17th – 18th May 2022 Valencia (Spain)

# Electromobility Technology Workshop:

## Driving a Greener Value Chain

by i-HeCoBatt

## *Exploring the promise of silicon anodes*

nanomakers

TITLE: Dr.
SPEAKER: Warda Hadouchi

i-HeCoBatt

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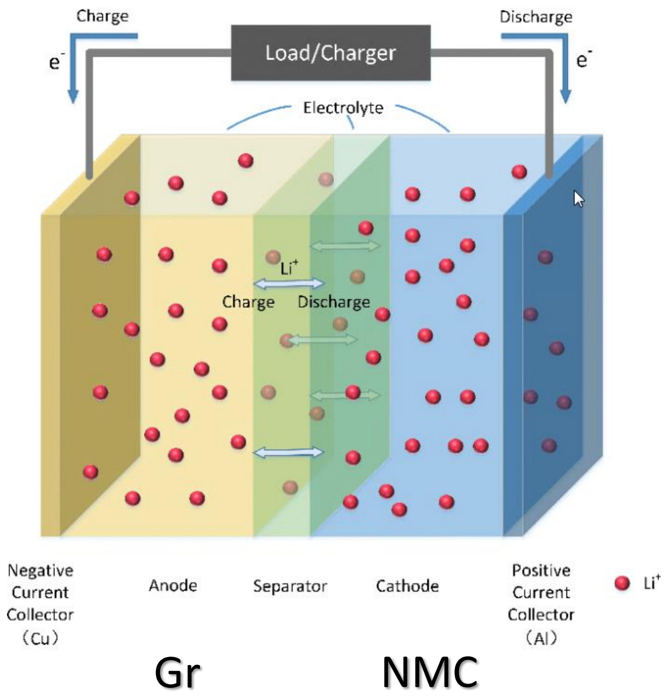
hosted by LOMARTOV [Applied Innovation Engineering]

