

Batteries & Supercaps

Supporting Information

Investigation of Polyacrylonitrile-Derived Multiple Carbon Shell Composites for Silicon-Based Anodes in Lithium-Ion Batteries

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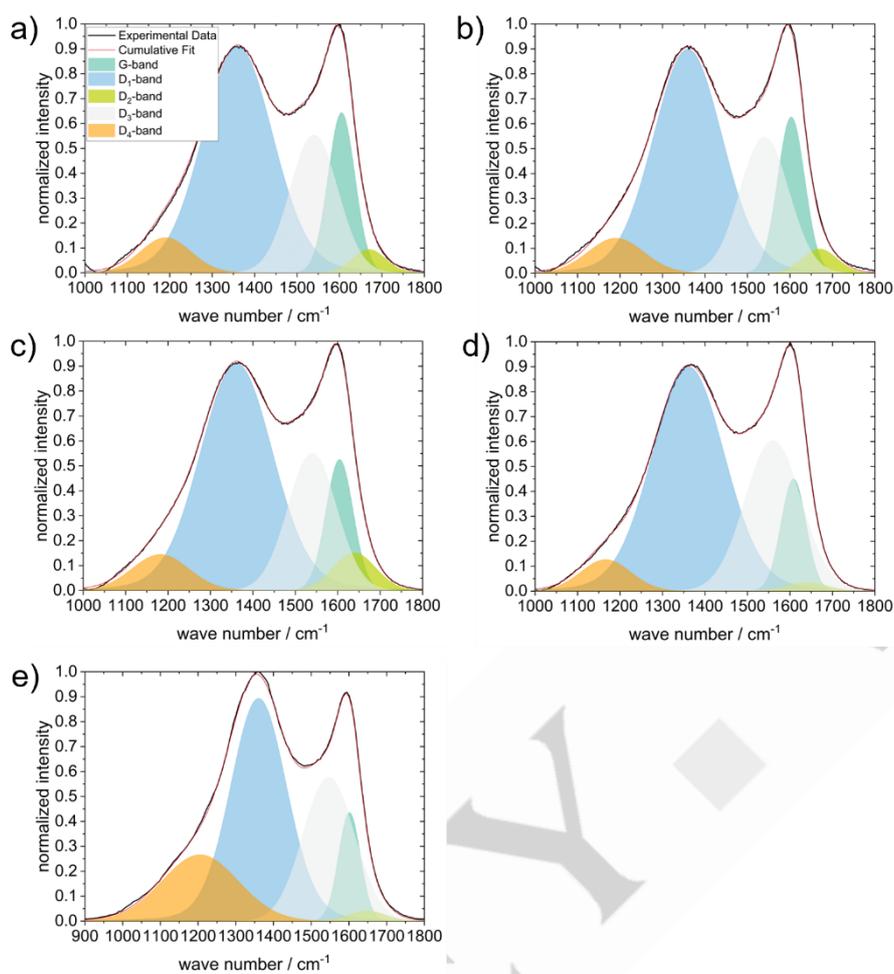


Figure S 1. Raman spectra with fits of the bands of the active materials a) Si@SCS-1000-70 b) Si@SCS-1000-50 c) Si@MCS-1000/1000-50, d) Si@MCS-1000/1000-30 and e) PAN-1000. A Gaussian peak type was used for the G-, D₂-, D₃- and D₄-band and a Voigt peak type for the D₁-band.

Table S 1. Degree of graphitization of graphene sheets calculated from fitted Raman spectroscopy measurements by dividing the area of the G-band by the total area of all bands.

| composite | degree of graphitization (A_G/A_{total}) / % |
|---------------------|--|
| Si@SCS-1000-70 | 14.3 |
| Si@SCS-1000-50 | 14.2 |
| Si@MCS-1000/1000-50 | 11.5 |
| Si@MCS-1000/1000-30 | 9.3 |
| PAN-1000 | 8.4 |

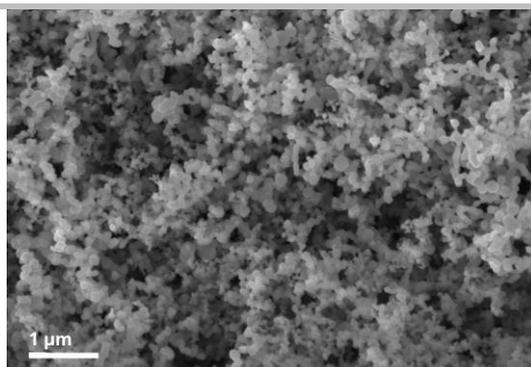


Figure S 2. Scanning electron microscopy micrograph of the pristine silicon nanoparticles.

