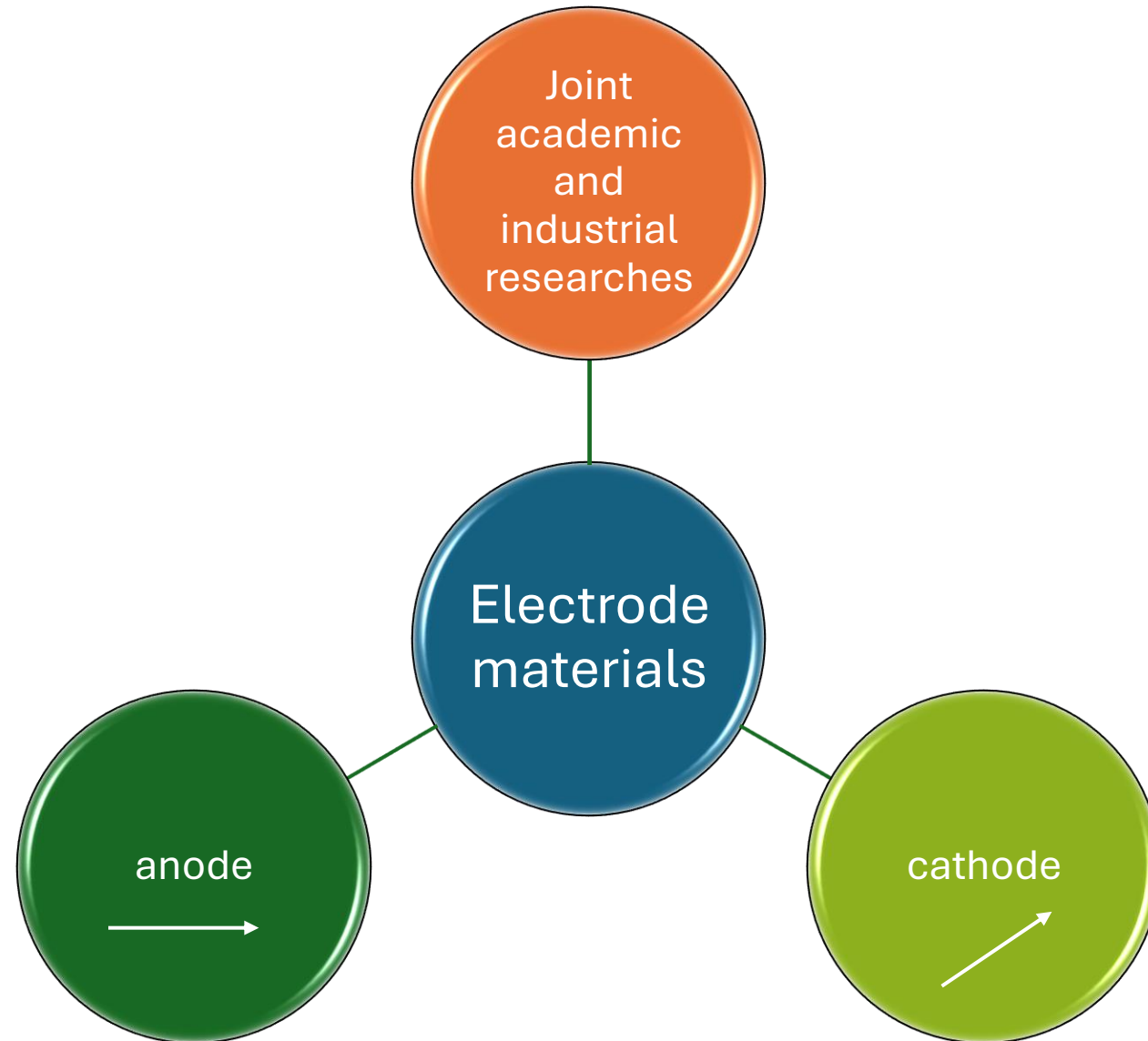


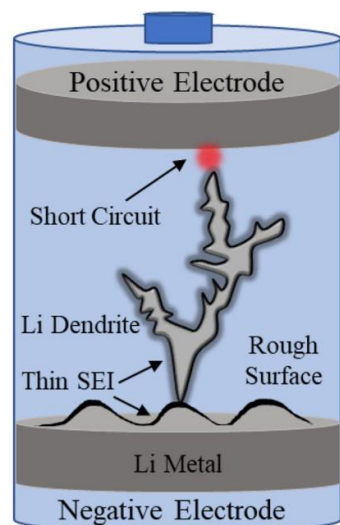


Dr. sc. Matea Raić,
professional advisor, Ruđer Bošković Institute
matea.raic@irb.hr

Advancements and Challenges of Silicon Anodes in Lithium-Ion Batteries



Nature offers us **two possibilities** for anode material:



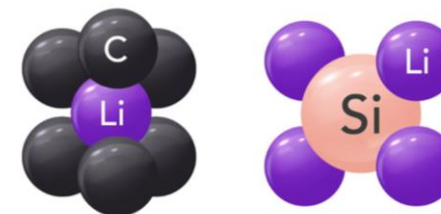
deposit lithium
as metal

- natural tendency to deposit in dendrites
- short circuit—and possibly a fire
- 1/1000000 cell need **fail** to force a recall



replacing
graphite with
silicon

1 Si atom – 4.4 Li $C_s = \mathbf{4200}$ mAh/g
6 C atoms – 1 Li $C_s = \mathbf{372}$ mAh/g



- 10-fold higher “specific capacity”
- an equivalent capacity anode will be thinner
- lower electrical resistance
- fast charge and discharge



