Impact of silicon content and particle size in lithium ion-battery anodes on particulate properties and electrochemical performance

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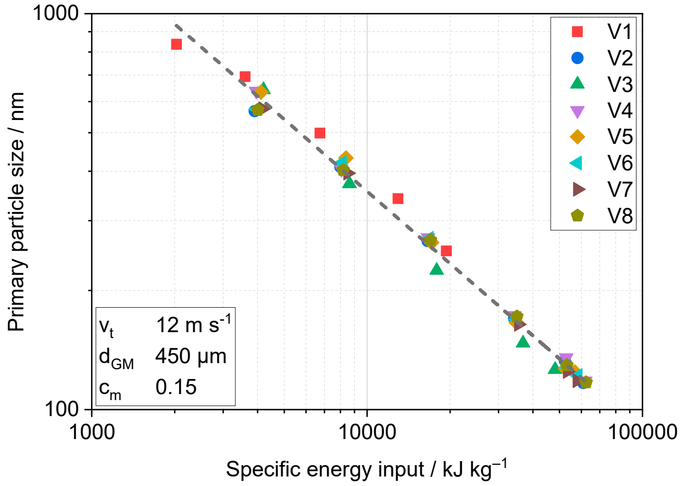

Figure S1. Primary particle size (measured by ultrasonic extinction) as a function of specific energy input during grinding (V1-V8 relate to separate experiments, all conducted under the same conditions)

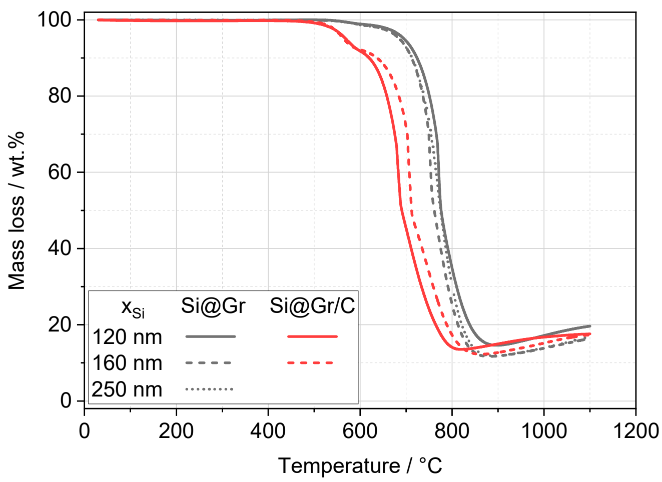

Figure S2. Thermogravimetric analysis of Si@Gr and Si@Gr/C composite particles with a variation of Si particle size

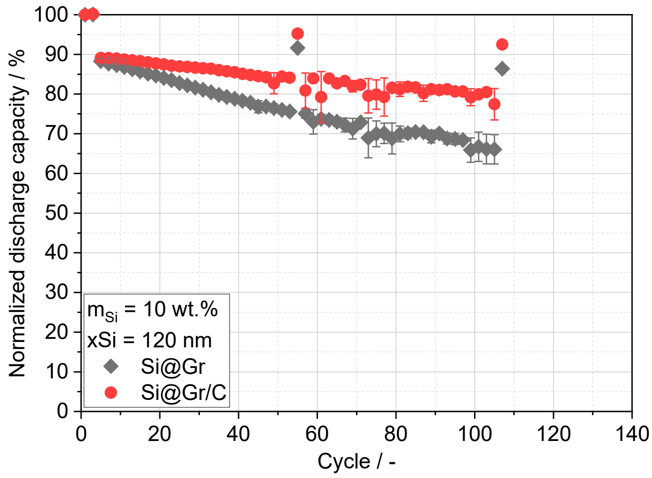

Figure S3. Normalized capacity of Si@Gr and Si@Gr/C anodes during long term cycling test (0.5C) in half cell configuration (normalized to the capacity at 0.1C before long-term cycling)