# Context



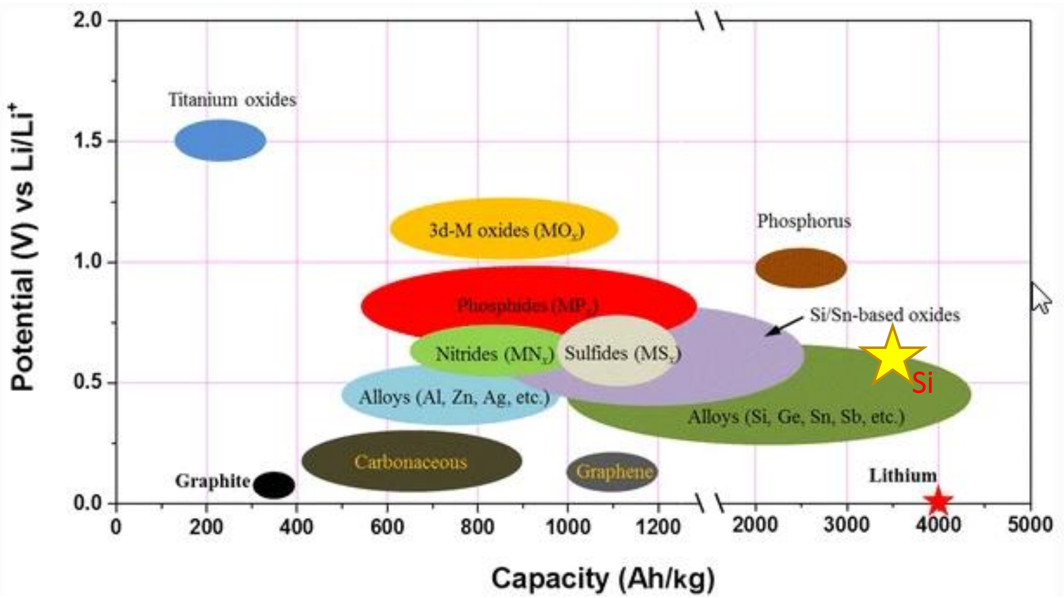

Development of electric vehicle→ need more autonomy at low cost

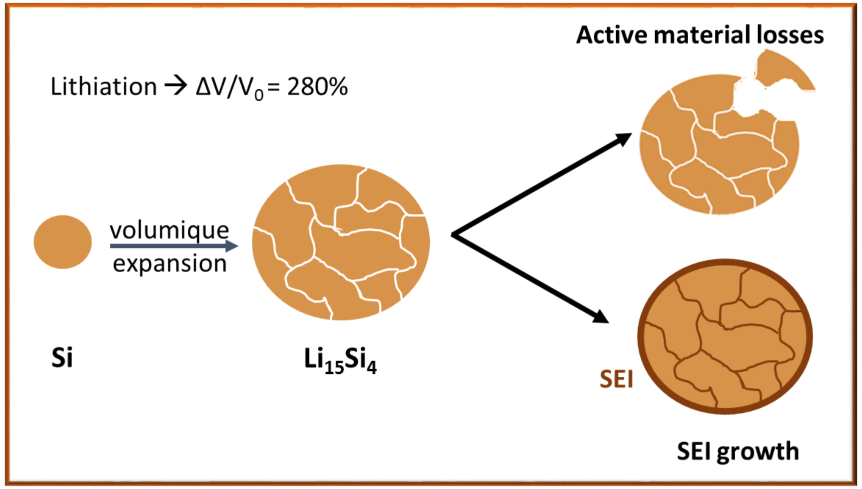
- Strong demand for innovation with major R&D efforts aiming at:
  i. **improving density** (autonomy)
  ii. improving **lifetime**
- Technical improvements have mainly taken place on the cathode material so far
- Industry research efforts currently cast on **improving anode capacity** using **silicon** instead of graphite, multiplying energy storage

# Silicon as anode material

+
- High specific capacity 3570 mAh/g for **$Li_{15}Si_4$**
- Low voltage ~0,5/Li/Li

–
- **Large volume expansion during cycling +280 %**
  - → material decohesion , cracking and decripitation
  - → loss of electronic connectivity and mechanical integrity
- **SEI**
  - → gradual electrolyte and lithium consumption
  - →Inherent non-passivating behaviour



# Silicon anode on the market

Due to capacity losses
→ Limitation of $SiO_x$ content in commercial cells (1-5%)

**Samsung SDI[a] :**

- *INR18650-32E* (100% Gr) → 238 Wh/kg
- *INR18650-35E* (1,5% SiOx) → 250 Wh/kg

**LG Chem[b]**

- *INR18650 MJ1* (3% SiOx) → 260 Wh/kg

↗ Energy density → ↗ Si content in anode

*Solving the cracking and SEI instability issues are* ***key enablers*** *for the* ***commercialization*** *of* ***new generation*** *Li-ion* ***batteries : Si/C composite***

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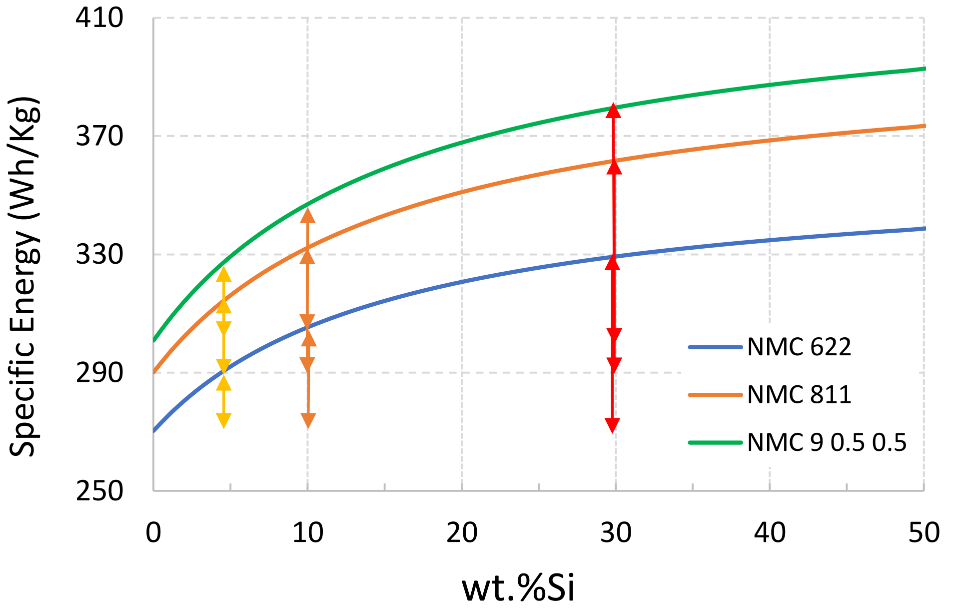
*(a) Kuntz et al. Identification of Degradation Mechanisms by Post-Mortem Analysis for High Power and High Energy Commercial Li-Ion Cells after Electric Vehicle Aging. Batteries 2021, 7 (3), 48.*

