Supporting Information

Cycling Behavior of Silicon-Containing Graphite Electrodes, Part A: Effect of the Lithiation Protocol

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S1. Cycling performance of silicon-free electrodes

Graphite electrodes (Figure S1, Figure S2, Figure S3) were cycled with various cycling protocols, applied in the study of graphite-Si electrodes, to assess the contribution of graphite, and thus determine the contribution of silicon in silicon-containing electrodes.

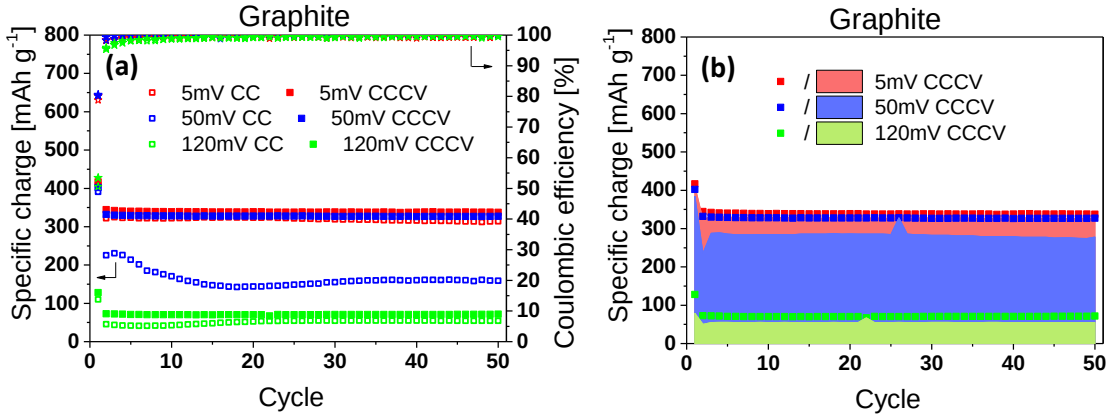

Figure S1. (a) Cycling performance (specific charge: squares, coulombic efficiency: stars) and (b) contribution of the galvanostatic charge (filled area) to the total specific charge (square symbols) of graphite electrodes with various cycling conditions.

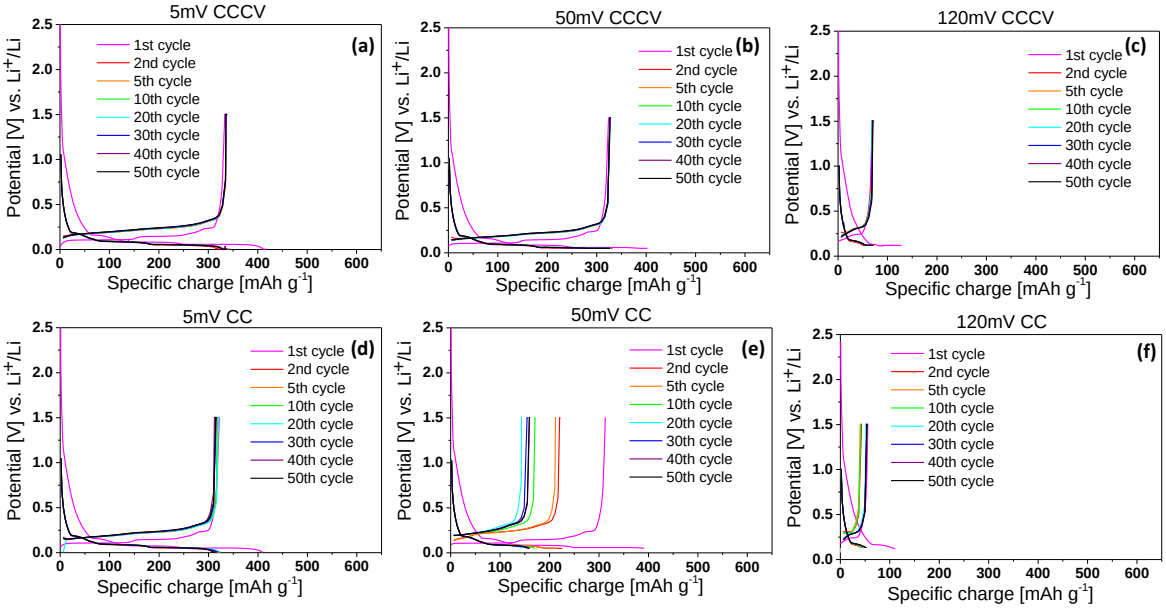

Figure S2. Voltage profiles of graphite electrodes using (a) 5 mV CCCV, (b) 50 mV CCCV, (c) 120 mV CCCV, (d) 5 mV CC, (e) 50 mV CC or (f) 120 mV CC cycling protocols.