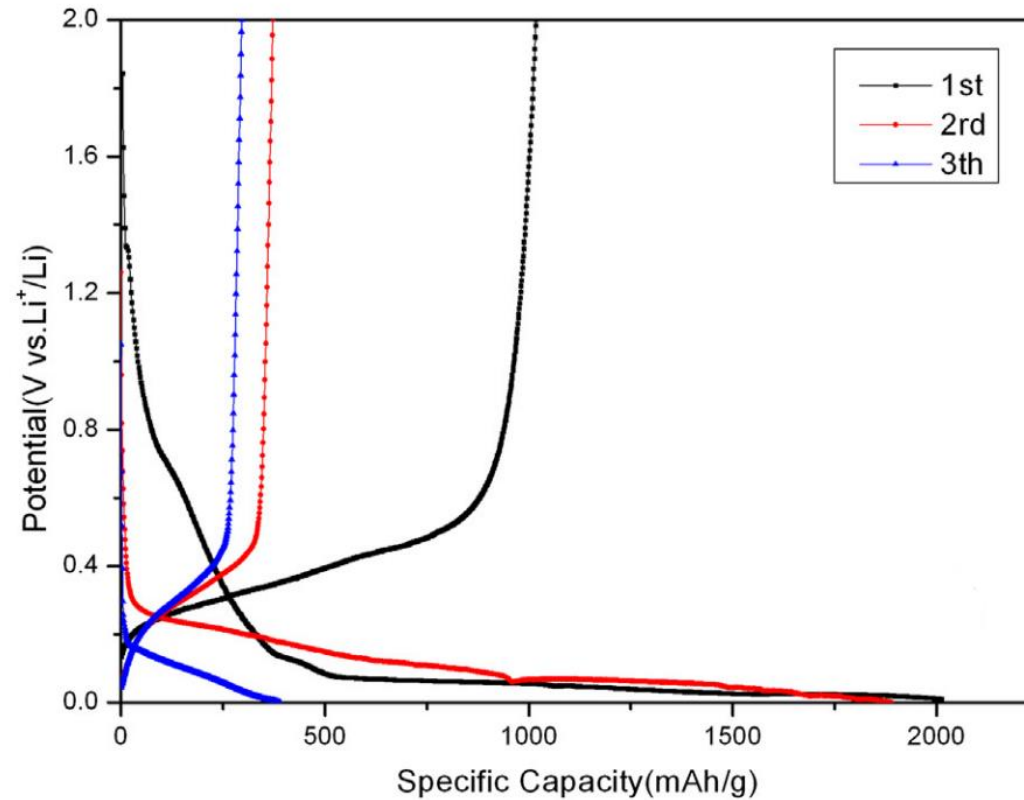
Recharge time ↓
Si cell widely regarded as a technology with $R_t < 10$ min

Cycle life?

Operation mechanism

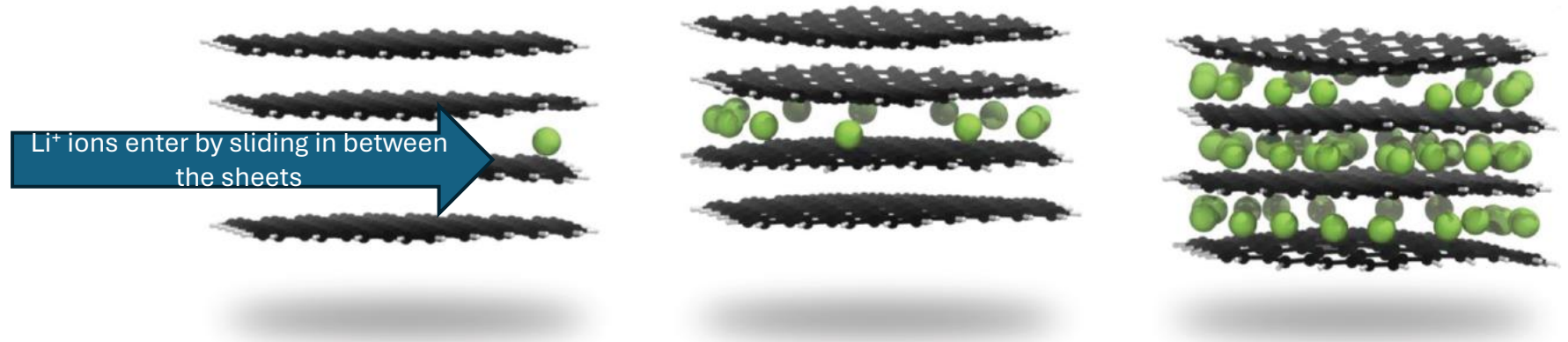
A graphite anode cell over **800** full charges.

Conventional silicon anodes
50-200 cycles.