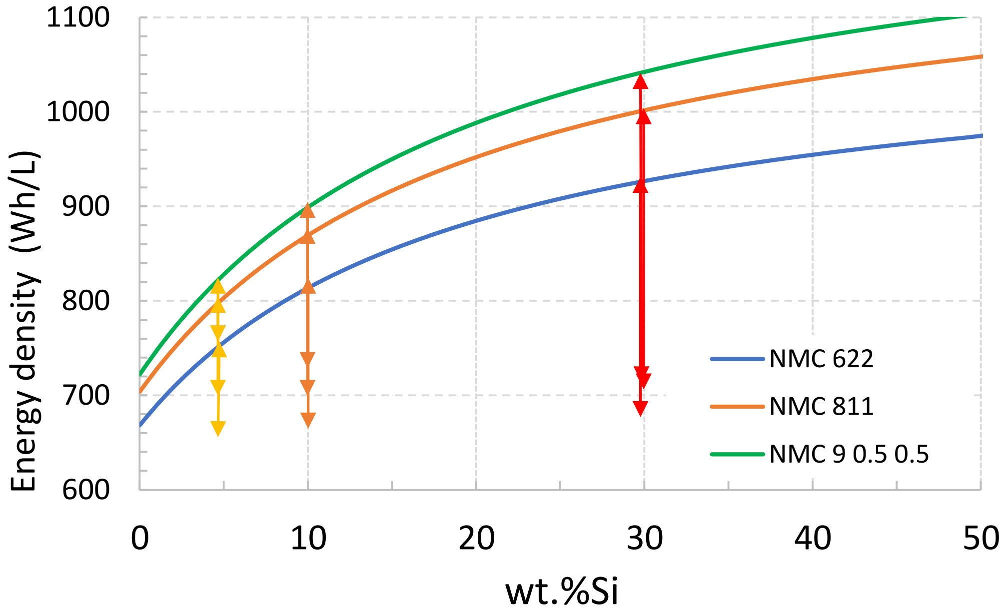
*(b) Li et al. Degradation Mechanisms of High Capacity 18650 Cells Containing Si-Graphite Anode and Nickel-Rich NMC Cathode. Electrochimica Acta 2019, 297, 1109–1120.*

# Modelization: influence of silicon content in the anode

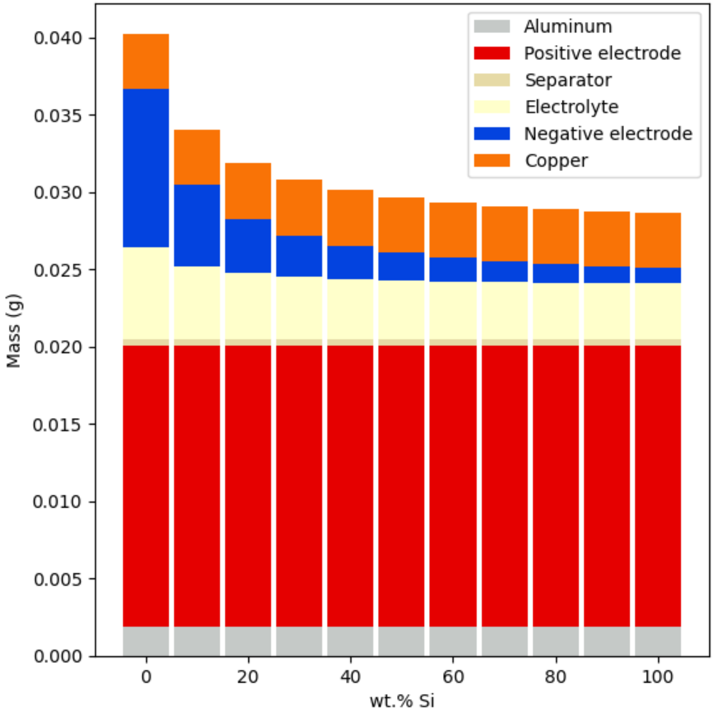
5%Si → +7 to 9%   10%Si → +11 to 13%   30%Si → +18 to 21%