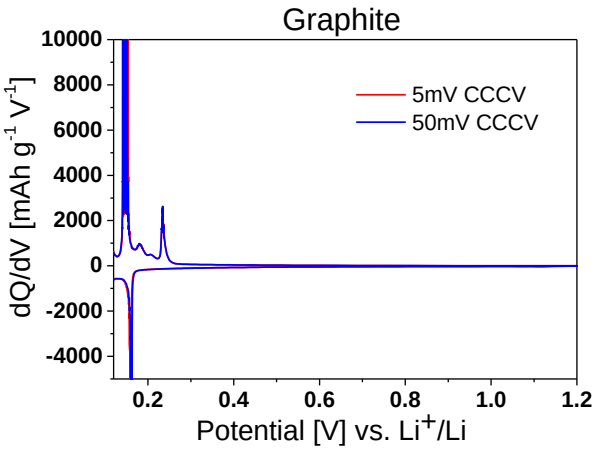

Figure S3. Differential capacity plots of the 1st cycle of graphite electrodes with 5 mV CCCV or 50 mV CCCV cycling protocols.

S2. Cycling performance of electrodes containing 10 wt % silicon

In order to compensate for the loss of specific charge due to incomplete lithiation of graphite at higher cutoff potentials, the relative amount of Si was increased to 10 wt %. The effect of the selected cutoff conditions on long-term cycling with these electrodes is shown in Figure S4.

First of all, it is observed that, for all cycling conditions, the performance fading is more pronounced and the specific charge is lower with Si 70−130 than with Si 30−50, confirming the trend found with 5 w .% silicon. Moreover, for both types of silicon nanoparticles, the effects of the cutoff potentials and the CV step on the specific charge and coulombic efficiency are similar to those observed with a lower relative amount of silicon. Indeed, the cycling behavior is identical for 5 mV CCCV, 5 mV CC and 50 mV CCCV protocols, and a very low specific charge is also reached with 120 mV CC for these electrodes. As expected from the increased amount of Si, a higher specific charge than for electrodes containing 5 wt % Si is obtained under most of the cycling conditions. In particular, almost 300 mAh g^{-1} is reached with Si 30−50 after 15 cycles for 120 mV CCCV thanks to the CV step.

For 50 mV CC, a discontinuity is observed in the cycling performance of electrodes containing Si 30−50. This is due to the fact that, for these cycling conditions, the lithiation is stopped on a plateau, where any change in the overpotential leads to huge changes in the lithiation depth and thus, in the obtained specific charge (Figure S5). Consequently, the specific charge reached in some cycles can be high even without a CV step, which is otherwise crucial to achieve full lithiation for such electrode compositions (Figure S4).

