



Electrochemical Impedance Spectroscopy study in micro-grain structured amorphous silicon anodes for lithium-ion batteries



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H I G H L I G H T S

- Deposition of micro-grain amorphous silicon on special copper foil.
- EIS study on silicon half-cells at various SoC's and various discharging currents.
- Lithiation mechanism is proposed.

A R T I C L E I N F O

Article history:

Received 14 June 2016

Received in revised form

23 August 2016

Accepted 12 September 2016

Keywords:

Lithium-ion batteries

Amorphous silicon

Electrochemical Impedance Spectroscopy

Lithiation mechanism

A B S T R A C T

In this paper, a study of the lithiation mechanism of micro-grain structured silicon anode is presented. Micro-grain amorphous silicon was deposited on special copper foil and it is shown that after several decades of galvanostatic cycles, it preserves its granular nature with minor degradation. In order to shed light on the lithiation mechanisms of the micro-grain silicon, Electrochemical Impedance Spectroscopy (EIS) was conducted on silicon half-cells at various State-of-Charge (SoC) and various discharging current values and the Solid-Electrolyte Interphase (SEI) R_{SEI} and polarization resistance R_{pol} were determined. Results reveal that R_{pol} highly increases for cell voltages lower than 0.2 V and it strongly depends on the discharging C-rate. From X-ray Photoelectron Spectroscopy (XPS) measurements combined with surface sputtering, the existence of a $Li_xSi_yO_z$ interlayer between SEI and silicon is confirmed, which is believed to play an important role to the lithium kinetics. Finally, combining our results, a lithiation mechanism of the micro-grain silicon anode is proposed.

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1. Introduction

The last decades Lithium-ion batteries are widely considered as the energy storage systems appropriate for use in low (laptops, cameras and smart cellular phones) and high (hybrid and all electric vehicles, renewables, aerospace) energy and power demand applications [1]. The main reason for this choice is the high specific energy and power density, which is the highest in batteries with non-aqueous electrolytes. Nevertheless, with the growing energy storage demands there is a strong need for energy storage systems with higher energy and power densities [2]. One way to achieve this goal concerns the development of new anode materials

alternative to graphite that is currently used in commercial lithium ion batteries. Silicon is considered as an alternative attractive high-capacity anode material for Li-ion batteries with theoretical specific capacity of Si (3579 mAh g^{-1}), almost 10 times higher than that of graphite (372 mAh g^{-1}) [3]. Moreover, silicon is a light and abundant element, so it presents itself as an ideal candidate for the next generation negative electrode in lithium ion batteries. However, volume variation during lithiation (charging)/delithiation (discharging) is the most important drawback of Li–Si alloys as it can reach up to 300% increase for the $Li_{15}Si_4$ structure, whereas only 10% of volume variation is observed for LiC_6 in graphite based anode materials [4]. This volume change inevitably leads to strong stress development, pulverization, lost of electrical contact between anode material and current collector and finally capacity loss [2–4].

Many alternatives have been proposed to alleviate this

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mechanical issue [2,3]. The main idea at these efforts was the reduction of anode material's size in nano-scale to buffer the volume change during lithiation and delithiation. Although some developed materials showed promising performance none of them make a substantial breakthrough towards commercialization because fabrication of nano-structured Si in general presents high capital and operational expenses. Extensive research effort has also been carried out regarding the influence of electrolyte composition in the performance of lithium ion batteries with silicon based anode materials. This implies that the problem is multi-sided and an ultimate solution could be given as long as the various mechanistic steps that take place during lithiation/delithiation are identified. Additionally, this identification should mainly be focused on the estimation of the resistance contribution during:

- Ionic lithium movement through the SEI,
- charge transfer in any interface (liquid/solid, solid/solid),
- diffusion of lithium atoms into the bulk of anode active material,
- formation of new solid structures.

The existence of these resistances is responsible for the cell voltage variation during lithiation and delithiation and the capacity determination. The knowledge of these contributions and more significant the capability of limiting the high resistance contributions, constitutes an excellent guide at the procedure of the optimum anode electrode design, for commercial lithium ion batteries. The present work moves towards this direction.

2. Experimental

2.1. Material synthesis and characterization

Silicon material was directly grown on copper foil in a commercial DC magnetron sputtering system. High purity argon was introduced into the chamber before the plasma ignition with a gas 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 100 W. Prior to the deposition, 15-min target cleaning at 100 W took place.