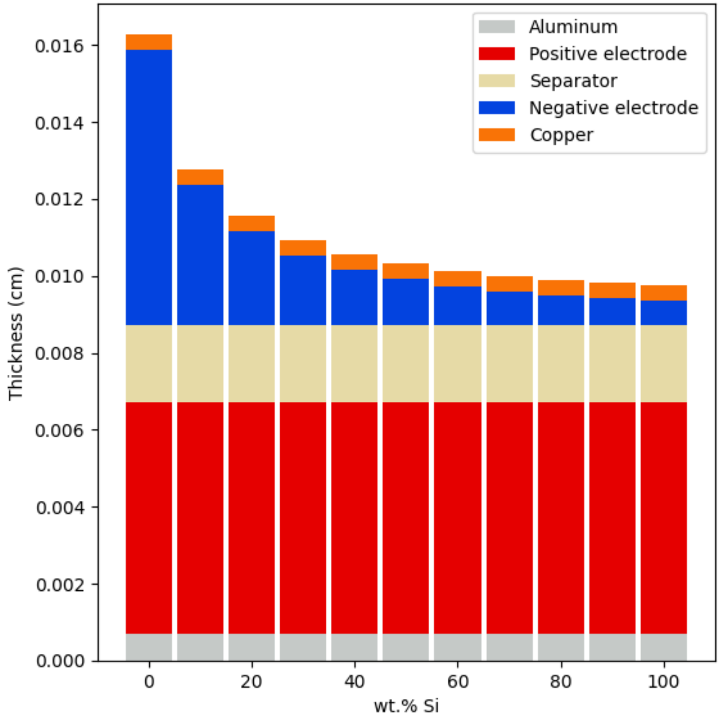



5%Si→ +11 to 13%   10%Si → +18 to 22%   30%Si → +28 to 30%



# Modelization: influence of silicon content in the anode

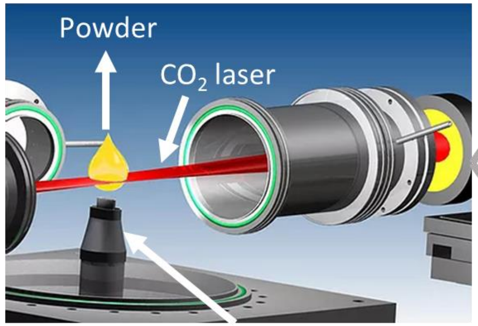



- Mass and thickness ↘ when wt.%Si/anode ↗
- For wt.%Si > 30 %, impact of Si content not interesting

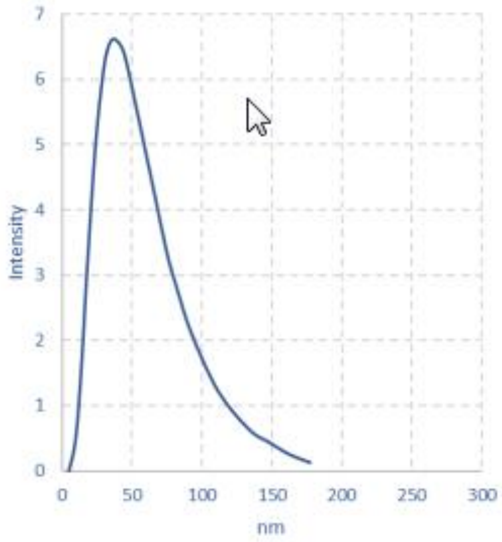
# Silicon nanoparticles synthesis by industrial process: **Laser pyrolysis**