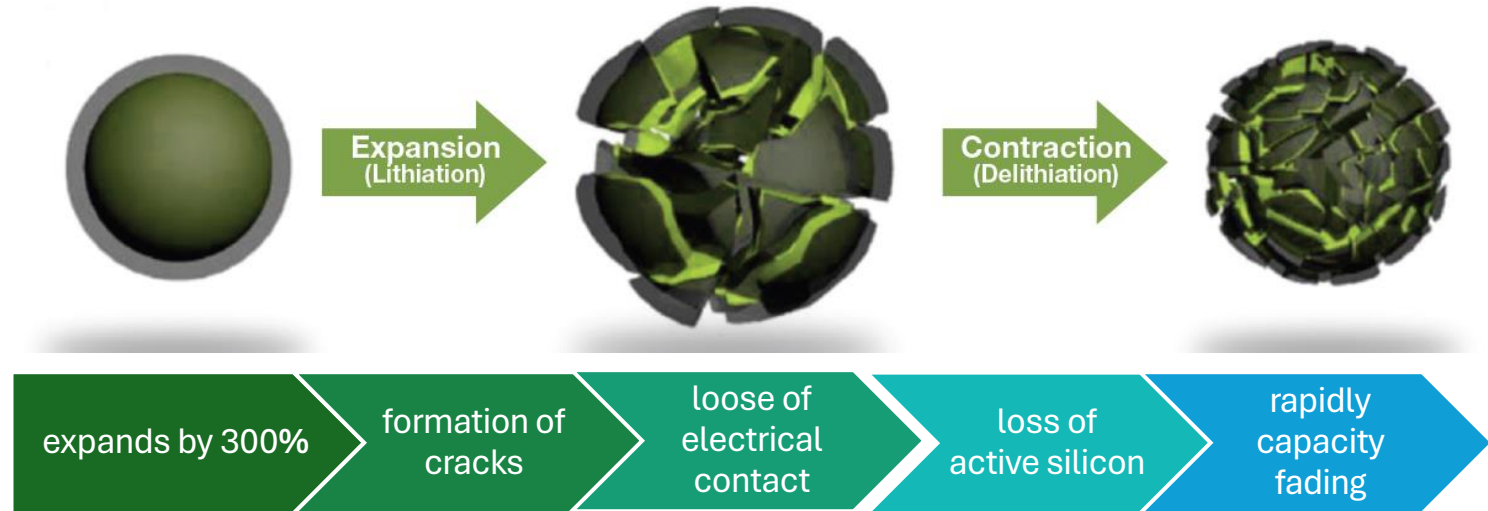
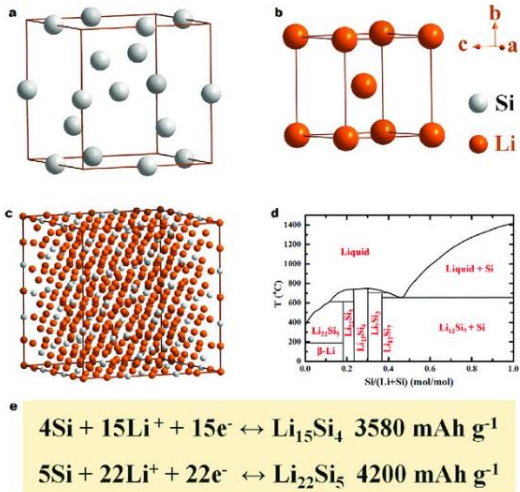


Initial capacity of nano silicon anode are **2013.8 mAh/g** and **1017.0 mAh/g**, respectively, the first columbic efficiency is only **50.5%** and the **specific capacity decays rapidly** in the following two cycles.

- Graphite's excellent reversibility
- "intercalation"** material
- expands by about 10%** when it's **fully lithiated** and then decreases back to its original size when delithiated.



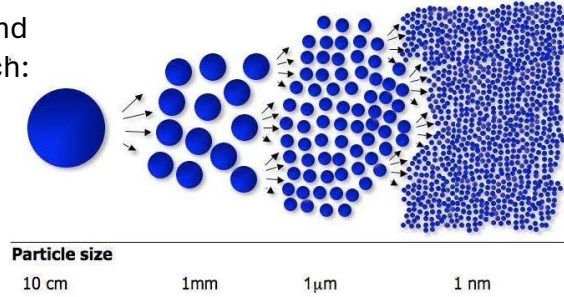
- Silicon is a **"conversion"** material.



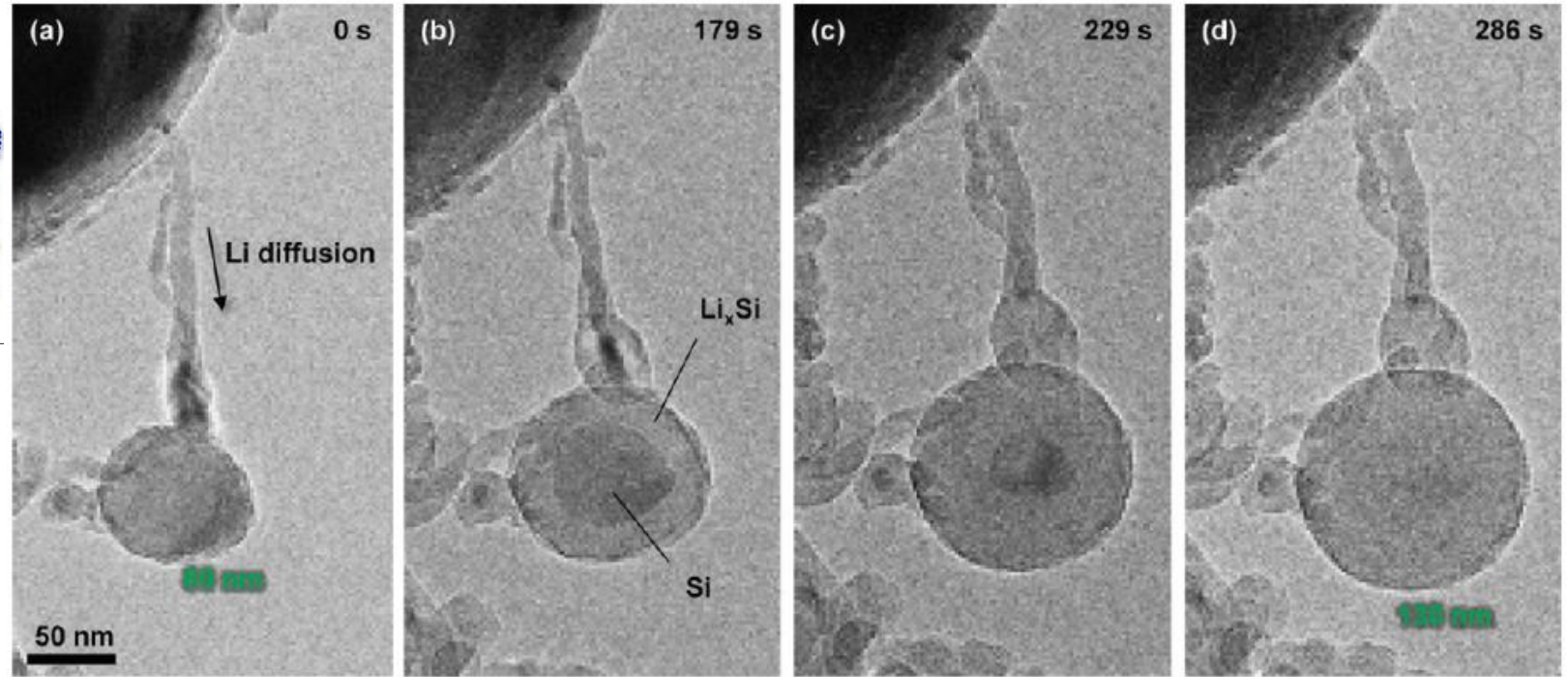
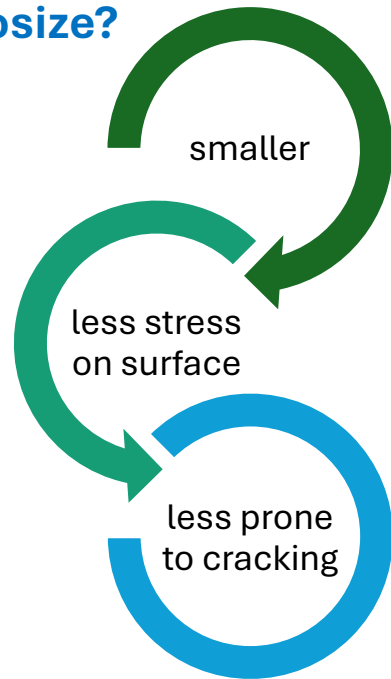
This **cycle life limitation** in turn limits the **amount of silicon** that can be added to an EV battery cell.