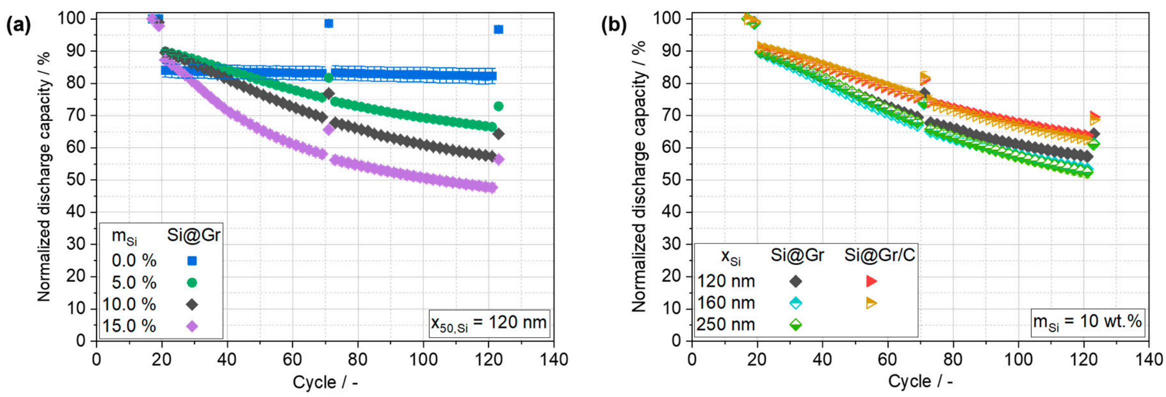

Figure S4. (a) Relative discharge capacity during long term cycling at 0.5C (normalized to the capacity at 0.1C after rate capability test and before long term cycling test, cycle 17); (a) Si@Gr with a variation of Si content; (b) Si@Gr and Si@Gr/C with a variation of particle size