*Laser pyrolysis*



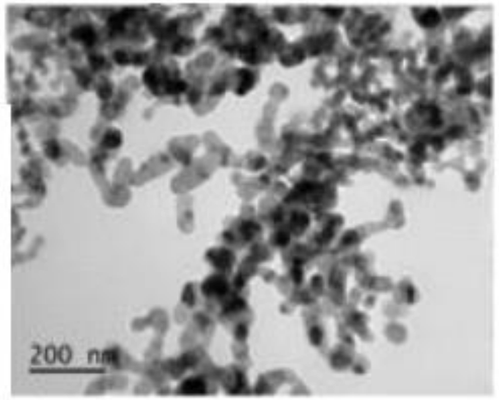

**Reagents**: $SiH_4$, puis $C_2H_2$

**Particle size disribution**

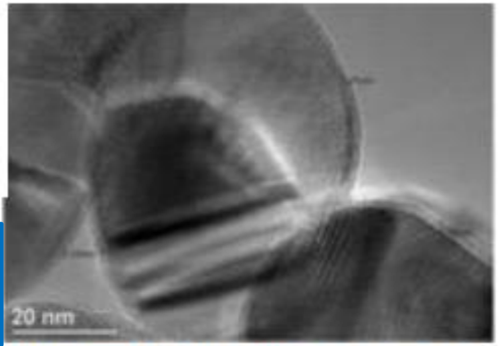



- Good size distribution
- Crystalline Si nanoparticles (ø=40 nm)
- Low oxygen content (< 5 wt.%)

**TEM / HRTEM ANALYSIS**




Sample TEM picture




Uniform carbon coating = 1 - 2 nm

**Carbon coated Silicon**

NMSiΩC99

| Strict crystal growth & size control | Bottom-up process |
|---|---|
| **Homogeneous** | **Highly pure** |
| Unique industrial practice | Adaptability to customer's needs |
| **Reproducible** | **Customizable** |

**Carbon** shell :

1. **protects Si** from direct **electrolyte** exposure,
2. **favors** the creation of a **stable SEI** layer, and
3. improves the **affinity of Si** with most **graphites** and **binders** (CMC, PAA…).