Table S 2. Elemental Analysis of Si/C composites after NaOH etching with and without additional thermal treatment at 1000 °C for 12 h.

| composite | C / wt.% | H / wt.% | N / wt.% | S / wt.% | residual / wt.% |
|----------------------------------|-------------|-------------|-------------|-------------|--------------------|
| Si@SCS-1000- 70_etched | 4.7 | 47.8 | 1.6 | 0.2 | 45.7 |
| Si@SCS-1000- 70_etched+T | 4.2 | 48.9 | 1.2 | 0.2 | 45.5 |
| Si@SCS-1000- 50_etched | 4.7 | 64.8 | 1.4 | 0.3 | 28.8 |
| Si@SCS-1000- 50_etched+T | 4.2 | 66.7 | 0.8 | 0.0 | 28.2 |
| Si@MCS-1000/1000- 50_etched | 3.7 | 48.1 | 0.5 | 0.2 | 47.4 |
| Si@MCS-1000/1000- 50_etched+T | 3.3 | 48.1 | 0.5 | 0.1 | 48.0 |
| Si@MCS-1000/1000- 30_etched | 4.4 | 65.0 | 0.4 | 0.2 | 30.1 |
| Si@MCS-1000/1000- 30_etched+T | 4.2 | 66.0 | 0.4 | 0.1 | 29.3 |

To evaluate whether oxygenic functionalization did occur during the etching, the etched samples were processed at 1000 °C for 12 hours. Similar fractions of C, H, N and S were measured for the samples with and without the thermal process step.

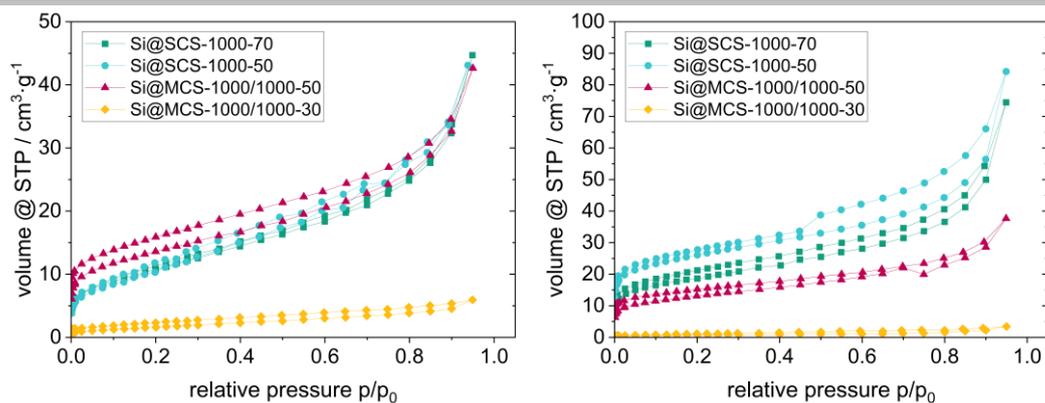


Figure S 3. N_2 -adsorption isotherms of the four Si/C composites.

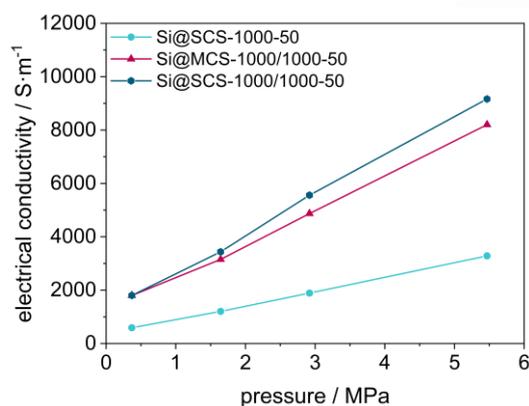


Figure S 4. Specific conductivity depending upon the applied pressure for the Si/C composites containing a silicon fraction of 50 wt.%.