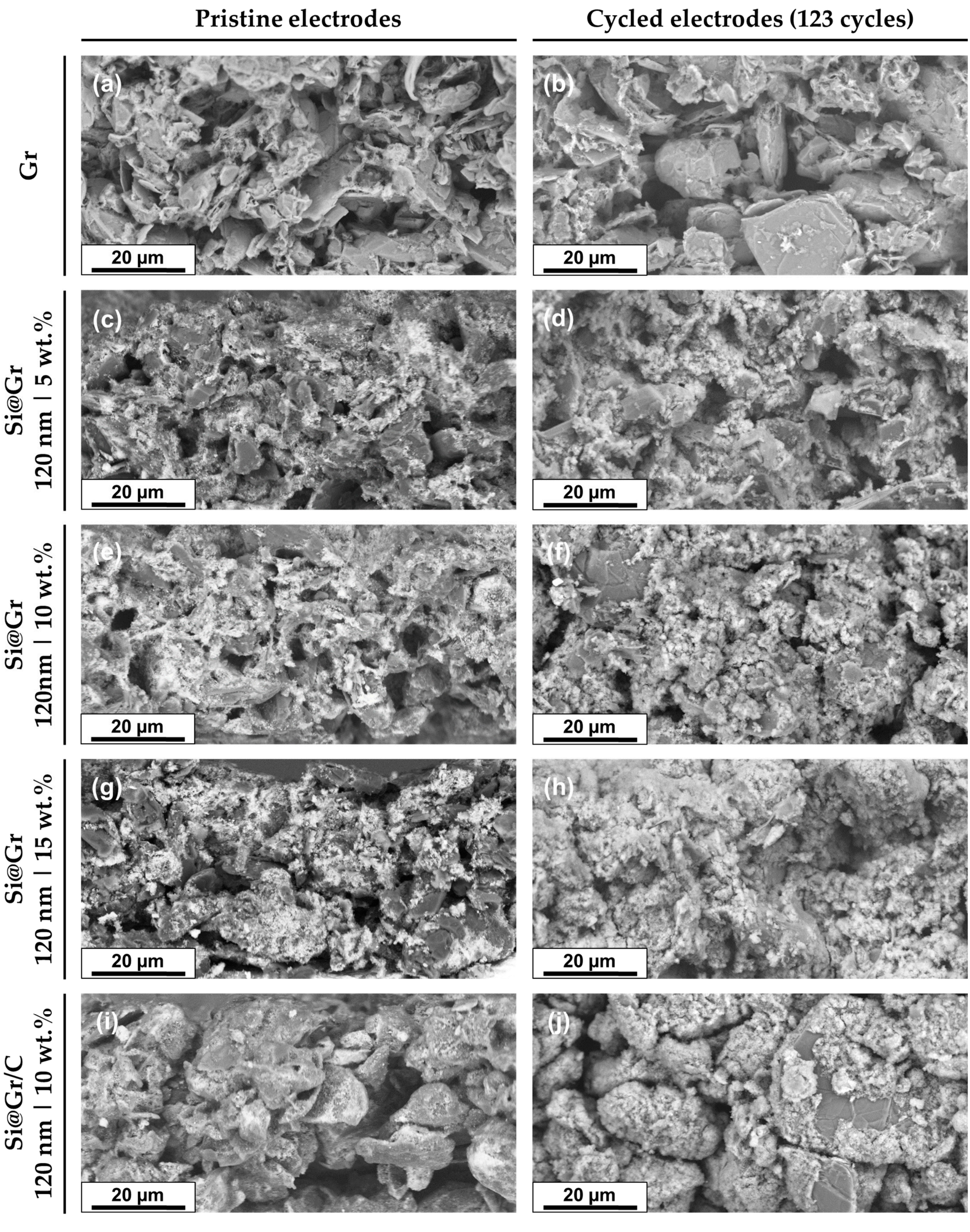

Figure S5. SEM images of Si@Gr and Si@Gr/C composite anodes before and after cycling for 123 cycles; (a-b) Gr; (c-d) Si@Gr, 5 wt.% Si, 120 nm; (e-f) Si@Gr, 10 wt.% Si, 120 nm; (g-h) Si@Gr, 15 wt.% Si, 120 nm; (i-j) Si@Gr/C, 10 wt.% Si, 120 nm