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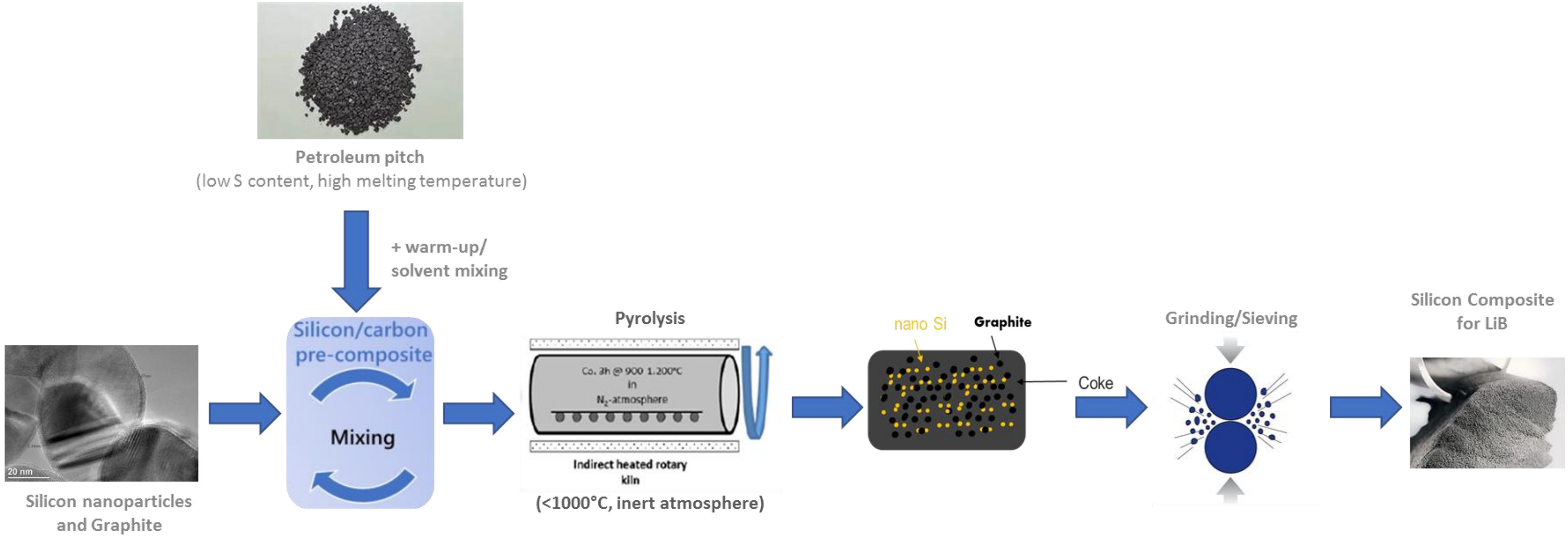
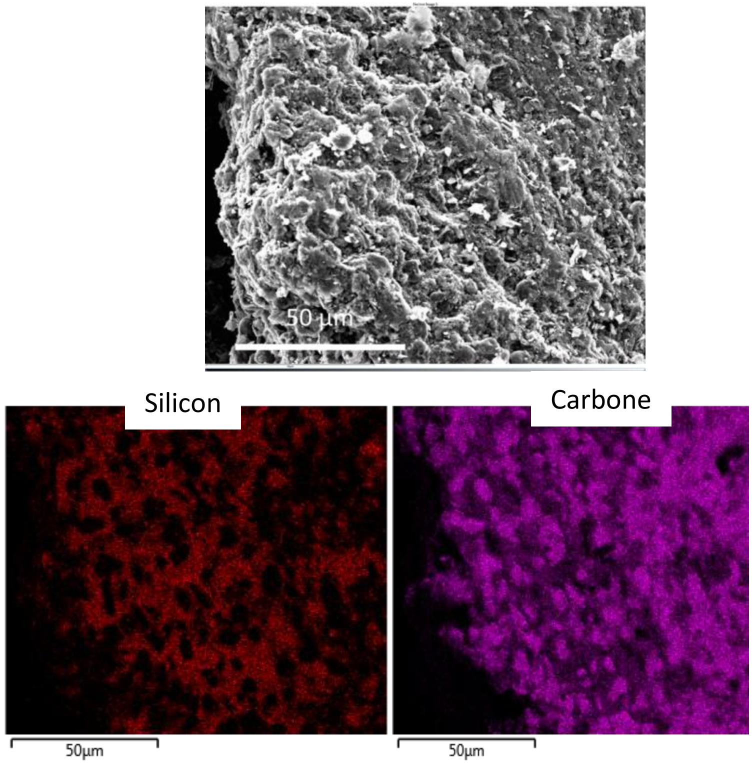
# Silicon/carbon composite synthesis by R&D process: Thermal pyrolysis

- Is not industrial process
- Development of formulation and guidelines for customer




