Silizium basierte Nanopartikel als Speichermaterial für Lithium Ionen Zellen

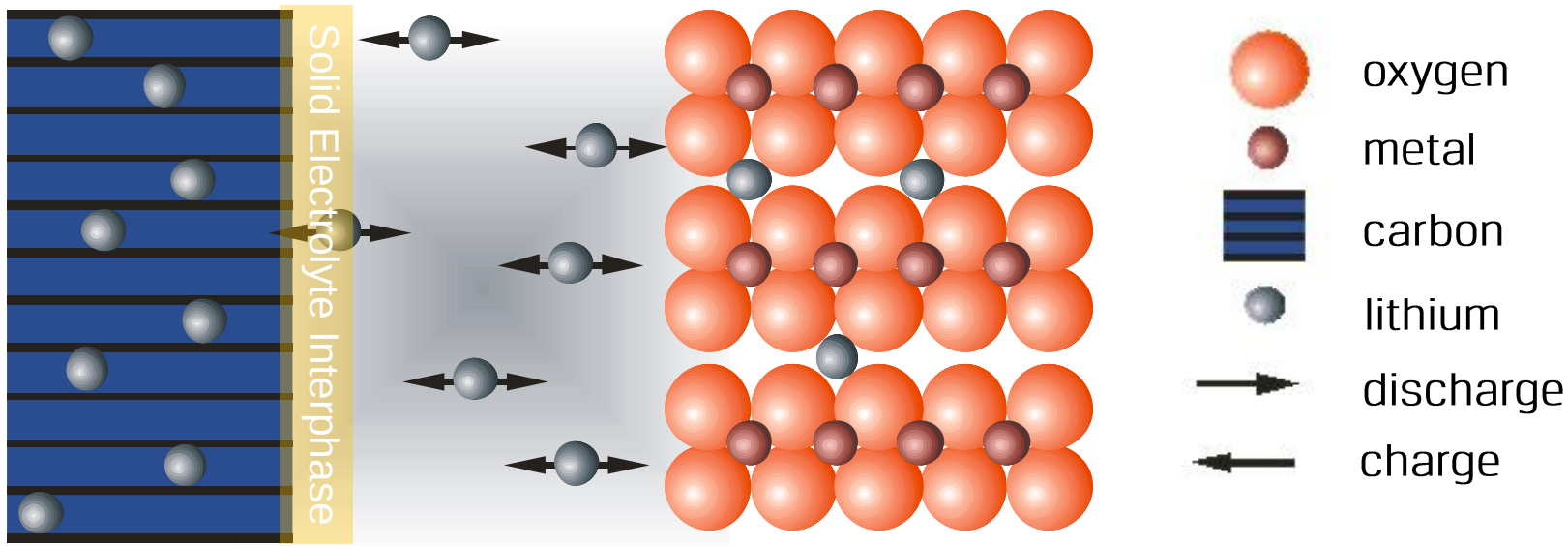
FachDialog - Chancen und Risiken der Anwendung von Nanotechnologien im Automobilsektor

Berlin, 27. September 2017

The Lithium Ionen Battery

$$Li_xC_n \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} C_n + x\,Li^+ + x\,e^-$$

$$Li_{1-x}MO_2 + x\,Li^+ + x\,e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} LiMO_2$$