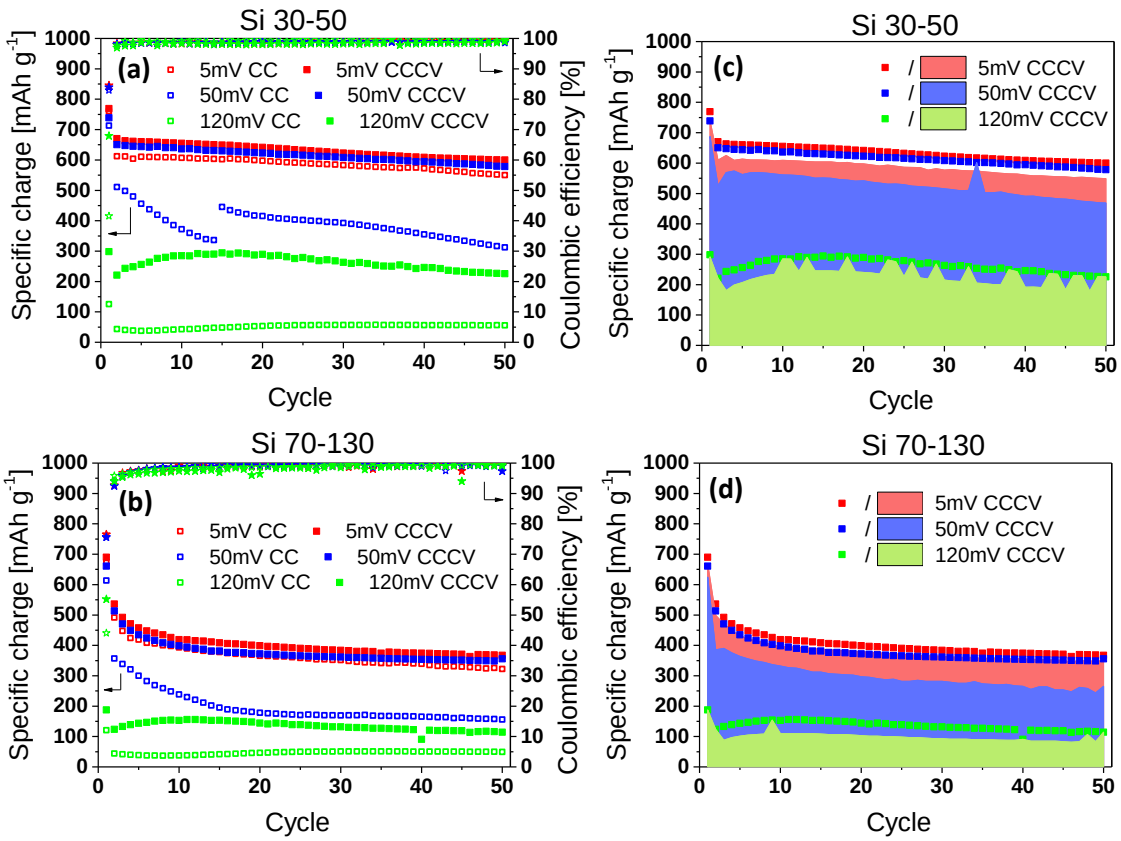

Figure S4. (a,b) Cycling performance (specific charge: squares, coulombic efficiency: stars) and (c,d) contribution of the galvanostatic charge (filled area) to the total specific charge (square symbols) of graphite electrodes with 10 wt % of (a,c) Si 30–50 and (b,d) Si 70–130, using various cycling protocols.

From the voltage profiles (Figure S5, Figure S6), it is also observed that the general behavior is similar to that of electrodes containing 5 wt % silicon. The major difference is the larger specific charge, including the longer delithiation plateau for 5 mV CCCV with Si 30–50 as well as for 5 mV and 50 mV with Si 70–130 with both CC and CCCV protocols, due to higher Si content, although this contribution quickly decreases in the case of the larger Si particles.

With 120 mV CCCV as lithiation cutoff condition, the gain achieved using a larger amount of Si (Si30–50) is clear after comparison of the corresponding voltage profiles with those of graphite electrodes. Indeed, while this cutoff condition is not suitable for graphite lithiation, it is sufficient to get reasonable specific charge from silicon due to the higher potential of the silicon lithiation processes.