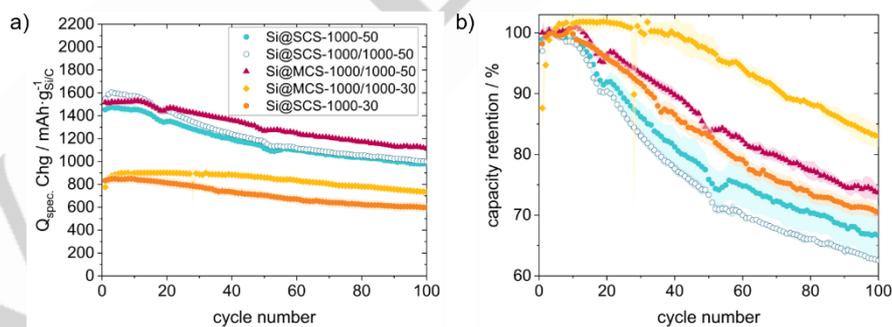


Figure S 5. Constant current constant voltage cycling measurement of selected Si@SCS and Si@MCS composites vs. Li/Li^+ at a rate of 0.5C between 0.01 V and 1.5 V. a) specific charge capacity and b) capacity retention.

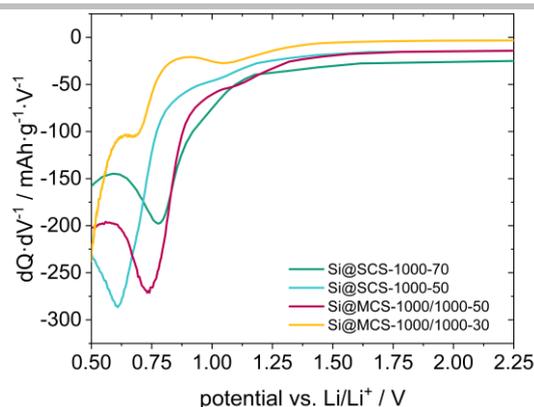


Figure S 6. Differential capacity analysis of the four evaluated Si/C composites during the initial lithiation within the decomposition potential window (0.5 V – 2.25 V) of the electrolyte (1 M LiPF₆ in EC: EMC 3:7 wt.% + 10 wt.% FEC + 2 wt.% VC). Potential and capacity were recorded in 10 s intervals, smoothing of recorded data was performed using a moving average including six data points.

Table S 3. Summary of publications evaluating silicon-carbon composites with multiple carbon shells.

| silicon particles | carbon source 1 st carbon shell | carbon source 2 nd carbon shell | cell configuration | initial delithiation capacity | first cycle efficiency | capacity retention | year, reference |
|------------------------------------|---|---|--|----------------------------------|---------------------------|---|---------------------------|
| Si nanoparticles (100 – 200 nm) | polyacrylonitrile | polyacrylonitrile | half-cell, CCCV @ 0.5 C (0.1 C CV cut-off) | 776 mAh·g ⁻¹ | 79.6 % | 96.9 % (50 cycles) 83.0 % (100 cycles) | 2023, this publication |
| Si nanoparticles (~30 nm) | resorcinol- formaldehyde resin | 2-methylimidazole + Co(NO ₃) ₂ ·6H ₂ O | half-cell, CC @ 0.5 C | 1515 mAh·g ⁻¹ | 79 % | 73 % (100 cycles) | 2018, [28] |
| crystalline mesoporous Si | fructose | preceramic organosilicon polymer | half-cell, CC @ ~ 0.15 C | 533 mAh·g ⁻¹ | 61 % | 91 % (50 cycles) | 2017, [29] |
| Si (200 – 800 nm) | polyurethane | polyaniline | half-cell, CC @ 0.1 C | 1011.8 mAh·g ⁻¹ | 87.03 % | 73.9 % (100 cycles) | 2023, [44] |
| porous Si microsphere | graphene | Al ₂ O ₃ + glycerin | half-cell, CC @ ~ 0.33 C | 1804.5 mAh·g ⁻¹ | 71.01 % | 77.2 % (100 cycles) | 2023, [45] |