NANOSTRUCTURED GERMANIUM THIN FILMS AS ANODE MATERIAL FOR LITHIUM-ION BATTERIES FOR AEROSPACE APPLICATIONS

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Dipartimento di Fisica e Scienze della Terra

Agenzia Spaziale Italiana

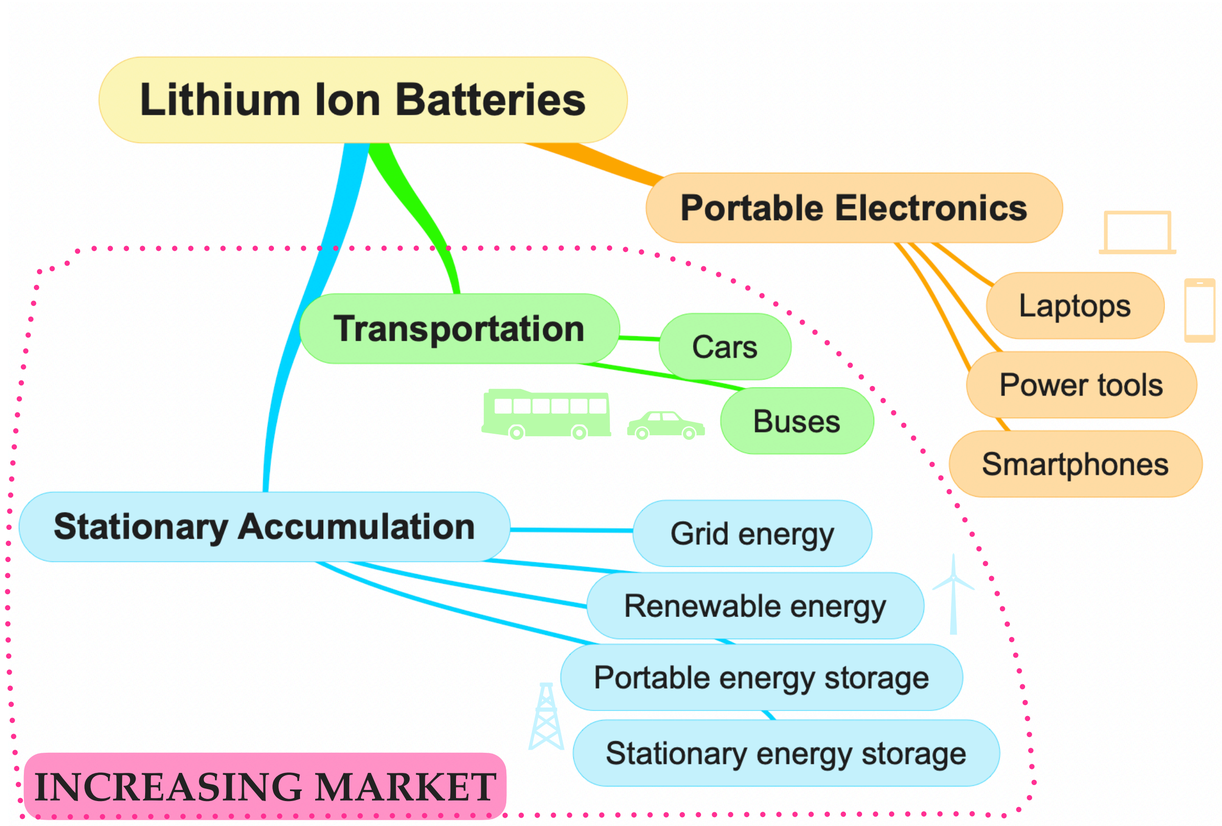
GLITTERY BATTERIE SPAZIALI

2023 NASA Aerospace Battery Workshop

LIBS GENERAL OVERVIEW

European Commission

" Batteries are an indispensable energy source. They are also a key technology in the transition to climate neutrality . . . Global demand for batteries is increasing rapidly and is set to increase 14 times by 2030. The EU could account for 17% of that demand."



Adapted from Electrochem. Energ. Rev. 2, 1–28 (2019). https://doi.org/10.1007/s41918-018-0022-z

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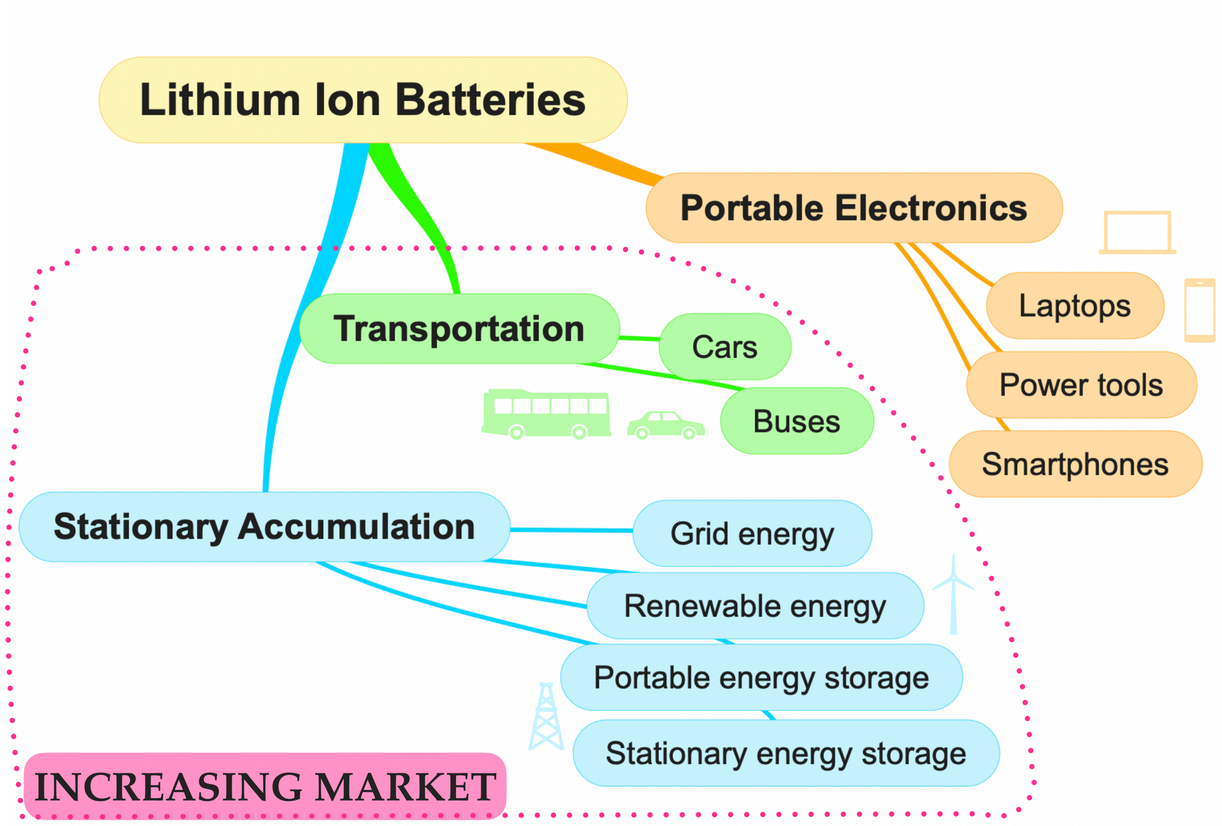
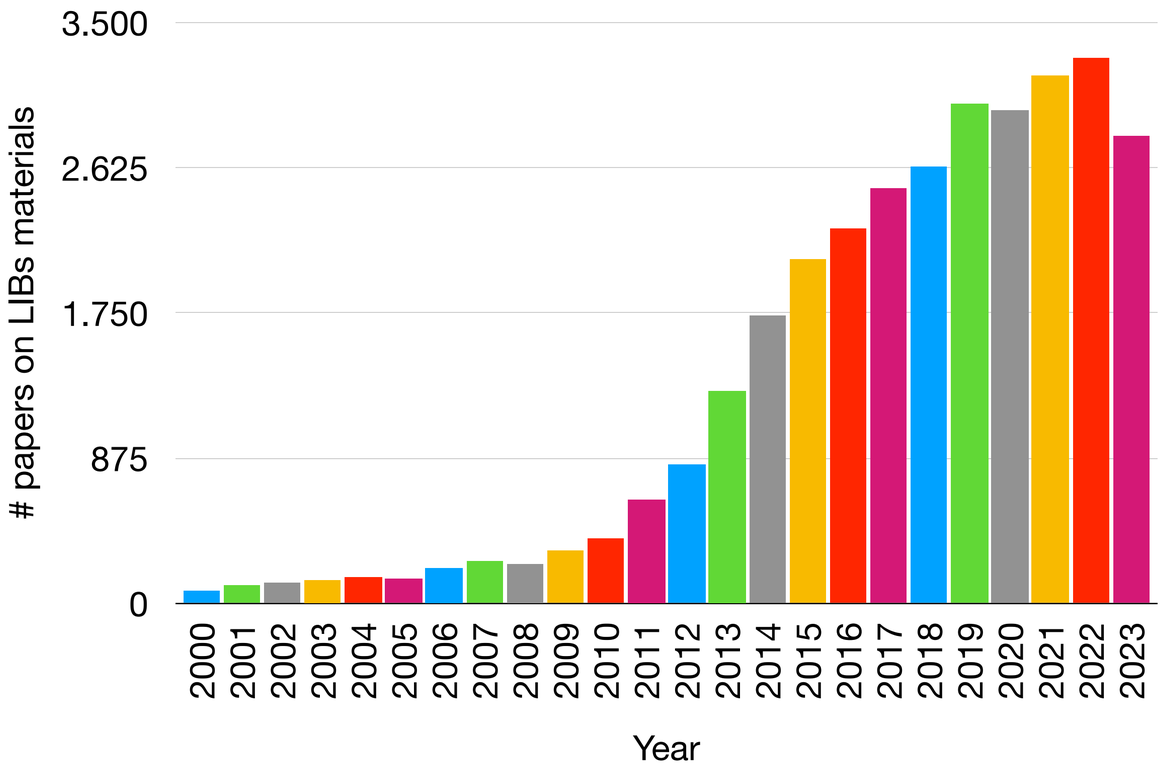


Time to push toward innovative materials research



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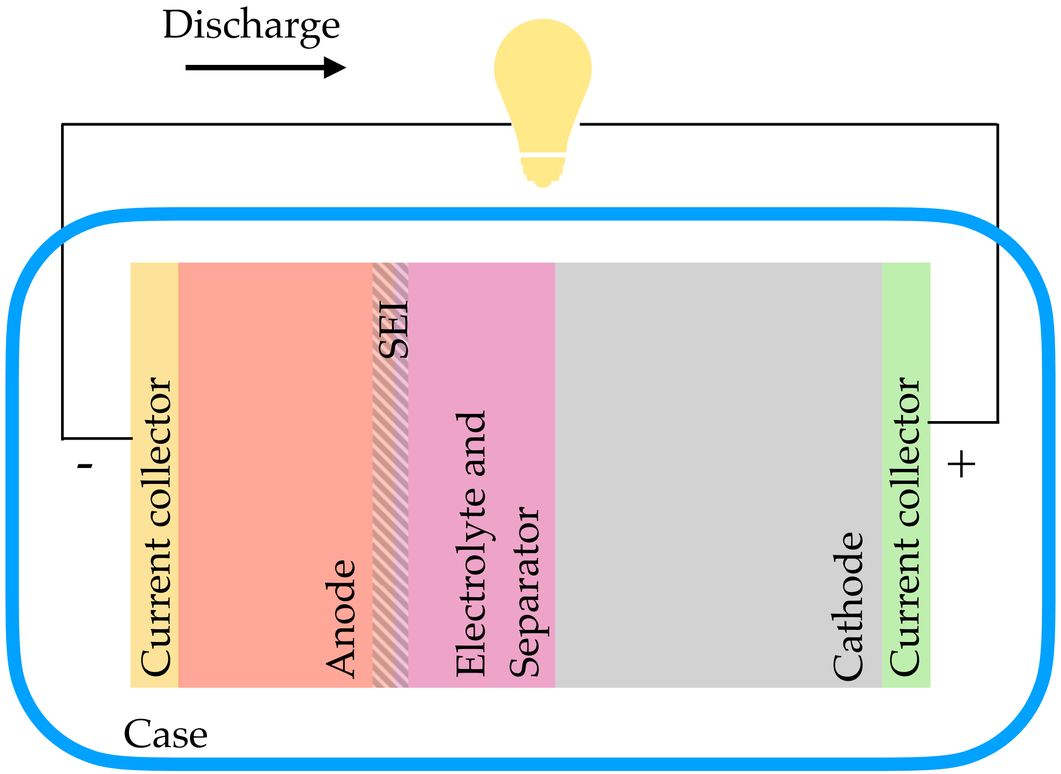
The voltage delivered depends on the **cell chemistry** hence on the **material** that forms it.



LIBs elements

- Negative electrode in which **oxidation** takes place.
- Positive electrode in which **reduction** takes place.
- Separator & Electrolyte
- Case

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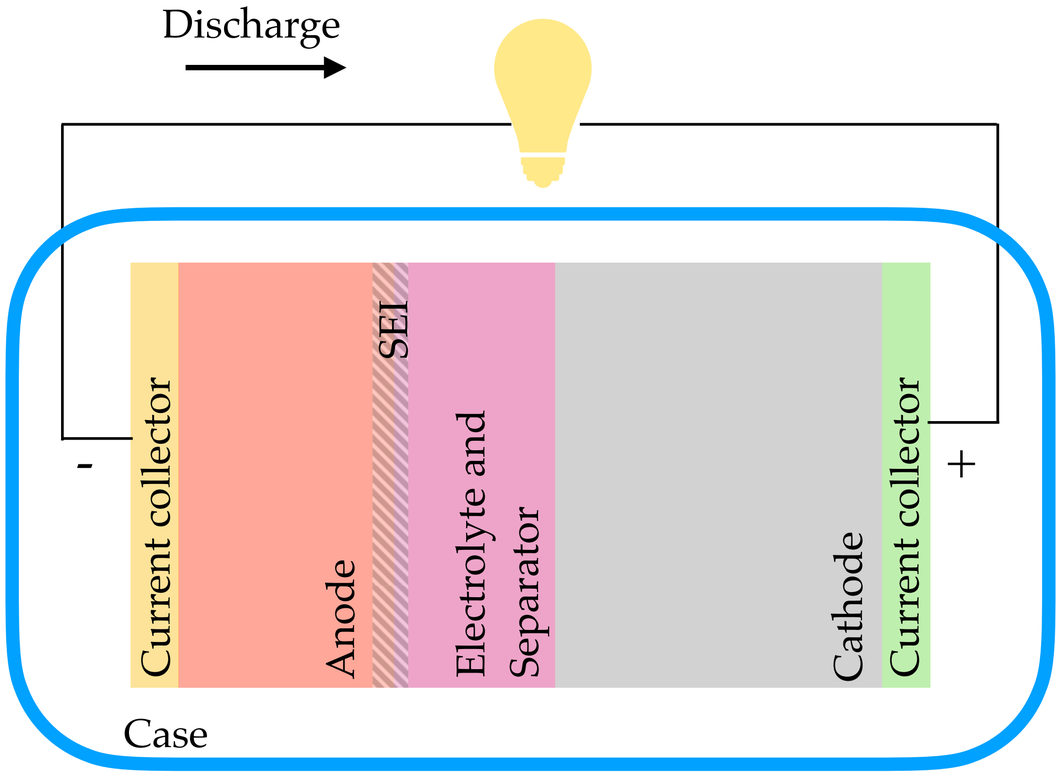

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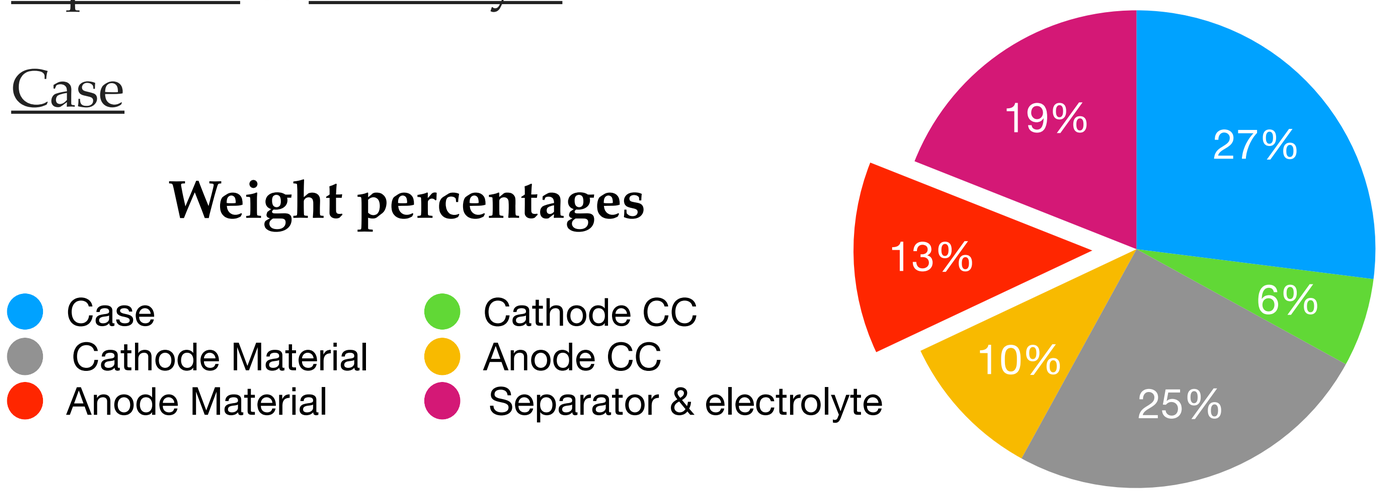
Weight percentages



👀 10% binder → we propose a **binder free approach**

[1] Adapted from RSC Adv., 2014,4, 3633-3642 . DOI: 10.1039/c3ra45748f

GLITTERY PROJECT

Germanium **L**ithium-**I**on ba**TTERY**

NASA TRL

TRL 9	Actual system "flight proven" through successful mission operations
TRL 8	Actual system completed and "flight qualified" through test and demonstration (ground or space)
TRL 7	System prototype demonstration in a space environment
TRL 6	System/subsystem model or prototype demonstration in a relevant environment (ground or space)
TRL 5	Component and/or breadboard validation in relevant environment
TRL 4	Component and/or breadboard validation in laboratory environment
TRL 3	Analytical and experimental critical function and/or characteristic proof-of-concept
TRL 2	Technology concept and/or application formulated
TRL 1	Basic principles observed and reported

Project final GOAL:

Produce a battery pack with pouch cell format lithium ion batteries using a porous Germanium electrode