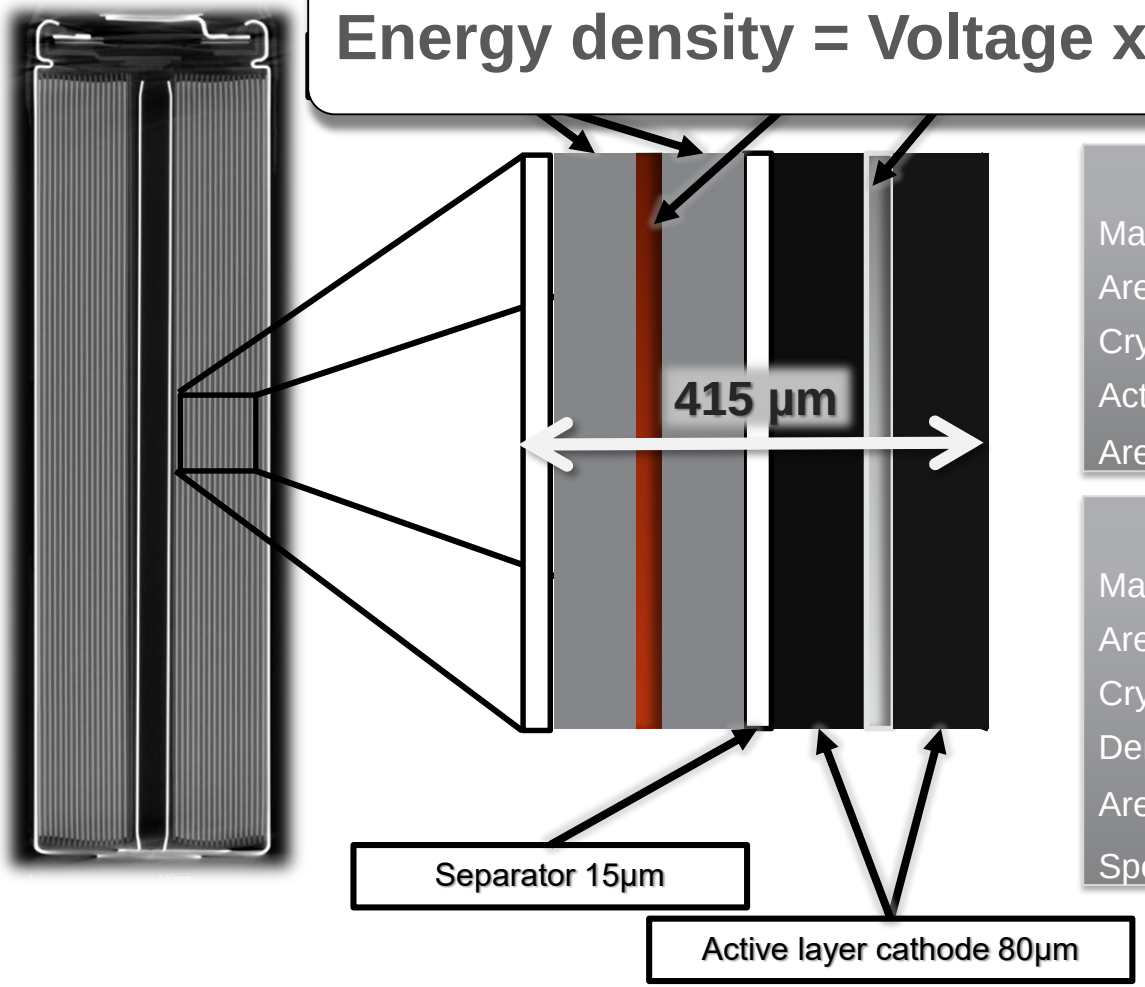
negative electrode **electrolyte** **positive electrode**

$$Li_{1-x}MO_2 + Li_xC_n \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} LiMO_2 + C_n$$

18650 Zelle **<u>1991</u>**: **<u>1Ah</u>** ⟶ **<u>2017</u>**: **<u>3.5Ah</u>**

Benchmark Energy Cell: Panasonic NCR 18650 B

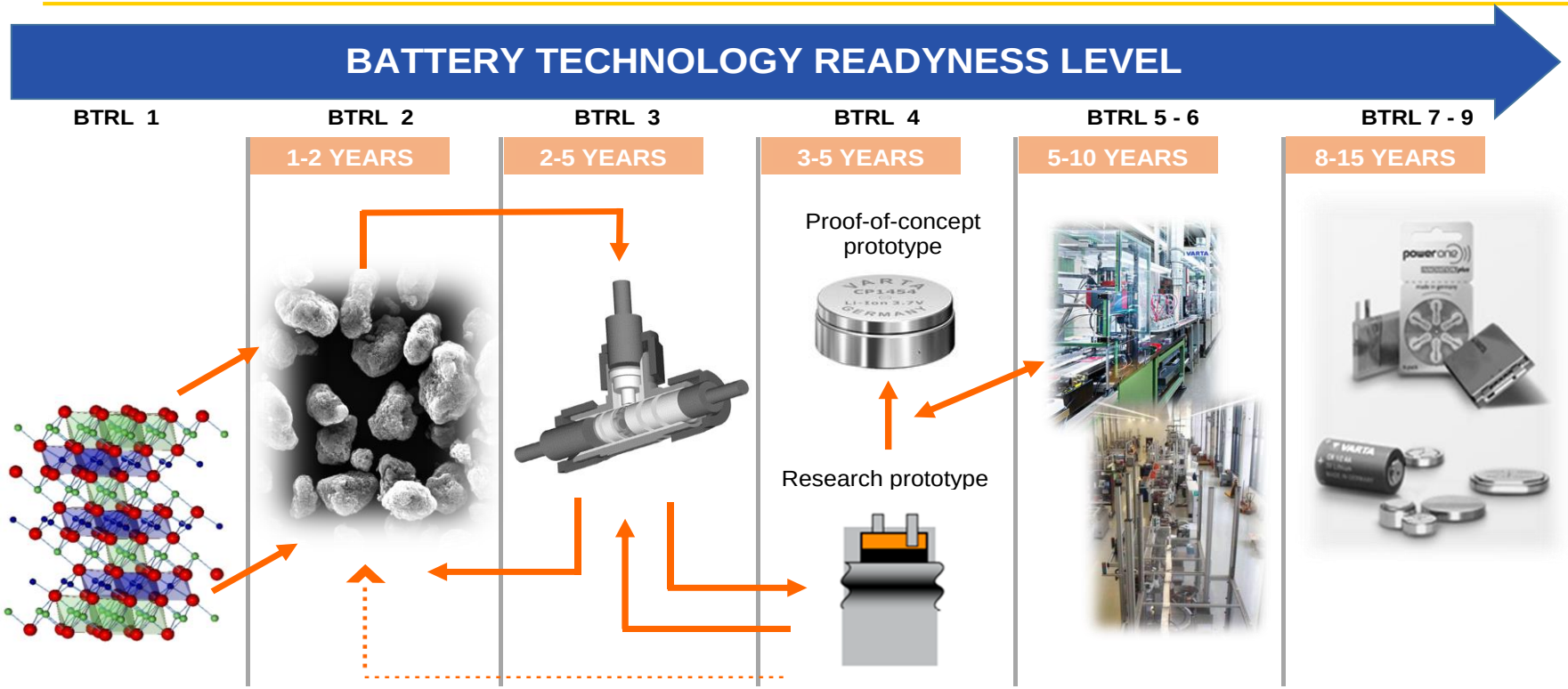
Energy density = Voltage x Charge density



