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

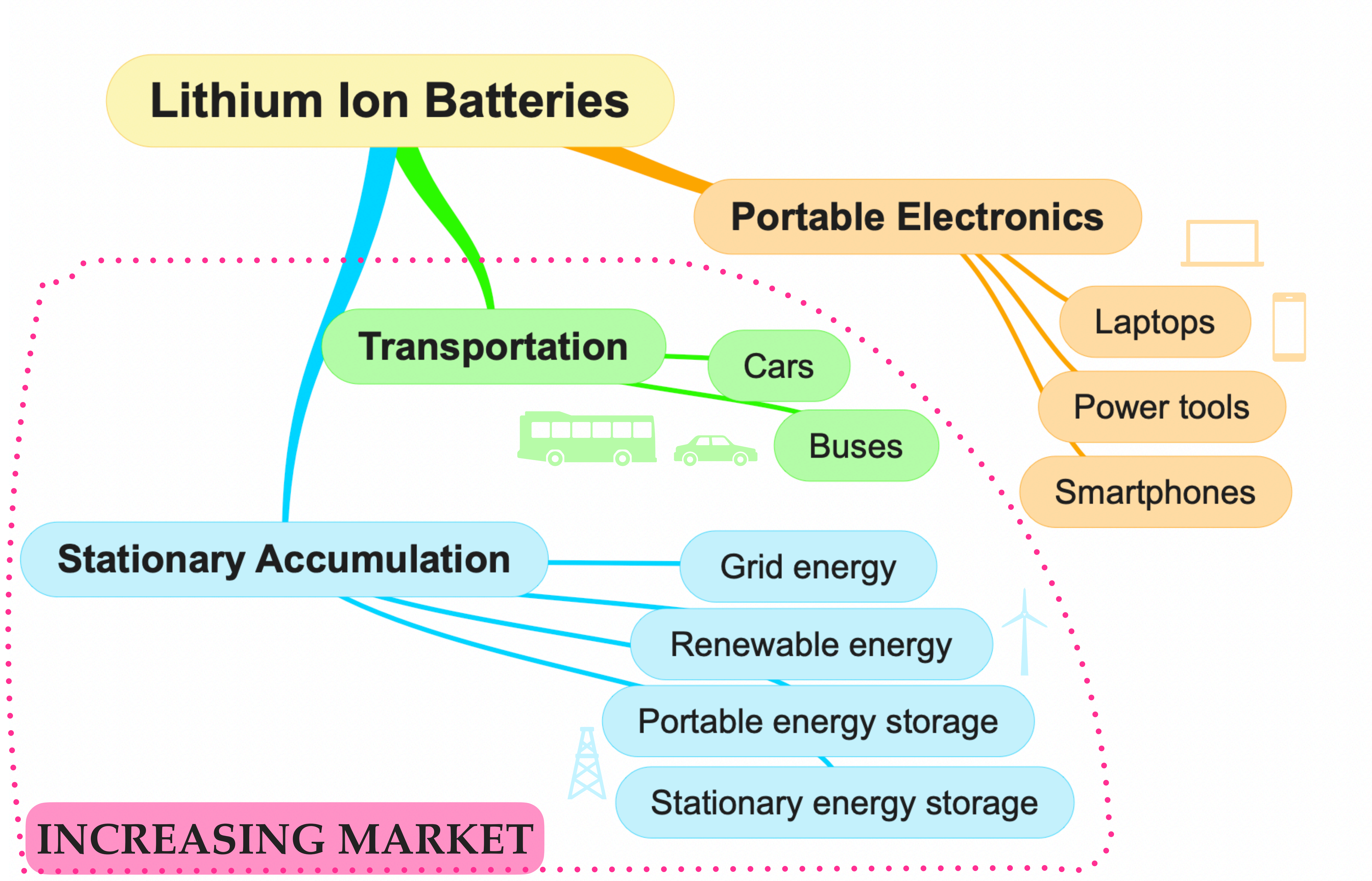
GLITTERY
BATTERIE SPAZIALI

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."



Lithium Ion Batteries

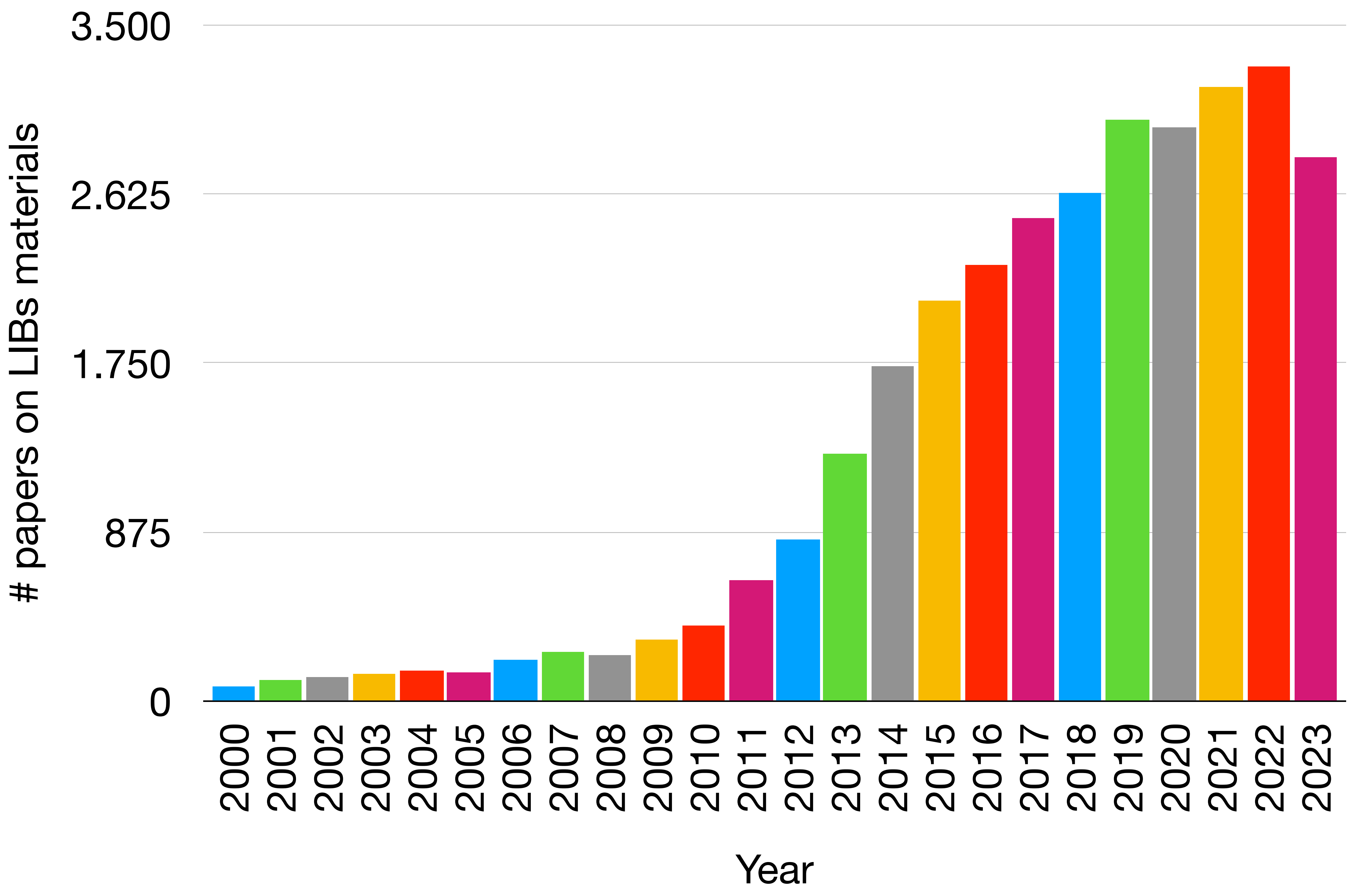
Portable Electronics
- Laptops
- Power tools
- Smartphones