EDX /TEM

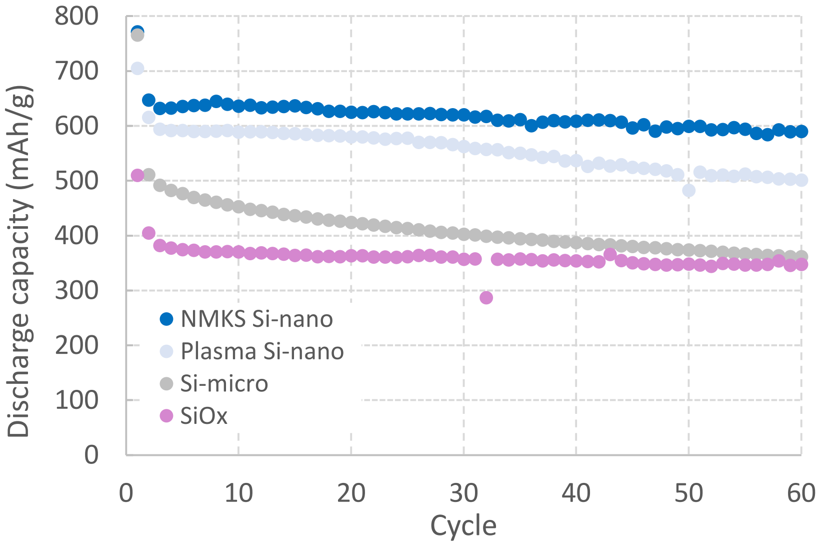


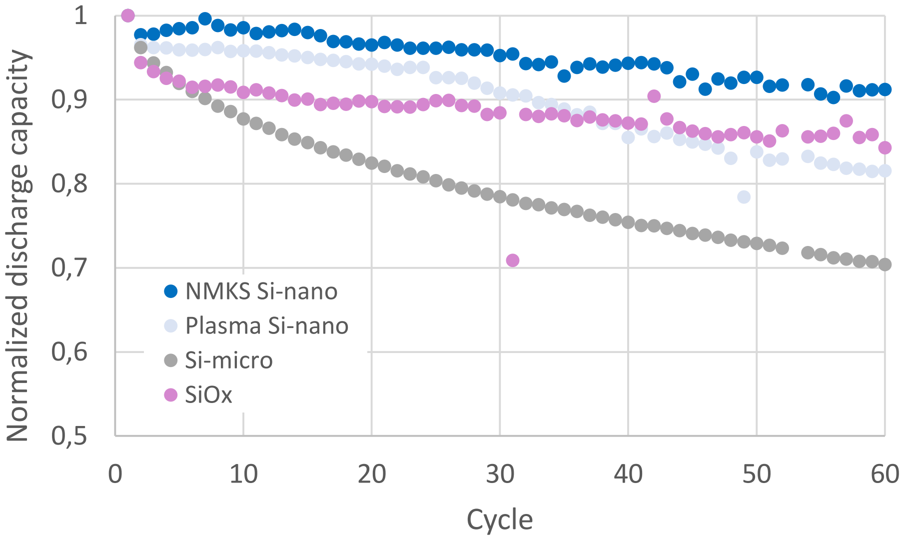

Good distribution of Si in the carbon matrix

Good process reproducibility

# Influence of different Si/C composite grade on electrochemistry performances

**Composite**: 7wt% Si/93 wt% coke




| | ICE (%) |
|---|---|
| NMSiΩC - 40 nm | 83 |
| Si plasma - 88 nm | 86 |
| µm si | 72 |
| SiOx | 76 |

- Half cell: Si/C vs. Li [10 mV and 1.5 V ]
- First cycle at C/20 then C/5
- Electrolyte: 1M $LiPF_6$ EC:PC:DMC (1:1:3) + 1 wt% VC and 5 wt% FEC
- Formulation: 80/2,5/2,5/15 composite/VGCF/$C_{45}$/CMC

➢ Best performances for NMSiΩC-40 nm (capacity and retention)
→ C-coating and particles size reduce cracking and SEI formation
➢ Good stability for SiOx but low capacity

