# Thin Film and Nanophase Si Electrodes

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There is currently considerable interest in the development of Li binary alloys for anodes in Li secondary cells. In addition to their low operating voltage vs. Li (~300 mV for Si), these alloys possess large theoretical energy densities, the largest of which is found in the Li-Si system. In the following electrochemical reaction, a number of stable phases are produced.

$$Si + xLi^+ + xe^- \xrightarrow{\text{charge}} Li_xSi$$
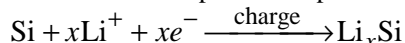
where crystallographic phases occur at x = 1.7, 2.3, 3.3, and 4.4.[1] If x is reversible between 0 and 4.4 the theoretical capacity of Si is 4200 mAh/g. Despite the obvious advantages of the binary alloy, these materials have a number of technological shortcomings. A large volume dilatation (~300 %) is associated with alloying 4.4 Li atoms per Si atom. As a result of the high mechanical stresses of alloying and the brittle nature of the alloy, the electrode is typically pulverized during the first few cycles.[2] The particle decrepitation coupled with the poor conductivity the material causes bulk Si to lose ~90 % of its capacity after the 5th cycle at ambient temperature.[3]

Nanocrystalline Si may not suffer from the same effects of mechanical stress, and may be able to minimize stress gradients and are therefore less affected by the volume changes that develop during cycling. In addition, nanostructured materials have a high concentration of grain boundaries to act as diffusion pathways and in general, the fast kinetics allow for high rate capabilities.

Nanostructured Si clusters were prepared by gas-phase ballistic consolidation. The as-deposited particles (5-20 nm) were found to be crystalline with an encompassing amorphous oxide layer as shown in Fig. 1. Electron energy-loss spectrometry (EELS) was used to measure the Li K and Si $L_{2,3}$-edges from the fully lithiated electrodes (Fig. 2). Elemental analyses of these edges confirmed the insertion of up to 4.3 Li atoms per silicon after the first discharge.

The measured capacities and capacity fade were affected by the substrate on which the nanocrystalline Si was deposited. Figure 3 shows that nano-silicon deposited onto the fibrous substrate showed reversible gravimetric capacities of up to 2100 mAh/g with some capacity retention after 30 cycles. The material deposited on a low surface area Cu substrate exhibited initial capacities of around 1100 mAh/g and an extended cycle life (50 % capacity retention after 50 cycles).

A Si thin film was prepared by evaporation directly onto the rough surface of a Ni coated coin cell. The structure of the evaporated Si was characterized with XRD and TEM and found to be a continuous amorphous film approximately 150 nm thick. Electrochemical cycling measurements revealed a gravimetric capacity of around 1500 mAh/g (Fig. 3). In addition to the high capacity, this electrode also exhibited a very stable cycle life with ~20 % capacity loss over 50 cycles.

References

[1] C. J. Wen and R. A. Huggins, J. Solid State Chem., **37** 271 (1981).
[2] J. Yang, M. Winter, and J. O. Besenhard, Solid State Ionics, **90** 281 (1996).
[3] H. Li, X. Huang, L. Chen, Z. Wu, and Y. Liang, Electrochem. Solid State Lett., **2** 547 (1999).

Fig. 1. High-resolution TEM image of the as-deposited nano-silicon. The lattice fringes reflect the Si (111) interplanar spacing of 3.1 Å.

Fig. 2. Li K-edge and Si $L_{2,3}$- edge from electrochemically alloyed Li$_x$Si. Inset shows the background subtracted Si L-edge.
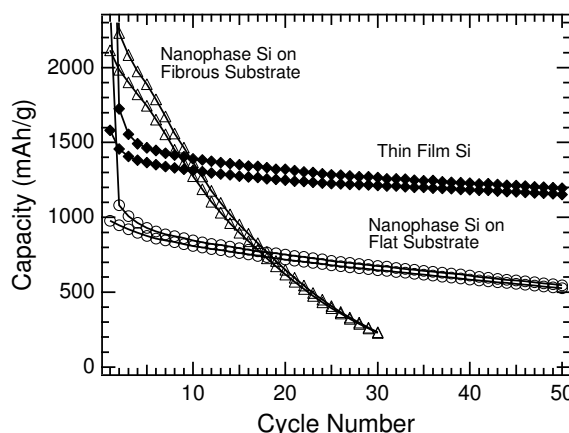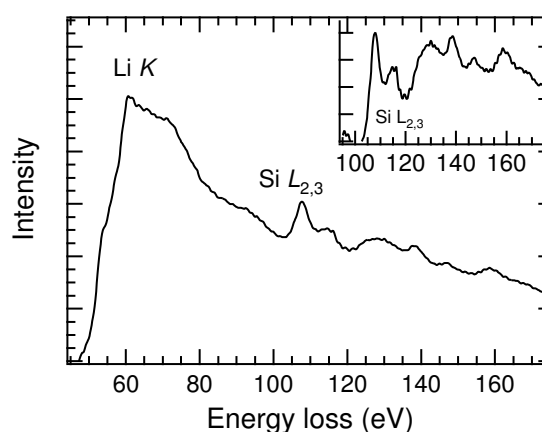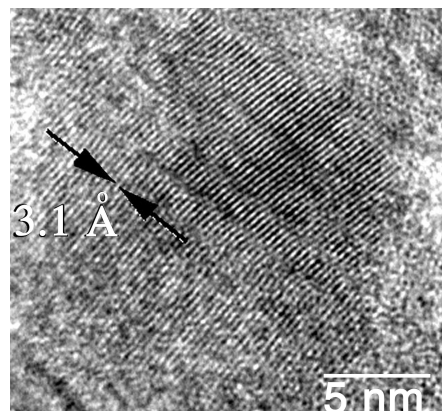

Fig. 3. Capacities of an evaporated Si thin film, nano-silicon deposited on a flat substrate, and nano-silicon on a high surface area fibrous substrate.