Transportation
- Cars
- Buses

Stationary Accumulation
- Grid energy
- Renewable energy
- Portable energy storage
- Stationary energy storage

INCREASING MARKET

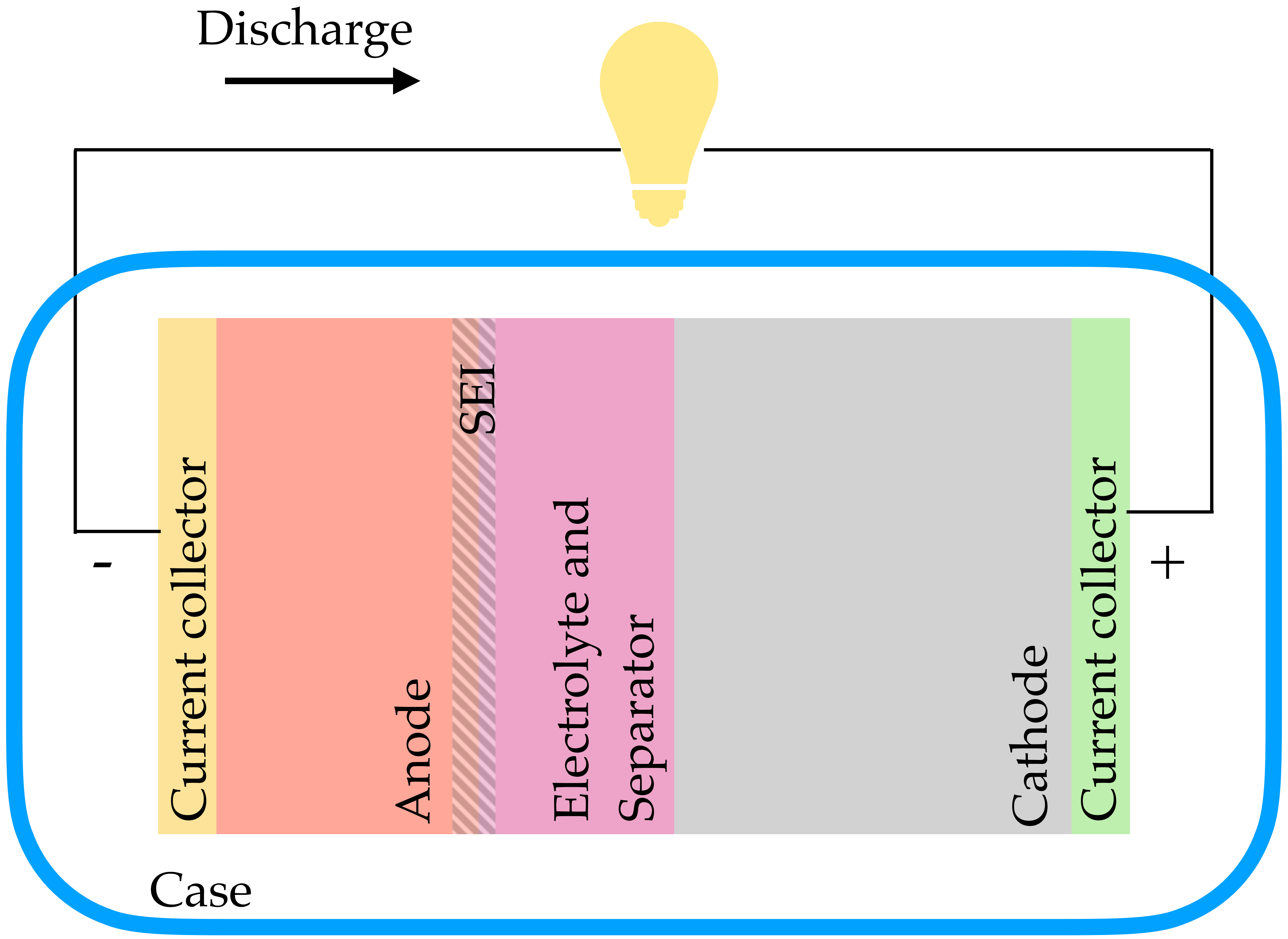
Time to push toward innovative materials research



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

LIBS GENERAL OVERVIEW

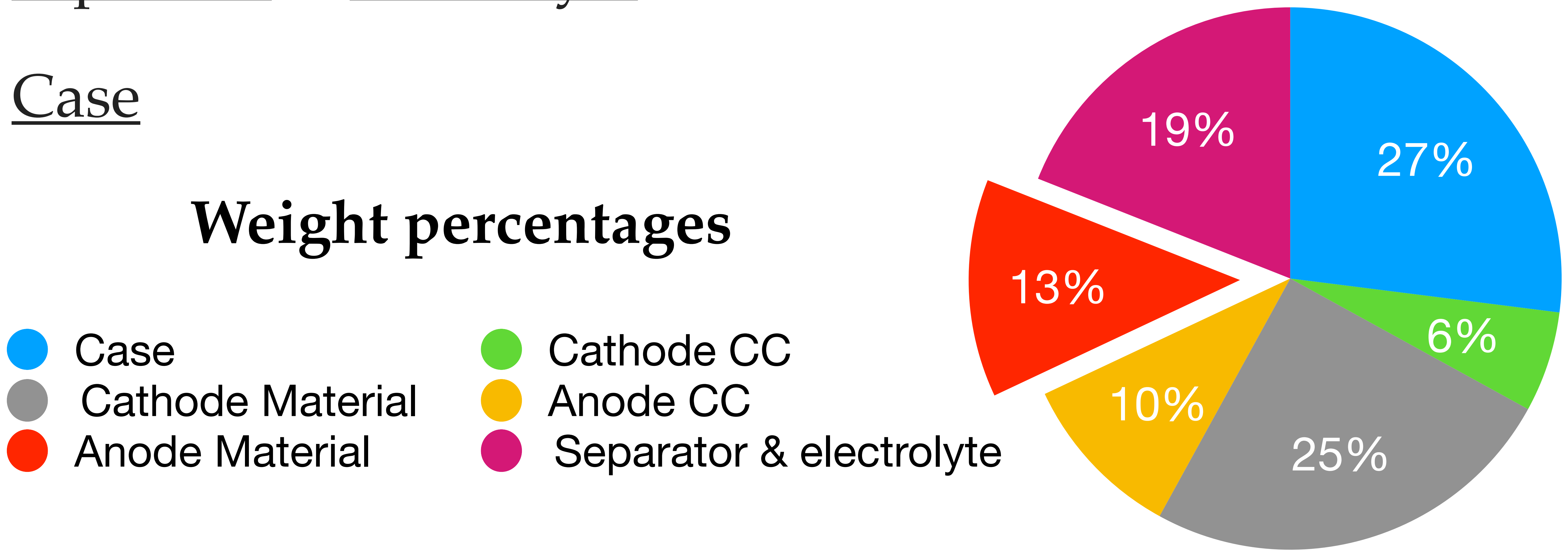
The voltage delivered depends on the **cell chemistry** hence on the **material** that forms it.