Project is entirely founded by the Italian Space Agency

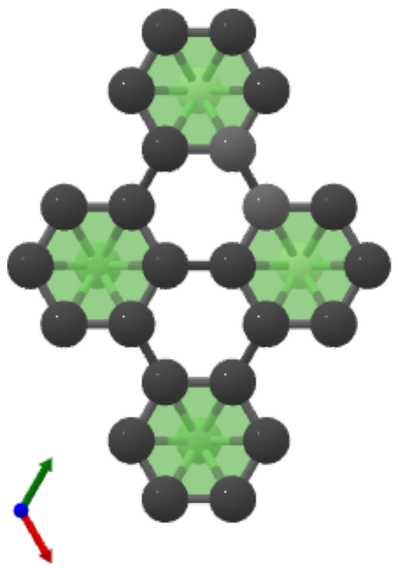
LIBS MATERIALS

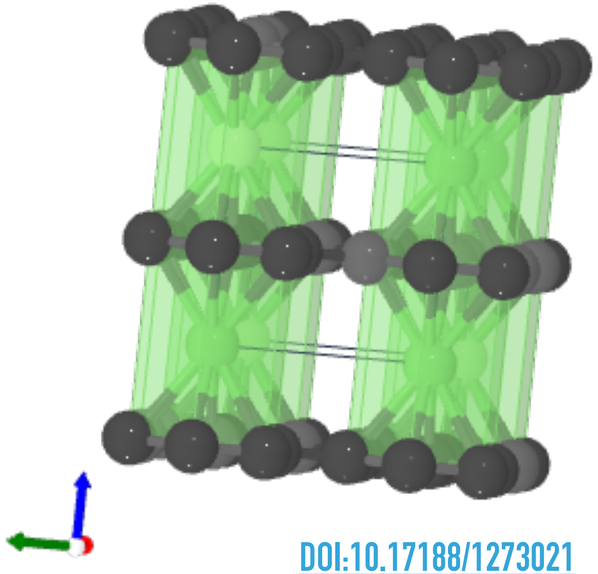
Electrode material	C	Li	Si	Ge
Lithiated phase	LiC_6	Li	$Li_{22}Si_5$	$Li_{22}Ge_5$
Theoretical specific capacity [mAh/g]	372	3 862	4 200	1 624
Volume change [%]	12	-	420	370

Standard materials used in commercial LIBs

BUT

- ❌ Low capacity
- ❌ Poor rate capabilities





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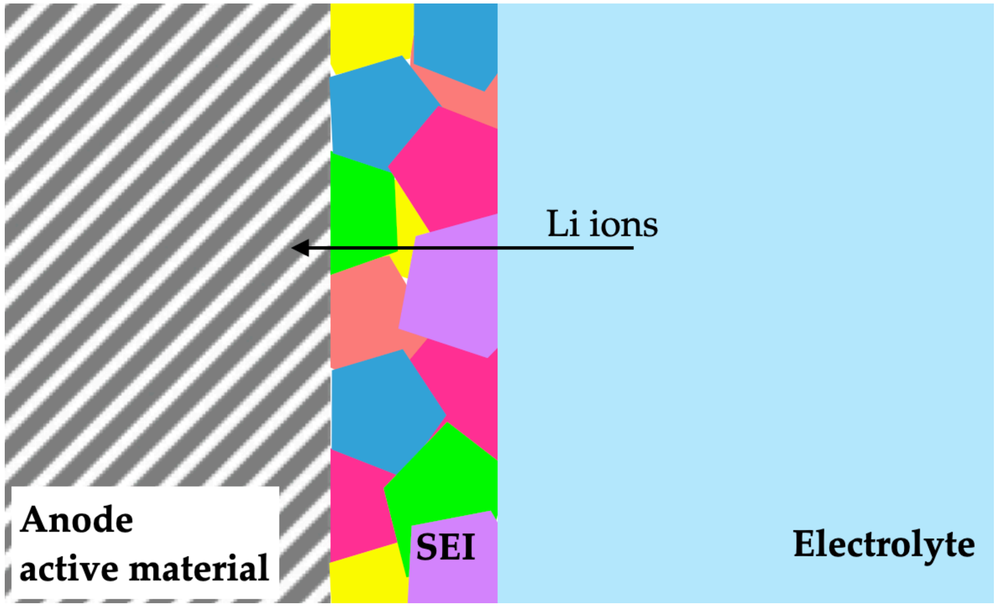

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- ✗ Supply shortage

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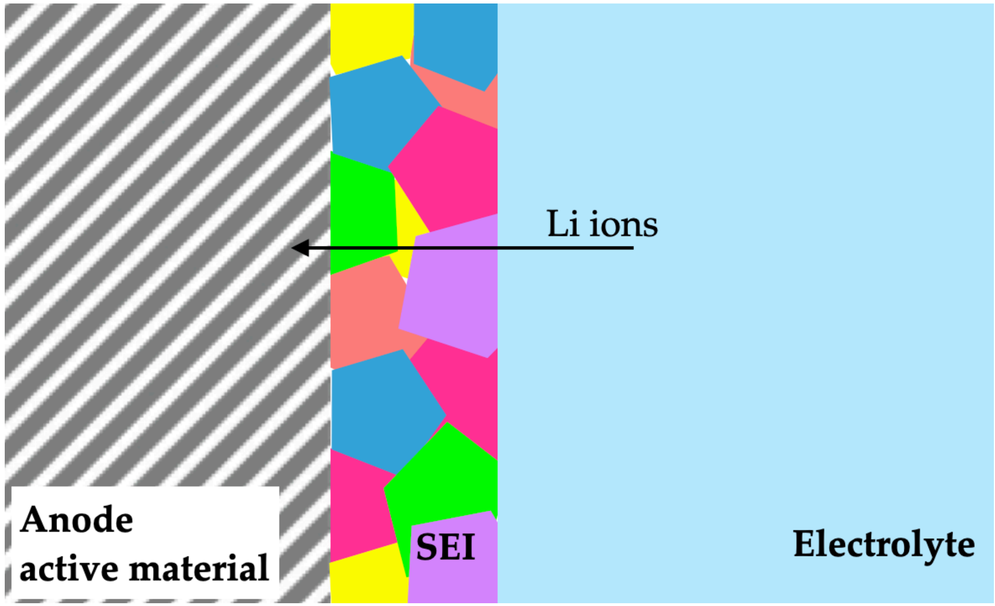

Lithium recycling

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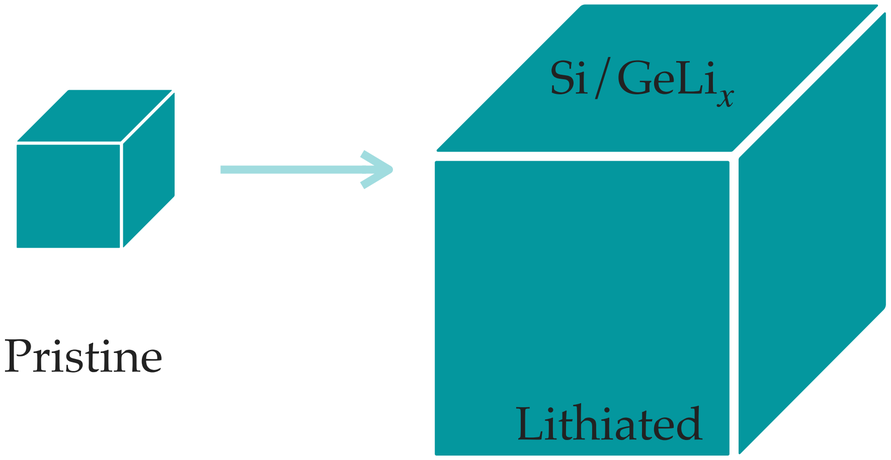
❌Huge volumetric expansion (~ 400 %) upon lithiation

leading to

❌Active material pulverisation

❌Cracks formation

❌Delamination from the substrate



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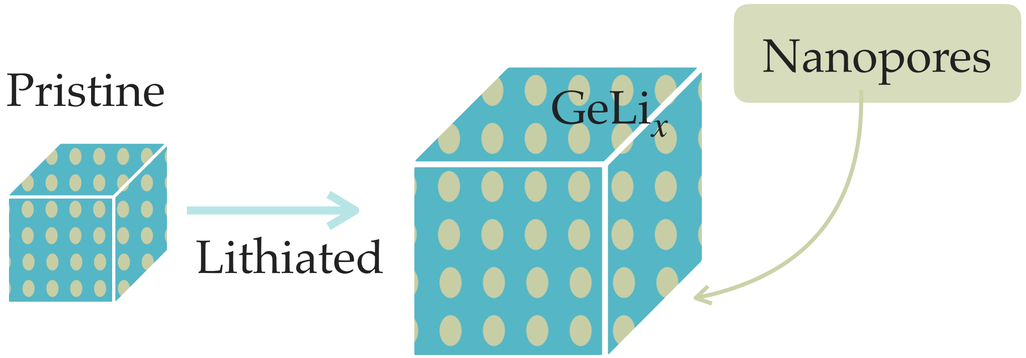


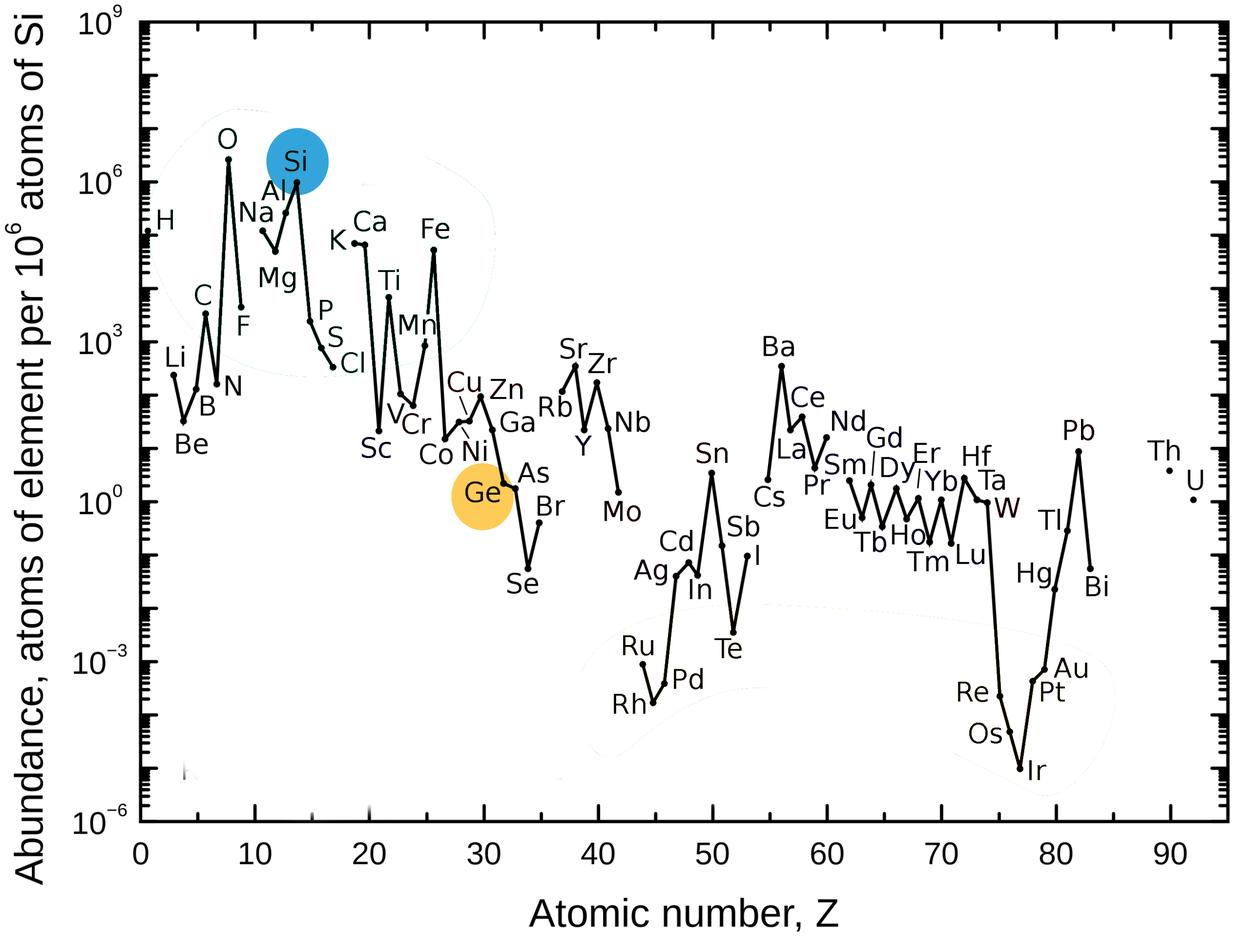
(volume accommodation by nano-pores)

Possible way to cope with this? Nanostructurization

LIBS MATERIALS

Ge-based electrode practical application is limited to sectors in which the **volumetric energy density [Wh/L]** is essential.

CRITICAL ROW MATERIAL



http://pubs.usgs.gov/fs/2002/fs087-02/

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Due to the **high theoretical specific capacity**

Promising materials for the AEROSPACE sector!

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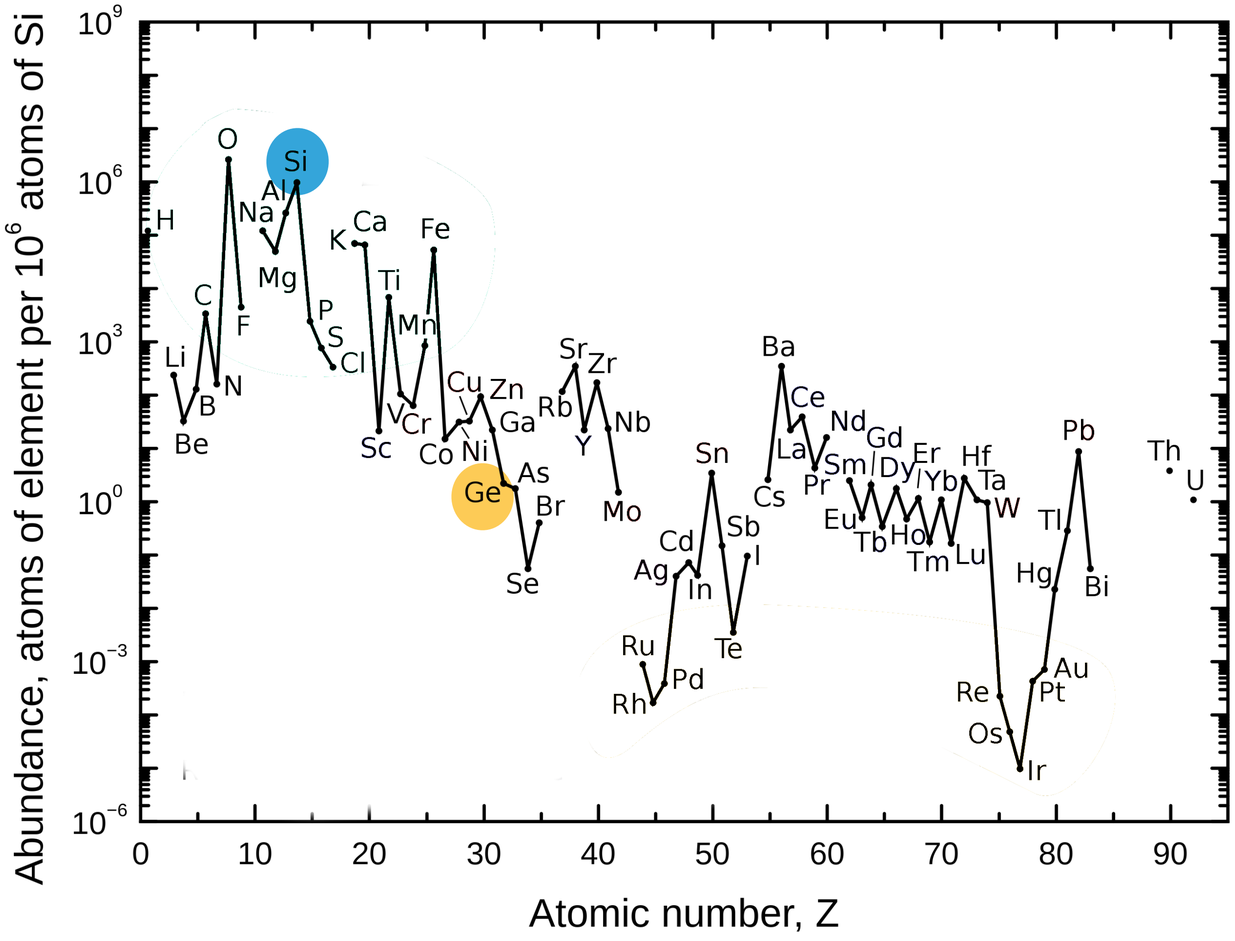

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WHY GERMANIUM

Ge vs Si

- ❌ Lower theoretical capacity [1624 mAh/g vs 4200 mAh/g]
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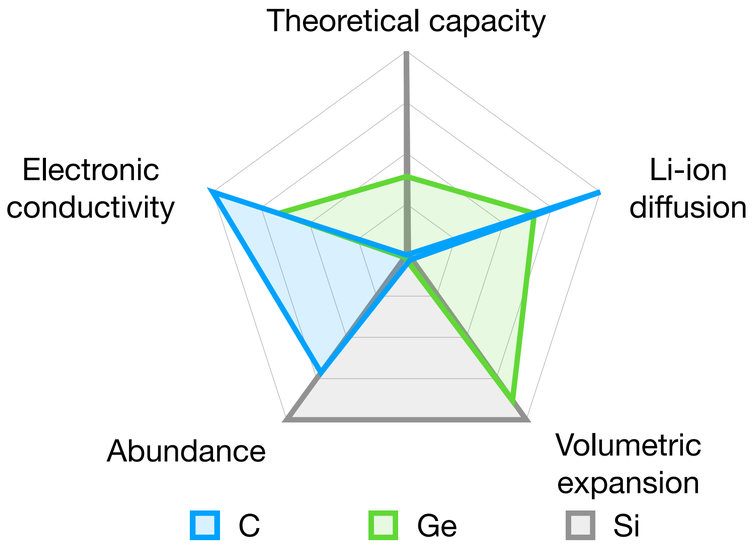

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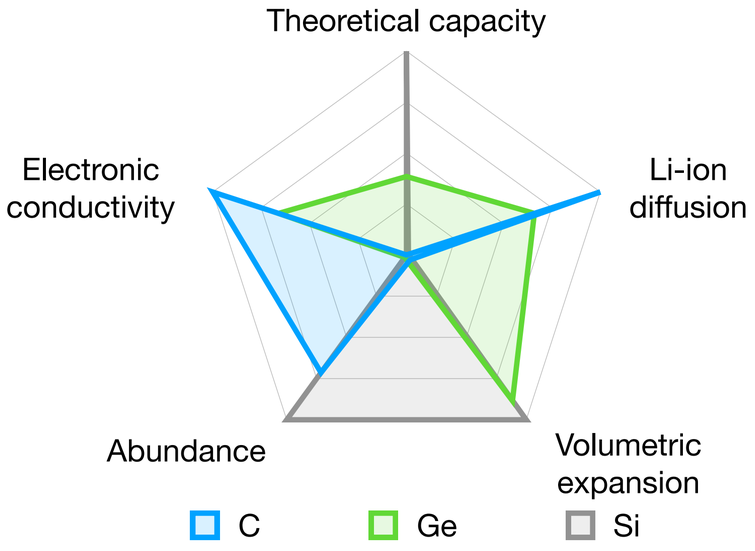

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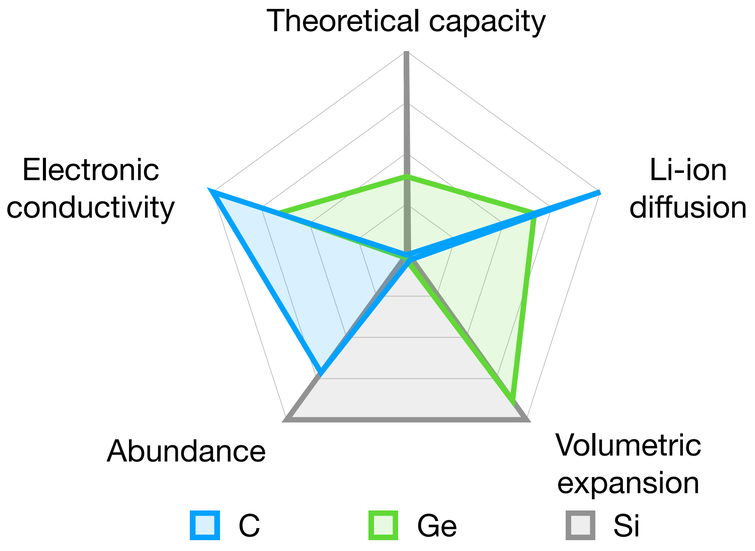

