

Nanoporous Silicon as an Electrode Material for Li-ion Batteries

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Abstract — We have developed a novel technique providing fabrication of nanoporous silicon films on nonsilicon substrates. Magnetron sputtering of an Al+Si composite target with subsequent selective etching off the aluminum from the deposited film were used to produce nanoporous silicon films on stainless steel substrates. These films were found to have a highly nanoporous skeleton formed by connected 20-200 nm silicon grains. They demonstrated an efficient Li accumulation/release during charging/discharging cycles combined with a high mechanical durability.

Keywords - nanoporous silicon; Li-ion battery.

I. INTRODUCTION

There has been an increasing research activity in development of high-capacity, reliable and durable energy sources, in particular Li-ion batteries, for compact electronic devices, electric vehicles and various energy systems. Major efforts are focused on finding new and improving existing materials for electrodes of the batteries. At that point silicon (Si) is of a considerable interest because it is characterized by a much higher charge/discharge capacity as compared to the commonly used carbon materials [1]-[3]. Meanwhile, a principal problem of Si anodes in the batteries is their mechanical durability during volume expansion accompanying the lithiation process resulting in cracking of the electrodes. Nanostructuring of the electrodes could overcome this problem.

In this paper we present experimental results on fabrication and study of nanostructured Si anodes for Li-ion batteries demonstrating appropriate accumulation properties and durability. Section II describes in detail preparation of the samples and the methods used for their analysis. The results and their discussion are presented in Section III.

II. SAMPLES AND EXPERIMENTAL TECHNIQUE

In the experiments performed, stainless steel foils were used as substrates. Composite Al+Si films were deposited by magnetron sputtering of Al target with Si insets covering 40 % of the erosion area (see [4], [5] for more details). The thickness of the deposited films was about 0.7 μm . Then the samples were immersed in H_3PO_4 water solution at 35 $^\circ\text{C}$ for 5 min in order to etch off Al selectively and to get nanostructured Si skeleton revealed. Subsequently, the samples with the flat surface area of 1.5 cm^2 were used as anodes in prototype Li-ion cells where cathode and polymer

separator were taken from commercial Li-ion batteries. 1 M LiClO_4 solution in propylene carbonate was used as an electrolyte in the prototype cells.

Charging of the cells was performed at two current densities of 6.67 mA/cm^2 and 33.33 mA/cm^2 using Autolab potentiostat/galvanostat PGSTAT100N. Before and after charge/discharge cycling the anodes were analyzed with scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

The nanostructured Si film after selective removal of Al is shown in Figure 1. Highly porous skeleton of Si is visible to be formed by connected 20-200 nm grains. Al is completely etched off while the Si crystalline grains left look to be covered with amorphous Si like it was previously observed in [6].

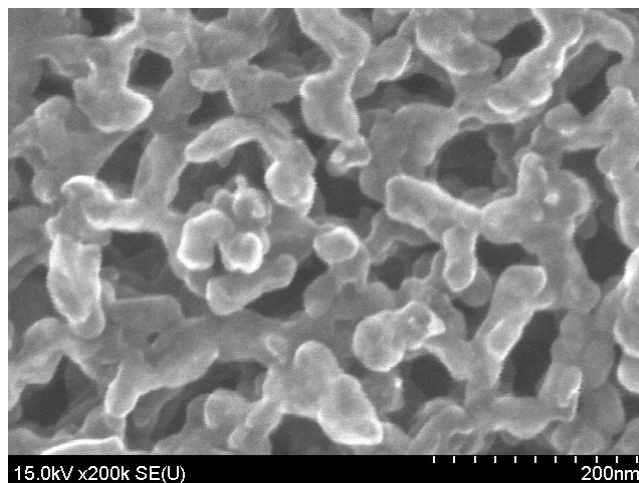


Figure 1. Surface SEM image of Al+Si film after selective etching off Al.

A voltage-time characteristic of the prototype Li-ion cell at charge/discharge cycling is shown in Figure 2. In general, it confirms conventional operation of Li-ion cell after the first charge cycle when the initial lithiation of the anode takes place.

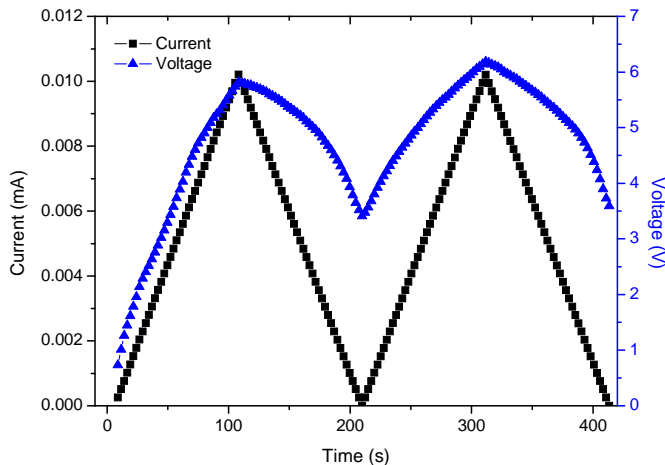


Figure 2. Typical voltage-time characteristic of the prototype Li-ion cell at cyclic lithiation. The straight lines show the test current variation for reference.