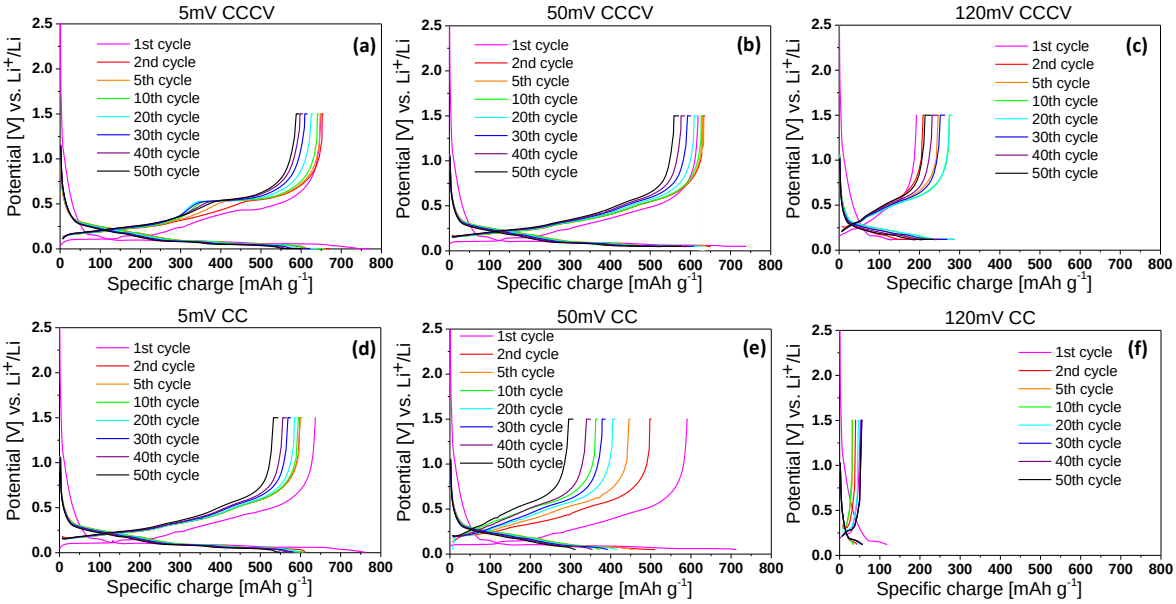

Figure S5. Voltage profiles of graphite electrodes with 10 wt % Si 30–50 with (a) 5 mV CCCV, (b) 50 mV CCCV, (c) 120 mV CCCV, (d) 5 mV CC, (e) 50 mV CC or (f) 120 mV CC cycling protocols.

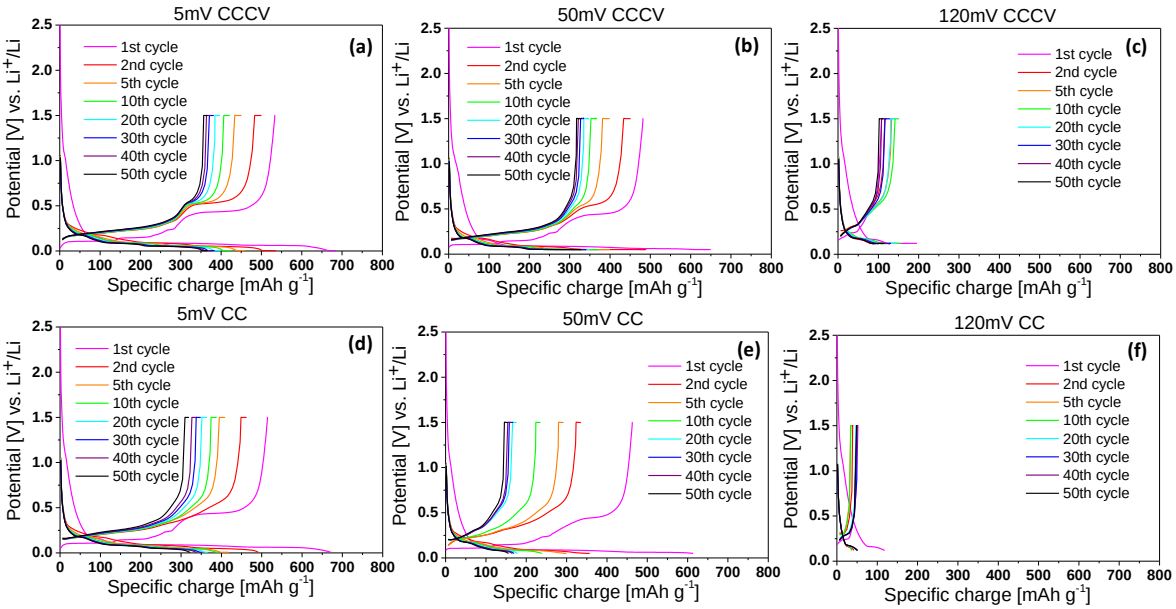

Figure S6. Voltage profiles of graphite electrodes with 10 wt % Si 70–130 with (a) 5 mV CCCV, (b) 50 mV CCCV, (c) 120 mV CCCV, (d) 5 mV CC, (e) 50 mV CC or (f) 120 mV CC cycling protocols.