Negative Electrode Panasonic	
Material	graphite
Area spec. mass [mg/cm²]	16,3
Crystal density [g/cm³]	2,26
Active layer density [g/cm³]	1,7
Area spec. capacity [mAh/cm²]	~5,5

Positive Elektrode Panasonic	
Material	NCA
Area spec. mass [mg/cm²]	26,8
Crystal density [g/cm³]	4,45
Density [g/cm³]	3,4
Area spec. capacity [mAh/cm²]*	4,9
Specific capacity [mAh/g]	~185

Battery Innovation Process



Scientific Breakthrough	New class of materials synthesized	Proven performance in half cells	Proven performance in lab-scale fulls cells	Material scale-up, cell testing and scale-up to pack	Product qualification Marked launch

Research Institutions
(Universities,
non-profit Research Organisations)

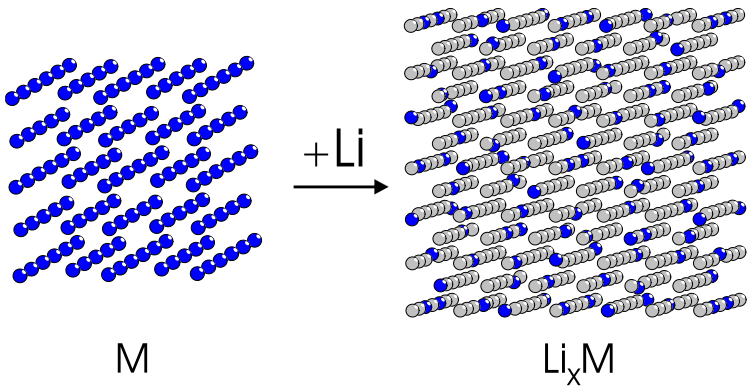
VARTA Advanced Development (VMI)

VARTA Product development

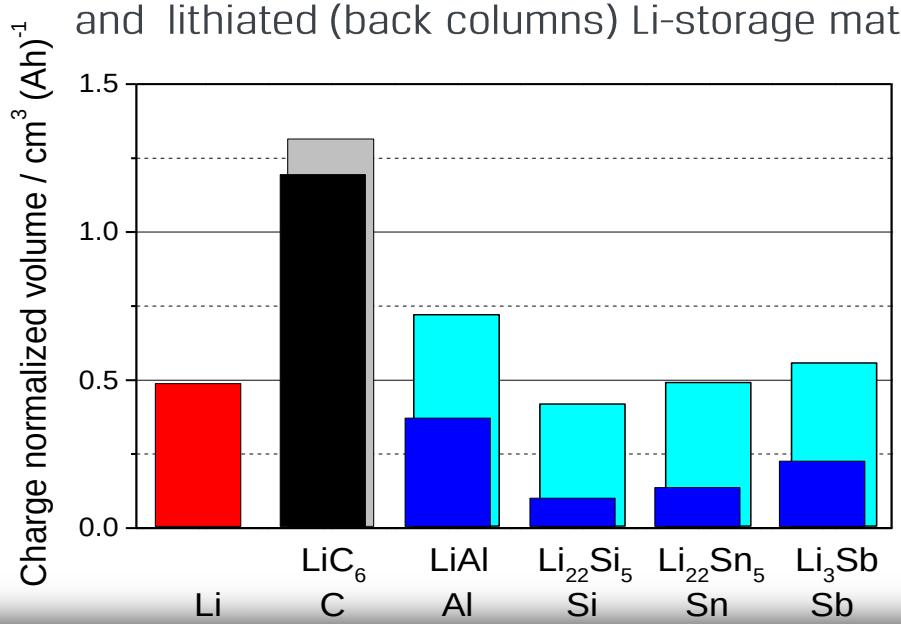
High Capacity → High Volume Changes

Reversible formation of intermetallic phases with Li ("Li-alloys"):

$$Li_xM \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} M + x\,Li^+ + x\,e^-$$



Charge Normalized Volumesof unlithiated (front columns and lithiated (back columns) Li-storage materials



Charge Densities:

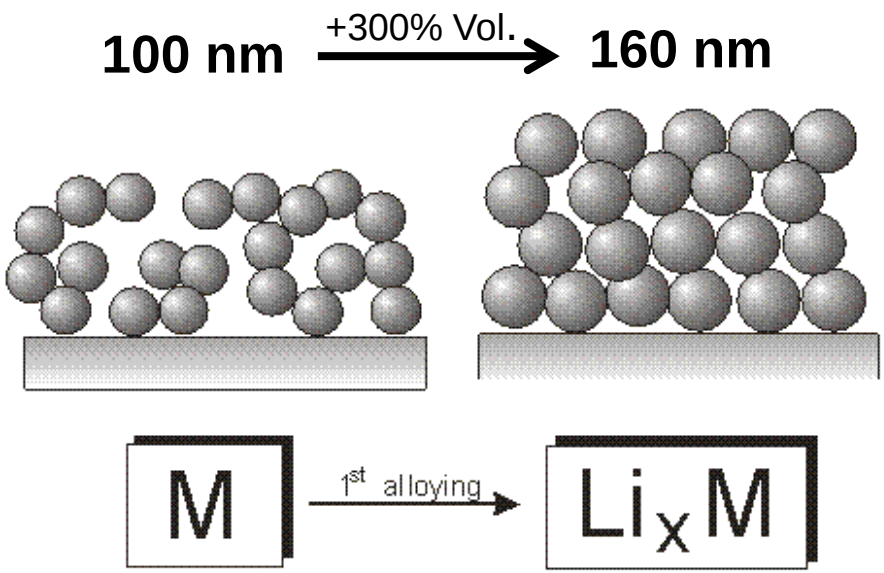
LiC_6:	759 Ah/L
LiAl:	1.8 x larger
Li_3Sb:	2.5 x larger
$Li_{22}Sn_5$:	2.7 x larger
$Li_{22}Si_5$:	3.1 x larger

→ Structural measures to overcome stability problems

Structural Measures to Improve Cycling Stability

"Going Nano" (1)

Small absolute volume Changes,
even when relative Volume changes are still large



(1) J.O. Besenhard, J.Yang, M. Winter, Journal of Power Sources, 68, 1997

Nano Materials – Good cycling stability but

Thin film electrodes

- ✘ Unfavourable ratio of active to inactive material

Nano structured materials
(e.g. particles, wires, etc.)

- ✘ High electrode porosity → low charge densitiy ($Ah \cdot L^{-1}$)
  → high surface area = large irreversible capacity

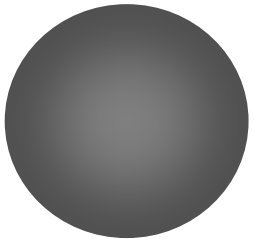
- ✘ Costs!? (Average anode material is ≈ 6% of the total cell cost)

- ✘ Potential safety and health risks

Candace K. Chan et. al., Nature Nanotechnology ,VOL 3 , (2008) 32

Desired Silicon based active material

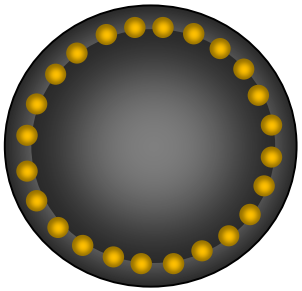
State of the Art
Graphite



372 mAh · g^{-1}

4 times more capacity
similar rate capability

Concept for an
Silicon/Graphite Composite



1500 mAh · g^{-1}

Desirable properties

- adjustable silicon content and therefore adjustable capacity
- Carbon coating to achieve a reasonable rate capability
- Suppression of continuous SEI formation trough minimization of electrolyte contact of silicon
- Similar particle size compared to graphite enabling easy implementation into the manufacturing process