Self-discharge dynamics of the prototype Li-ion cell is shown in Figure 3. Despite the losses (of about 35 % within an hour) associated with the imperfection of the experimental system and the presence of leaks, the fabricated prototype Li-ion cell has demonstrated considerable potential for further improvement.

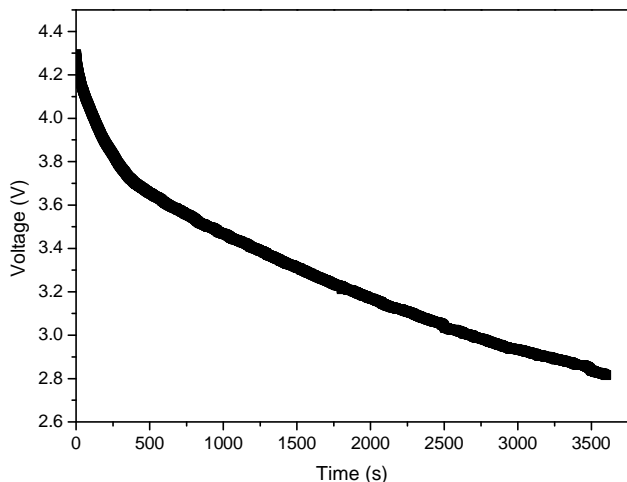


Figure 3. Self-discharge dynamics of the prototype Li-ion cell.

The nanostructured Si film morphology after 20 charge/discharge cycles is shown in Figure 4. The test sample has retained the original coral-like structure, but microcracks have appeared therein. The number of the microcracks correlates with the current density used for charging the cells. Nevertheless, microcracks have not led to the fragmentation of the whole structure. The microcracks appearance is associated with the quite hard test conditions owing to high current density through the cell.

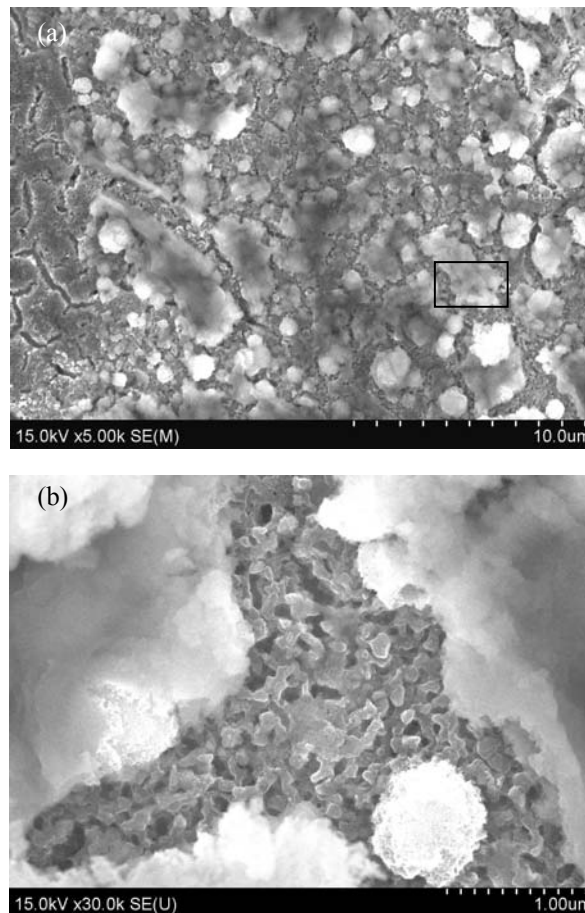


Figure 4. Surface SEM images of nanostructured Si film after 20 charge/discharge cycles: a) general view b) fragment of the structure.

Rather thick cracked layer can be also seen on the upper surface of the anode. Apparently, it is a solid-electrolyte interphase (SEI), which is formed on the anode surface as a product of the electrolyte reduction [7]. Formation of thick SEI layers on Si nanostructures was observed in [3], [8]. They were noted to play a stabilizing role providing an increase of mechanical durability of anode materials.

It is obvious that the coral-like structure is more mechanically strong in comparison to needle or tubular ones because its grains are interconnected to each other over the whole film thickness.

IV. CONCLUSION

The coral-like nanostructured Si films fabricated by magnetron sputtering of the composite Al+Si target and selective etching off Al have clearly demonstrated an ability to accumulate Li during charging and to maintain a certain level of voltage on a discharge time. Herewith, they have excellent mechanical durability even at high charging current densities which is their undoubted advantage. An extended study of the role of porosity and crystal structure of the grains has to optimize their performance in Li-ion batteries.

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