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$1C = 1h$ charge/discharge

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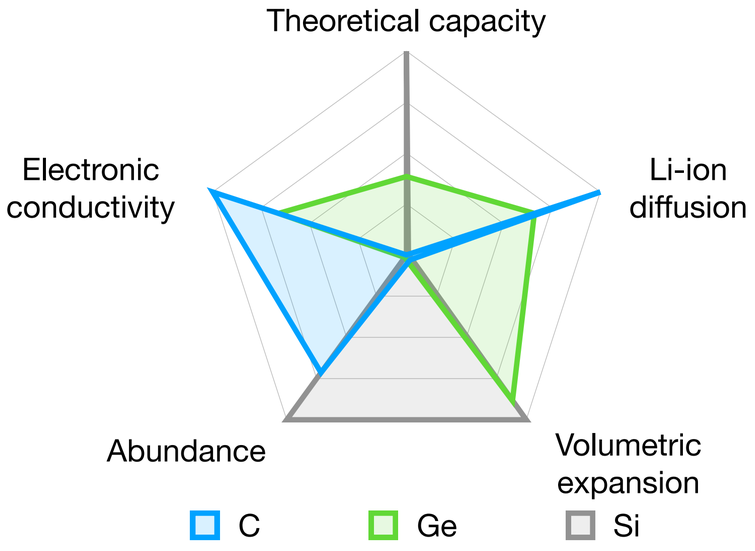
✅ Surface stability : Ge less reactive than Si towards O molecules[1]
Intrinsic suppression of irreversibile capacity loss due to Li_2O formation



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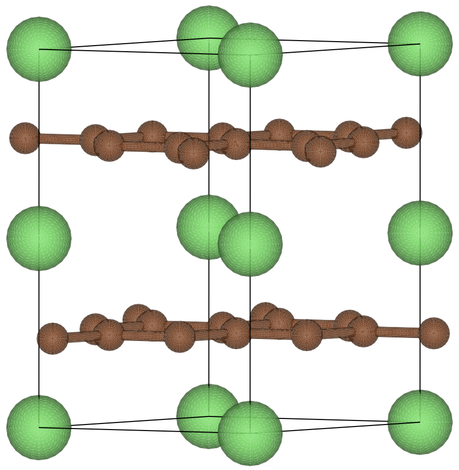
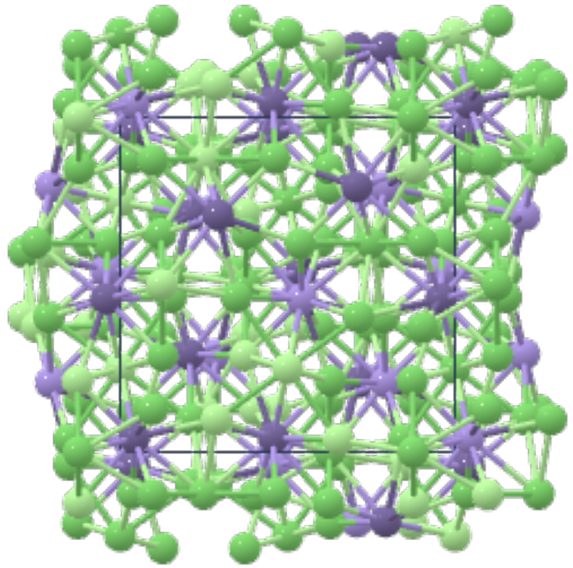
[1] doi:10.1088/1757-899X/41/1/012007

ALLOYING MATERIALS

Intercalation mechanism





Alloying mechanisms

GRAVIMETRIC CAPACITY : the charge stored per unit mass of active material in the electrode

STANDARD TECHNOLOGY

LiC_6 $$C_{\text{Graphite}} = \frac{1}{6}\frac{F}{\text{Carbon Molar Mass}} \approx 372\ \text{mAh g}^{-1}$$

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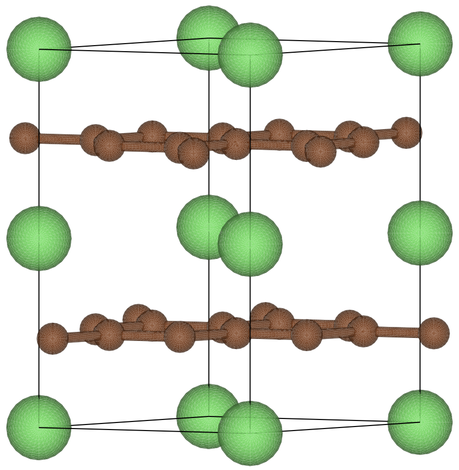

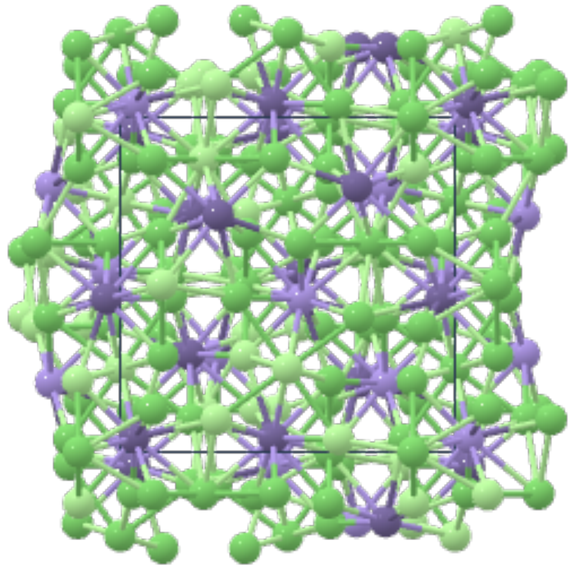

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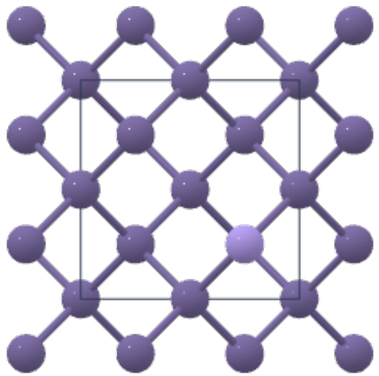
GE-BASED TECHNOLOGY

$Li_{22}Ge_5$

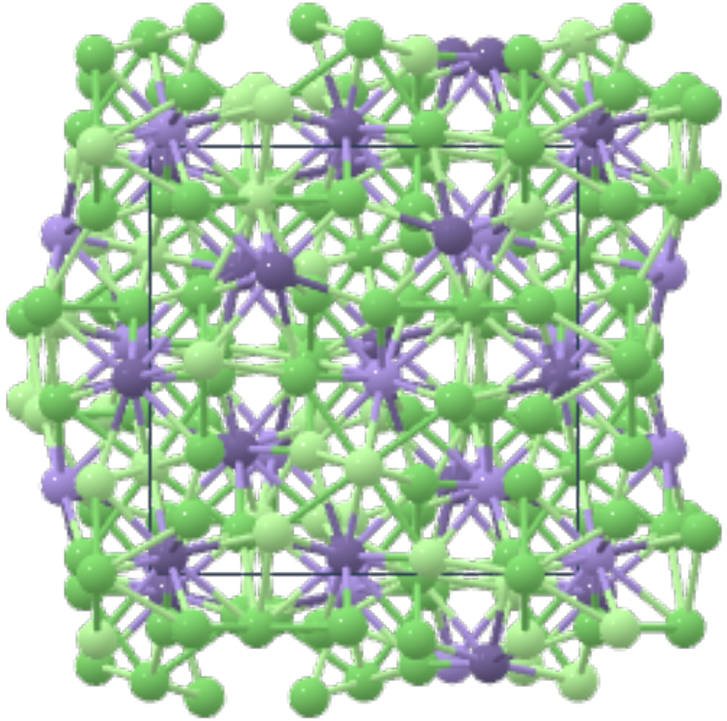
$$C_{\text{Ge}} = \frac{22}{5}\frac{F}{\text{Ge Molar Mass}} \approx 1624\ \text{mAh g}^{-1}$$

GERMANIUM LITHIATED PHASES

$Ge \longrightarrow Li_{15}Ge_4 \longrightarrow Li_{22}Ge_5$



DOI: 10.17188/1206032



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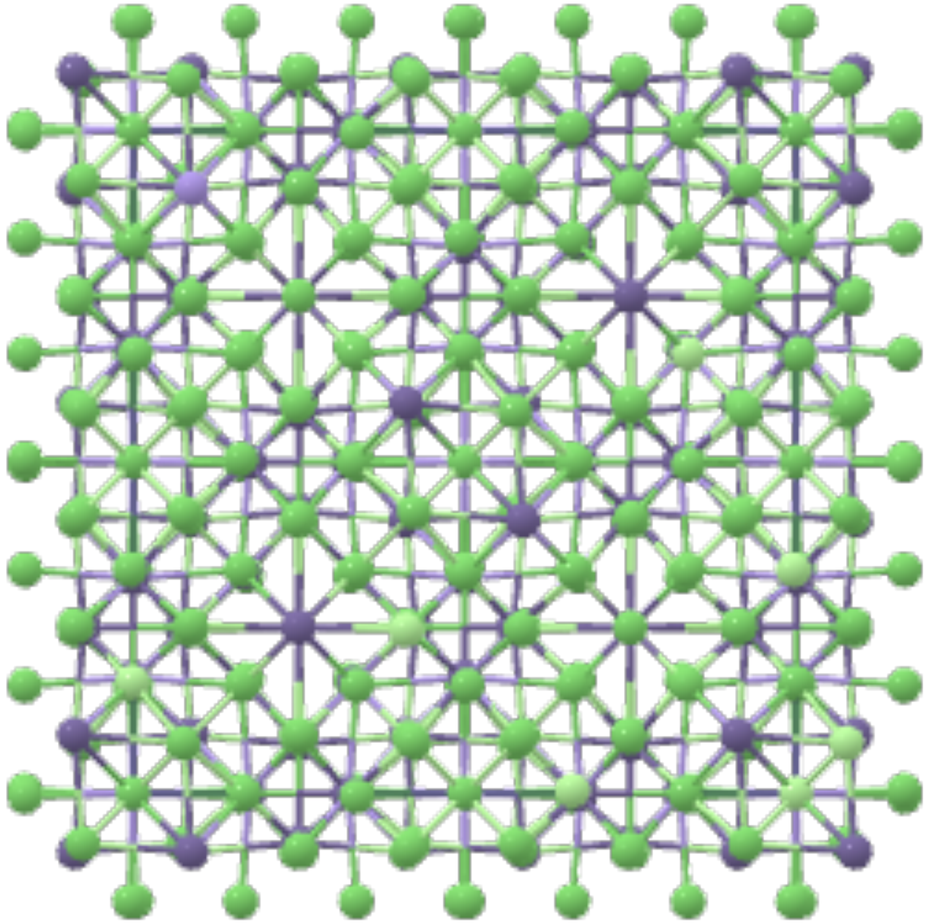
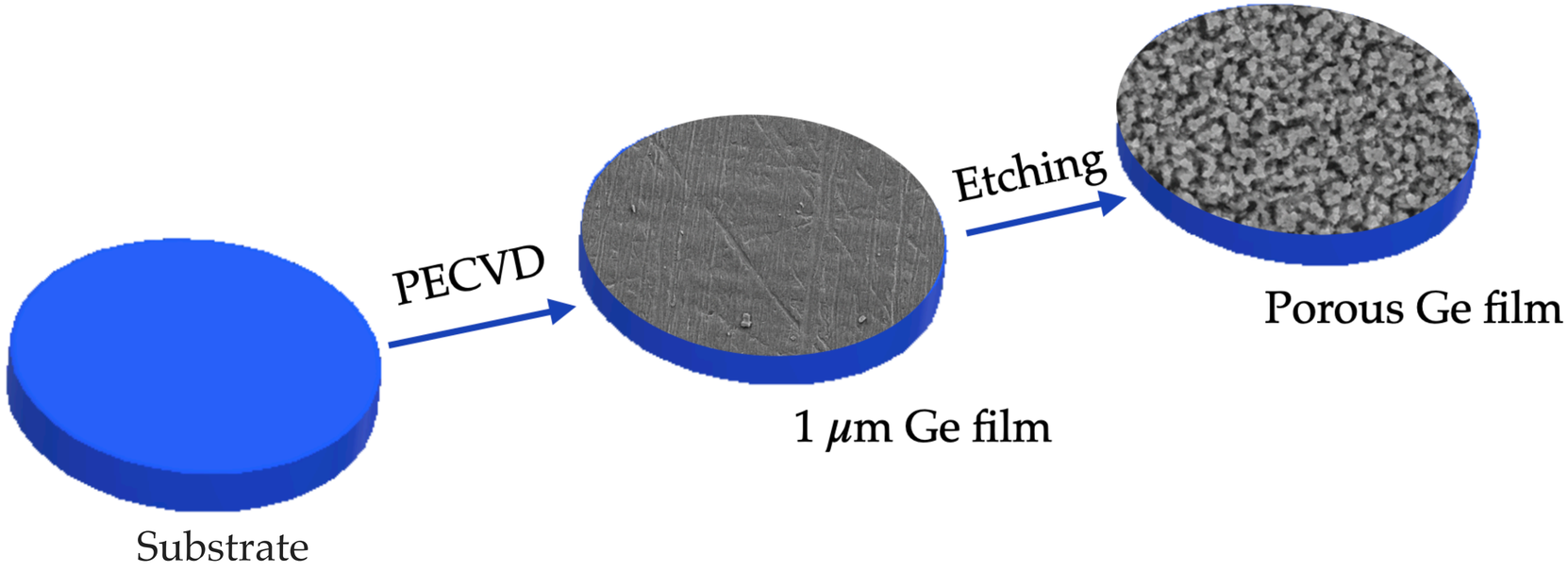


Data retrieved from the Materials Project for Li22Ge5 (mp-1204063) from database version v2022.10.28

TWO STEPS SAMPLE PREPARATION:

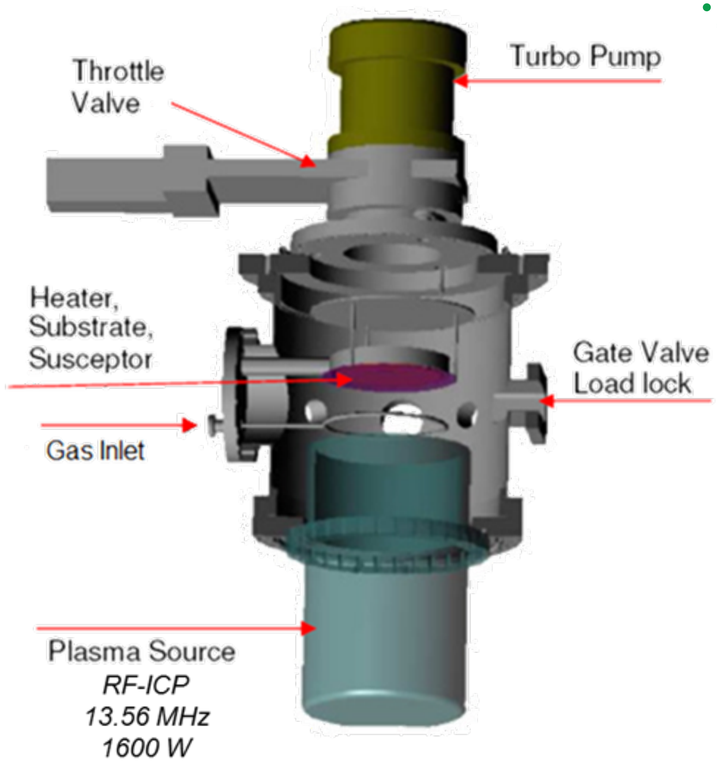
1. DEPOSITION
   via Chemical Vapor Deposition

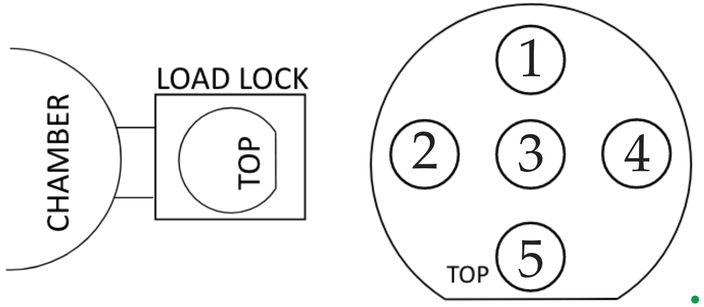
2. NANOSTRUCTURATION
   via Electrochemical Etching



TOP-DOWN APPROACH

PECVD - PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION





The **precursors** of the element to be deposited are decomposed in **reactive species**

React chemically to produce a film on the target substrate.

Precursor gas: **GeH_4**

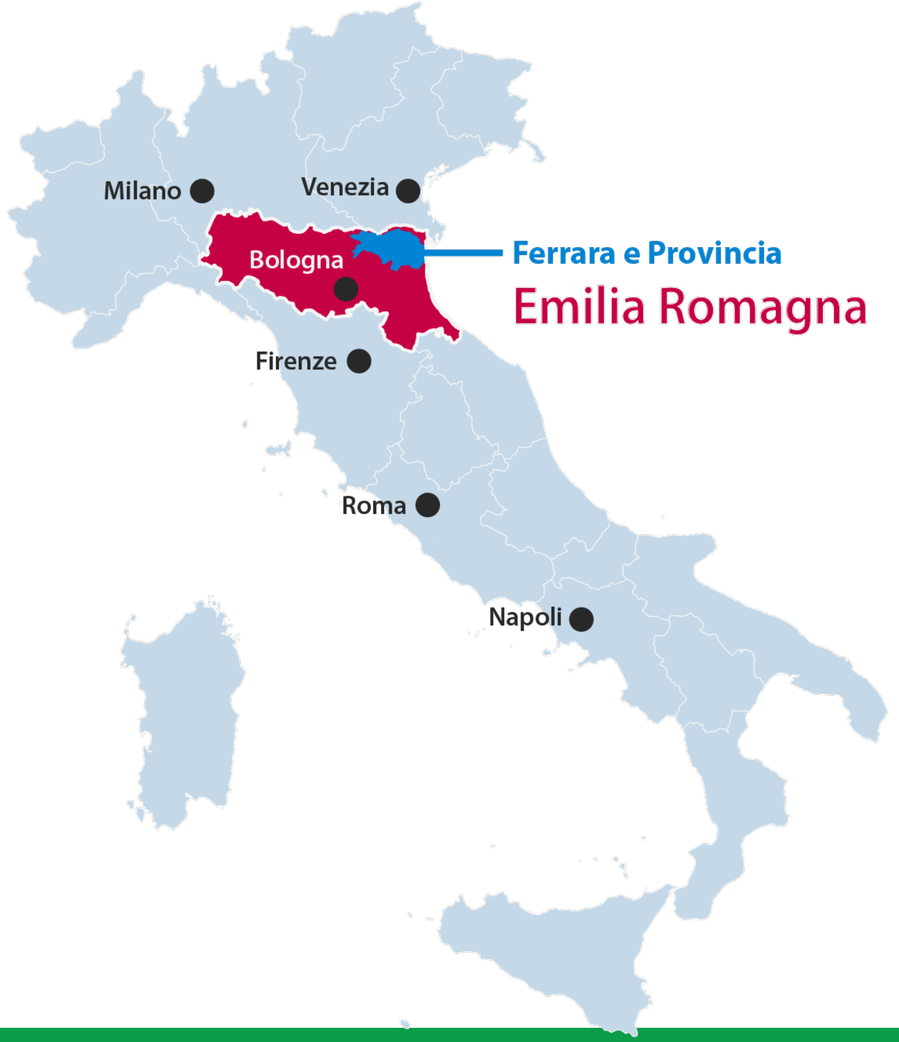
Growth rate: 1.265 nm/s

BINDER FREE ANODE

Active material ONLY!