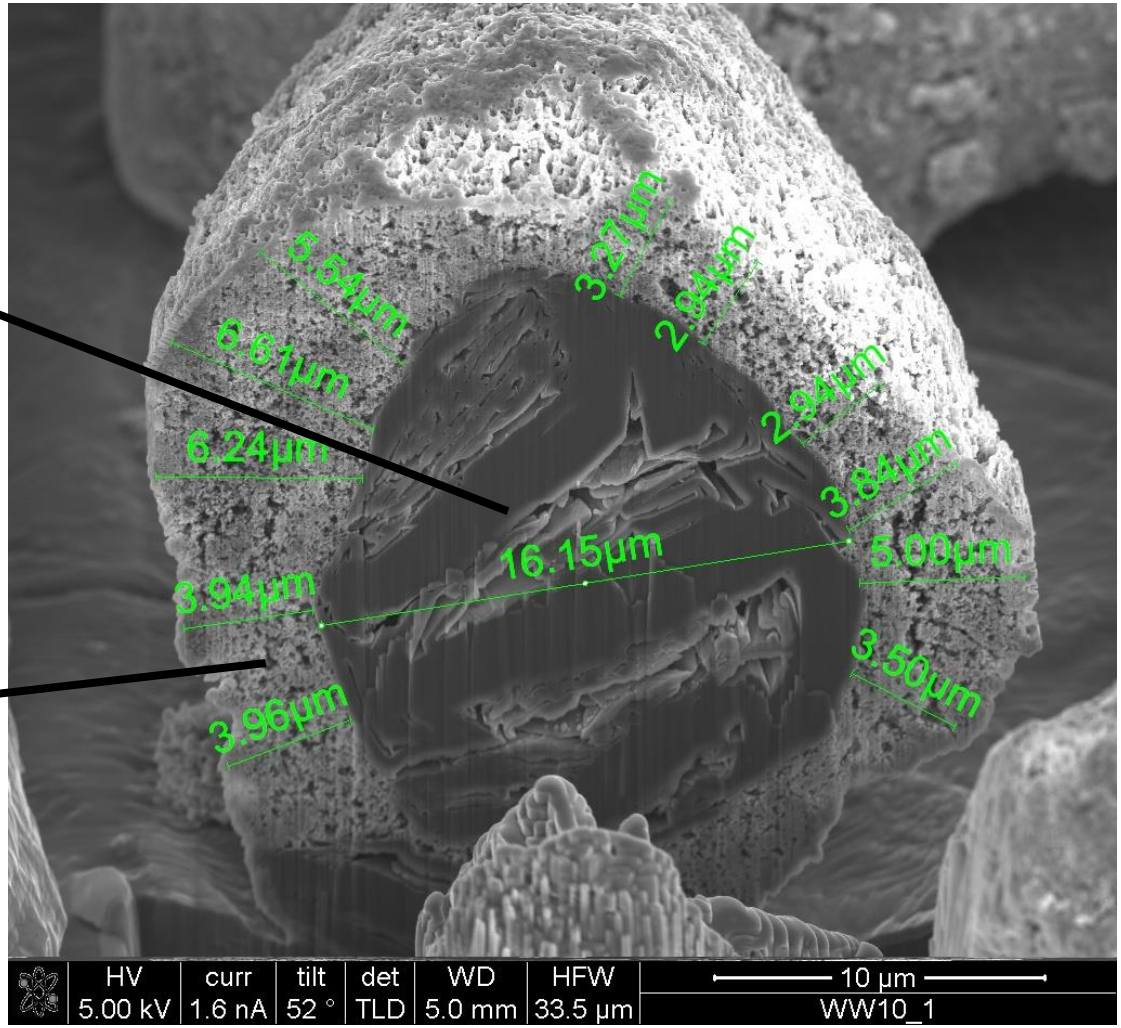
VMI Silicone/Graphite Composite

Core

→ natural graphite

Shell

→ silicon nano particles (50nm) embedded in amorphous carbon

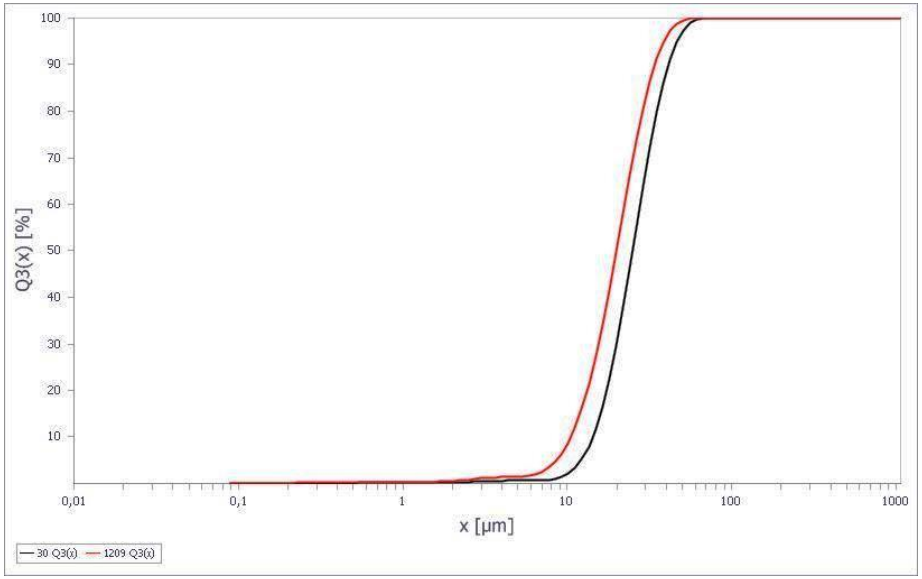


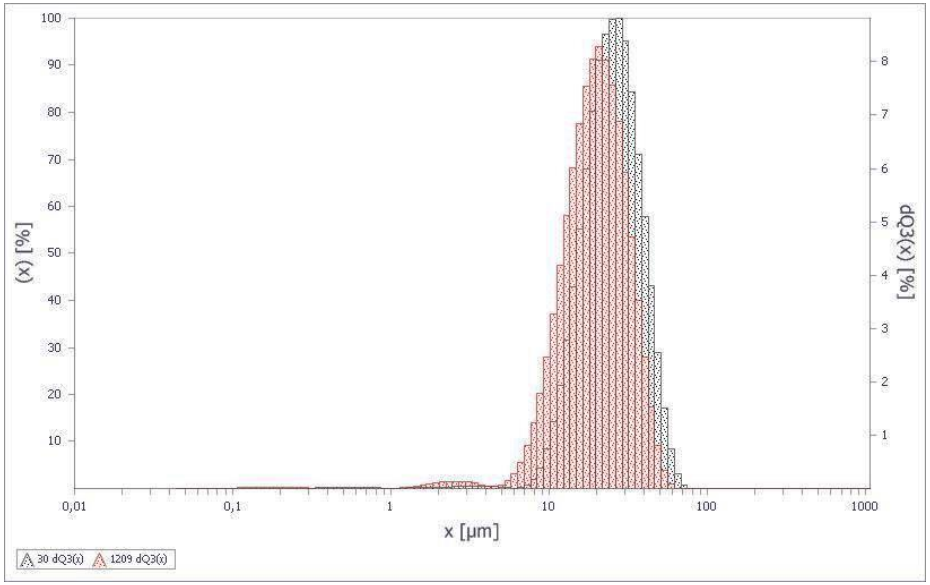
VMI Silicone/Graphite Composite - Particle Size Distribution