Challenge: to prevent the expansion and contraction of silicon from undermining battery life.

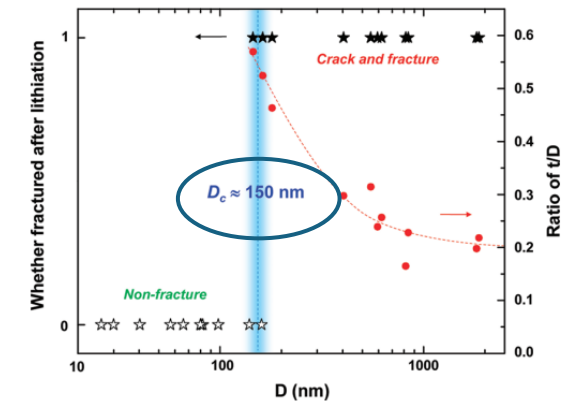
The most **popular** and **successful** approach:



Nanosize?

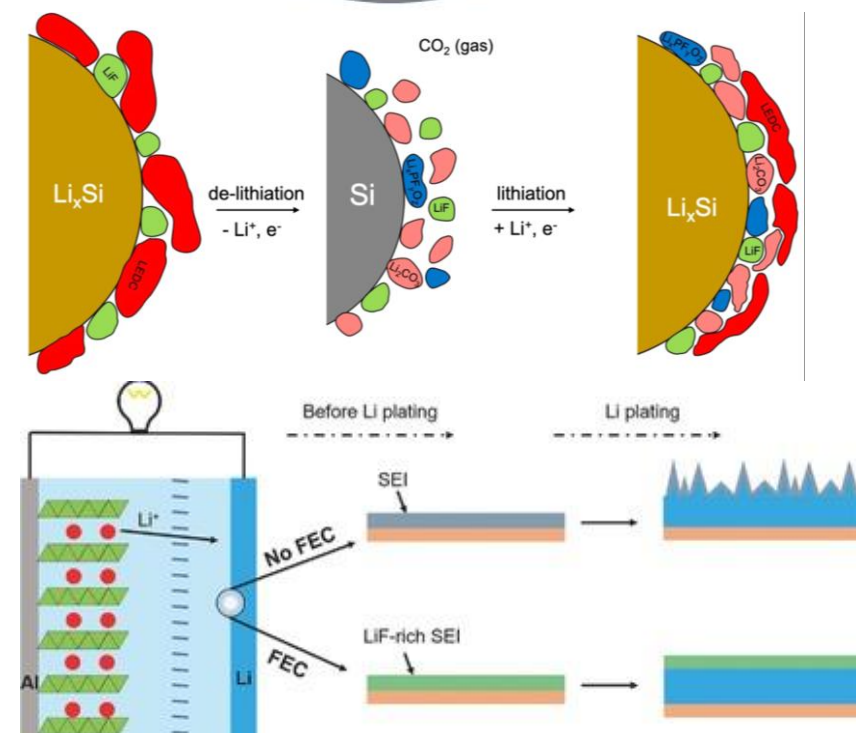


-80-nm SiNP uniformly expanded to 130 nm after lithiation
-despite the volumetric expansion of around 300%.



The **critical particle size** below which structural failure does not occur.