PECVD - PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

PECVD equipment at the **University of Ferrara** -
Department of Physics and Earth Science

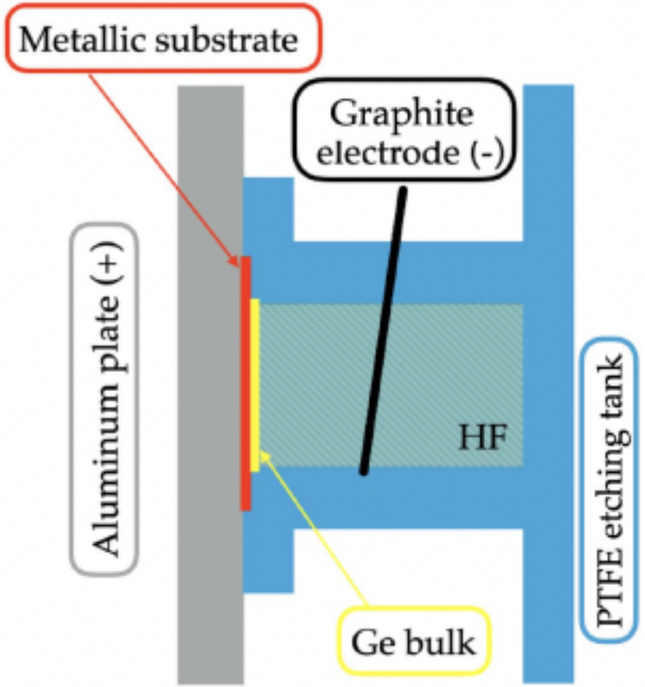


Università degli Studi di Ferrara

ELECTROCHEMICAL ETCHING

Electrochemical etching involves non-spontaneous reactions to

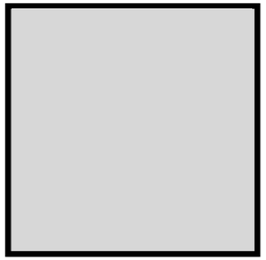
→ **create nano-pores to better accomodate Li ions**



+ connected to the Aluminum plate

- clamped to a Graphite rod

40 mA current for **180 s**



Scheme:
-square: metal foil (3x3 cm)
-dark grey circle: bulk germanium (d=2.8 cm)
-red circle: porous germanium (d=2.5 cm)
-green circle: anode area (d=1.5 cm)

<u>Etching solution</u>:
HF (50 % w/w in H_2O): ethanol

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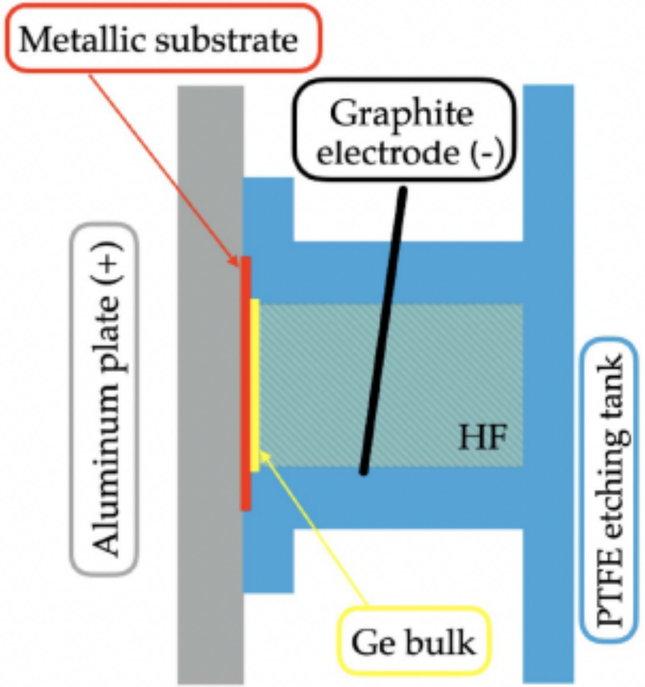

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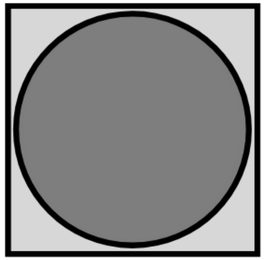

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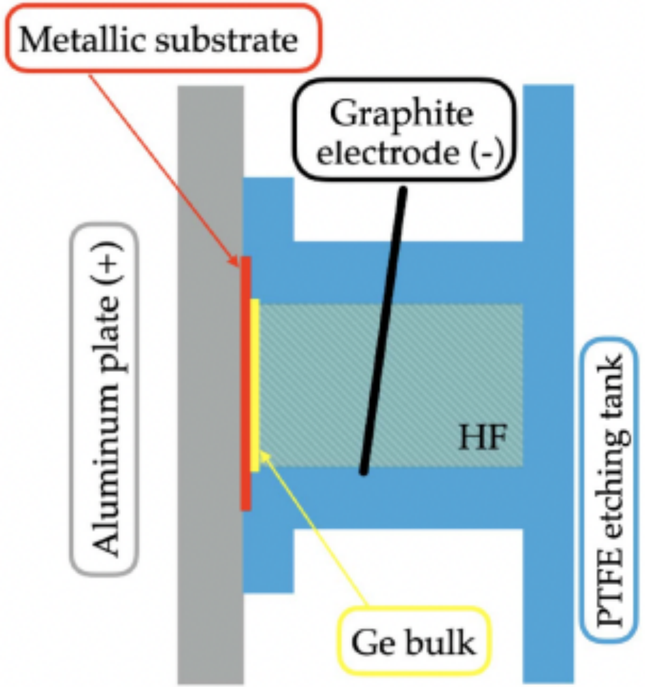

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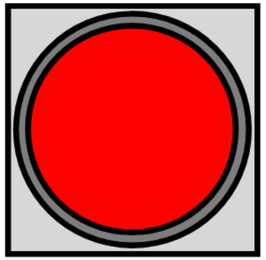


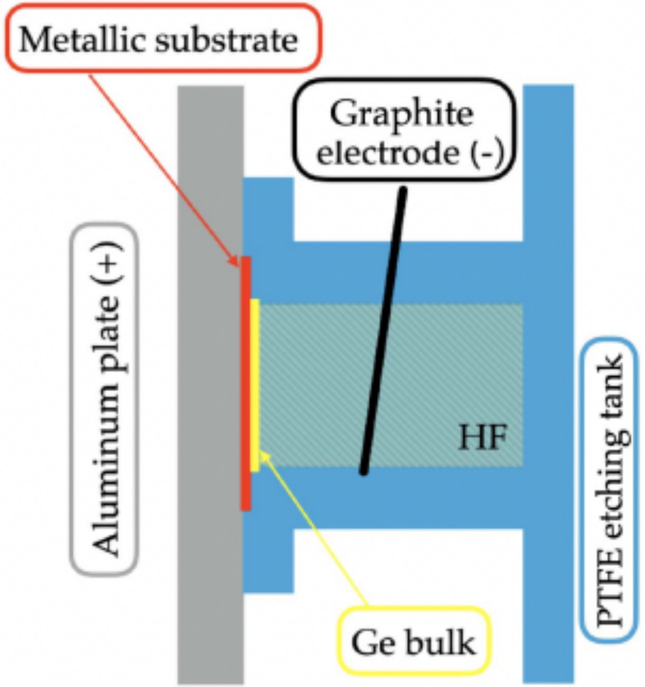
Scheme:
-square: metal foil (3x3 cm)
-dark grey circle: bulk germanium (d=2.8 cm)
-red circle: porous germanium (d=2.5 cm)
-green circle: anode area (d=1.5 cm)

<u>Etching solution</u>:
HF (50 % w/w in H_2O): ethanol

ELECTROCHEMICAL ETCHING

Electrochemical etching involves non-spontaneous reactions to

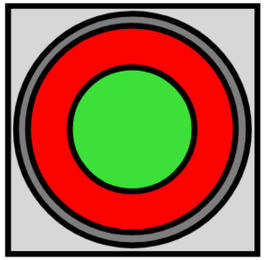
→ **create nano-pores to better accomodate Li ions**



+ connected to the Aluminum plate

- clamped to a Graphite rod

40 mA current for **180 s**



Scheme:
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-green circle: anode area (d=1.5 cm)

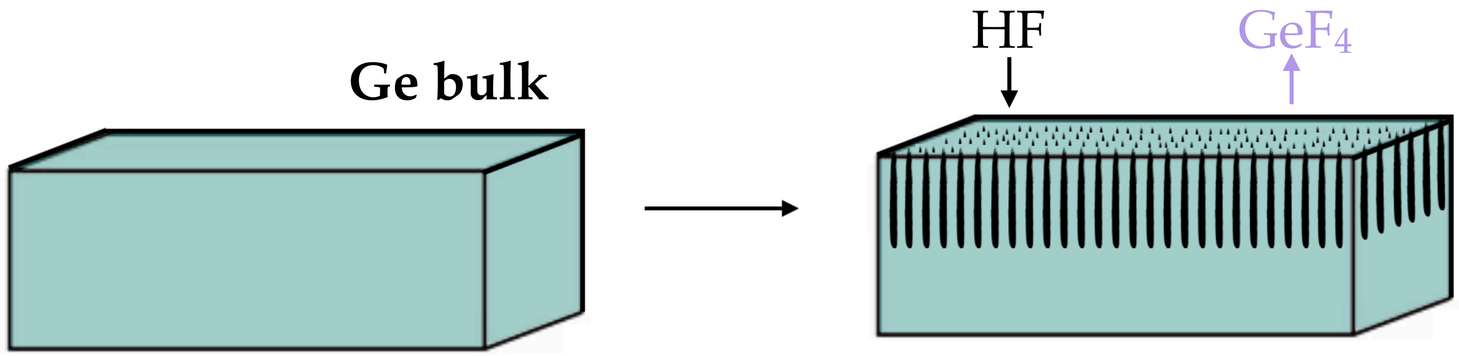
<u>Etching solution</u>:
HF (50 % w/w in H_2O): ethanol

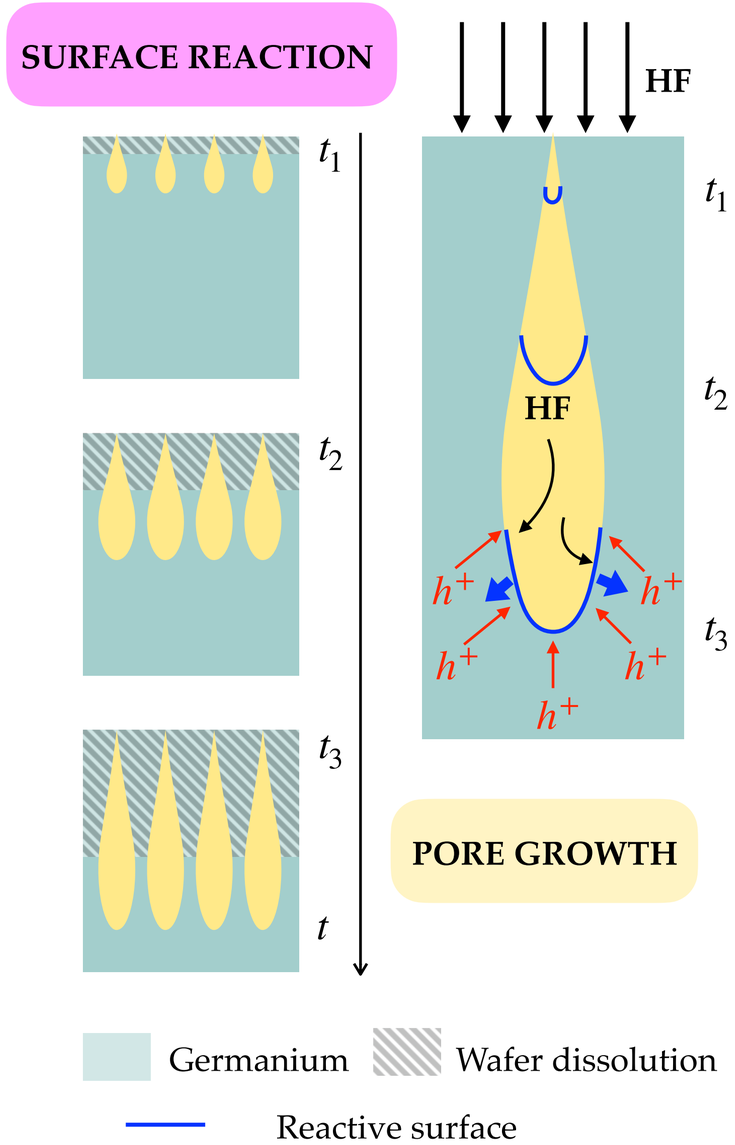
GE ANODIC DISSOLUTION IN HF – THEORETICAL MODEL[2]

Divalent and tetravalent dissolution processes

(1) $$Ge + 6HF + 2h^+ \rightarrow GeF_6^{2-} + 4H^+ + H_2$$

(2) $$Ge + 6HF + 4h^+ \rightarrow GeF_6^{2-} + 6H^+$$



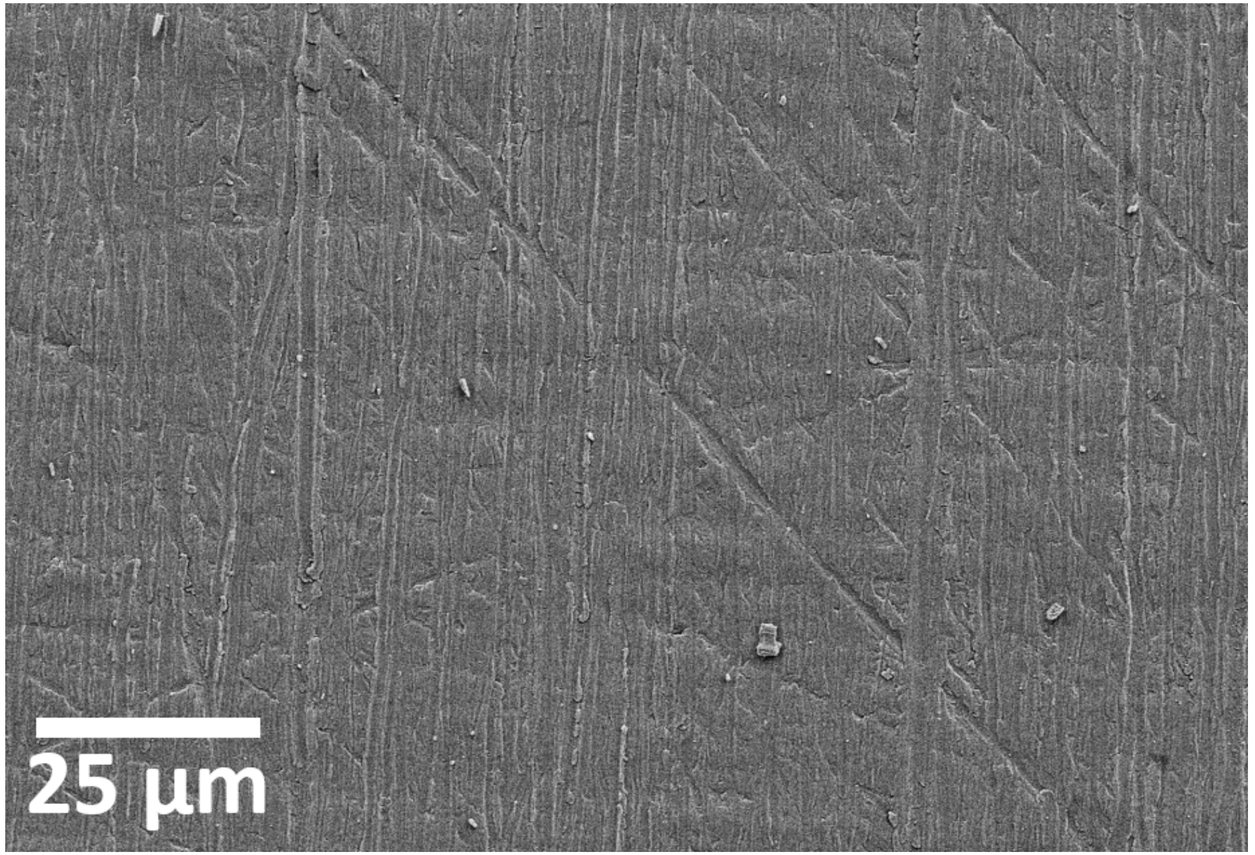


Adapted from Dupuy et al , **Electrochimica Acta (2021)**, https://doi.org/10.1016/j.electacta.2021.137935

MORPHOLOGY

MO SAMPLE

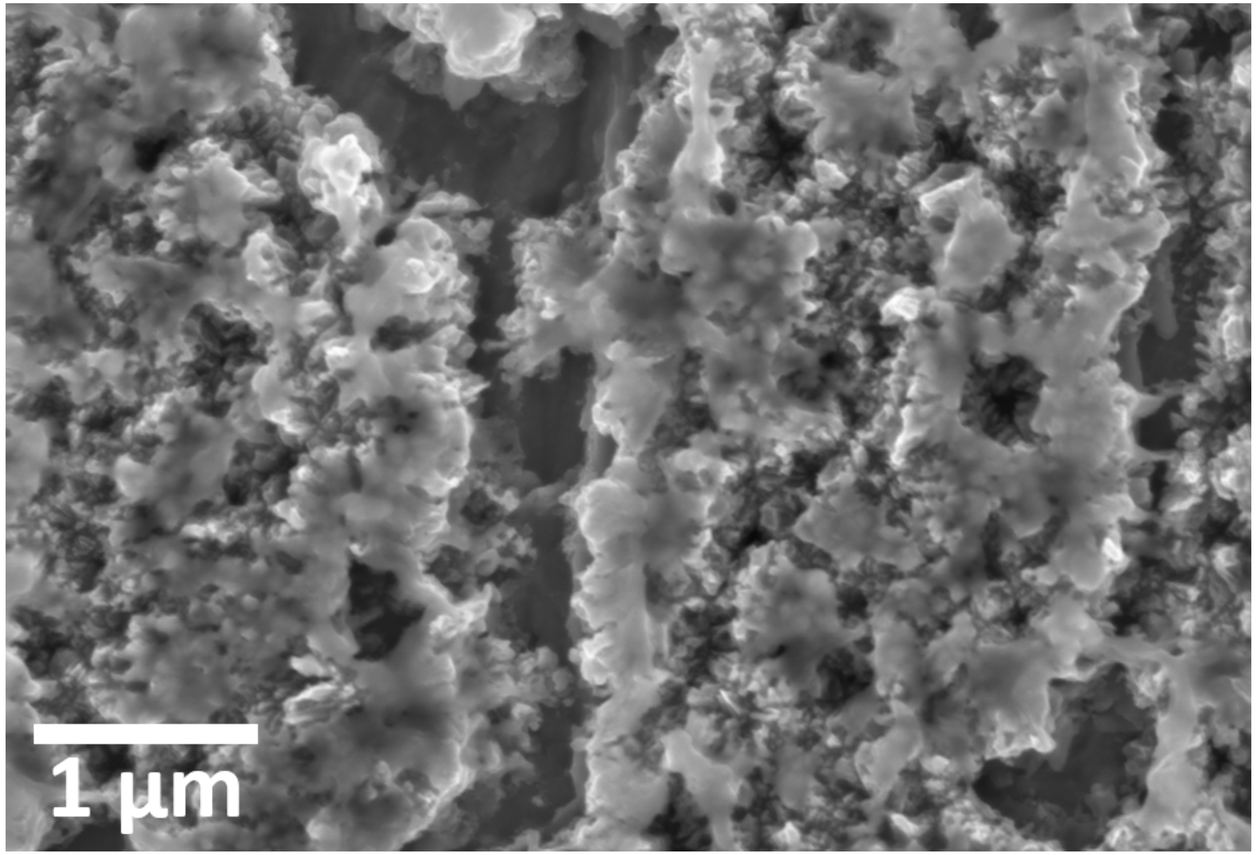
GE BULK



Bulk Ge (1μm)