LIBs elements

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

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

GLITTERY
BATTERIE SPAZIALI

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

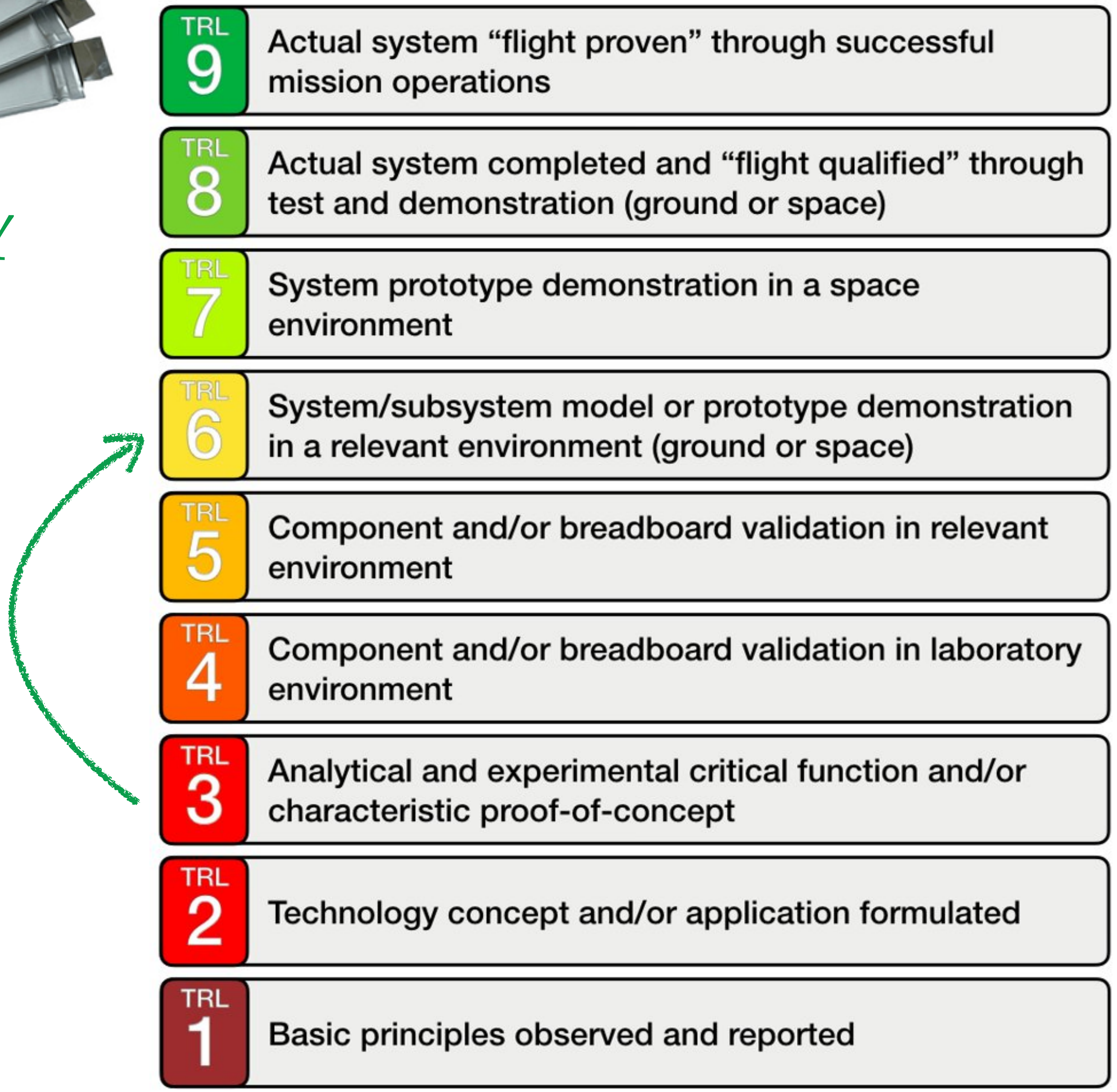
Project final GOAL:

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

Agenzia Spaziale Italiana

Project is entirely founded by the Italian Space Agency

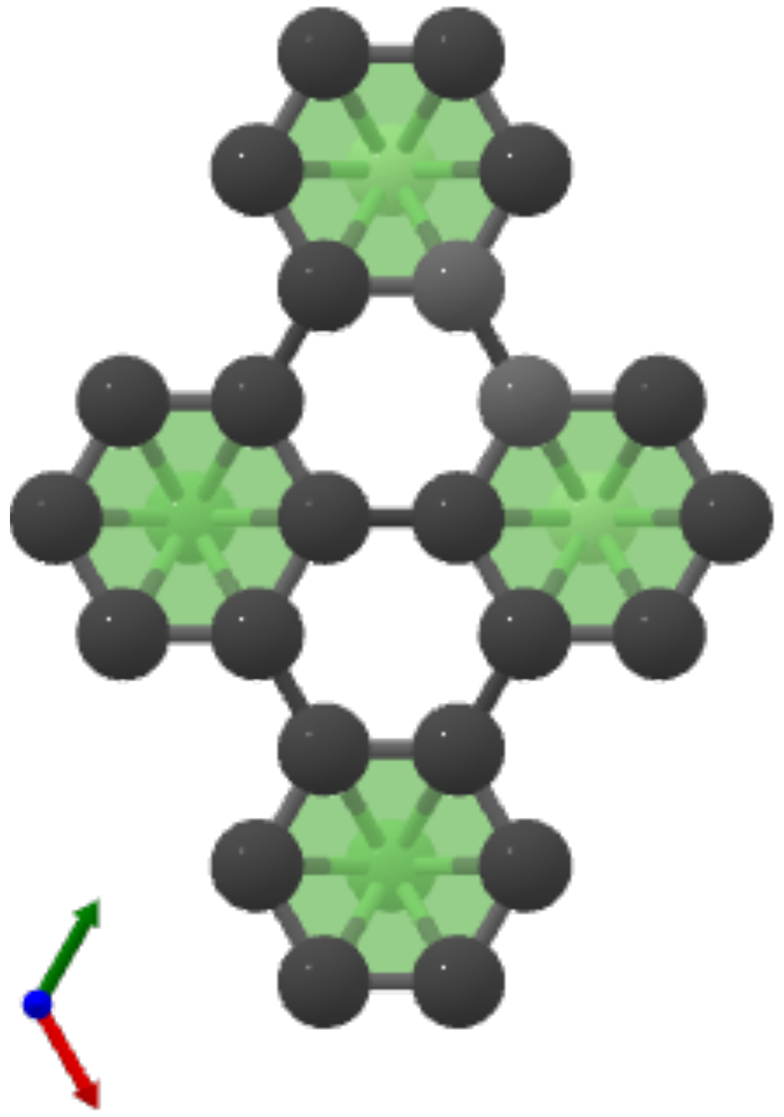
NASA TRL

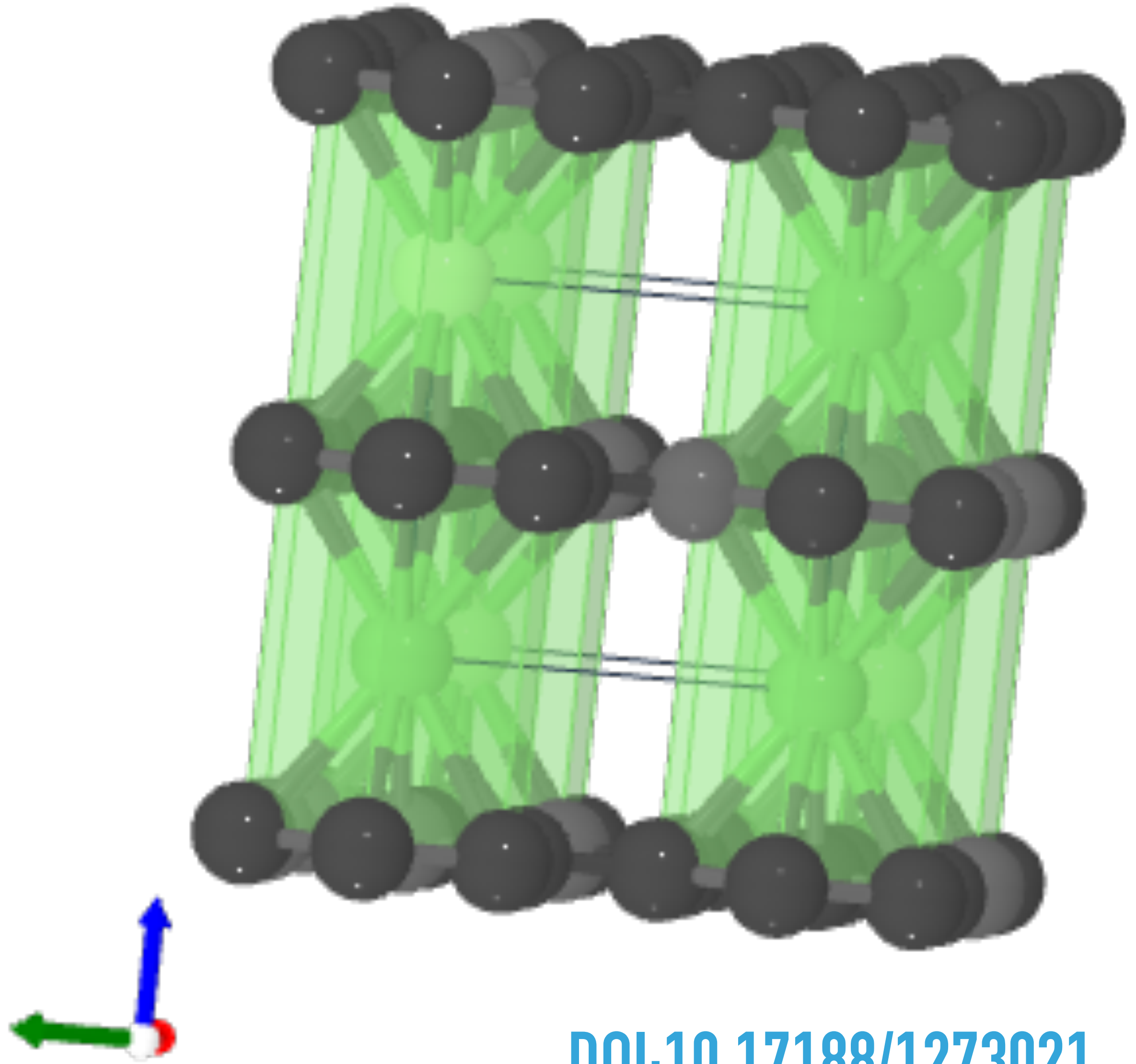


TRL 9	Actual system “flight proven” through successful mission operations
TRL 8	Actual system completed and “flight qualified” through test and demonstration (ground or space)
TRL 7	System prototype demonstration in a space environment
TRL 6	System/subsystem model or prototype demonstration in a relevant 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

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





DOI:10.17188/1273021

Standard materials used in commercial LIBs

BUT

❌ Low capacity

❌ Poor rate capabilities

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

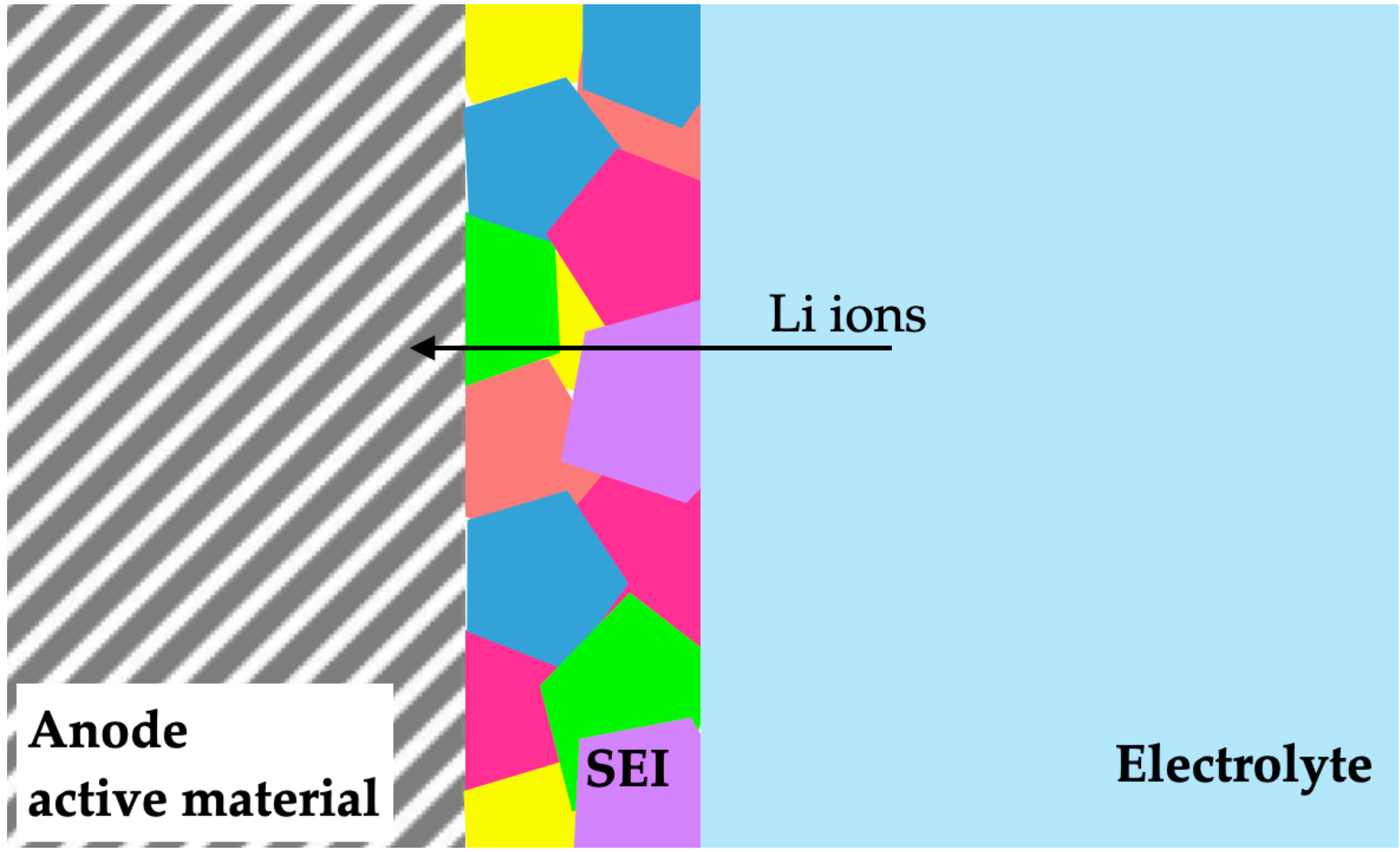
Best theoretical specific capacity BUT

↓

- ❌ High reactivity (H_2O, O_2)
- ❌ Uncontrollable dendrite formation
- ❌ Unstable anode/electrolyte interface
- ❌ Supply shortage

