

Batteries & Supercaps

Supporting Information

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

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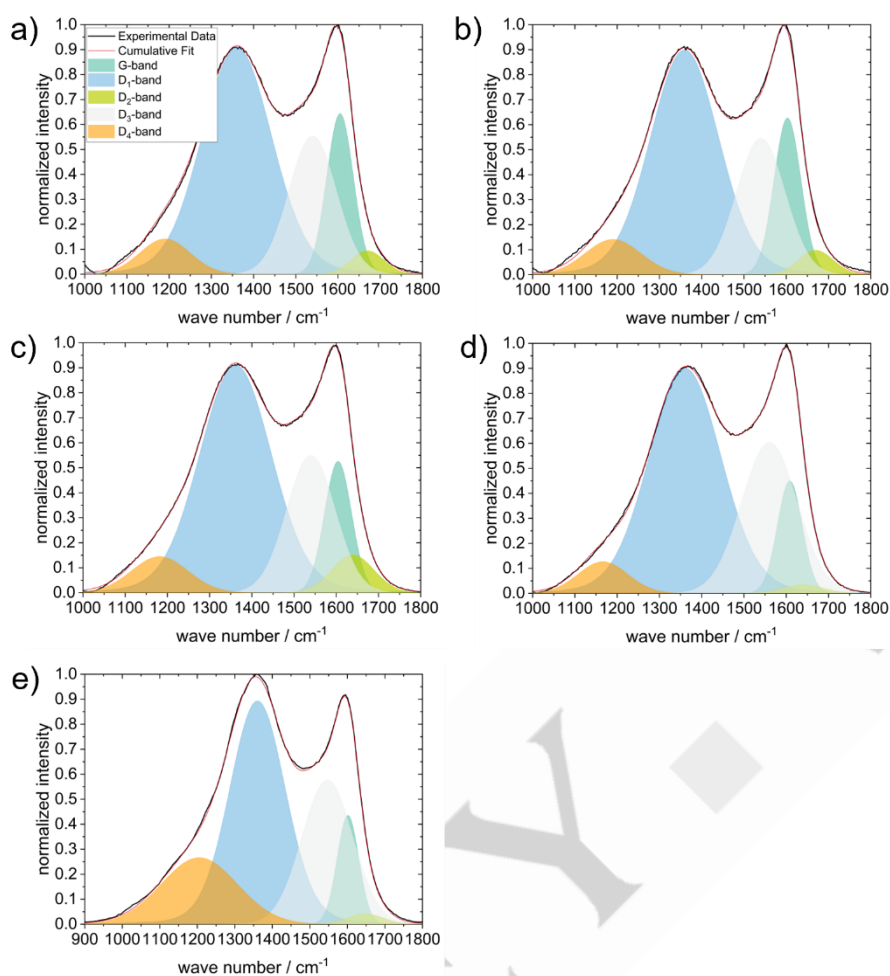


Figure S 1. Raman spectra with fits of the bands of the active materials a) Si@SCS-1000-70 b) Si@SCS-1000-50 c) Si@MCS-1000/1000-50, d) Si@MCS-1000/1000-30 and e) PAN-1000. A Gaussian peak type was used for the G-, D₂-, D₃- and D₄-band and a Voigt peak type for the D₁-band.

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

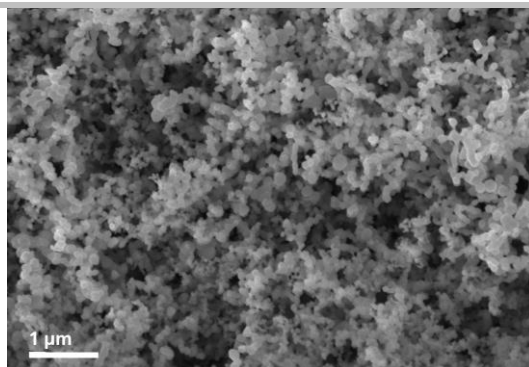


Figure S 2. Scanning electron microscopy micrograph of the pristine silicon nanoparticles.

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.