Approach	Challenges	Improvements
Silicon-Oxide (SiOx) Anodes	<ul style="list-style-type: none"> - Low conductivity - Initial capacity loss due to lithium consumption 	<ul style="list-style-type: none"> - Pre-lithiation to compensate for lithium loss - Doping with metal oxides to enhance conductivity - Nano-engineering to reduce stress from volume expansion
Silicon-Carbon (Si-C) Composite	<ul style="list-style-type: none"> -High volume expansion (~300%) - Pure carbon has lower capacity 	<ul style="list-style-type: none"> - Graphene/carbon nanotube integration for better conductivity - Porous carbon frameworks to accommodate expansion - Advanced polymer binders (e.g., PAA, alginate) for better flexibility
Coated Silicon Nanoparticles	<ul style="list-style-type: none"> -Minimize silicon exposure to electrolyte -inhibit SEI formation 	<ul style="list-style-type: none"> - Conductive coatings - Core-shell structures (SiO₂, Al₂O₃) to stabilize SEI formation - Hollow/yolk-shell designs to allow silicon expansion without breaking
Including Additives in the Electrolyte	<ul style="list-style-type: none"> -Formation of stable SEI layer - Electrolyte decomposition reduces efficiency 	<ul style="list-style-type: none"> - Fluoroethylene Carbonate (FEC) for stable SEI formation - Lithium Nitrate (LiNO₃) to enhance SEI stability - Self-healing polymers to dynamically repair SEI



*Holland, Julian, et al. “Ab initio study of lithium intercalation into a graphite nanoparticle.” Materials Advances 3.23 (2022): 8469-8484.

*Zhou, Xiaozhong, et al. “Research progress of silicon suboxide-based anodes for lithium-ion batteries.” Frontiers in Materials 7 (2021): 628233

*X.Q. Zhang, X.B. Cheng, X. Chen, C. Yan, Q. Zhang, Fluoroethylene Carbonate Additives to Render Uniform Li Deposits in Lithium Metal Batteries, Adv. Funct. Mater. 27 (2017)

*J. Wang, C. Gao, Z. Yang, M. Zhang, Z. Li, H. Zhao, Carbon-coated mesoporous silicon shell-encapsulated silicon nano-grains for high performance lithium-ion batteries anode, Carbon Vol. 192 (2022) 277–284.

COMPANY	CHARACTERISTICS
SilaNano	C/Si composite Panasonic Energy Mercedes Benz- C/Si=50:50 wt% 1600-1900 mAh/g
Group14	C/Si composite Porsche 1800-1850 mAh/g
IonBlox	Silicon oxide anode
Amprius	Si nanowires-expensive Sold under brand SiCore >500 cycles
Enovix	C/Si composite-high pressure-dense packing
Enevate	Flexible glassy C/Si layer Binder free



BENCHMARK



COMMERCIAL CONSIDERATIONS OF SILICON ANODES

- Synthetic graphite today has a market price of \$7.00-\$7.50/kg
- Cost of **raw metallurgical silicon** is less than \$5/kg at scale.
- A commonly discussed short-term market price range for **silicon/carbon anode** material is between **\$50-75/kg**.

synthesized from **expensive silane gas** and are combined with relatively expensive **carbon scaffolding** and **specialized coatings**

• SCIENTIFIC APPROACH

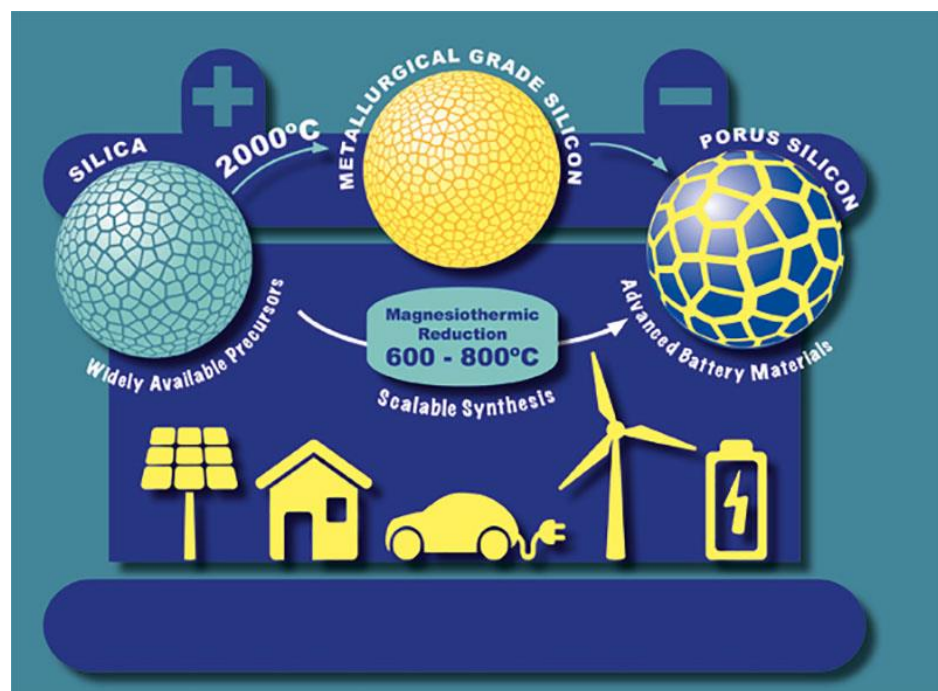


Cost-competitive manufacture of porous-silicon anodes via the magnesiothermic reduction: A techno-economic analysis

Maximilian Yan^{a,b}, Sarah Martell^b, Mita Dasog^b, Solomon Brown^a, Siddharth V. Patwardhan^{a,*}