♻ Lithium recycling

SEI (Solid Electrolyte Interphase)



LIBS MATERIALS

Electrode material	C	Li	Si	Ge
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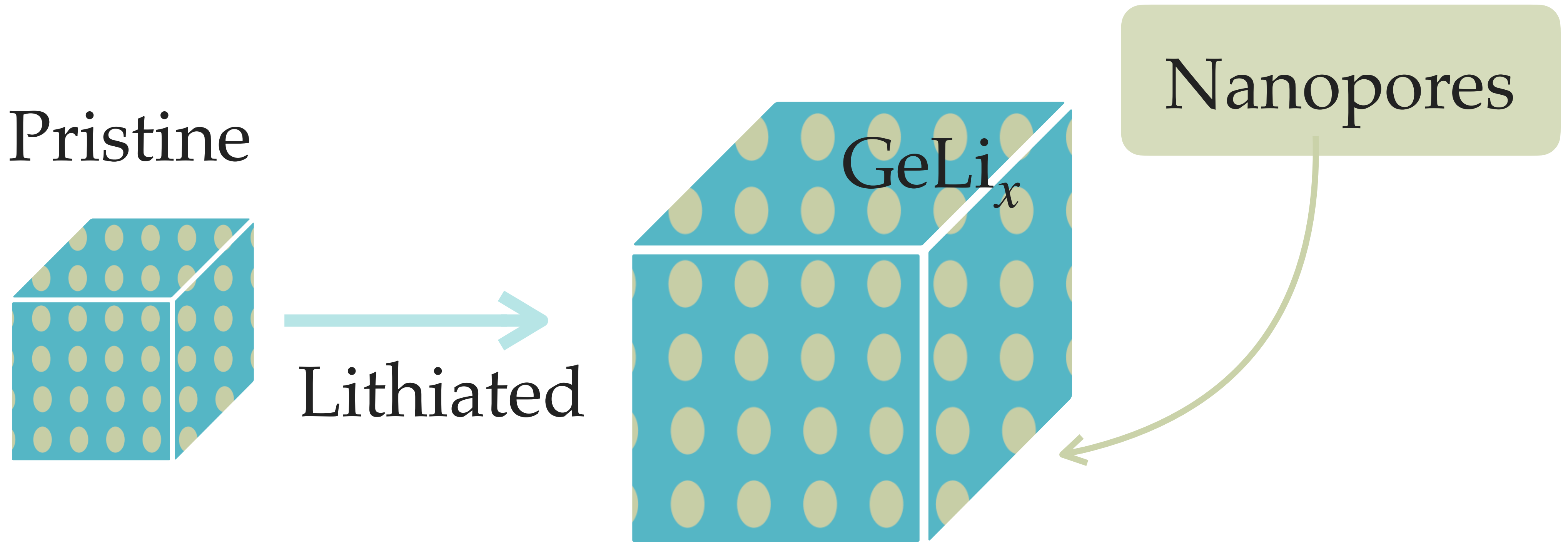
Theoretical specific capacity [mAh/g]	372	3 862	4 200	1 624
Volume change [%]	12	-	420	370

High theoretical specific capacity BUT

❌Huge volumetric expansion ($\sim 400\,\%$) upon lithiation

leading to

- ❌Active material pulverisation
- ❌Cracks formation
- ❌Delamination from the substrate



(volume accommodation by nano-pores)

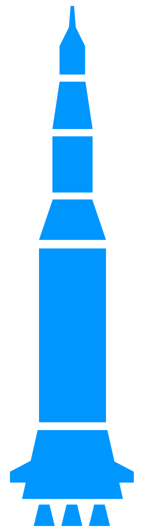
Possible way to cope with this? Nanostructurization

LIBS MATERIALS

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

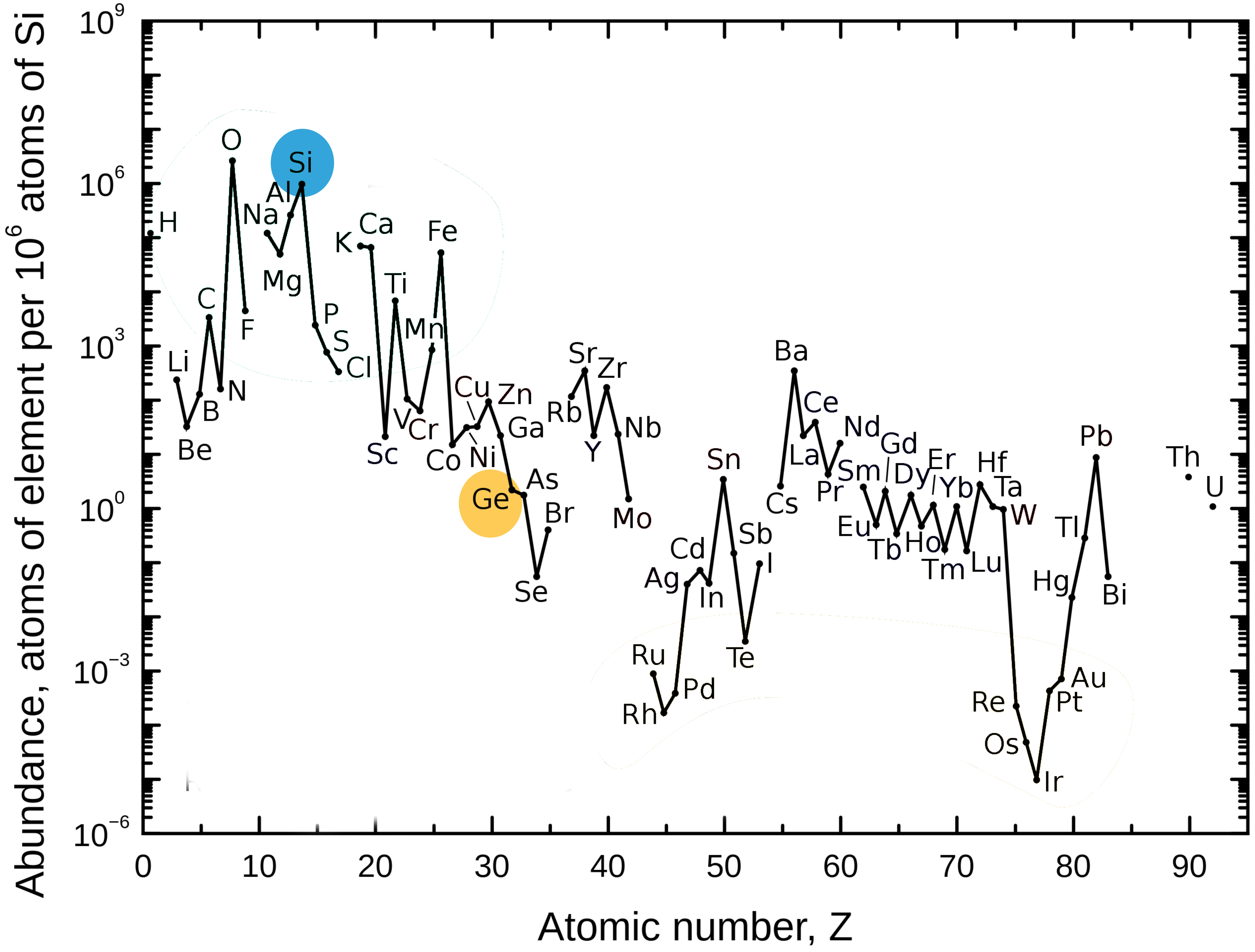
Electrode material	C	Li	Si	Ge
Theoretical specific capacity [mAh/g]	372	3 862	4 200	1 624

Due to the **high theoretical specific capacity**



Promising materials for the AEROSPACE sector!