- Increase of average particle size from

$$d50_{Graphit} = 19\ \mu m \rightarrow d50_{Si/C\text{-}Komposit} = 25\ \mu m$$

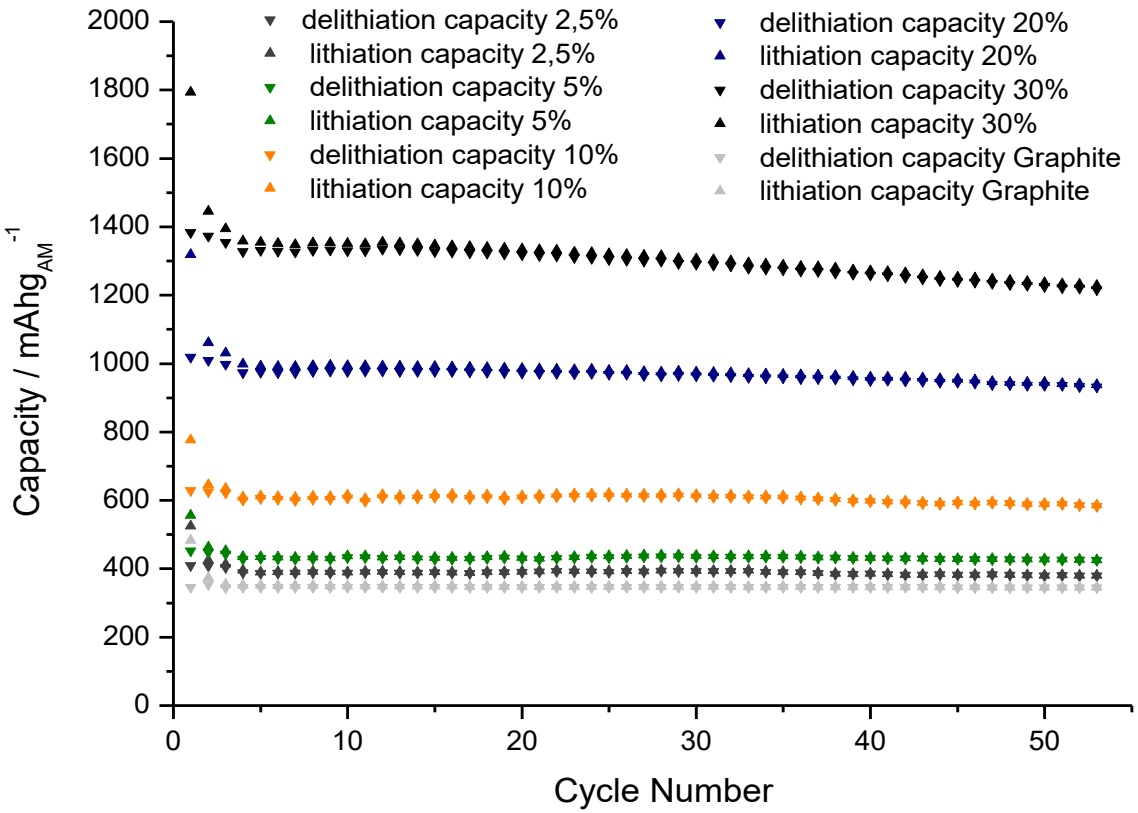
- Homogeneous coating process leads to equal particle size distribution