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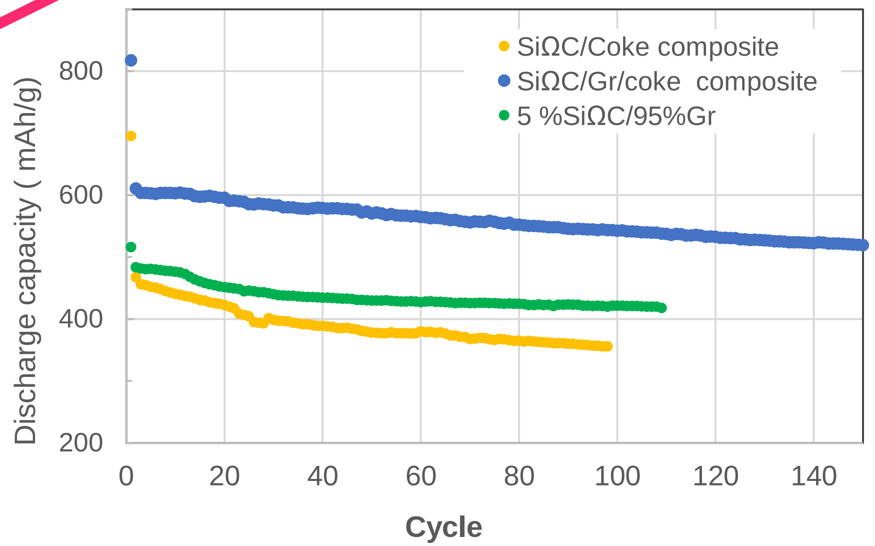
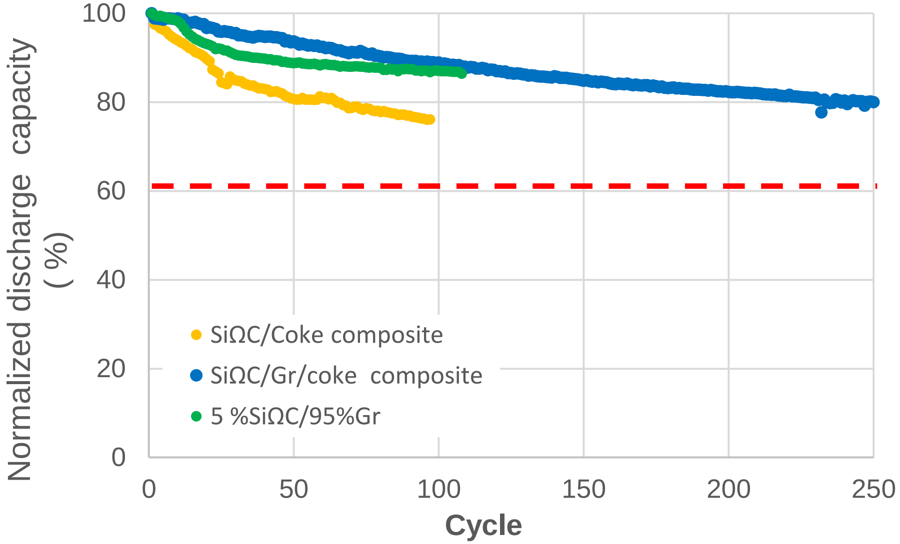
# Presence of Graphite in Silicon anode




**Composite:** [(a)]

- SiΩC/Coke → 12 wt.% / 88 wt.%
- SiΩC/Coke/Gr → 12 wt.% / 28 wt.% / 60 wt.%

- Half cell: Si/C vs. Li [10 mV and 1.5 V ]
- First cycle at C/20 then C/5
- Electrolyte: 1M $LiPF_6$ EC:PC:DMC (1:1:3) + 1 wt% VC and 5 wt% FEC
- Formulation: 80/2,5/2,5/15 composite/VGCF/$C_{45}$/CMC

- ➢ Addition of Gr in the composite ↗ ICE, capacity and improve the retention
- ➢ Carbon matrix → protects Si from direct contact with electrolyte and accommodates volume expansion

**Silicon content increase is possible by considering two key factors:**

→ The composition of the carbon matrix: important effect of the pitch on Si coating
→ An electrolyte more adapted to the chemistry of Silicon

*(a) Gutierez et al. Towards a better understanding of the degradation mechanisms of Li-ion full cells using Si/C composites as anode. Journal of Power sources. 2022..*

# Perspective: Nanomakers involved in Astrabat europeen project

**All Solid State** : Using NM SiΩC as main anode material combining with solid electrolyte and NMC cathode to make All Solid-State Battery.

Interest:

- Stabilize the SEI → limit Li comsumption
- Control silicon volume expansion
- Provide a safer system fo LiB
- Multiply speficic capacity

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# Thank you for your attention

For more question
Contact: whadouchi@nanomakers.fr