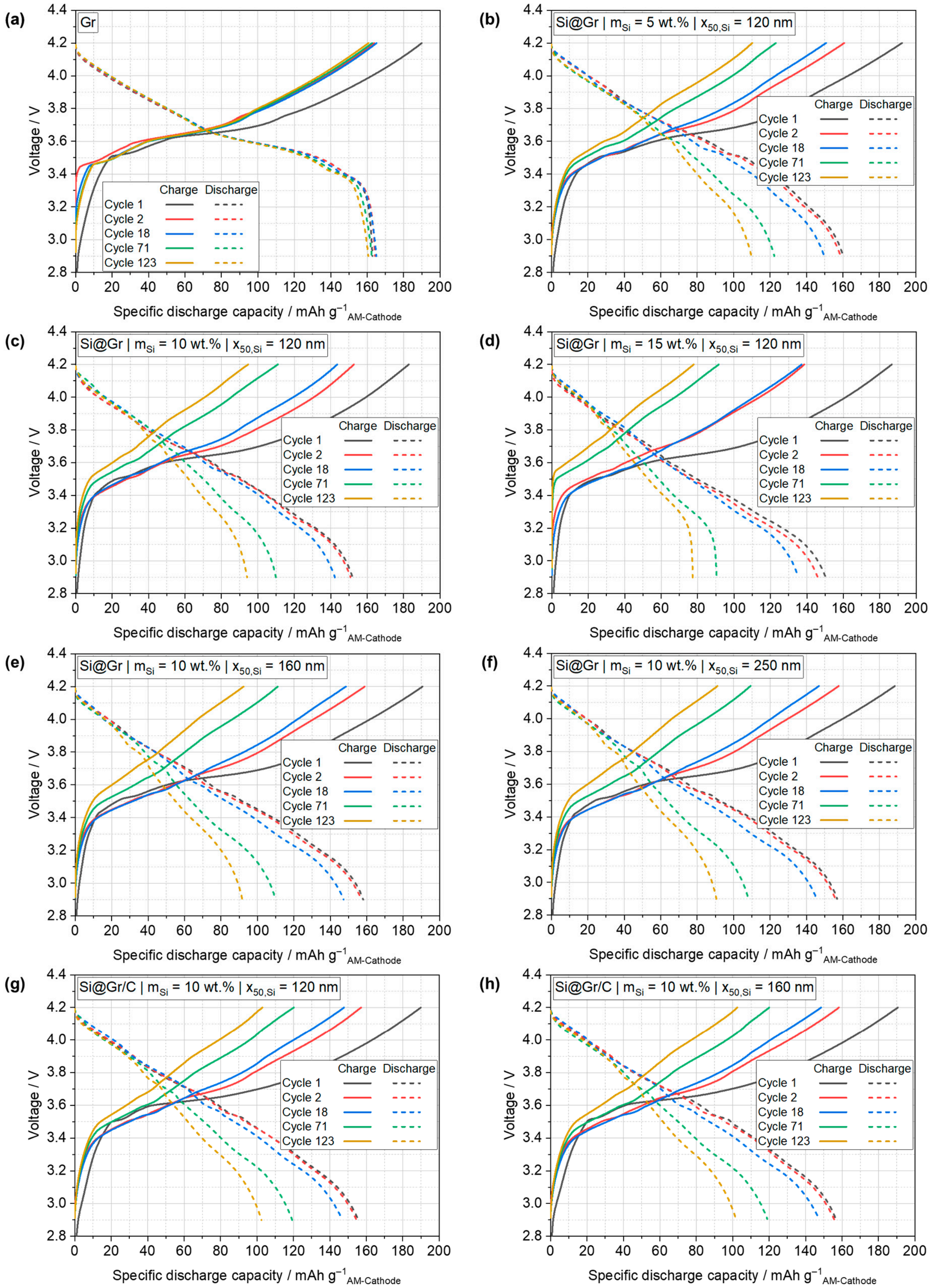

Figure S6. Voltage curves at different cycles (all at 0.1 C); (a) Gr; (b) Si@Gr, 5 wt.% Si; (c) Si@Gr, 10 wt.% Si; (d) Si@Gr, 15 wt.% Si, (e) Si@Gr, 160 nm Si; (f) Si@Gr, 250 nm Si; (g) Si@Gr/C, 120 nm Si; (h) Si@Gr/C, 160 nm Si

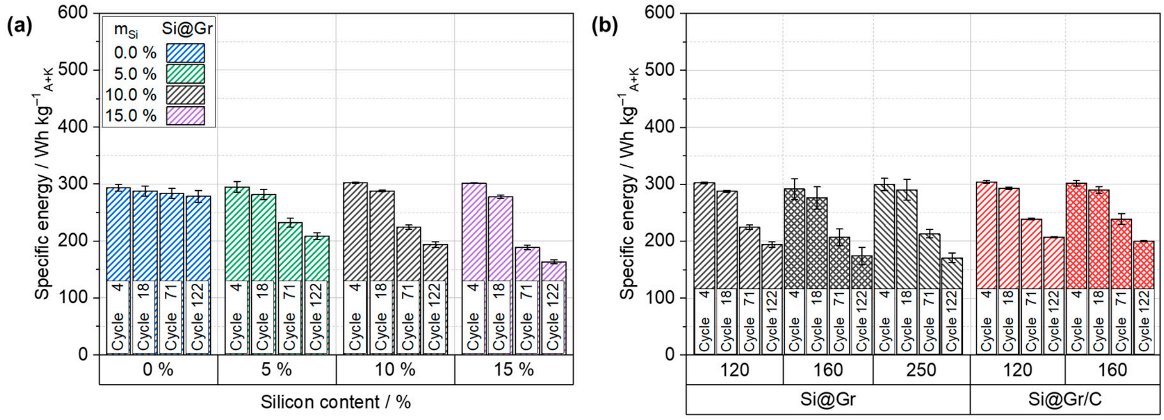

Figure S7. Specific energy (Wh kg^{-1}); (a) of Si@Gr as a function of Si content for 120 nm Si NP; (b) of Si@Gr and Si@Gr/C as a function of Si particle size for 10 wt.% Si