CRITICAL RAW MATERIAL



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

WHY GERMANIUM

Ge vs Si

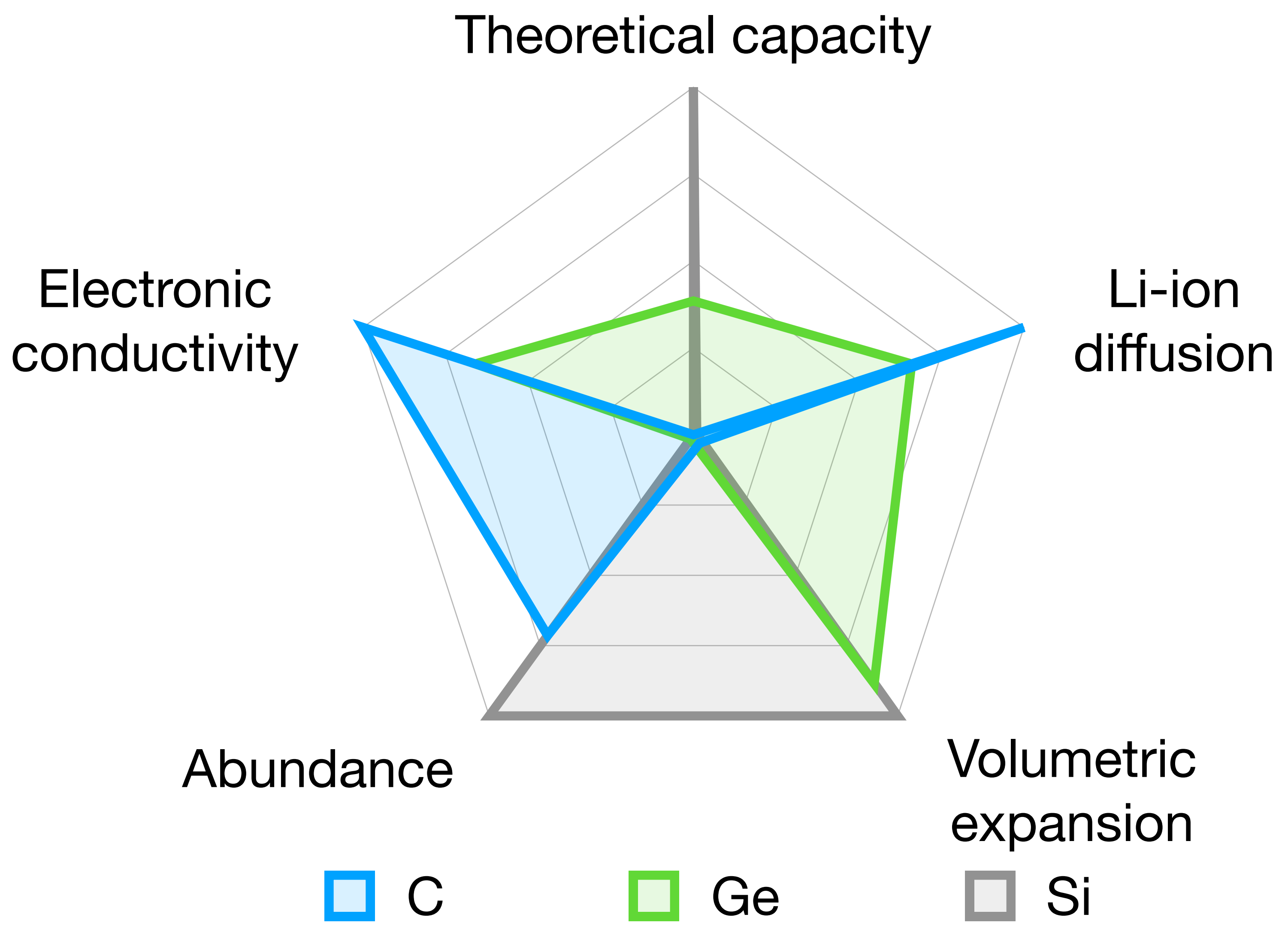
❌ Lower theoretical capacity [1624 mAh/g vs 4200 mAh/g]

❌ Si is more abundant (hence cheaper) than Ge

✅ High electronic conductivity : 10^4 times higher in Ge than Si
$[E_g(Ge) = 0.66$ eV vs $E_g(Si) = 1.1$ eV @ 300K].

✅ Fast Li-ions diffusion : 400 times faster in Ge than Si

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



C-RATE:

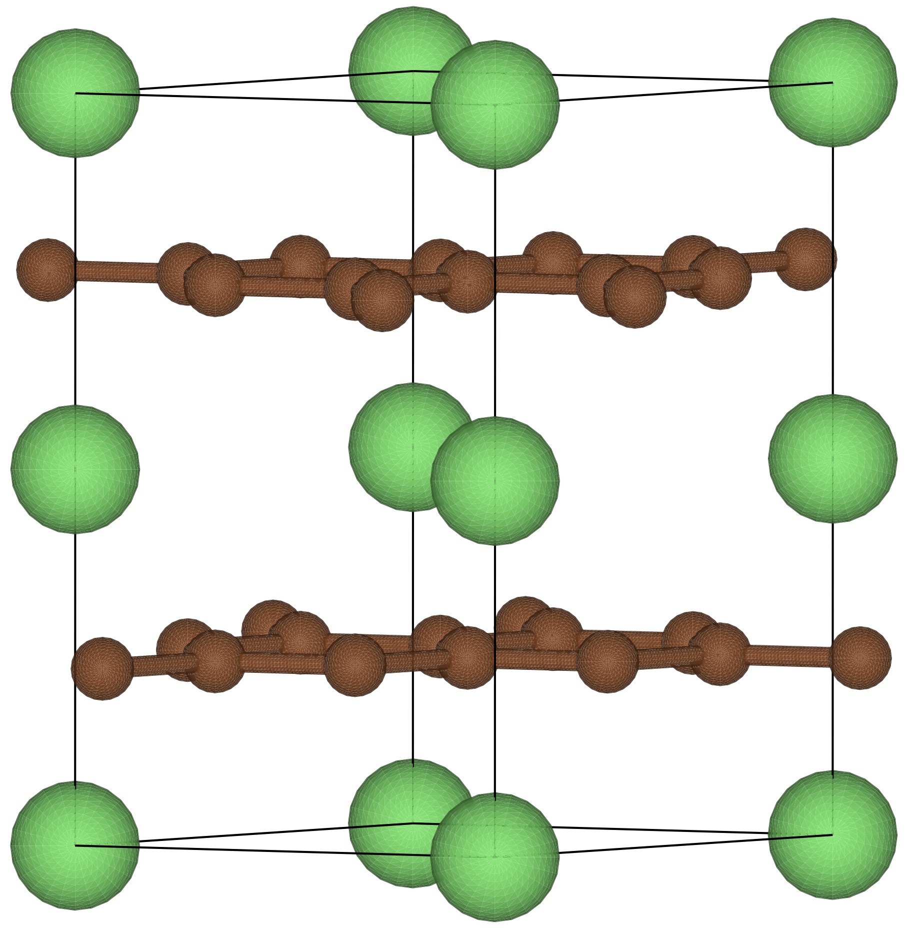
$$\text{C-rate} = \frac{\text{specific capacity [mAh g}^{-1}] \cdot \text{ mass loading [g]}}{\text{time [h]}}$$