VMI Silicone/Graphite Composite - Specific Capacity vs. Cycling Stabiltiy*

→ Adjustable silicon content results in different capacities



Silicon content

30% Si → 1400 mAh·g^{-1}

20% Si → 1012 mAh·g^{-1}

10 % Si → 750 mAh·g^{-1}

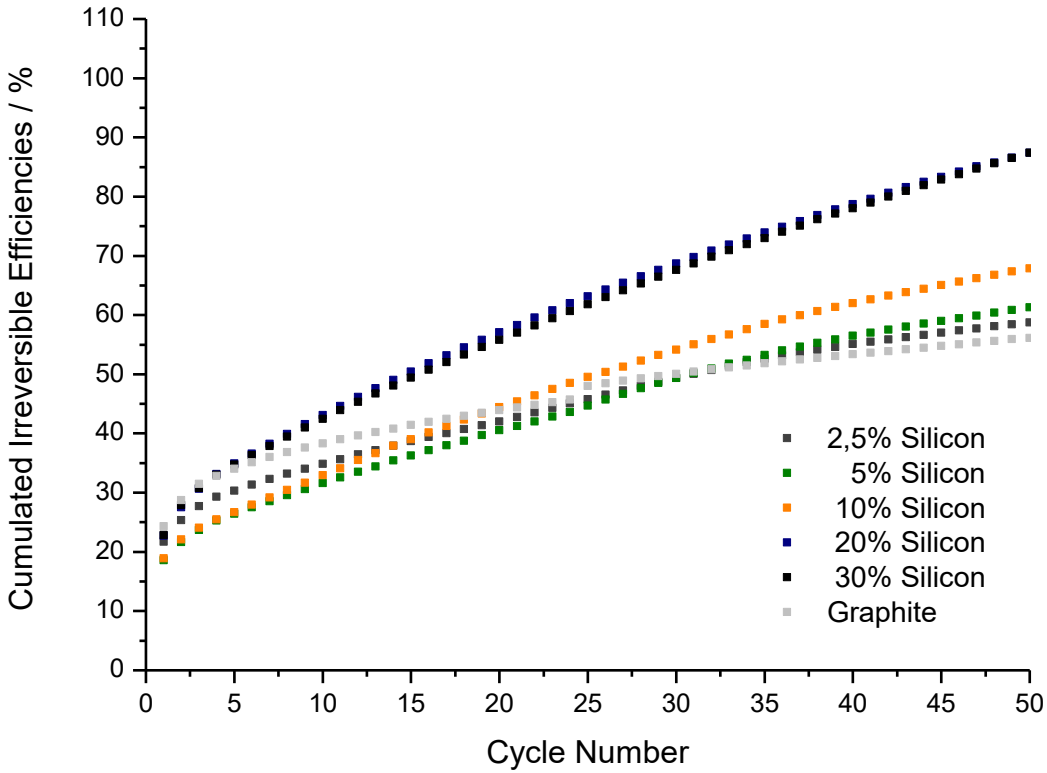
5% Si → 550 mAh·g^{-1}

2,5% Si → 450 mAh·g^{-1}

*Swagelok cell vs. metallic lithium

VMI Silicone/Graphite Composite - Silicon Content vs. Irreversible Capacity*

Influence of BET surface area on cumulated irreversible capacity