Calculation of the energy density

$$W_V = \frac{W}{V_{Anode} + V_{Cathode} + \frac{1}{2} \cdot (V_{Cu} + V_{Al})}$$

$$= \frac{W}{A_{Anode} \cdot h_{Anode} + A_{Cathode} \cdot h_{Cathode} + \frac{1}{2} \cdot (A_{Cu} \cdot h_{Cu} + A_{Al} \cdot h_{Al})}$$

$$with$$

$$A_{Anode} = A_{Cathode} = A_{Cu} = A_{Al} = 254.47\ mm^2 = 2.54 \cdot 10^{-4} m^2 \qquad (S1)$$

$$h_{Cu} = 10\ \mu m = 1 \cdot 10^{-5} m$$

$$h_{Al} = 20\ \mu m = 2 \cdot 10^{-5} m$$

W_V	Energy density / Wh L^{-1}
W	Energy / Wh
V_{Anode}	Volume of the anode coating / L
$V_{Cathode}$	Volume of the cathode coating / L
V_{Cu}	Volume of the copper substrate / L
V_{Al}	Volume of the aluminium substrate / L
A_{Anode}	Area of the anode / m^2
$A_{Cathode}$	Area of the cathode / m^2
A_{Cu}	Area of the copper substrate / m^2
A_{Al}	Area of the aluminium substrate / m^2
h_{Anode}	Height of the anode coating / m
$h_{Cathode}$	Height of the cathode coating / m
h_{Cu}	Height of the copper substrate / m (10 µm, $1 \cdot 10^{-5} m$)
h_{Al}	Height of the aluminium substrate / m (20 µm, $2 \cdot 10^{-5} m$)

Calculation of the specific energy

$$W_m = \frac{W}{m_{Anode} + m_{Cathode} + \frac{1}{2} \cdot (m_{Cu} + m_{Al})} \qquad (S2)$$

W_m	Specific energy / Wh m⁻¹
W	Energy / Wh
m_{Anode}	Coating mass of the anode / kg
$m_{Cathode}$	Coating mass of the cathode / kg
m_{Cu}	Mass of the copper substrate / kg
m_{Al}	Mass of the aluminium substrate / kg

Table S1. Overview of the anode coating thickness for the different produced electrodes; Thickness of used copper foil: $h_{S,Cu}$ = 10 µm

Si content m_{Si}	Si particle size x_{Si}	Carbon coating	Initial coating thickness $h_{C,A,0}$	Coating thickness 123 cycles $h_{C,A,123}$	Rel. thickness increase
wt.%	nm	-	µm	µm	%
0.0	120	-	101	105	3.96
5.0		-	74	94	27.03
10.0		-	56	83	48.21
15.0		-	47	88	87.23
10.0	160	-	63	94	49.21
	250	-	56	92	64.29
	120	Yes	73	98	34.25
	160	Yes	73	103	41.10

Theoretical calculation of the specific surface area (SSA)

The specific surface area was calculated based on the particle shape of Si NPs. In the following an exemplary calculation for 1 g of Si@Gr composite with <u>spherical</u> Si NPs (x_{Si} = 120 nm, m_{si} = 5 wt.%) is shown:

1. Volume of one Si NP $V_{Si,total}$

$$V_{Si,total} = \frac{m_{Si}}{\rho_{Si}}$$
$$V_{Si,total} = \frac{0.05\ g}{2.33\ \frac{g}{m^3}} = 2.15 \cdot 10^{-8}\ m^3 \quad (S3\text{-}1)$$

2. Total volume of <u>spherical</u> Si NPs $V_{Si,particle}$

$$V_{Si,particle} = \frac{1}{6} \cdot \pi \cdot x_{Si}^3$$
$$V_{Si,particle} = \frac{1}{6} \cdot \pi \cdot (1.2 \cdot 10^{-7}\ m)^3 = 9.05 \cdot 10^{-22}\ m^3 \quad (S4\text{-}1)$$

3. Total amount of Si NPs $N_{Si,total}$ in the sample

$$N_{Si,total} = \frac{V_{Si,total}}{V_{Si,particle}}$$
$$N_{Si,total} = \frac{2.15 \cdot 10^{-8}\ m^3}{9.05 \cdot 10^{-22}\ m^3} = 2.37 \cdot 10^{13} \quad (S5\text{-}1)$$