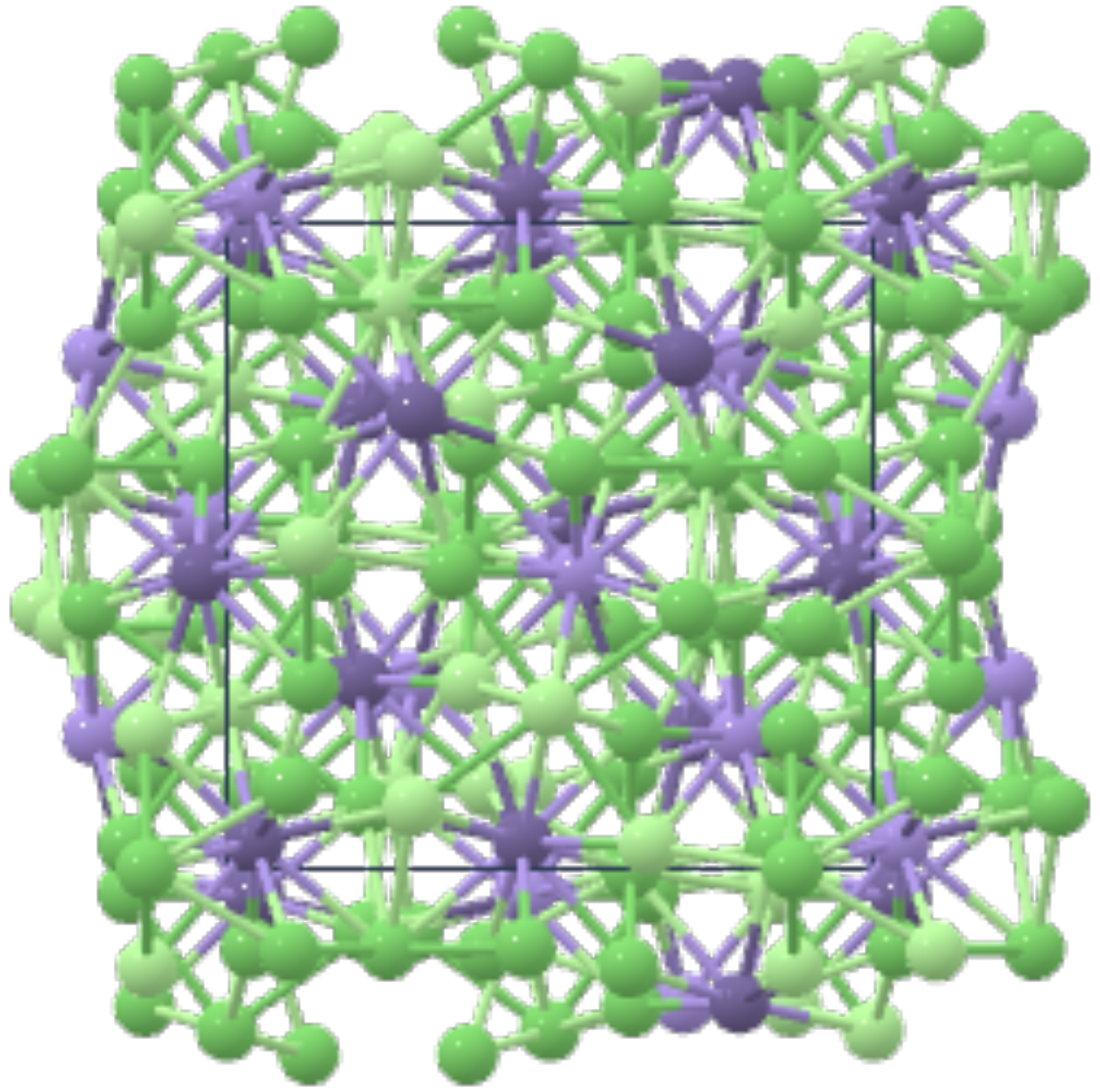
$1C = 1h$ charge/discharge
$C/2 = 2h$ charge/discharge
$2C = \frac{1}{2}h$ charge/discharge

[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

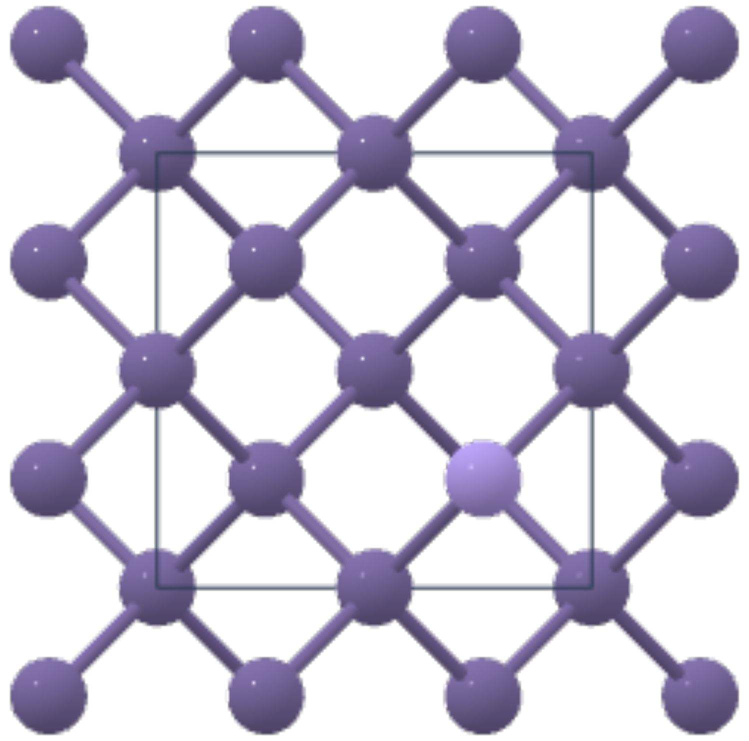
$$C_{\mathrm{Graphite}} = \frac{1}{6}\frac{\mathrm{F}}{\mathrm{Carbon\ Molar\ Mass}} \approx 372\ \mathrm{mAh\ g^{-1}}$$