Metallic Substrate

GE NANO-STRUCTURED



Nanostrutured Ge (1μm)

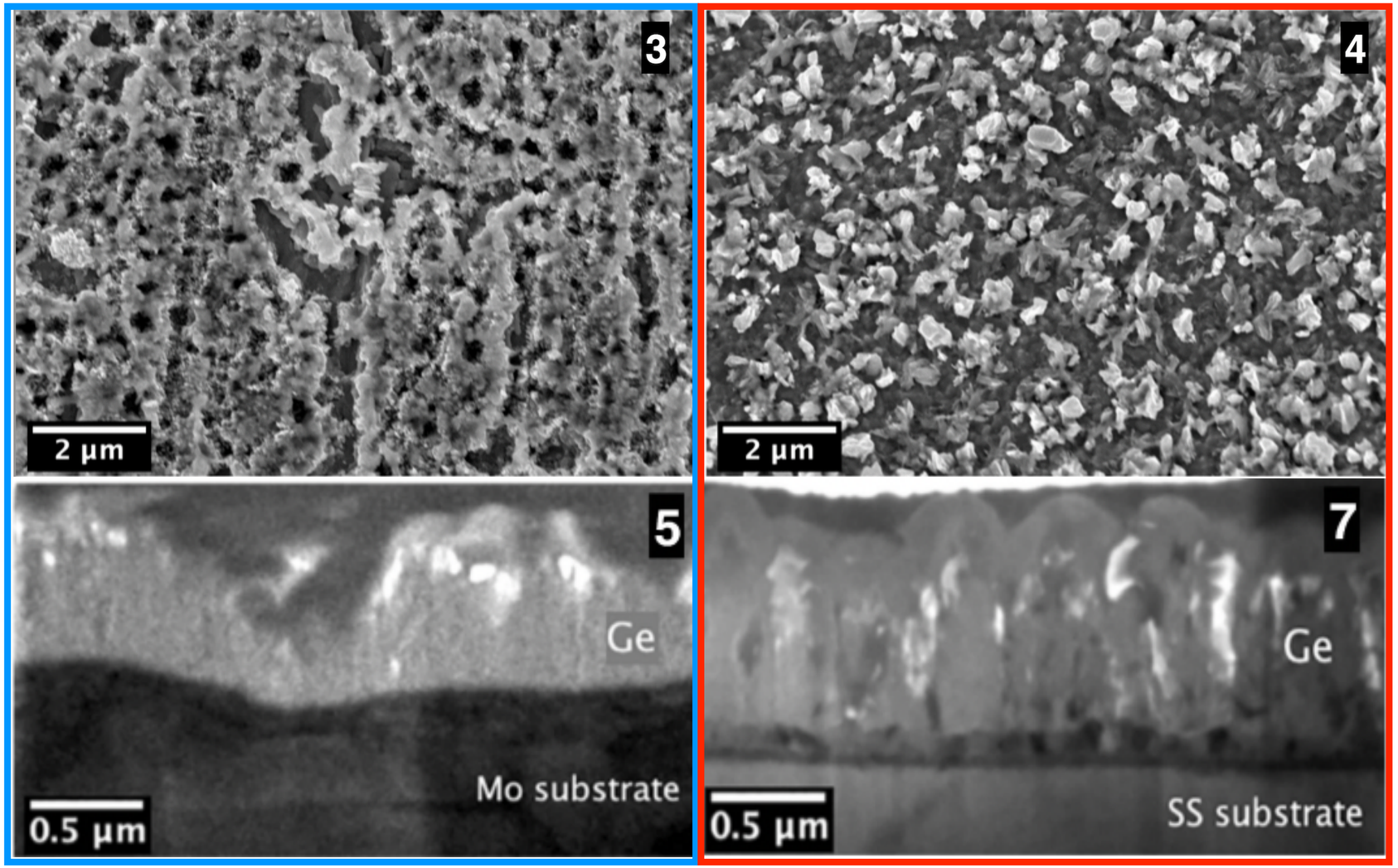
Metallic Substrate

V. Diolaiti, A. Andreoli et al, **IEEE International Conference on Nanotechnology, (2022)** DOI: 10.1109/NANO54668.2022.9928666

MO VS SS SUBSTRATE

MO SAMPLE

SS SAMPLE



V. Diolaiti, A. Andreoli et al, IEEE TNANO Vol 22, (2023) DOI: 10.1109/TNANO.2023.3311757

SEM and **cross-sectional TEM bright field** images:

- Ge layer appears compact and uniform over the entire area
- Good adhesion of the film for both substrates
- Nanostrutures along all the deposition thickness

CELL ASSEMBLY

Ar-filled MBraun glovebox

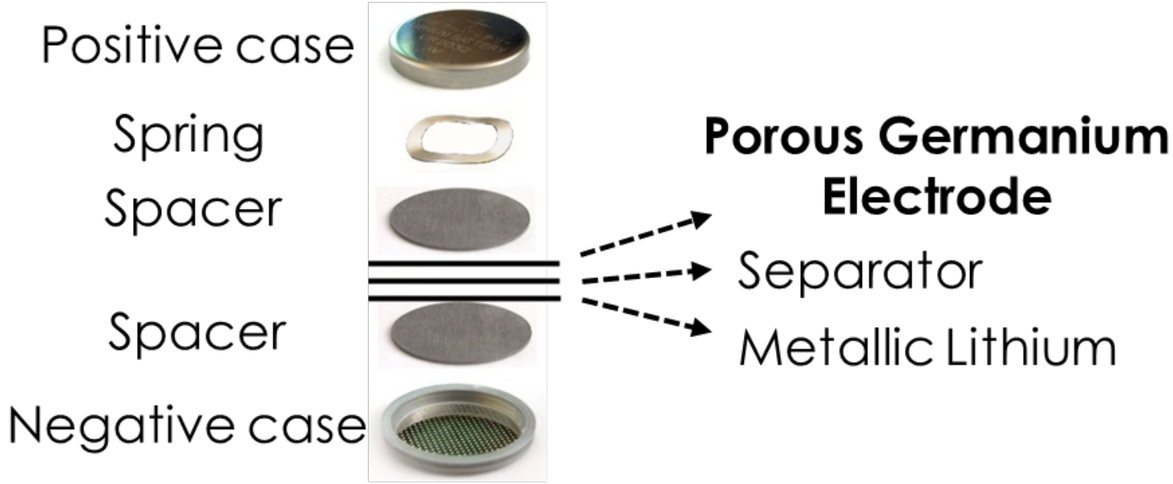
LP30

+

FEC additive
(fluoroethylene carbonate)

Mass loadings ~ 0.3 mg
for 1 μm Ge film

HALF CELL CONFIGURATION FOR A CR2032 CELL

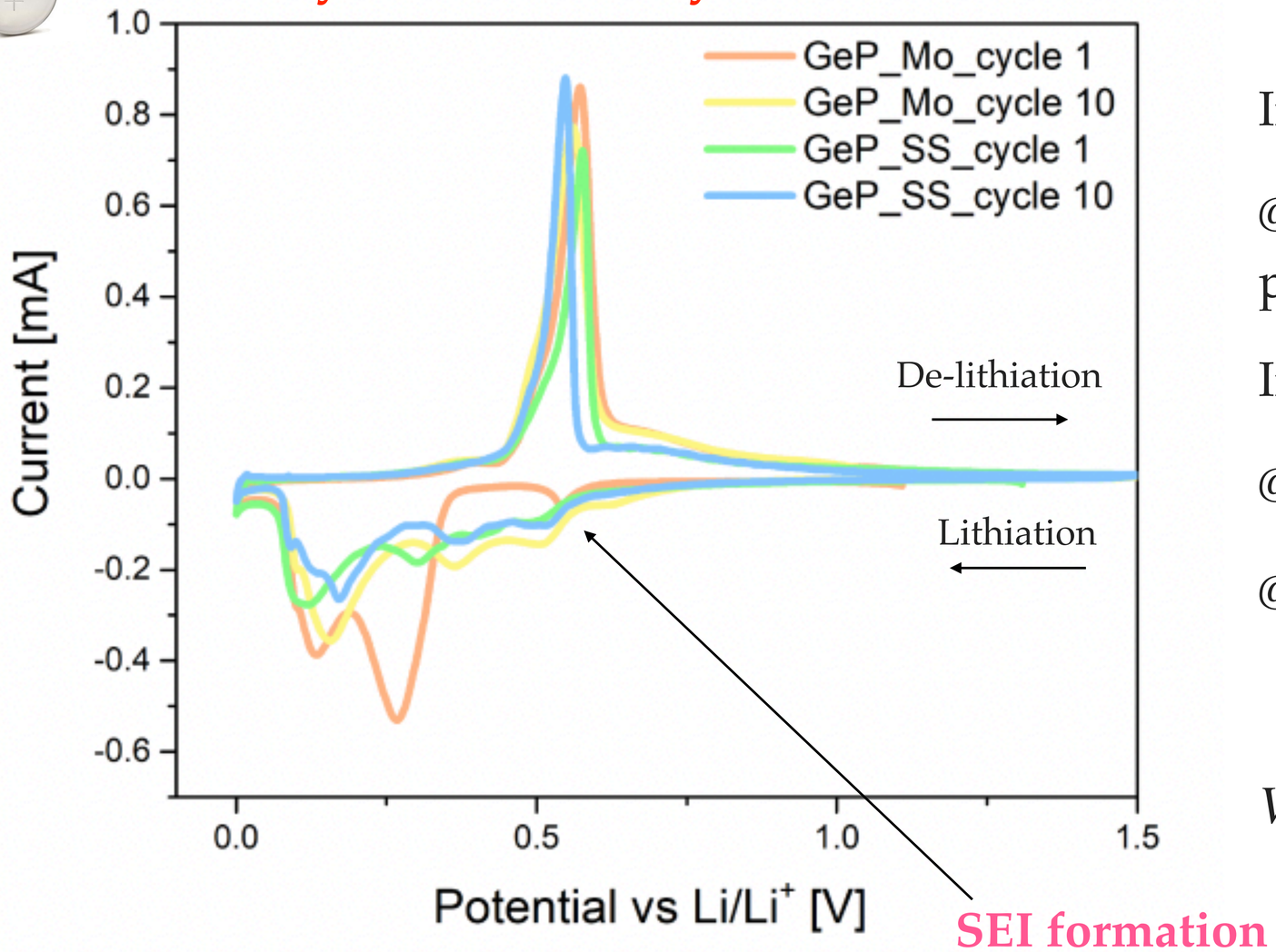


LP30 : 1M **$LiPF_6$** in EC:DMC=1:1 vol

Solvent in the electrolyte:
DMC : dimethyl carbonate $[M+H+MeOH]^+$
EC : ethylene carbonate $[M+H]^+$

Conducting salt **$LiPF_6$** lithium hexafluorophospate

Cyclic voltammetry on SS and Mo



$V \in [0.01 - 1.5]$ V

In **cathodic scan**:

@$V = 0.6$ V delithiation of the Li_xGe phases into aGe

In **anodic scan**:

@ $V \sim 0.25$ V: cGe $\rightarrow Li_7Ge_3$

@ lower V structural transformation

$$cLi_7Ge_3 \rightarrow aLi_7Ge_3$$

$V \in [0.15 \div 0]$ V conversion

$$aLi_7Ge_3 \rightarrow Li_{15}Ge_4$$

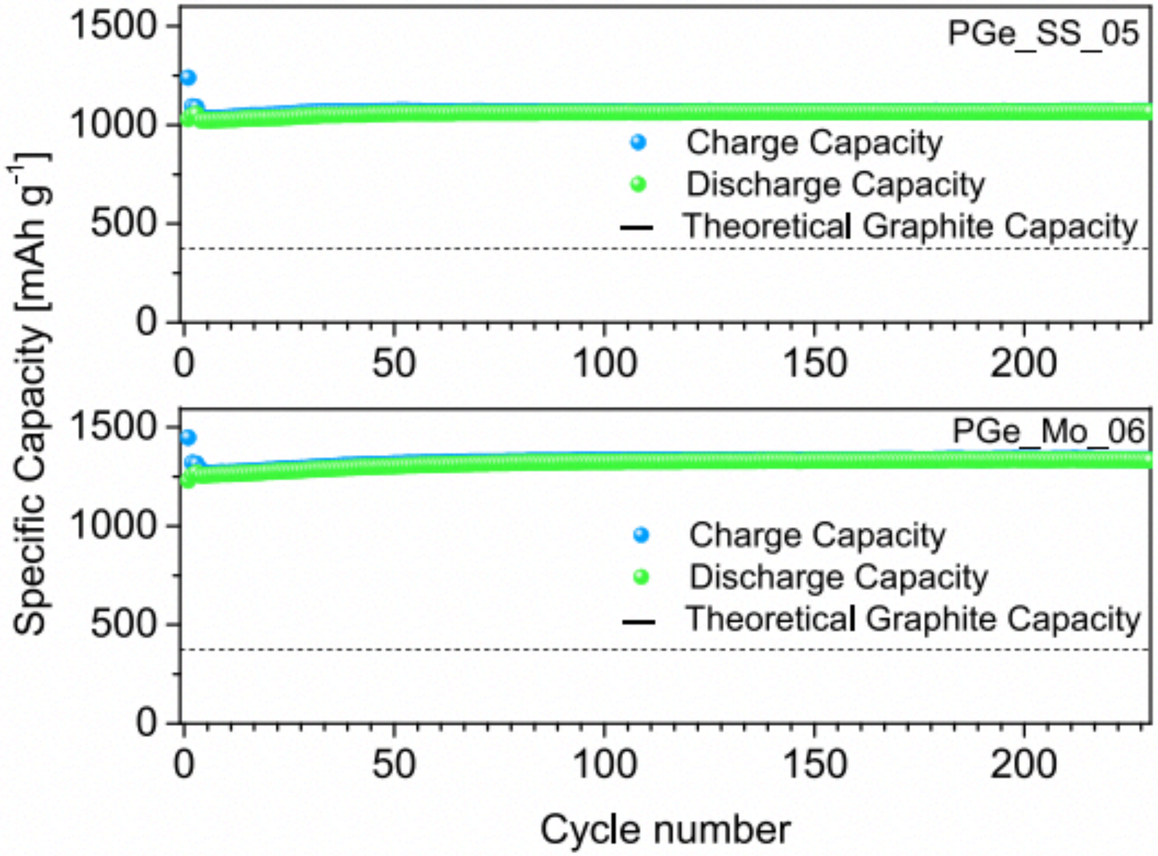
V. Diolaiti, A. Andreoli et al, IEEE TNANO Vol 22, (2023) DOI: 10.1109/TNANO.2023.3311757

ELECTROCHEMICAL ANALYSIS

INTERESTING FOR AEROSPACE APPLICATIONS!!

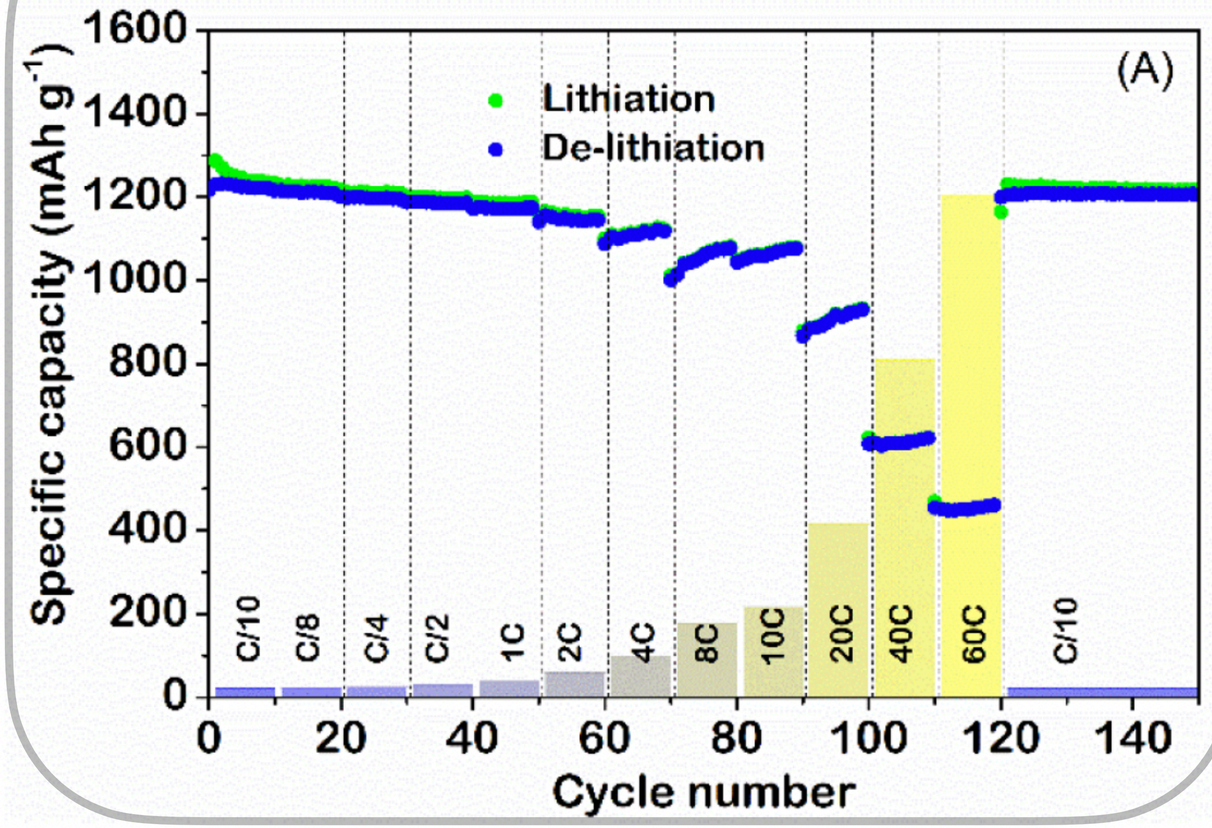
THANK TO SILVIO FUGATTINI FOR THIS MEASUREMENT

Capacity @ 1C on SS and Mo



V. Diolaiti, A. Andreoli et al, IEEE TNANO Vol 22, (2023) DOI: 10.1109/TNANO.2023.3311757

Capacity @ different C-rates on Mo

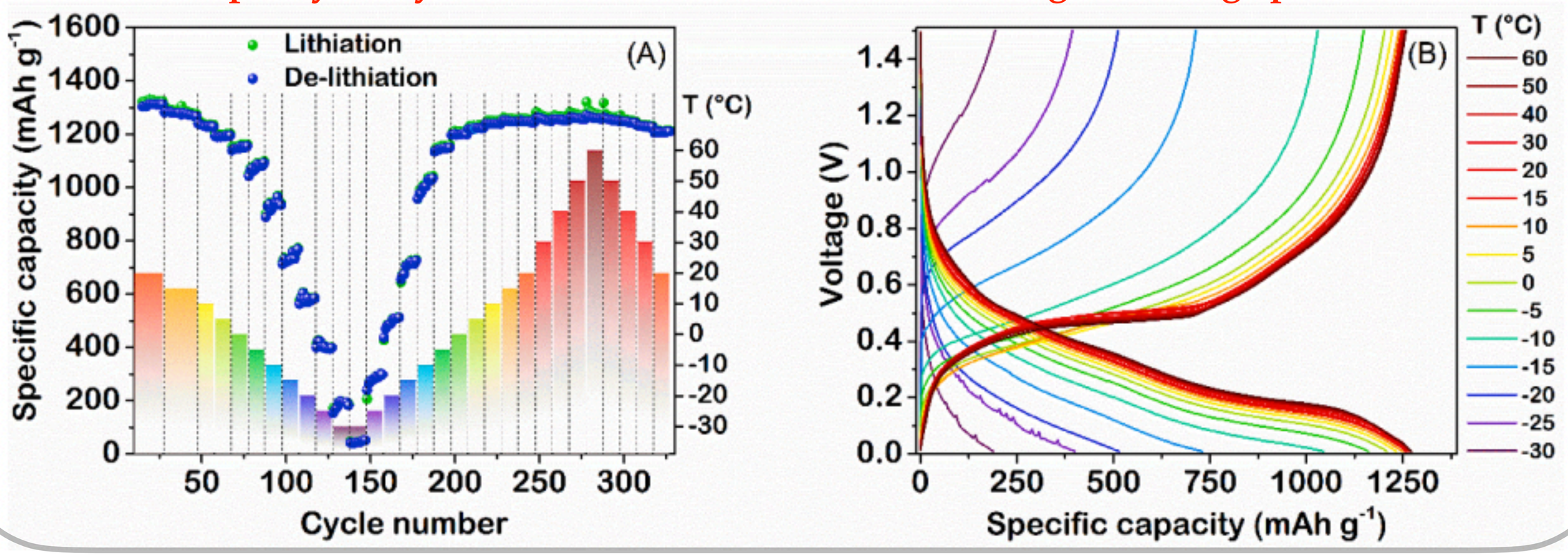


S. Fugattini, A. Andreoli et al, Electrochimica Acta, Volume 411 (2022) 139832, ISSN 0013-4686 https://doi.org/10.1016/j.electacta.2022.139832