As substrate and current collector, special roughened copper foil manufactured by Schlenk was used. The pre-treated copper consisted of electrolytically deposited nodular copper grains, which greatly increase the real (active) surface of the foil and a chromate-based passivation of several atomic layers was performed to protect against oxidation. The surface and morphology of the electrodes before and after galvanostatic cycling were studied by Scanning Electron Microscopy (SEM) using a LEO Supra 35VP microscope. The silicon thickness was 1.2 μm .

2.2. Electrochemical testing

To evaluate the electrochemical properties of Si-based anodes, small half cells containing testing electrode with 1.13 cm^2 surface area, separator, electrolyte 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_6 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 galvanostatic charge-discharge cycling of the two-electrode cells in the potential range of 0.05–0.7 V at 25°C. AC impedance spectra were recorded with a potentiostat/galvanostat (Autolab PGSTAT302N) at various cell voltages (0.05–0.35 V) during galvanostatic lithiation. The frequency range was from 50 kHz to 100 mHz with 10 mV of

amplitude. The impedance data were fitted using the ZSimpWin computer program. For the calculation of the specific capacity (mAh g^{-1}) the silicon mass was estimated by weighing the electrode before and after the deposition via the aid of a high accuracy balance. The anode mass loading was 0.3 mg cm^{-2} .

2.3. XPS characterization

Photoemission experiments were carried out in an ultra high vacuum system (UHV) that consists of a fast entry specimen assembly, a sample preparation area and an analysis chamber. The base pressure in both chambers was 1×10^{-9} mbar. Unmonochromatized $\text{AlK}\alpha$ line at 1486.6 eV and an analyzer pass energy of 97 eV, giving a full width at half maximum (FWHM) of 1.7 eV for the Au 4f7/2 peak, were used in all XPS measurements. The XPS core level spectra were analyzed using a fitting routine, which can decompose each spectrum into individual mixed Gaussian-Lorentzian peaks after a Shirley background subtraction. Regarding the measurement errors, for the XPS core level peaks we estimate that for a good signal to noise ratio, errors in peak positions are of about 0.05 eV. Calibration of the analyzer's kinetic energy scale was performed according to ASTM-E 902-88.

3. Results and discussion

Fig. 1 shows the SEM top view images for silicon that has been deposited on top of rough copper foil before cycling and after 50 galvanostatic cycles at T-cell configuration described in the experimental section. It is observed that before lithiation (Fig. 1a–c) silicon forms multiple grains with an average grain size of around 1 μm and high specific area in a rather uniform distribution over a large area. Raman measurements [5] demonstrated that the grains consist of amorphous silicon as no crystalline or microcrystalline nature was detected. Details on the morphology and the properties of such silicon can be found elsewhere [5]. After the silicon anode having performed 50 galvanostatic cycles at C/10 rate (Fig. 1d), it is witnessed that silicon exhibits uniform square-like form fragmentation with deep and wide cracks of around 1–2 μm width. It is also noted that within the network of cracks, silicon regions preserve their grain nature even after 50 galvanostatic cycles as illustrated in more detailed SEM pictures (Fig. 1e and f). The fragmentation pattern of silicon after lithiation and delithiation resembles a commonly referred mud crack pattern, which is in general attributed to the tensile biaxial mechanical stress of the deposited films and strongly depends on the substrate – film bonding properties and film thickness [6–8].

Therefore, it can be assumed that even though silicon is grown in micro-grains, when subjected to mechanical stress due to the lithiation/delithiation mechanism, macroscopically it behaves like a uniform film. Nevertheless, once the cracks are created and the energy is released, microscopically, the silicon grains remain relatively robust during cycling. A closer observation of silicon surface (Fig. 1f) shows the transformation of silicon micro-grains into nanoparticles with discrete boundaries, differentiating the anode surface and possibly containing additional material phases.

In order to study the lithiation mechanisms within micro-grain silicon, half-cells were subjected to lithiation (discharging) at currents in the range 0.025 mA–0.325 mA (0.022 mA cm^{-2} – 0.288 mA cm^{-2}) and the voltage vs. capacity curves are shown in Fig. 2.

The discharge capacity depends on the discharge current i.e. for 0.025 mA discharging current the capacity obtained is more than 3200 mAh g^{-1} whereas for 0.325 mA current the capacity is limited to 1750 mAh g^{-1} . The voltage – discharge capacity curves for all currents can be described as follows: first, when lithiation starts,

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