Electronic Supplementary Information

In Situ and Operando Atomic Force Microscopy of High-Capacity Nano-Silicon Based Electrodes for Lithium-Ion Batteries

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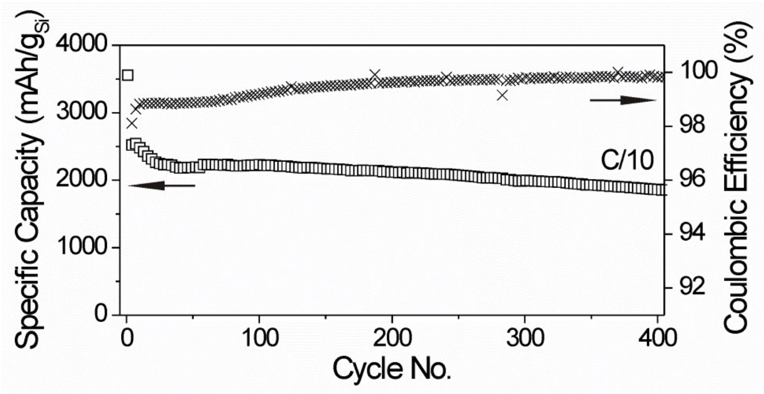

Fig. S1 Cycling performance of a nano-Si electrode containing PVA binder and carbon black additive. Both the capacity retention and Coulombic efficiency are shown versus the cycle number. After the initial cycle at C/20 was completed, the C-rate was increased to C/10 for further cycle life study.

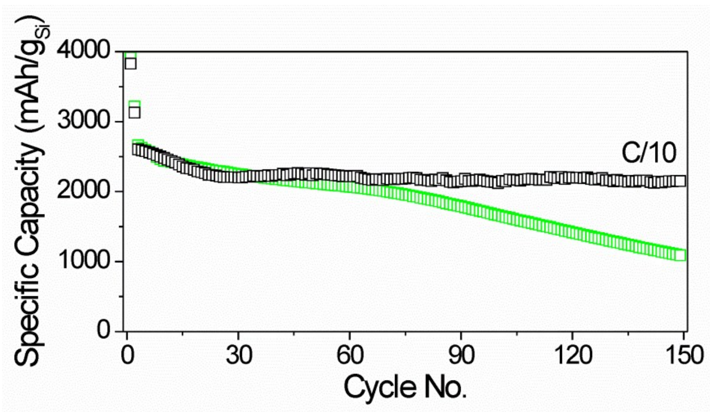

Fig. S2 Comparison of nano-Si electrodes with (black) “stable” and (green) “unstable” cycling behavior at C/10. As discussed in the manuscript, the different performance is correlated with the fraction of surface cracks and pinholes.

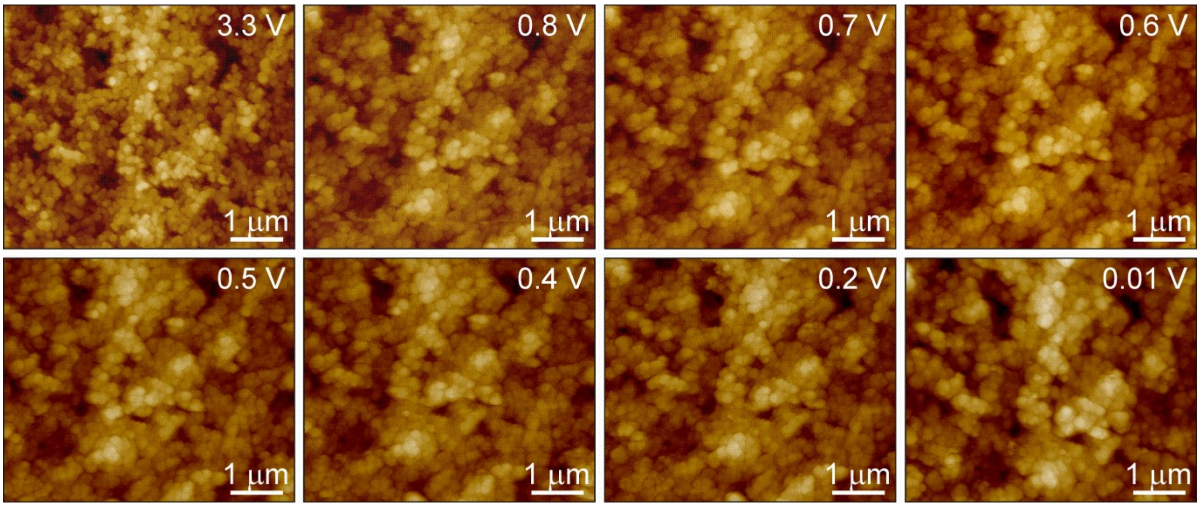

Fig. S3 AFM height images of a nano-Si electrode obtained in situ during the first lithiation cycle. Each image shows the same area of the top surface.

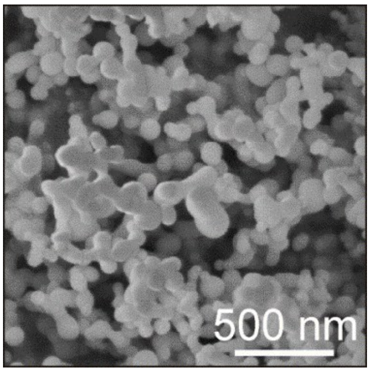

Fig. S4 SEM image of the <100 nm Si particles used in this work.