ELECTROCHEMICAL ANALYSIS

THANK TO SILVIO FUGATTINI FOR THESE MEASUREMENTS

Temperature investigation: both plots show the performance of a porous Ge based electrode cycled @ 1C

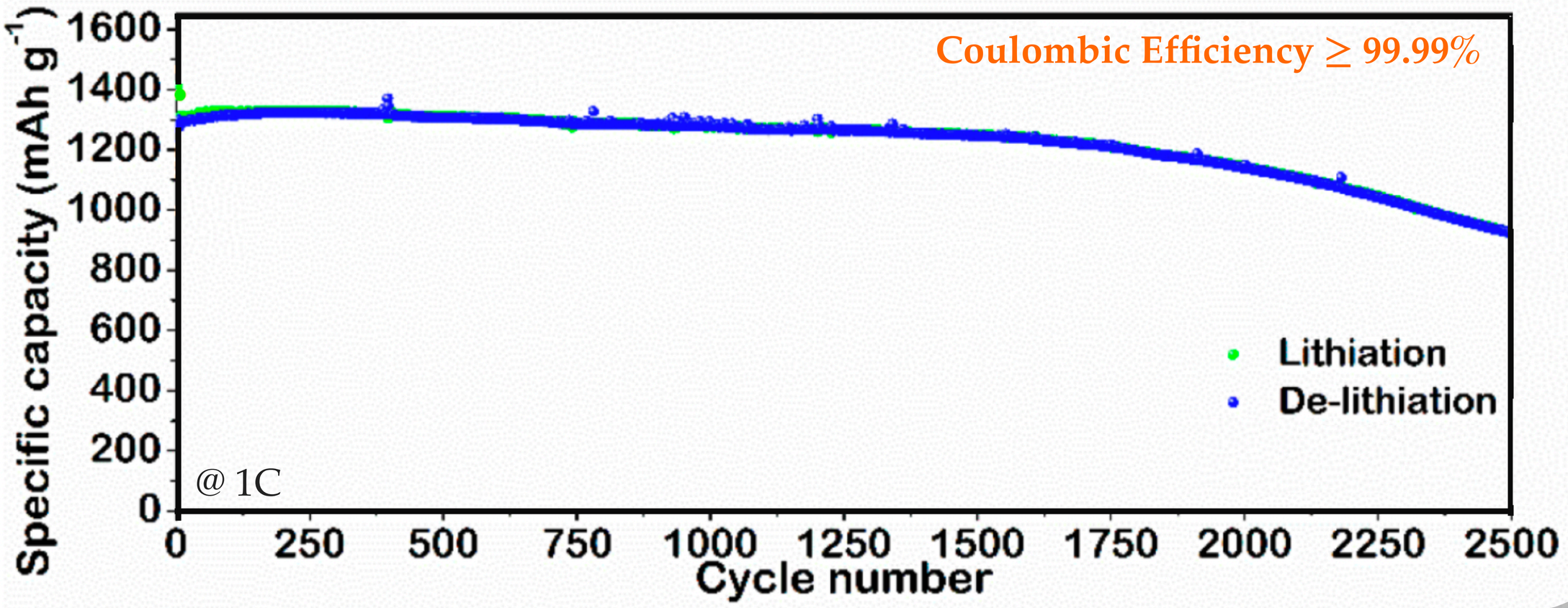


S. Fugattini, A. Andreoli et Al, Electrochimica Acta, Volume 411 (2022) 139832, ISSN 0013-4686 https://doi.org/10.1016/j.electacta.2022.139832

ELECTROCHEMICAL ANALYSIS

THANK TO SILVIO FUGATTINI FOR THIS MEASUREMENT

BEST RESULT ACHIEVED SO FAR!



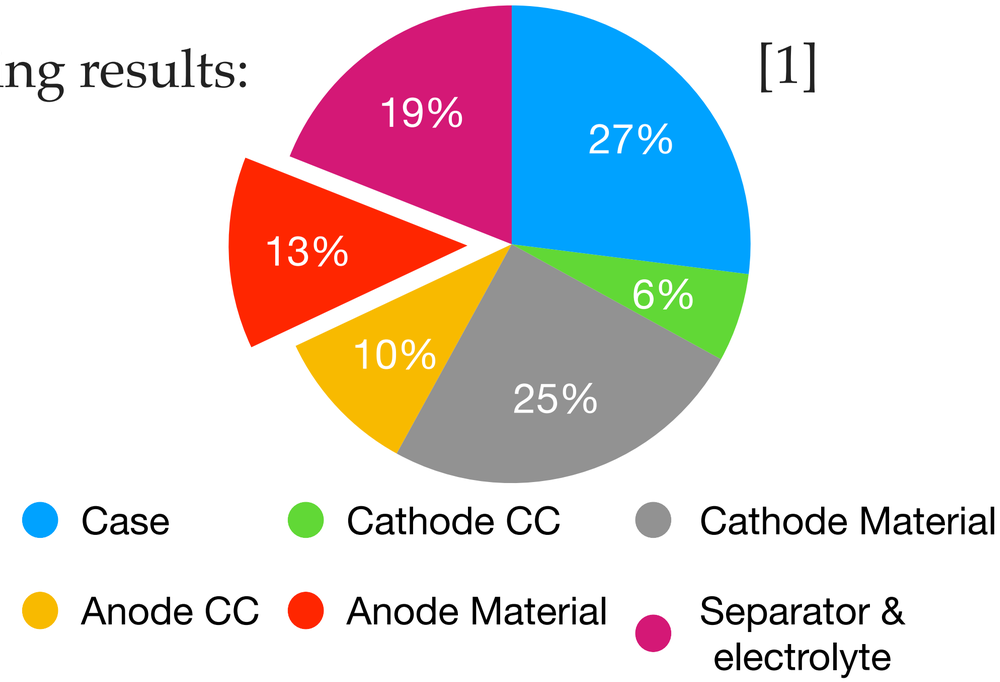
S. Fugattini, A. Andreoli et Al, Electrochimica Acta, Volume 411 (2022) 139832, ISSN 0013-4686 https://doi.org/10.1016/j.electacta.2022.139832

CONCLUSIONS

The here proposed Porous Germanium anode shows promising results: [1]

- Specific capacity over **3x higher than standard graphite**

only 1/3 of the active material is needed



From [1] the total cell mass of a LFP | Graphite 18650 cell is 38.8 g
→ 5.04 g Graphite

→ only 1.68 g of Germanium

Saving 8.7% of weight!

[1] Adapted from RSC Adv., 2014,4, 3633-3642 . DOI: 10.1039/c3ra45748f

CONCLUSIONS

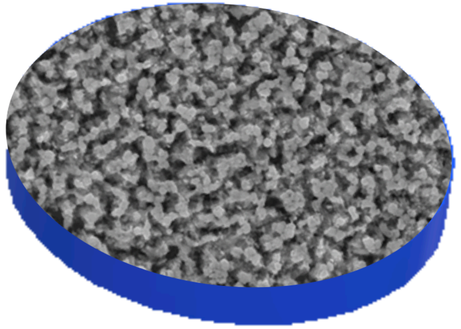
The here proposed Porous Germanium anode shows promising results:

- Specific capacity over **3x higher than standard graphite**
- Impressive stability for hundreds of cycles
- High rate capability

RELIABLE & HIGH-PERFORMING

NEXT STEPS

- Mass loading increase
- Coin and pouch full cells
- SEI formation mechanisms



CONCLUSION

The activities shown have been supported and funded by the Italian Space Agency, in the framework of the invitation to tender “Interdisciplinary Enabling Technologies” (ASI loan agreement N. 2021-2-U.0), project GLITTERY (Germanium Lithium-Ion baTTERY).

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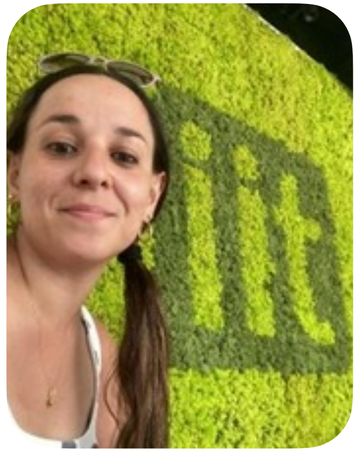
Remo P. Zaccaria - IIT



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Professor **Donato VINCENZI** -
UNIFE: donato.vincenzi@unife.it

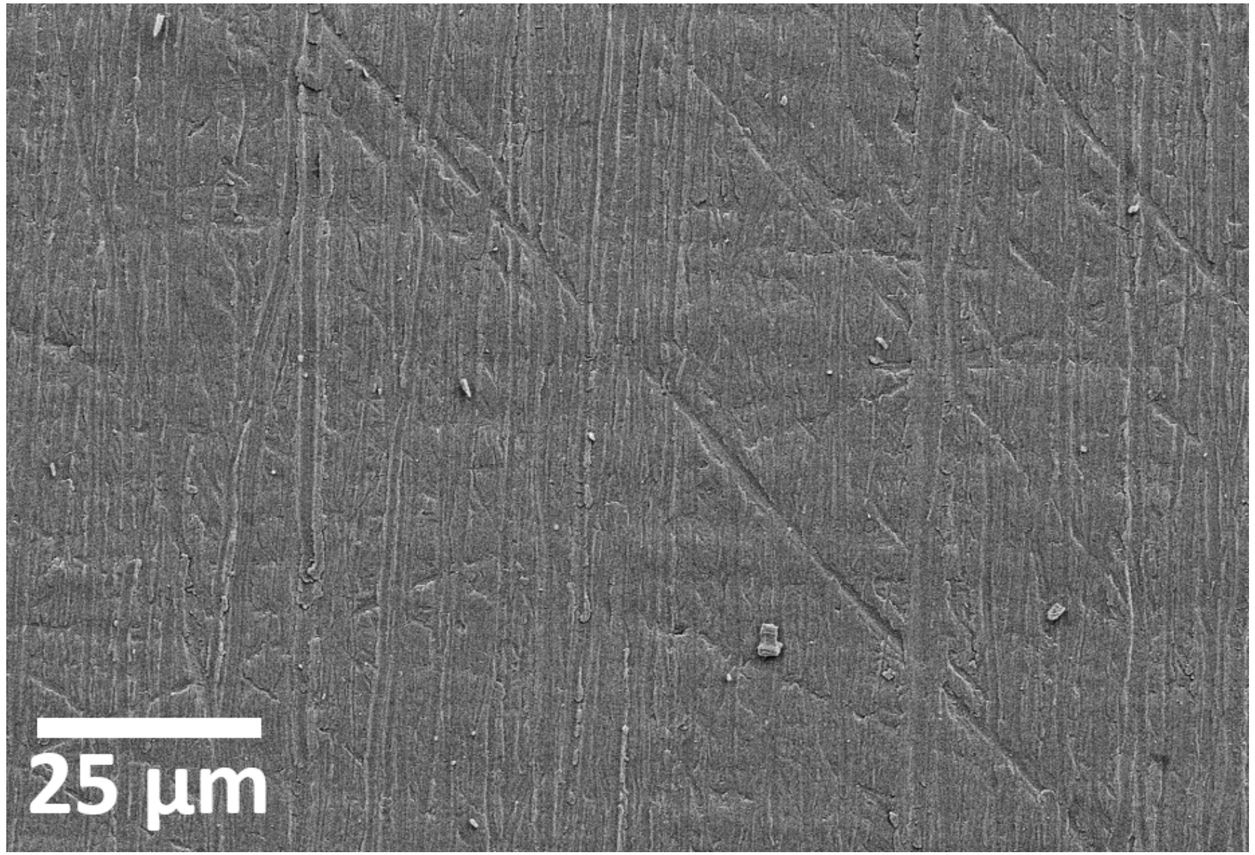
THANK YOU FOR YOUR ATTENTION!

BACKUP SLIDES

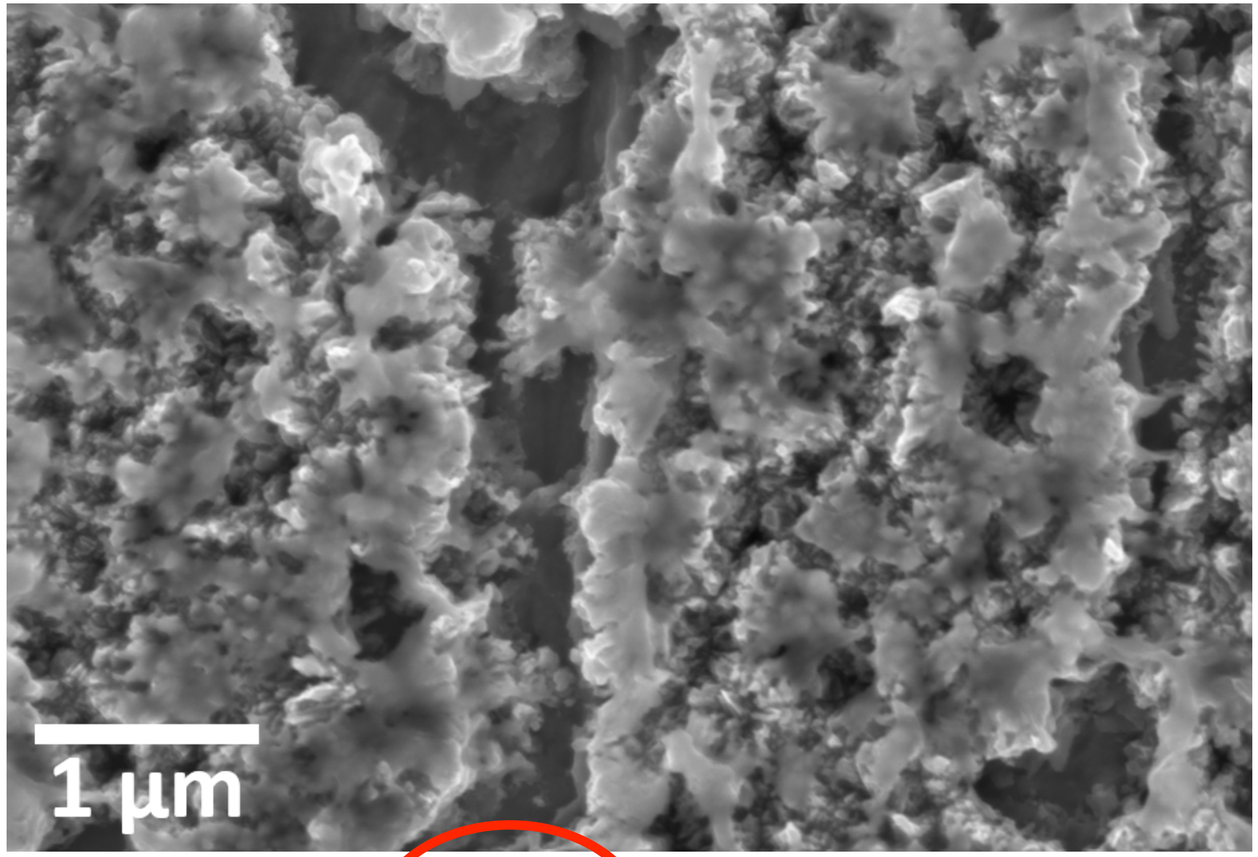
BACK UPS- POROSITY CALCULATION

MO SAMPLE

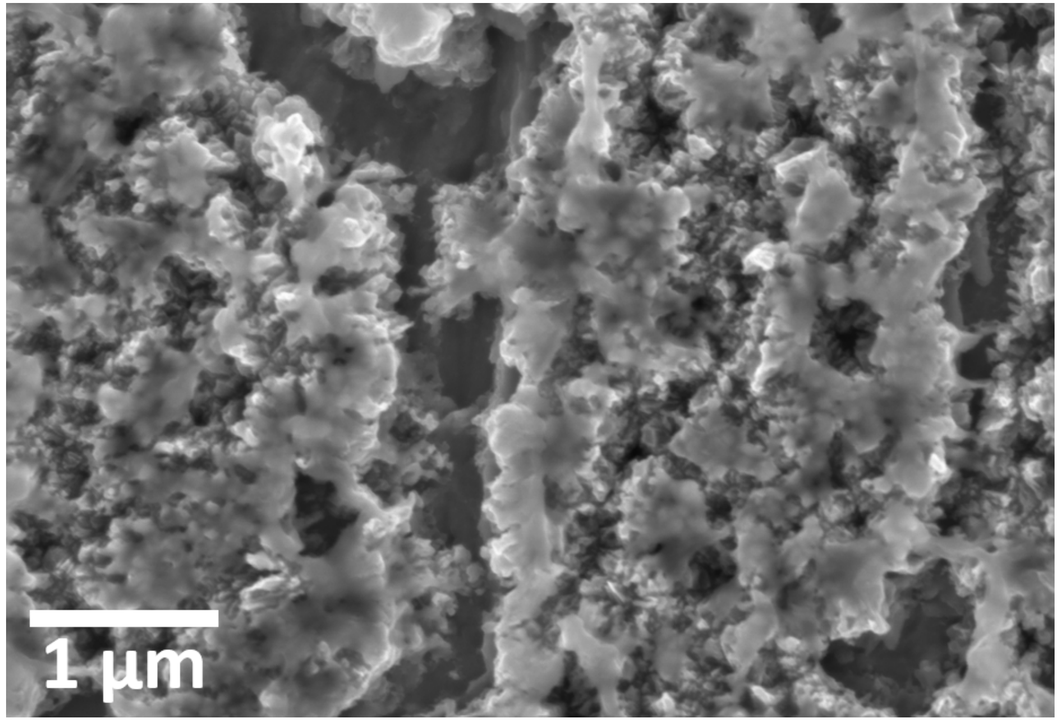
GE BULK

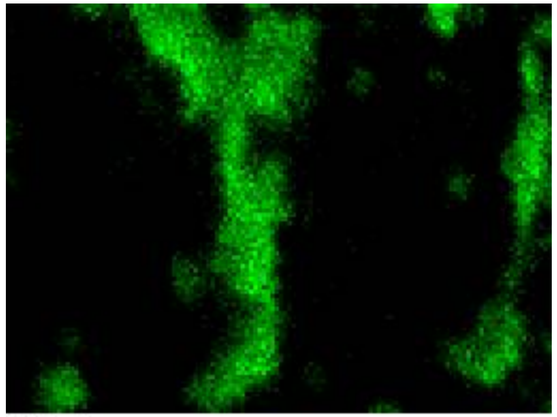


GE NANO-STRUCTURED

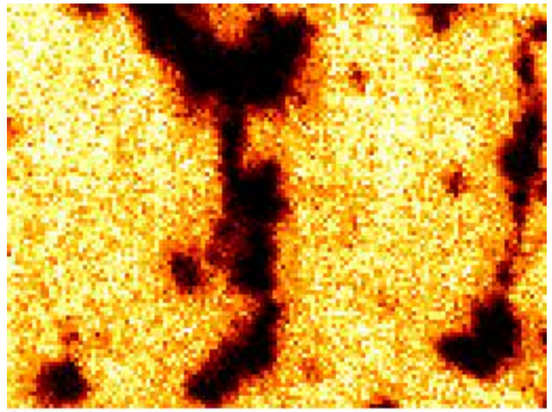


$$\text{Porosity} = \frac{\text{void volume}}{\text{layer total volume}} = \frac{\text{mass removed}}{\text{total mass}} \sim 70\,\%$$