The individual contributions of graphite and Si were then extracted from the experimental data and compared to the theoretical specific charge (Figure S7). Again, the general behavior is similar to that observed with 5 wt % Si.

On the one hand, the specific charge attributed to Si 70−130 is lower than the theoretical value for the first cycles and, after 50 cycles, less than 60 mAh g^{-1} is reached, independently of the cutoff conditions, due to poor cycling stability of this silicon type.

On the other hand, silicon contribution of Si 30−50 is close to the theoretical value for the first cycles with 5 mV and 50 mV, both with and without a CV step. After long-term cycling, however, the performance fading with 10 wt % silicon is more pronounced that with 5 wt %, and about 60 mAh g^{-1} is lost after 50 cycles, probably due to more pronounced Si volume changes and a lower amount of carbon to buffer them. Despite this loss, the specific charge of 10 wt % Si 30−50 contributes to half of the total electrode specific charge. Moreover, the use of a CV step with a cutoff potential of 120 mV results in a silicon specific charge of ~165 mAh g^{-1}, while graphite is almost inactive at such high cutoff potential. Nevertheless, this corresponds to a silicon utilization of only ~46% whereas ~63% Si 30-50 was utilized in electrodes containing 5 wt % silicon under similar cycling conditions.

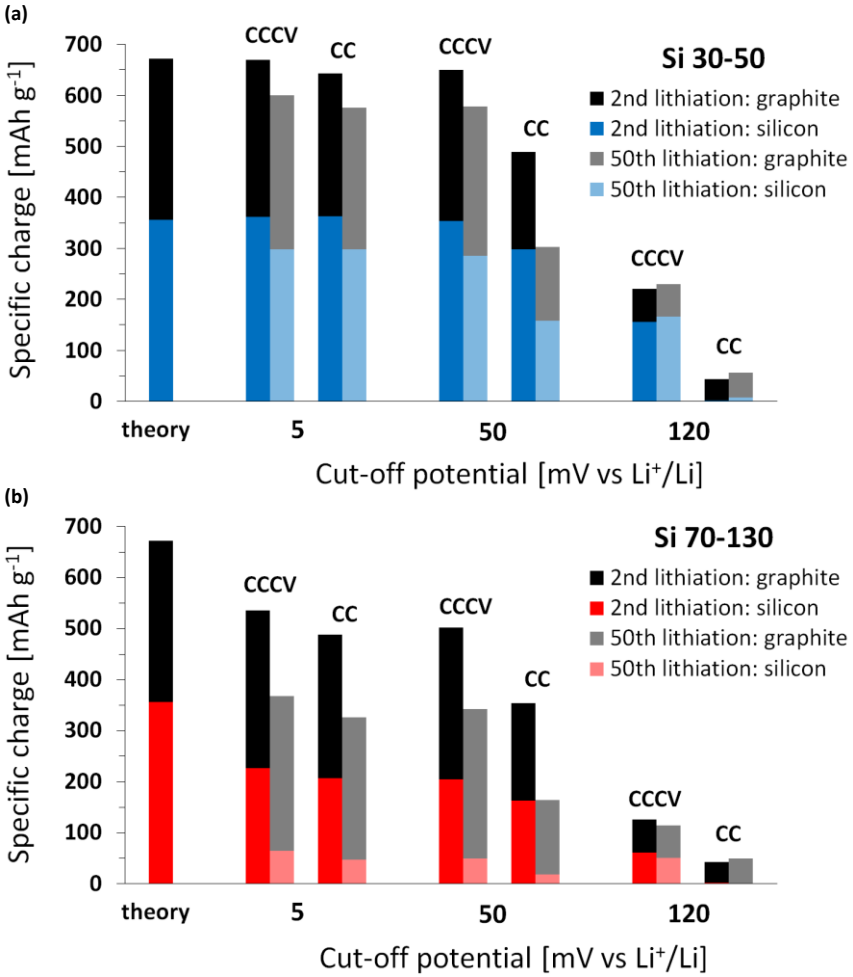

Figure S7. Contribution of graphite (black) and silicon to the total specific charge of graphite electrodes with 10 wt % (a) Si 30–50 (blue) and (b) Si 70– 130 (red) for the 2nd lithiation (dark colors) and the 50th lithiation (light colors) with various lithiation cutoff conditions.