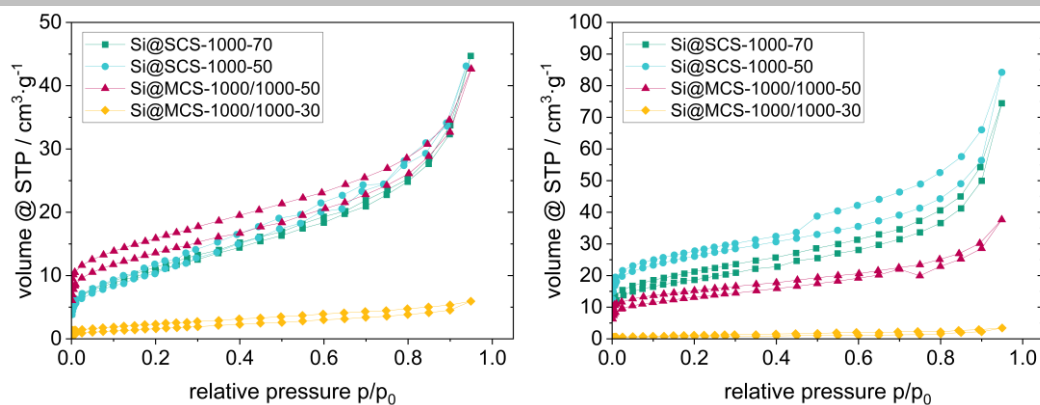


Figure S 3. N_2 -adsorption isotherms of the four Si/C composites.

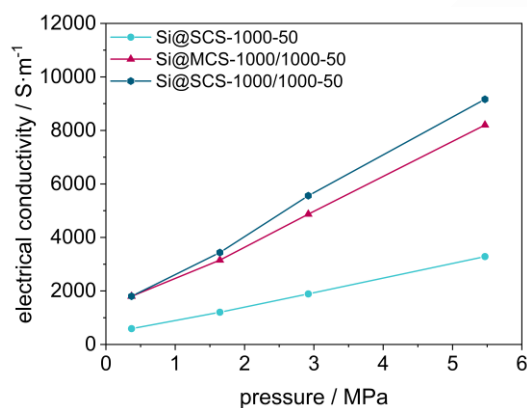


Figure S 4. Specific conductivity depending upon the applied pressure for the Si/C composites containing a silicon fraction of 50 wt.%.

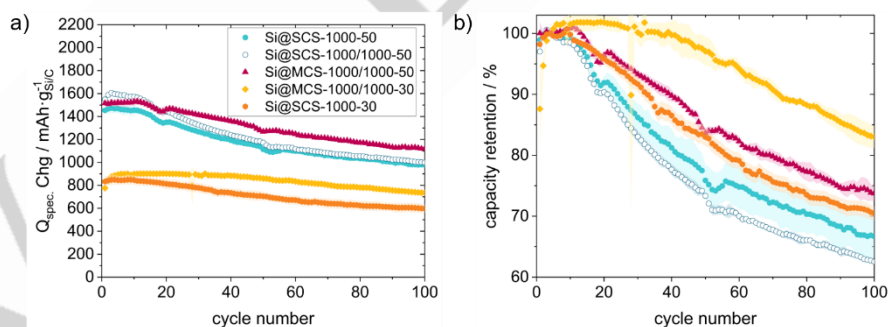


Figure S 5. Constant current constant voltage cycling measurement of selected Si@SCS and Si@MCS composites vs. Li/Li^+ at a rate of 0.5C between 0.01 V and 1.5 V. a) specific charge capacity and b) capacity retention.

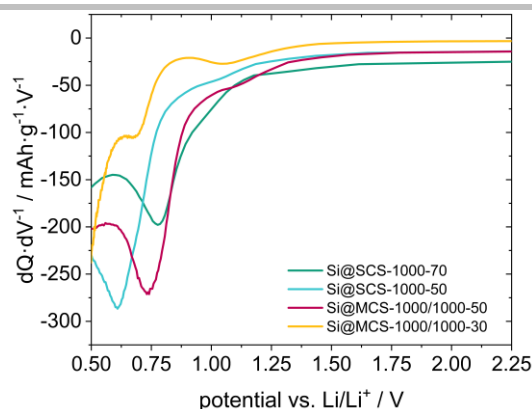


Figure S 6. Differential capacity analysis of the four evaluated Si/C composites during the initial lithiation within the decomposition potential window (0.5 V – 2.25 V) of the electrolyte (1 M LiPF₆ in EC: EMC 3:7 wt.% + 10 wt.% FEC + 2 wt.% VC). Potential and capacity were recorded in 10 s intervals,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