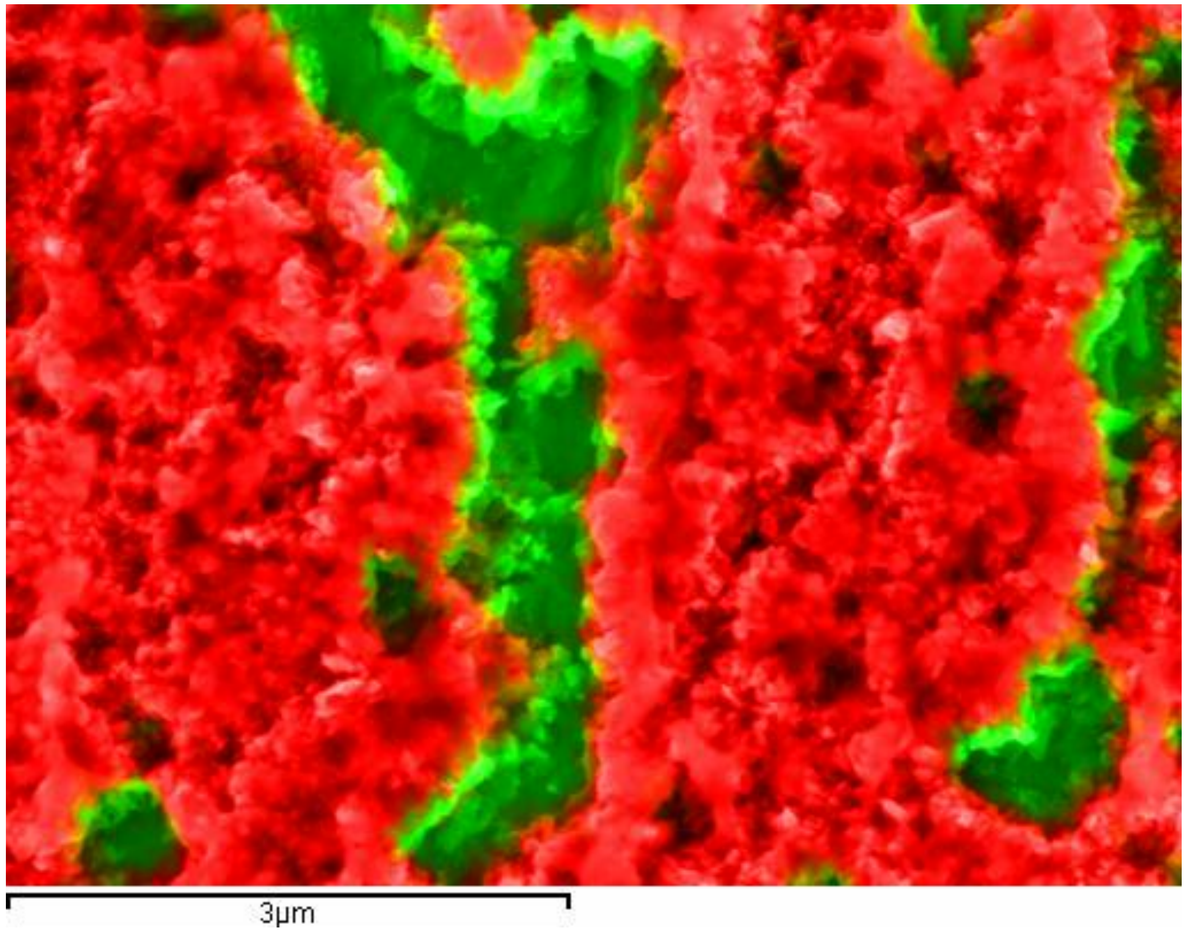


Mo La1



Ge La1_2

SEM-EDX ANALYSIS

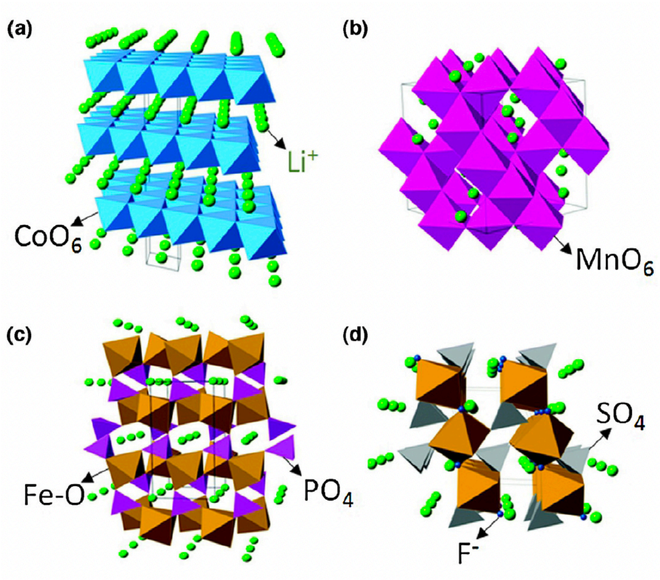


CATHODE MATERIALS

An intercalation cathode is a solid host which can store guest ions which can be inserted and removed in a reversible way.

Crystal structures of representative intercalation cathodes

Layered



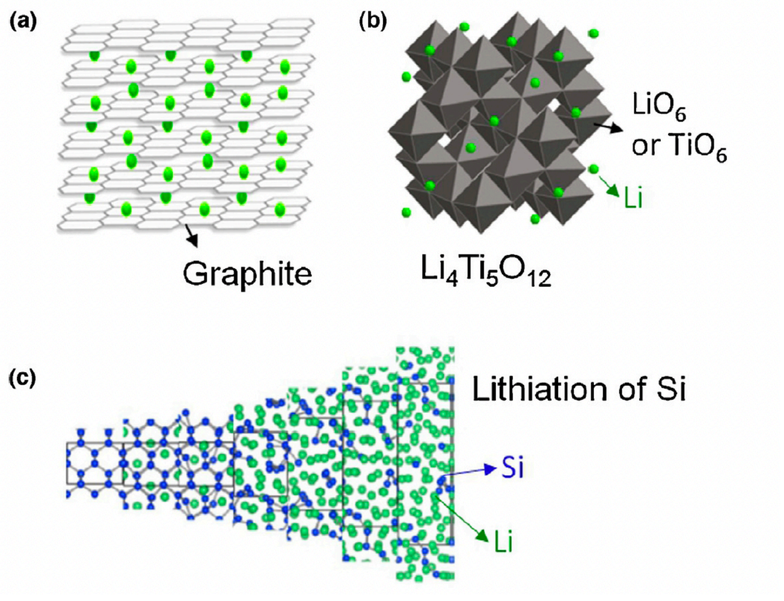
Layered

Olivine

Tavorite

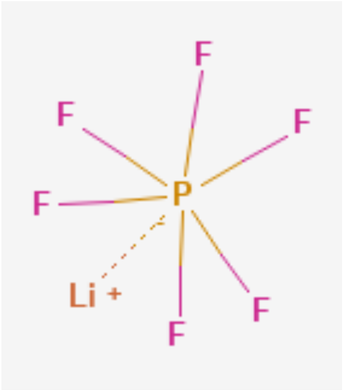
ANODE MATERIALS

Commercial LIB use graphite anodes which has a layered structure, but tha anode material also includes Li-alloy



[4] *NItta et al, "Li-ion battery materials: present and future", http://dx.doi.org/10.1016/ j.mattod.2014.10.040*

BACK UPS - LIPF6



The most used conducting salt is **$LiPF_6$**

✅ the protection of Al current collectors

❌ chemical and thermal instability in organic carbonates —> electrolyte ageing

The formation of ageing products begins with the reaction with organic carbonate with PF_5.

The electrochemical reaction of the electrolyte compounds at the charge anode build a protective layer on the anode, the Solid Electrolyte Interface (SEI)

In battery applications one exploits:

- its high solubility in non-aqueous polar solvents
- Inertness of PF_6 anion towards strong reducing agents such as metallic Li

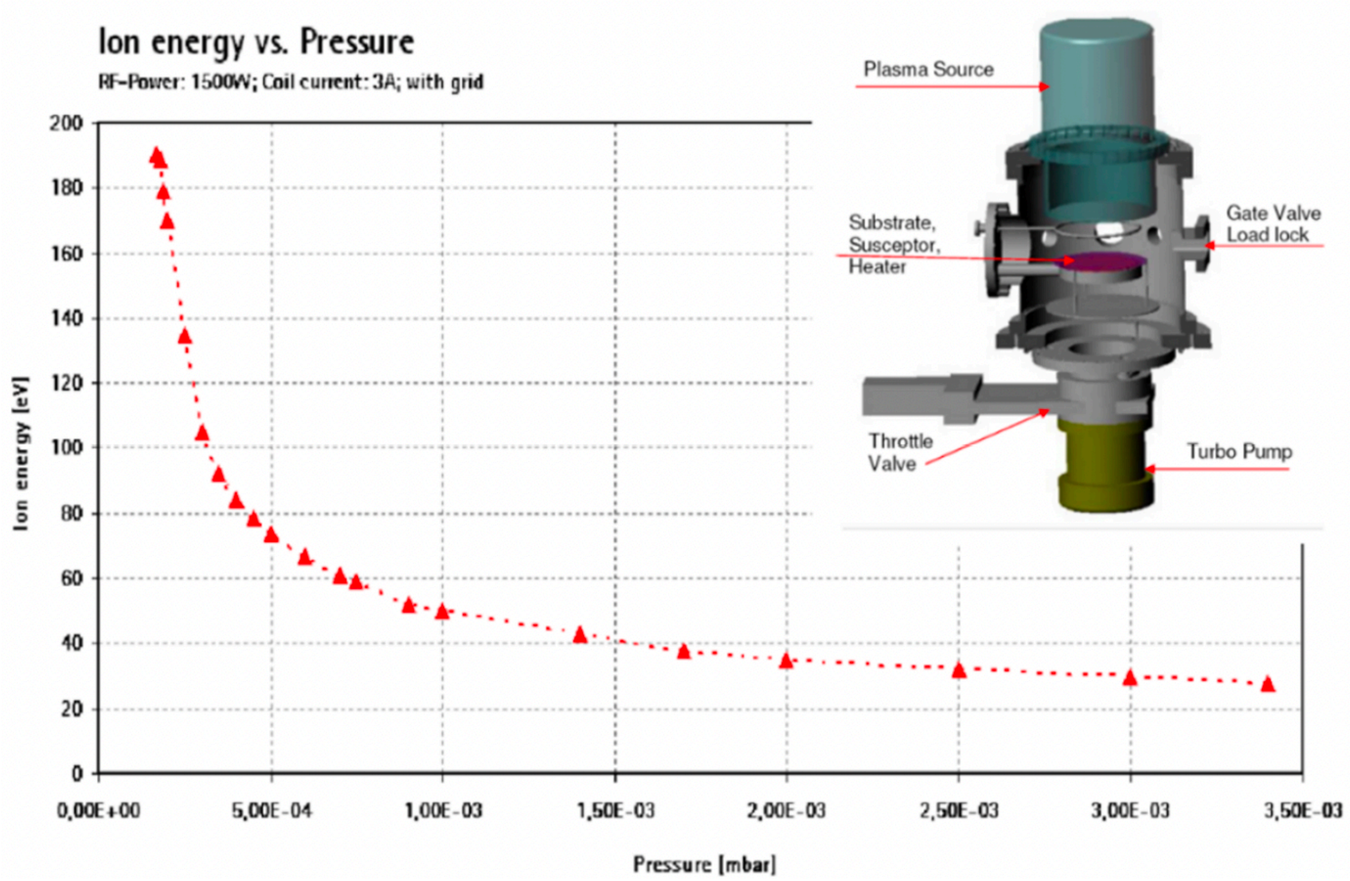
BACK UPS - PECVD

A low energy plasma is used to avoid damage to the crystal structure from high-energy ions.

The plasma is excited at a $\nu = 13.56$ **MHz**

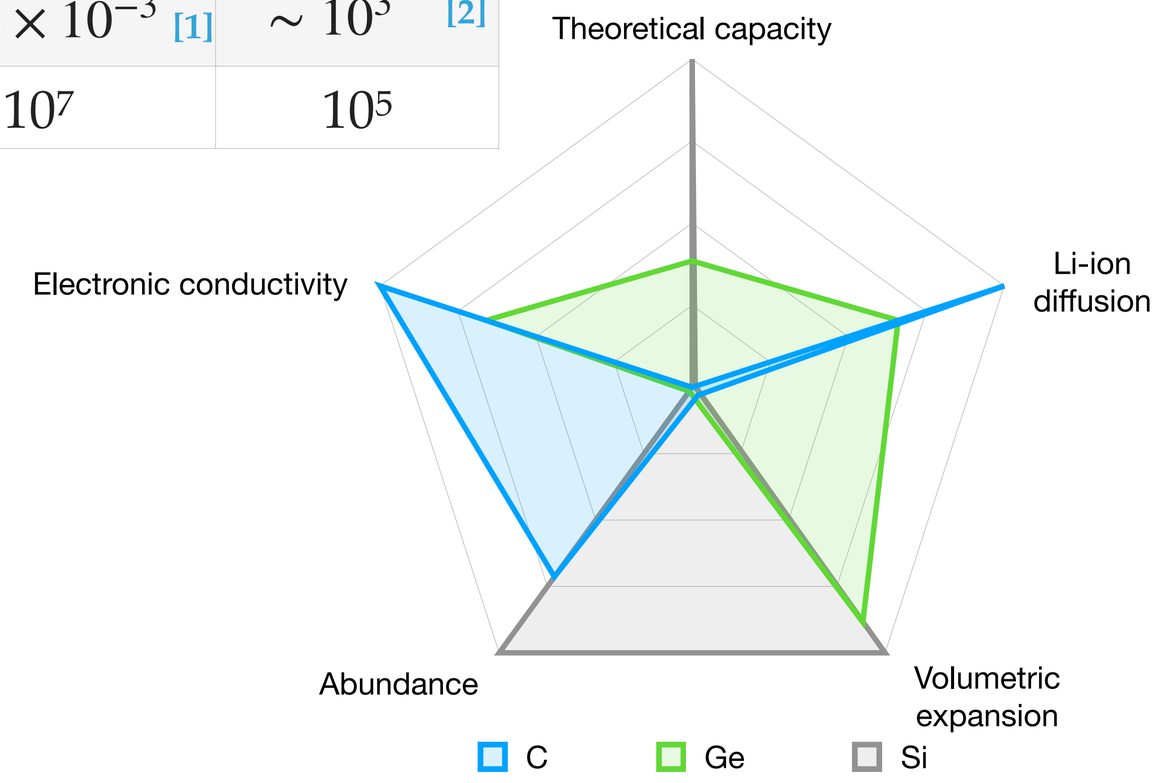
only e^- are effectively accelerated

energy transfer to the heavy particles occurs only via collision



BACK UPS - RADAR PLOT

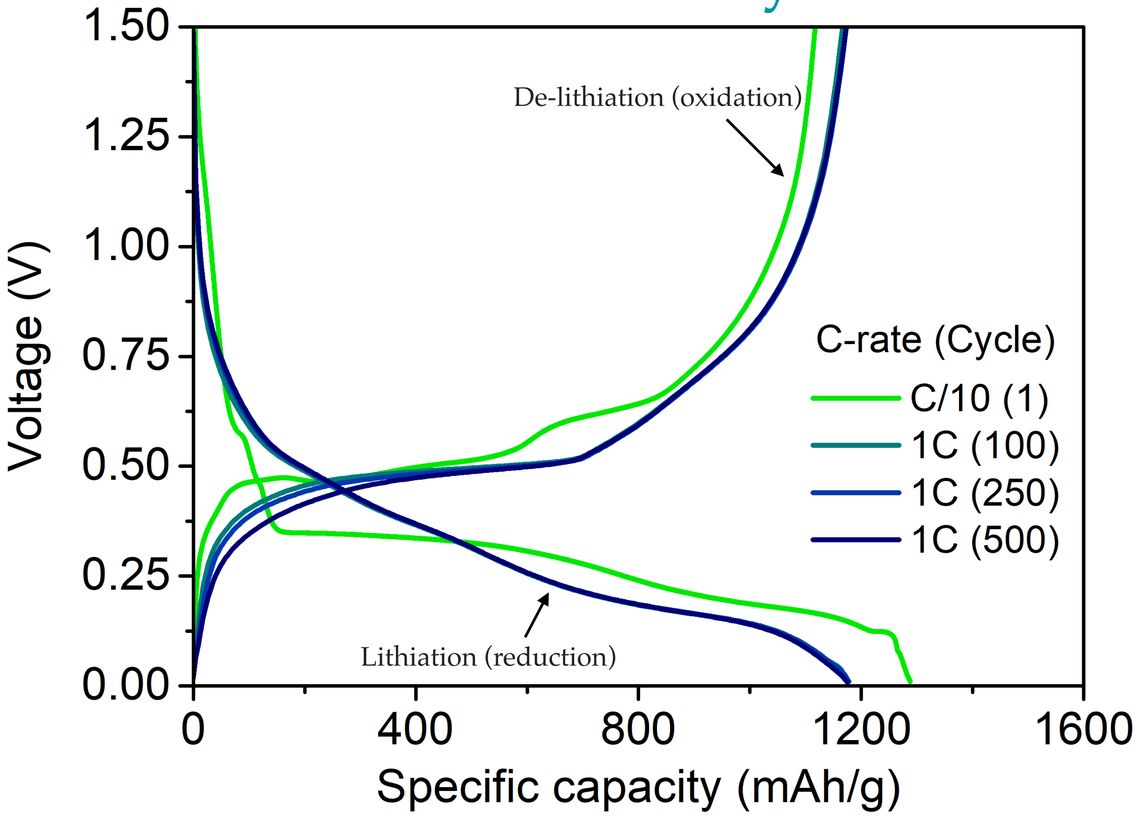
	Ge	Si	C
Theoretical capacity [mAh/g] [1]	1624	4200	372
Volume expansion [%] [1]	370	420	12
Li ion diffusion [cm²/s]	6.51×10^{-12} [1]	1.41×10^{-14} [1]	$\sim 10^{-11}$
Electronic conductivity [S/m]	2.1 [1]	1.6×10^{-3} [1]	$\sim 10^{3}$ [2]
Abundance	10^{0}	10^{7}	10^{5}