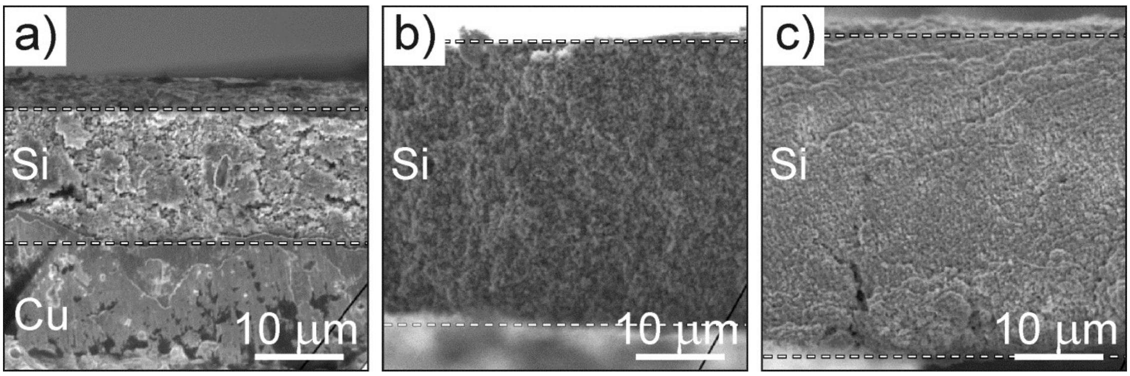

Fig. S5 Cross-sectional SEM images of nano-Si electrodes (a) before and after (b) 1 and (c) 2 cycles. The electrodes expand significantly in the free direction during the initial cycle, from about 14 µm to 32 µm. The thickness increase in the subsequent cycle is only about 4 µm, which is in good agreement with the height changes measured by means of AFM.

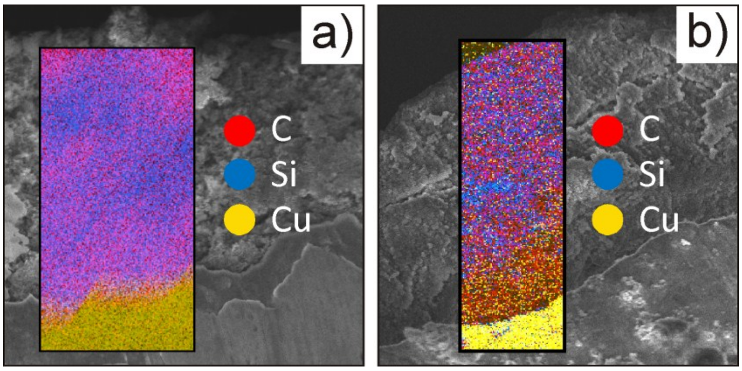

Fig. S6 SEM-EDS maps showing the homogeneous distribution of Si and C (a) before and (b) after 2 cycles.

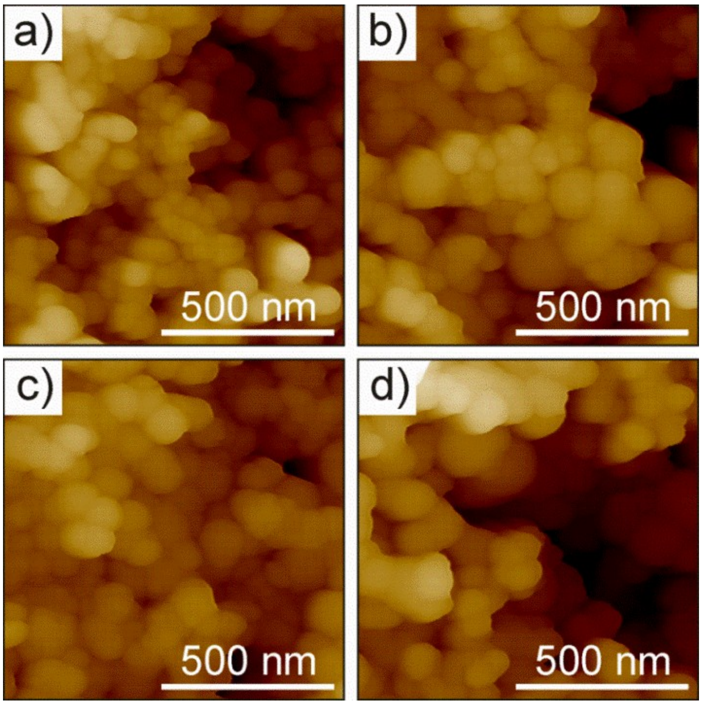

Fig. S7 AFM height images corresponding to the phase images shown in **Fig. 9** in the manuscript.

Monte Carlo method for topographical images

The topographical images shown in manuscript were transformed in part into SEM-like images by use of the program Gwyddion. The procedure is based on a Monte Carlo method.[1-3]

Each pixel on the surface represents the starting point of a number of lines with random directions and Gaussian length distribution. If the line ends above the surface, i.e., the endpoint hits free space, the pixel brightness is increased. In contrast, if the line ends below the surface, i.e., the endpoint hits material, the brightness is decreased. The quality and integration parameter define the number of lines and the standard deviation of the Gaussian length distribution, respectively.

1 David Nečas, Petr Klapetek, Gwyddion: an open-source software for SPM data analysis, *Cent. Eur. J. Phys.*, **10**(1), (2012), 181-188

2 Gwyddion homepage, http://gwyddion.net/documentation/user-guide-en/presentations.html#semsim (accessed January 2016)

3 Quantitative Data Processing in Scanning Probe Microscopy published by Elsevier (ISBN: 9781455730582)