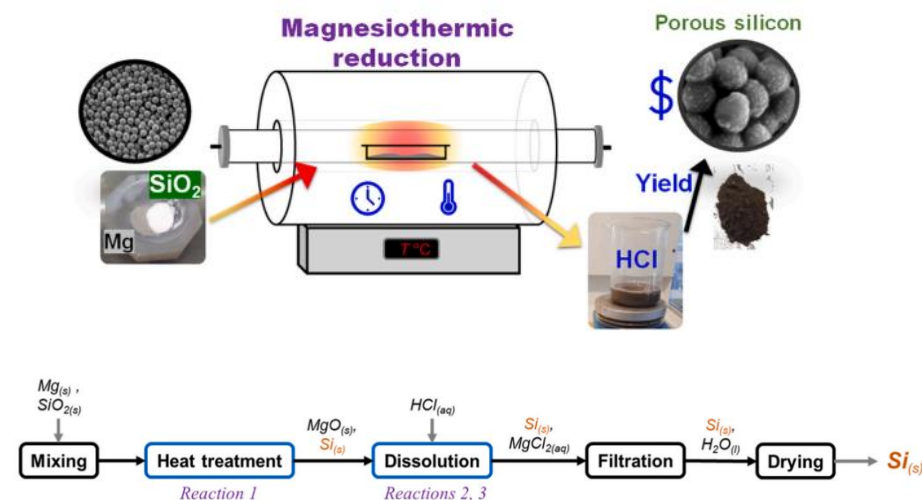
^a Department of Chemical and Biological Engineering, The University of Sheffield, Mappin Street, Sheffield, S1 3JD, United Kingdom

^b Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax, NS, B3H 4R2, Canada



EXAMPLE OF SCIENTIFIC APPROACH

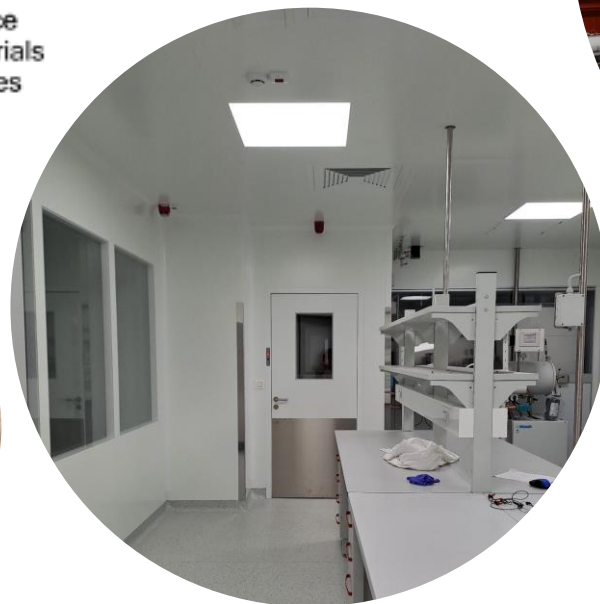
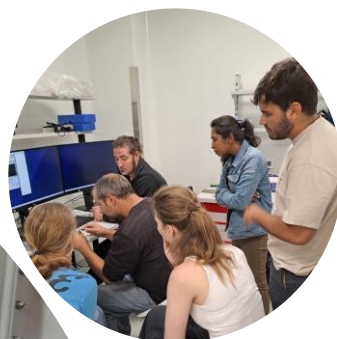
- low-cost** method for silicon anode production
- abundant silica sources**
- operating at **lower temperatures (~600-700°C)** compared to traditional methods



reduces energy costs

reduces raw material expenses

scalable and profitable approach

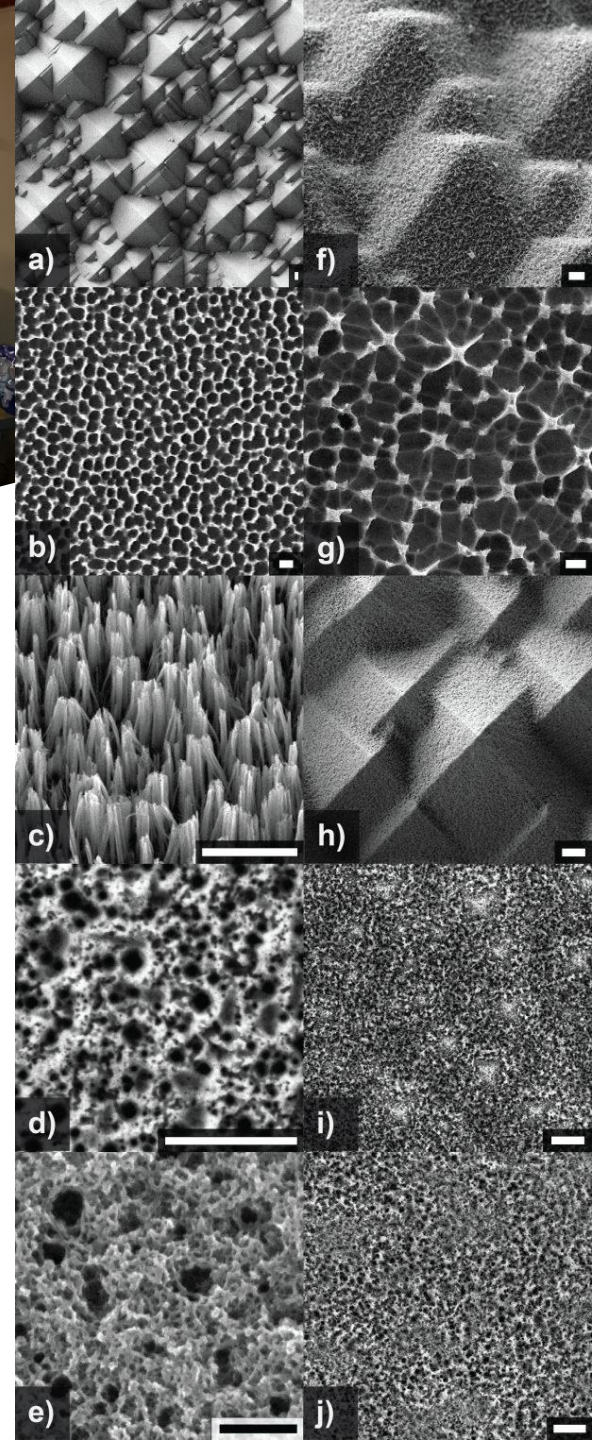


Laboratory for molecular physics and synthesis of new materials

head: dr. sc. Mile Ivanda

Research focus:

