) formation, voltage profiles demonstrate that Li alloying occurs at higher potential which can be explained by the improvement of the anode's conductivity. Finally, we have to note that for these cells the irreversible capacity during the first charging-discharging cycle is lower than 20%.

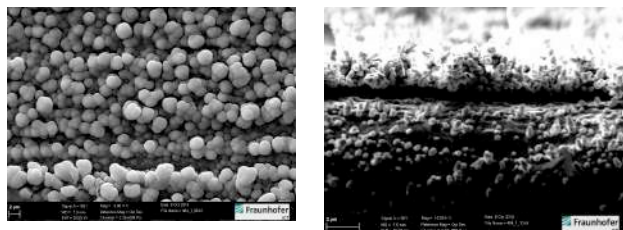


Fig. 1. SEM top view (left) and cross-section (right) images of silicon deposited on special copper foil. Silicon mass loading:  $0.5 \text{ mg cm}^{-2}$ .

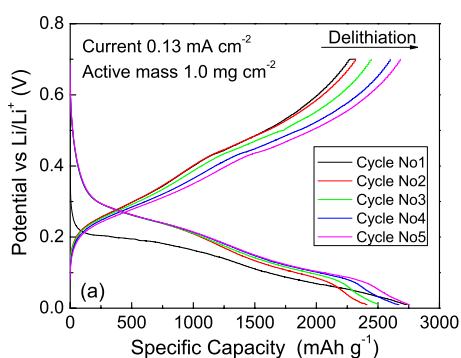


Fig. 2. Anode potential vs specific capacity profile of half-cell with silicon anode during 5 galvanostatic cycles.

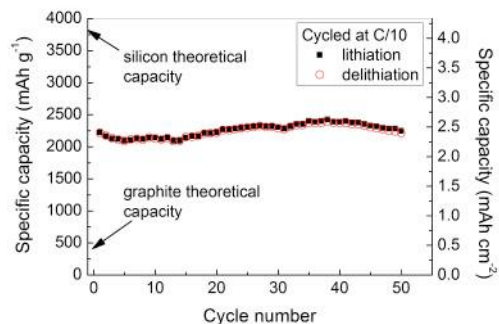


Fig. 3. Specific capacity as a function of cycles during charging/discharging operation of half cell with silicon anode (mass loading:  $1.0 \text{ mg cm}^{-2}$ )

Fig. 3 demonstrates the lithiation-delithiation capacity as a function of cycles (current  $0.64 \text{ mA cm}^{-2}$ ) for half-cell having  $1.0 \text{ mg cm}^{-2}$  of silicon mass loading. The cell exhibits stable performance in terms of specific capacity delivering more than  $2000 \text{ mAh g}^{-1}$  even after 50 continuous galvanostatic cycles. In addition, by comparing lithiation-delithiation capacity, it appears that the Coulombic efficiency is higher than 99.5% at

least after the first couple of cycles and once the SEI is well formed. We have to note that this behavior is similar to all half-cells prepared with the silicon loading.

Fig. 4 illustrates the areal specific capacity of cells cycled with various currents as a function of their silicon mass loadings. Up to  $1.0 \text{ mg cm}^{-2}$  of silicon mass loading, anode specific capacity linearly scales with the electrode's active mass with a slope of around  $2200 \text{ mAh g}^{-1}$ , which is the average stabilized specific capacity value that most of the cells attain after several cycles. These results clearly demonstrate that the capacity scales linearly with the mass loading at least up to  $1.0 \text{ mg cm}^{-2}$  and commercial anodes with more than  $2.5 \text{ mAh cm}^{-2}$  of stable capacity can be obtained with such technology.

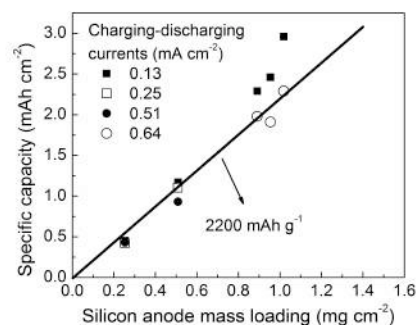


Fig. 4. Areal specific capacity as a function of the silicon mass loading. Capacity values were extracted from half-cells with various silicon mass loadings cycled at various currents.

#### IV. CONCLUSION

In this paper various loadings of amorphous silicon have been deposited by DC sputtering on top of rough copper foil that served as current collector. SEM demonstrated that silicon is grown in micro-grain structure. The average grain size varies between fraction of  $\mu\text{m}$  to several  $\mu\text{m}$  depending on the silicon mass. Half-cells were prepared with the above silicon as anodic electrode and it was demonstrated that high-density anodes with stable capacity that exceeds  $2200 \text{ mAh g}^{-1}$  (or  $2.0 \text{ mAh cm}^{-2}$ ) and irreversible capacity of less than 20% were obtained.

#### ACKNOWLEDGMENT

This work is supported by European Regional Development Fund and National Funds/German-Greek Bilateral R&D Cooperation Initiative/2013-2015.

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