4. Surface area of one <u>spherical</u> Si NP $S_{Si,particle}$

$$S_{Si,particle} = \pi \cdot x_{Si}^2$$
$$S_{Si,particle} = \pi \cdot (1.2 \cdot 10^{-7}\ m)^2 = 4.52 \cdot 10^{-14}\ m^2 \quad (S6\text{-}1)$$

5. Total surface area of <u>spherical</u> Si NPs $S_{Si,total}$ in the sample

$$S_{Si,total} = N_{Si,total} \cdot S_{Si,particle}$$
$$S_{Si,total} = 2.37 \cdot 10^{13} \cdot 4.52 \cdot 10^{-14}\ m^2 = 1.07\ m^2 \quad (S7\text{-}1)$$

6. Total surface area of Gr particles $S_{Gr,total}$ in the sample

$$S_{Gr,total} = S_{Gr} \cdot m_{Gr}$$
$$S_{Gr,total} = 2.89\ m^2 \cdot 0.95 = 2.75\ m^2 \quad (S8\text{-}1)$$

7. Total surface area S_{total} in the sample

$$S_{total} = S_{Gr,total} + S_{Si,total}$$
$$S_{total} = 2.75\ m^2 + 1.07\ m^2 = 3.82\ m^2 \quad (S9\text{-}1)$$

In order to take a plate-like shape of the Si NPs into account, equations ***S2-1*** and ***S4-1*** are replaced by equation ***S2-2*** and ***S4-2***, respectively. The rest of the calculation remains the same. A good correlation was found for a diameter to height ratio of 8.

$h_{Si} = \frac{1}{8} \cdot x_{Si} = \frac{1}{8} \cdot 1.2 \cdot 10^{-7}\, m = 1.5 \cdot 10^{-8}\, m.$

2. Total volume of <u>plate-like shaped</u> Si NPs $V_{Si,particle}$

$$V_{Si,particle} = \frac{1}{6} \cdot \pi \cdot x_{Si}^2 \cdot h_{Si}$$
$$V_{Si,particle} = \frac{1}{4} \cdot \pi \cdot (1.2 \cdot 10^{-7}\, m)^2 \cdot 1.5 \cdot 10^{-8}\, m = 1.70 \cdot 10^{-22}\, m^3 \quad (S4\text{-}2)$$

3. Total amount of Si NPs $N_{Si,total}$ in the sample

$$N_{Si,total} = \frac{V_{Si,total}}{V_{Si,particle}}$$
$$N_{Si,total} = \frac{2.15 \cdot 10^{-8}\, m^3}{9.05 \cdot 10^{-22}\, m^3} = 1.26 \cdot 10^{14} \quad (S5\text{-}2)$$

4. Surface area of one <u>plate-like shaped</u> Si NP $S_{Si,particle}$

$$S_{Si,particle} = \left(\frac{1}{4} \cdot \pi \cdot x_{Si}^2\right) \cdot 2 + \pi \cdot x_{Si} \cdot h_{Si}$$
$$S_{Si,particle} = \left(\frac{1}{4} \cdot \pi \cdot (1.2 \cdot 10^{-7}\, m)^2\right) \cdot 2 + \pi \cdot 1.2 \cdot 10^{-7}\, m \cdot 1.5 \cdot 10^{-8}\, m = 2.83 \cdot 10^{-14}\, m^2 \quad (S6\text{-}2)$$

5. Total surface area of <u>plate-like shaped</u> Si NPs $S_{Si,total}$ in the sample

$$S_{Si,total} = N_{Si,total} \cdot S_{Si,particle}$$
$$S_{Si,total} = 1.26 \cdot 10^{14} \cdot 2.83 \cdot 10^{-14}\, m^2 = 3.58\, m^2 \quad (S7\text{-}2)$$

6. Total surface area of Gr particles $S_{Gr,total}$ in the sample

$$S_{Gr,total} = S_{Gr} \cdot m_{Gr}$$
$$S_{Gr,total} = 2.89\, m^2 \cdot 0.95 = 2.75\, m^2 \quad (S8\text{-}2)$$

7. Total surface area S_{total} in the sample

$$S_{total} = S_{Gr,total} + S_{Si,total}$$
$$S_{total} = 2.75\, m^2 + 3.58\, m^2 = 6.32\, m^2 \quad (S9\text{-}2)$$