synthesis of silicon-based materials for various applications





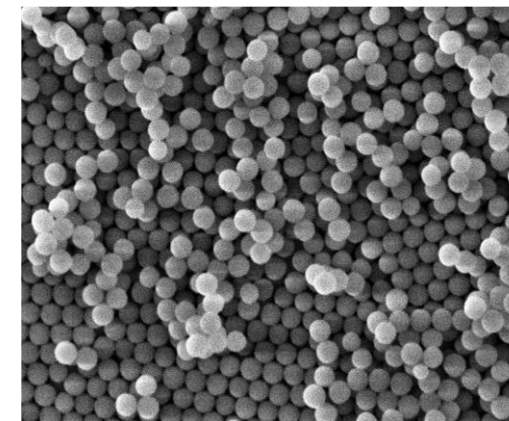
Ag decorated porous Si structure as potential high-capacity anode material for Li-ion cells

Matea Raić^{a,b}, Lara Mikac^{a,b}, Marijan Gotić^{a,b}, Marko Škrabić^c, Nikola Baran^{a,b}, Mile Ivanda^{a,b,*}

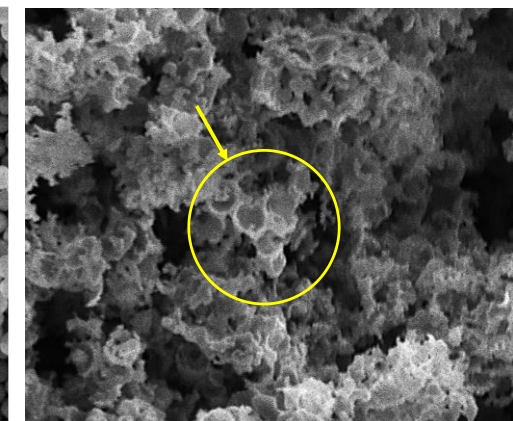
^aLaboratory for Molecular Physics and Synthesis of New Materials, Ruder Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia

^bResearch Unit New Functional Materials, Center of Excellence for Advanced Materials and Sensing Devices, Bijenička c. 54, 10000 Zagreb, Croatia

^cDepartment of Physics and Biophysics, School of Medicine, University of Zagreb, Šalata 3b, 10000 Zagreb, Croatia