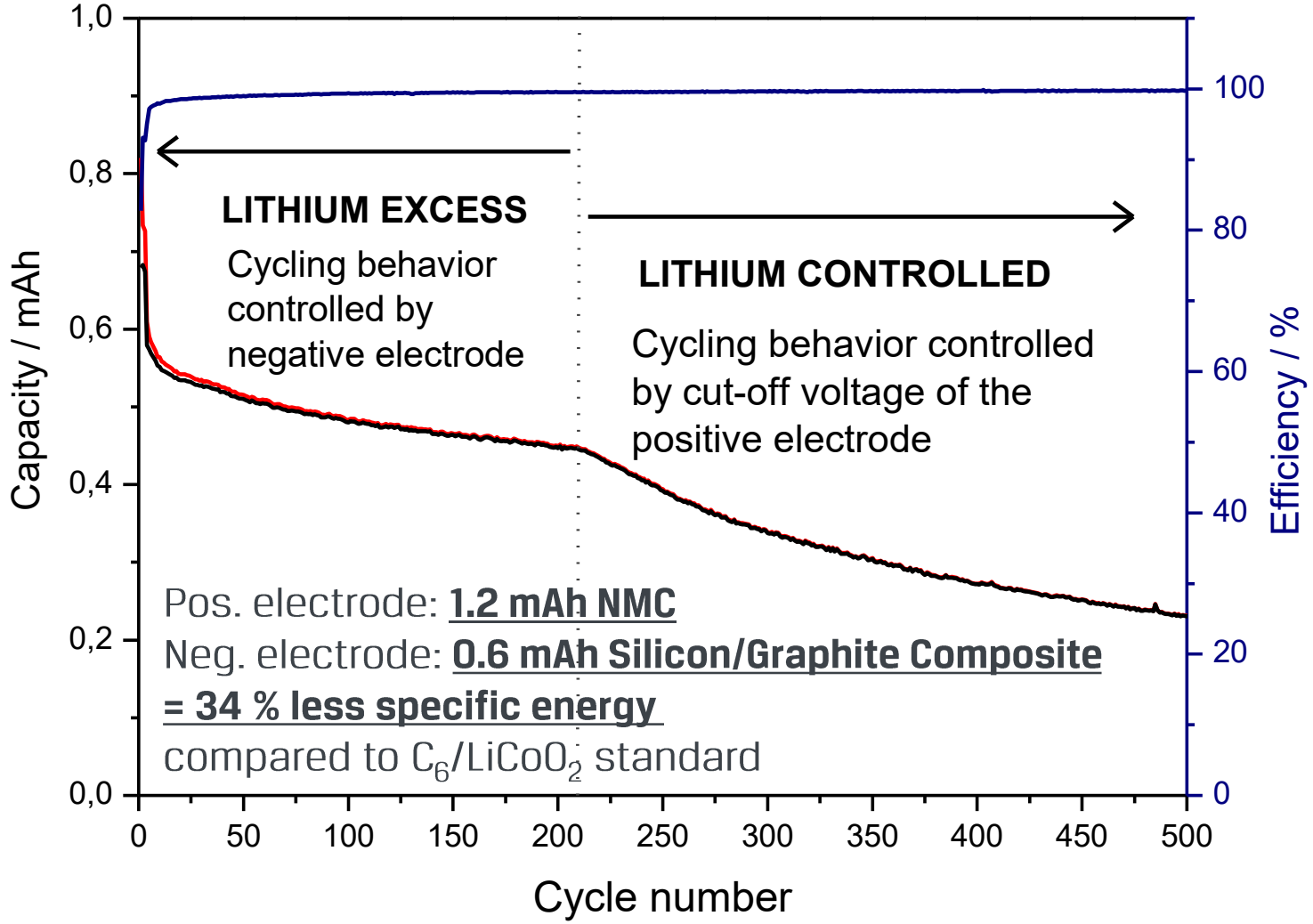


Dependence of BET surface area on silicon content

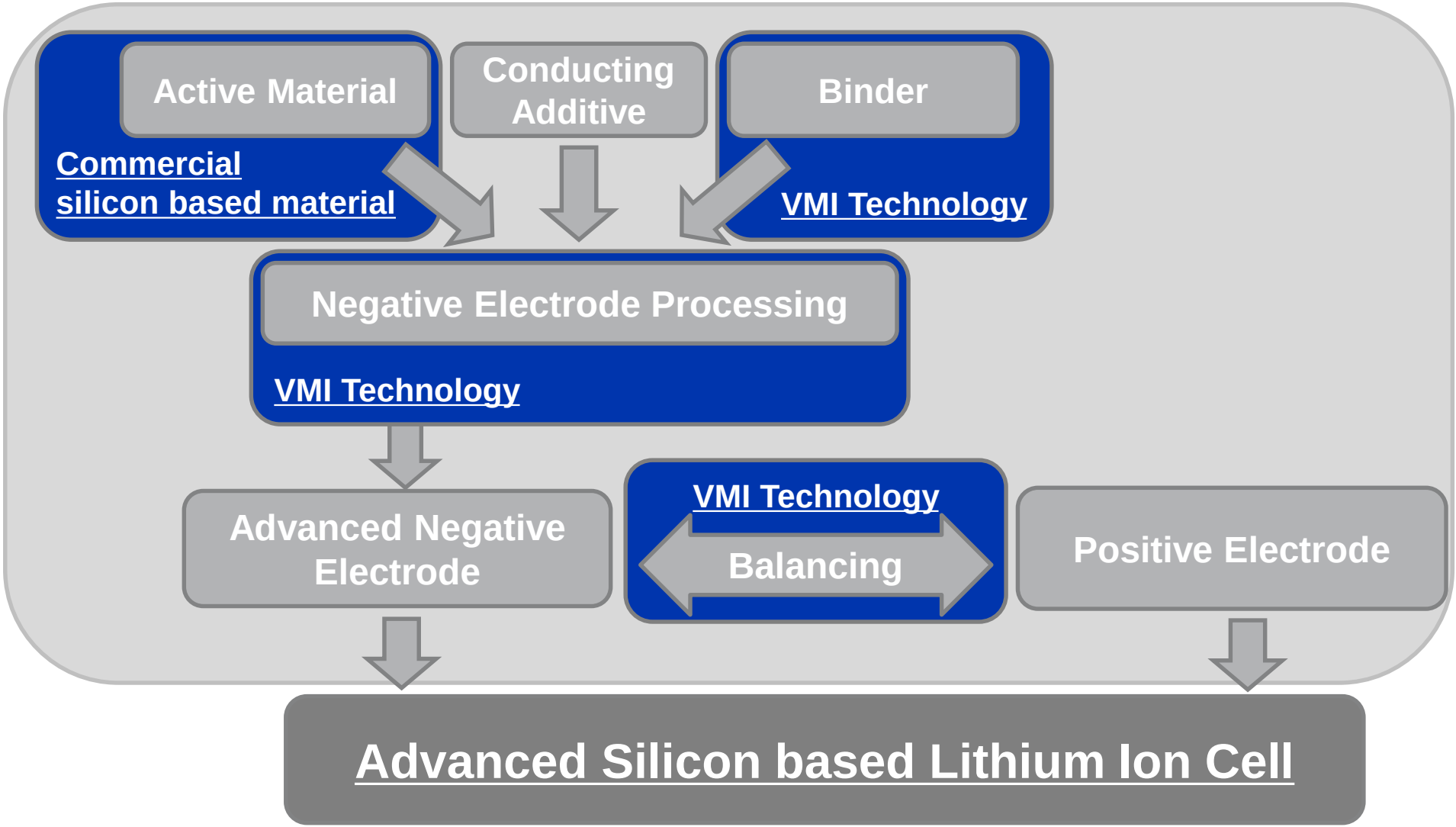
Name	BET [m^2/g]
Graphite	4,85
2,5% Si	5,96
5% Si	8,31
10% Si	11,87
20% Si	21,33
30% Si	26,14
nano Si	63,04

*Swagelok cell vs. metallic lithium

Silicon/Graphite Composite vs. NMC



Implementation Strategy: Silicon Based Electrode Materials



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Thanks for your Attention!