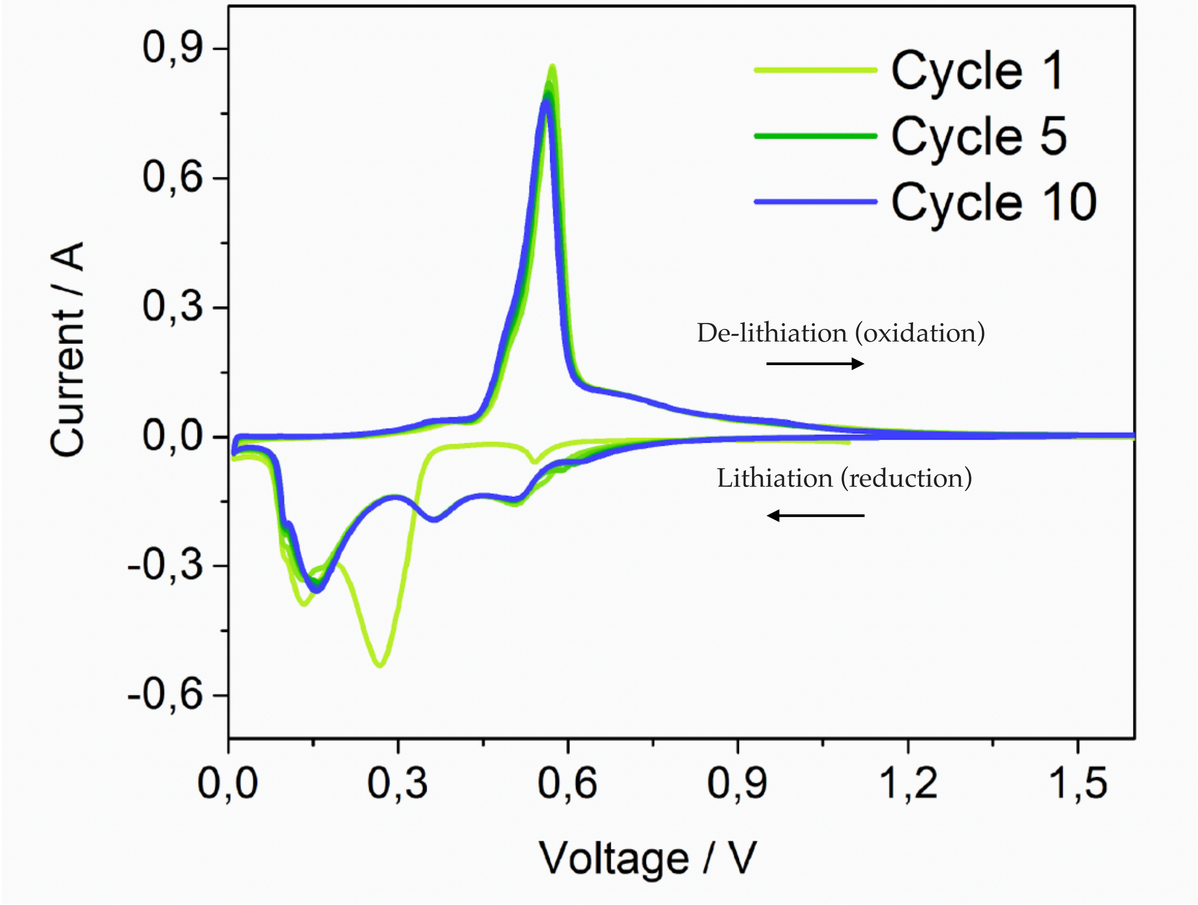
[1] https://doi.org/10.1016/j.ensm.2020.05.010
[2] https://doi.org/10.1021/jz100188d

ELECTROCHEMICAL CHARACTERISATIONS

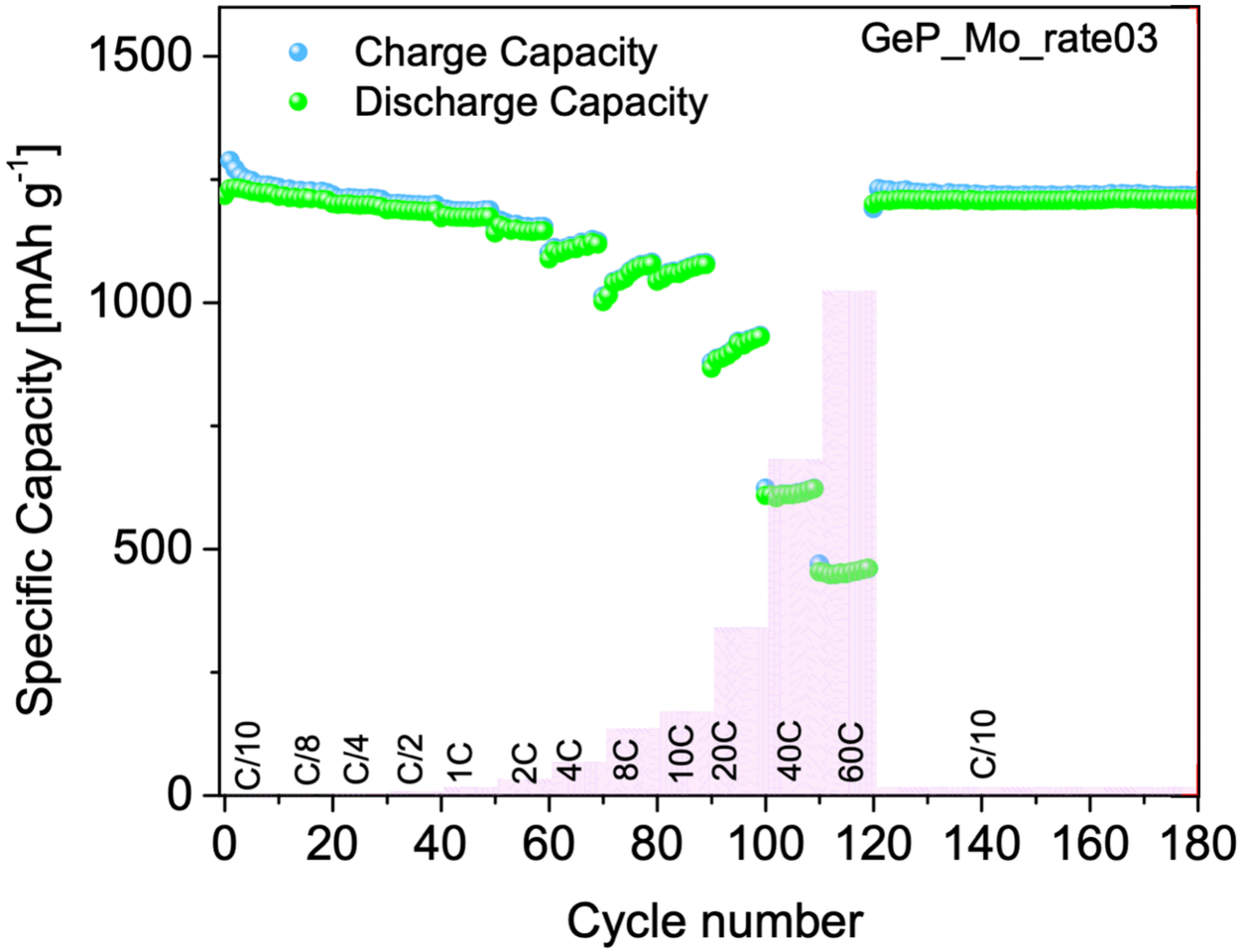
Galvanostatic cycles

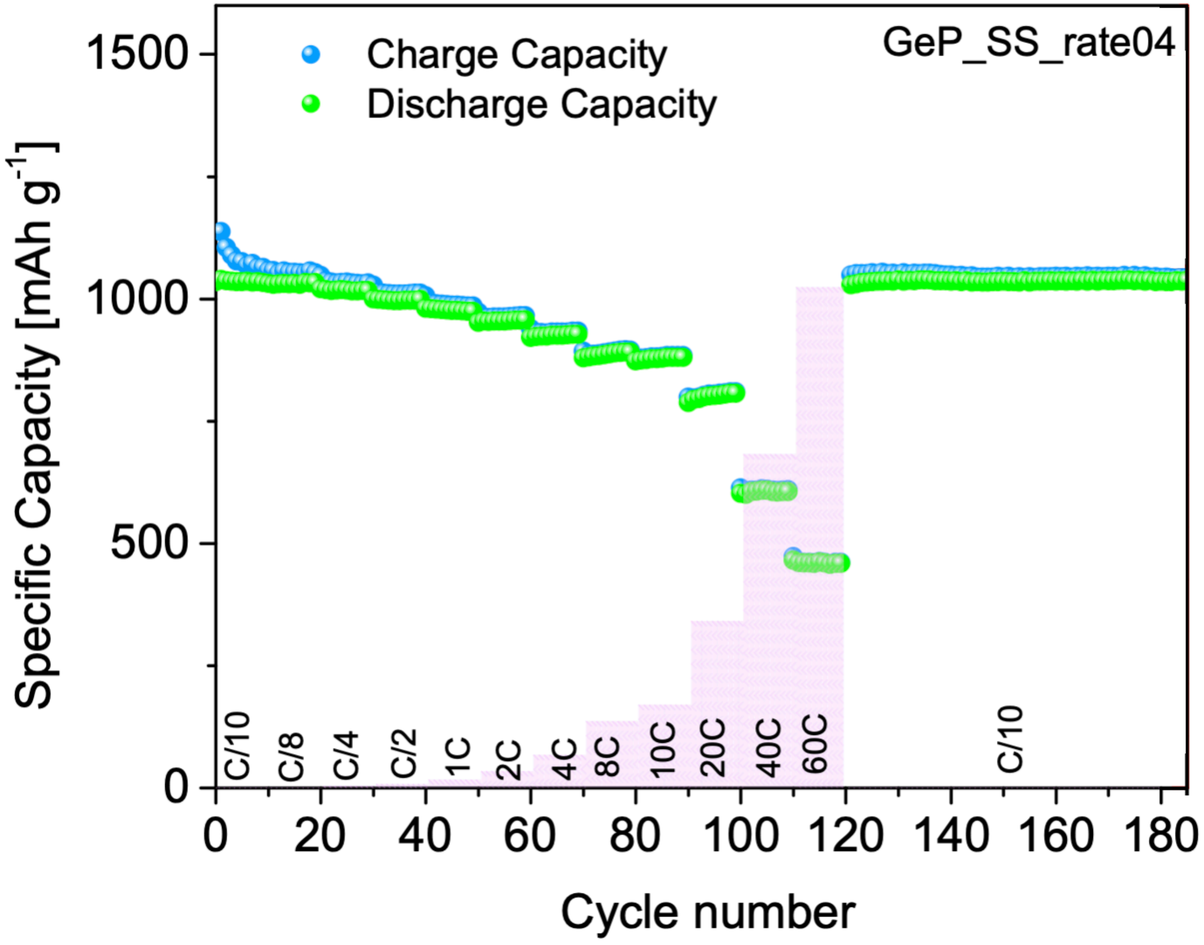


Cyclic Voltammetry

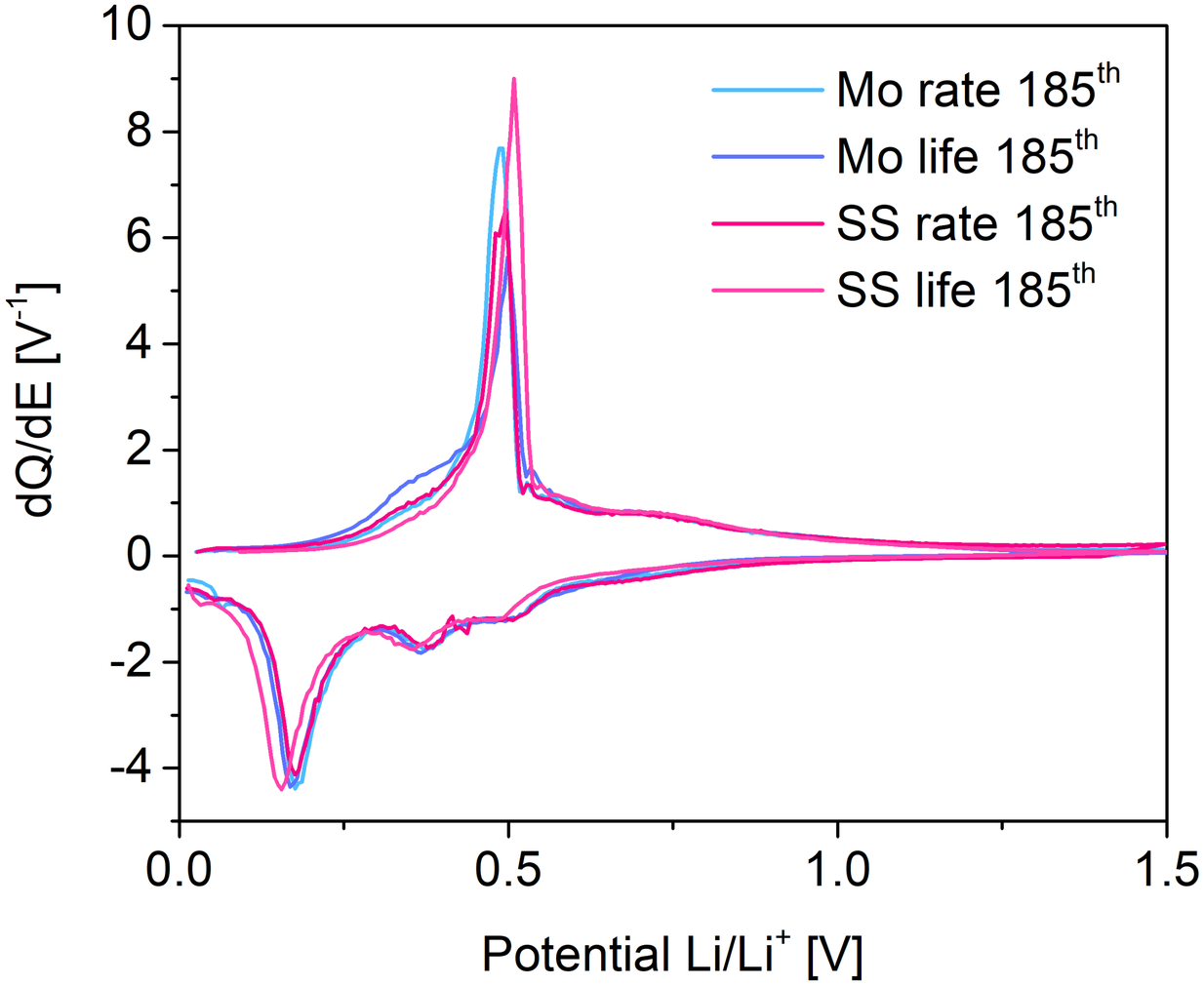


BACK UPS - C-RATE ON MO AND SS



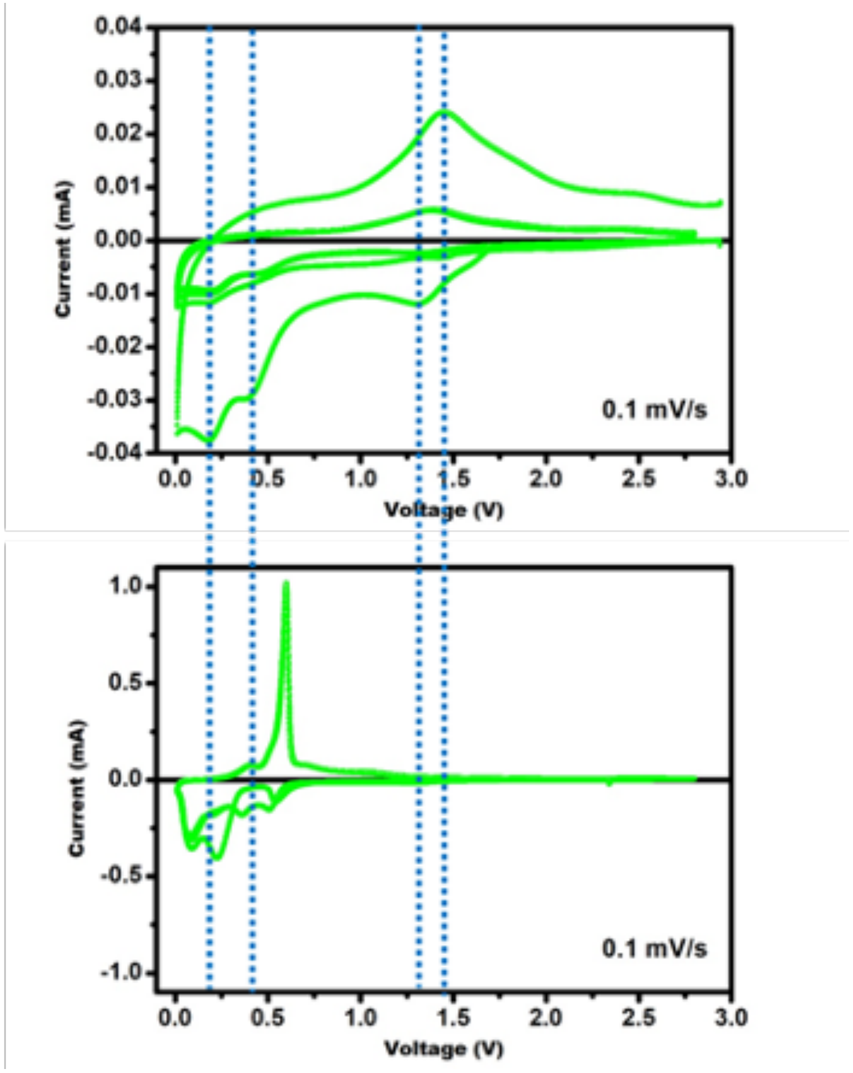


BACK UPS - DIP


Mo rate 185th
Mo life 185th
SS rate 185th
SS life 185th
dQ/dE [V-1]
Potential Li/Li+ [V]
10
8
6
4
2
0
-2
-4
0.0
0.5
1.0
1.5

BACK UPS - V vs Li

Pristine Molybdenum

No contribution from the substrates

Porous Germanium on Molybdenum