200 nm



200 nm

High Surface Area

- more lithium-ion storage and faster charge/discharge rates

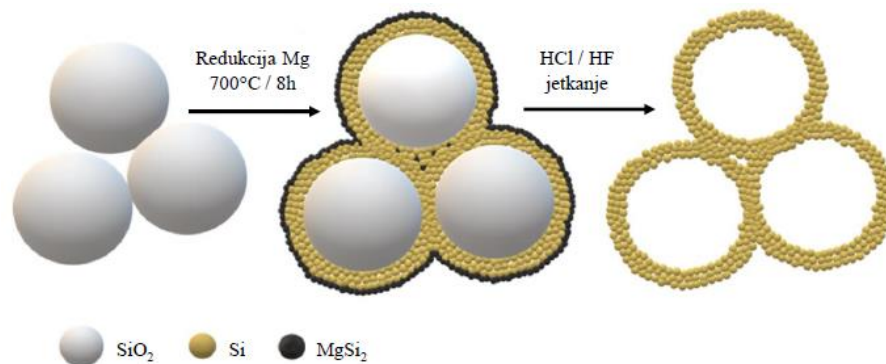
Accommodates Volume Expansion

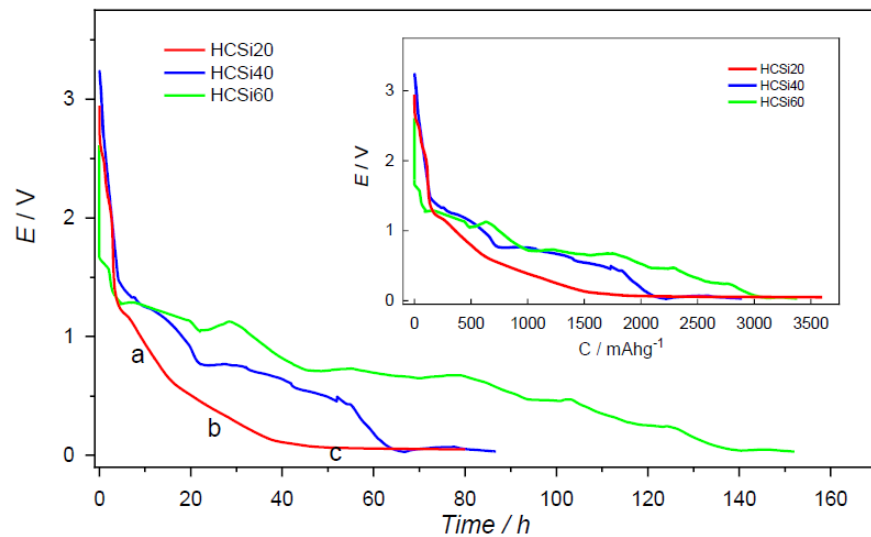
- prevents electrode degradation

Magnesiothermic
reduction

Nanoporous
silicon

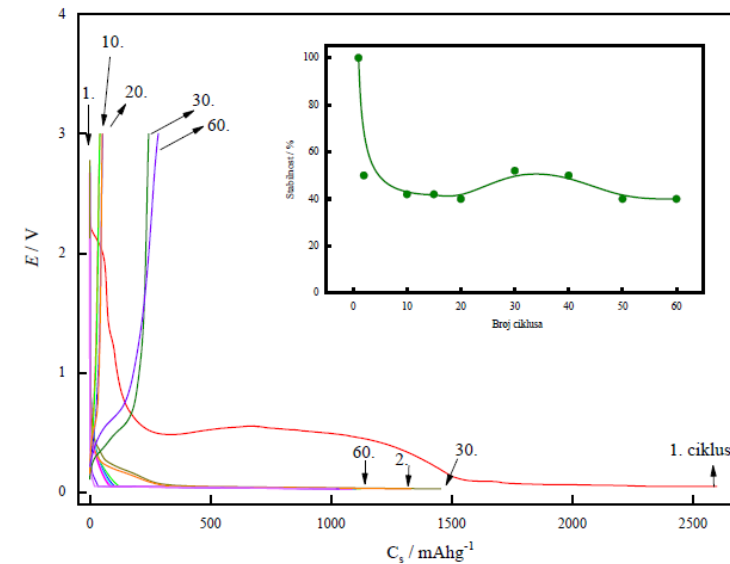
Decorated with
Ag nanoparticles



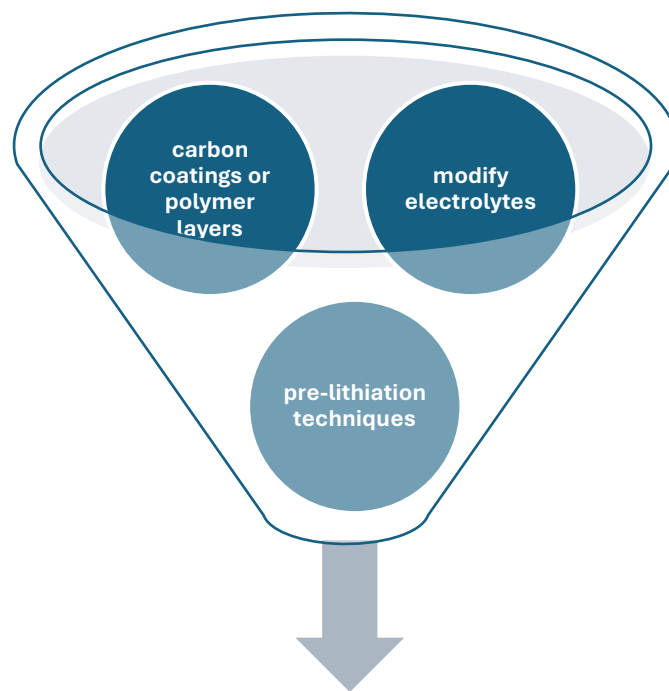


- High capacity in 1st cycle (**≈3500 mAh/g**)
- Capacity drops to **20% in 50 cycles**
- Additive increases up to **80 cycles**

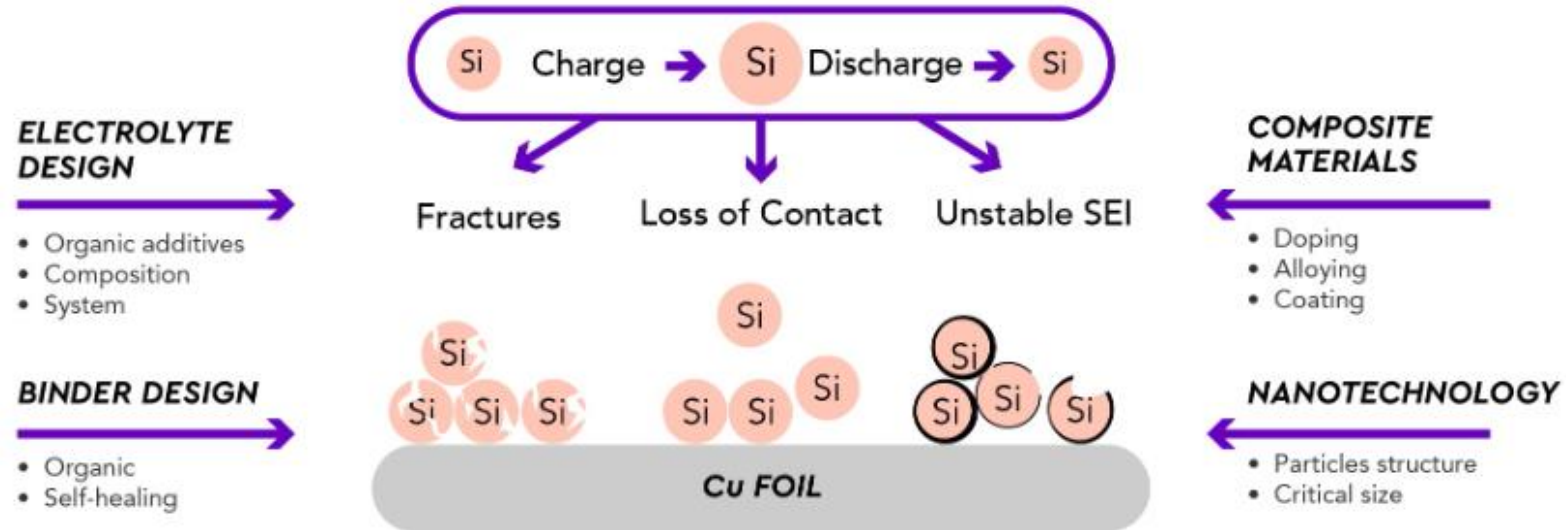
+FEC



Future plans:



Improve cyclability



Future perspectives

Innovation in the **chemistry of materials** to improve Li-ion battery components.

Thank you for attention!