GE-BASED TECHNOLOGY $Li_{22}Ge_5$

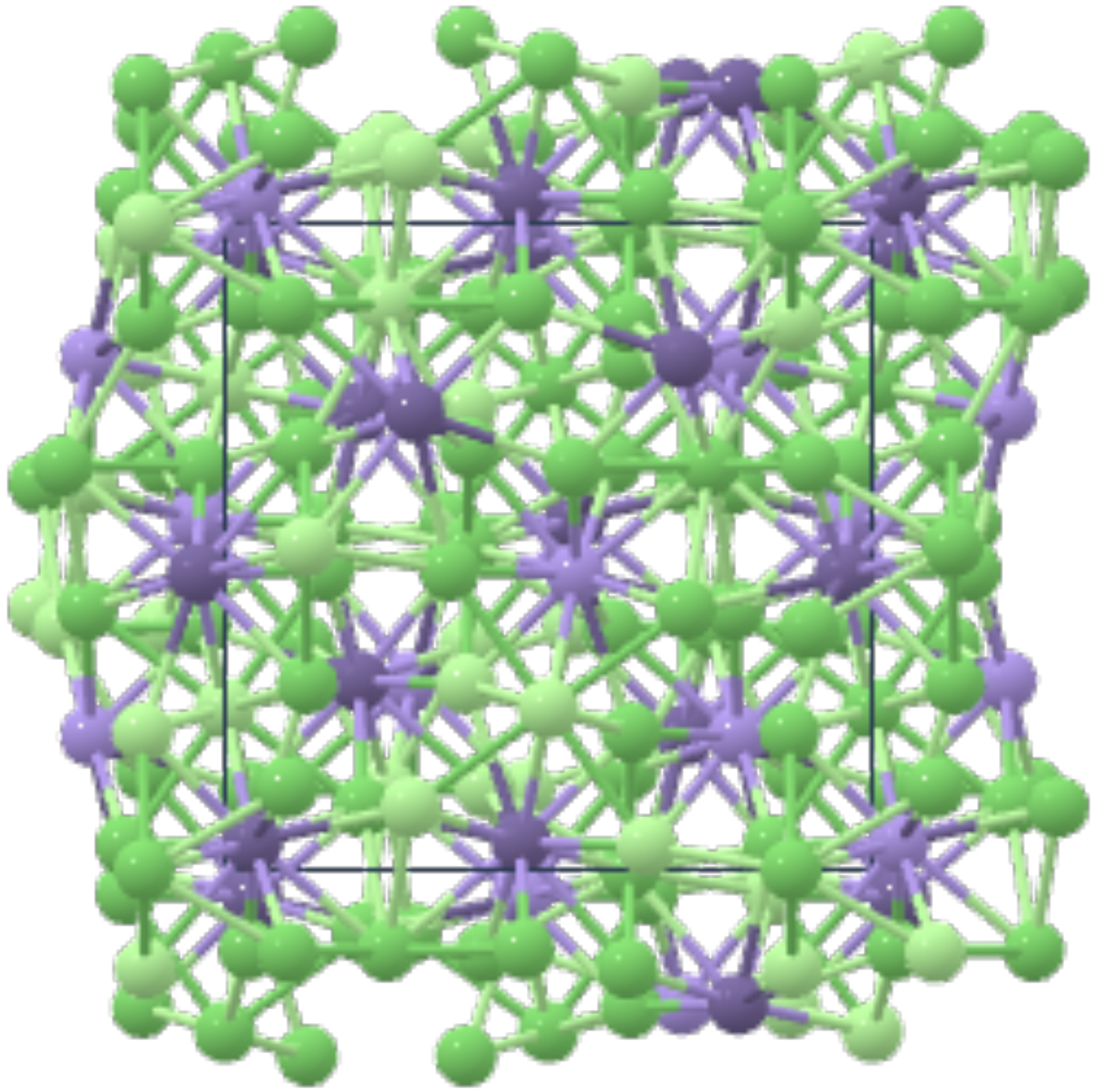
$$C_{\mathrm{Ge}} = \frac{22}{5}\frac{\mathrm{F}}{\mathrm{Ge\ Molar\ Mass}} \approx 1624\ \mathrm{mAh\ g^{-1}}$$

GERMANIUM LITHIATED PHASES

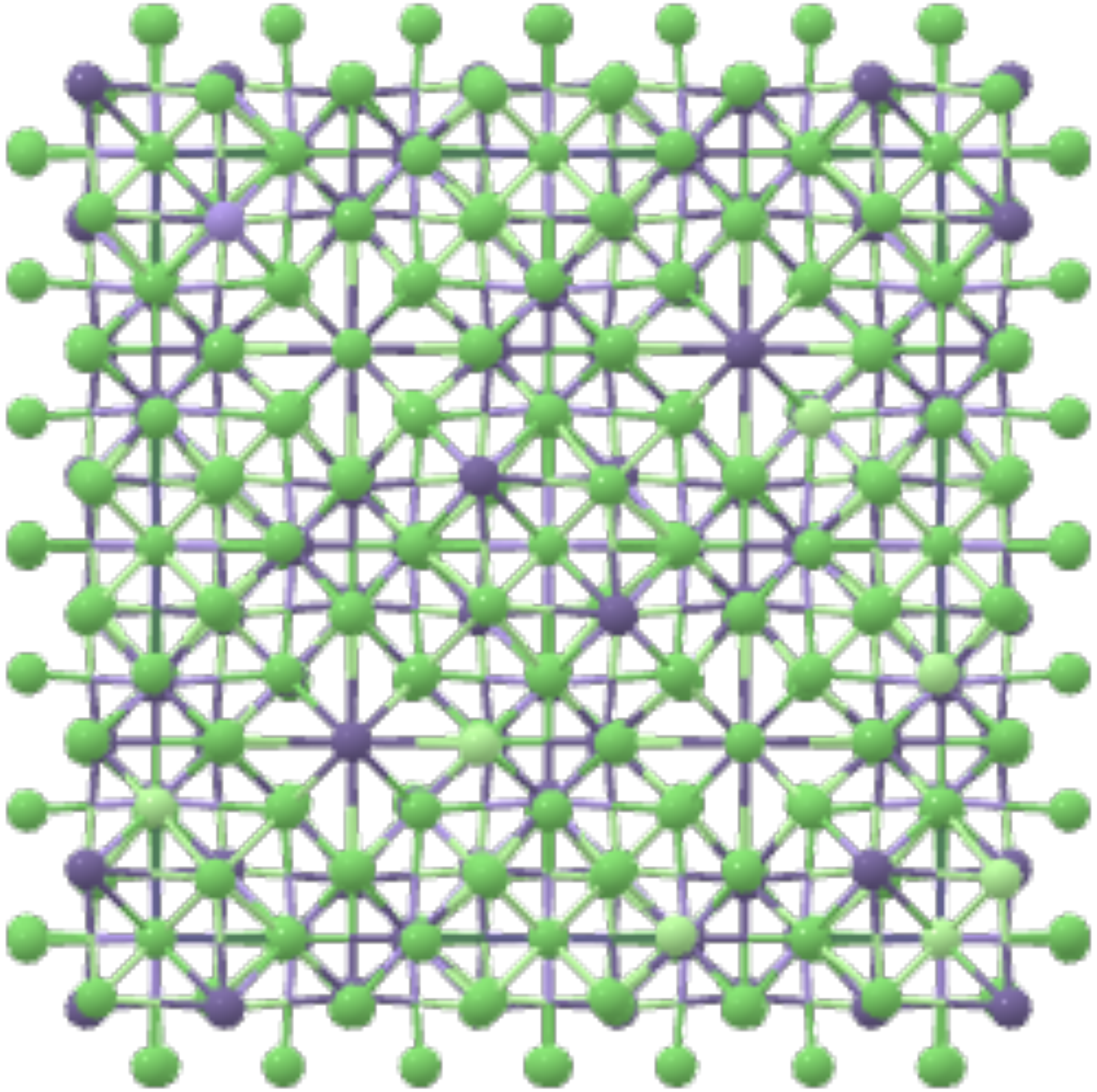
$$Ge \longrightarrow Li_{15}Ge_4 \longrightarrow Li_{22}Ge_5$$



DOI: 10.17188/1206032



DOI: 10.17188/1192682



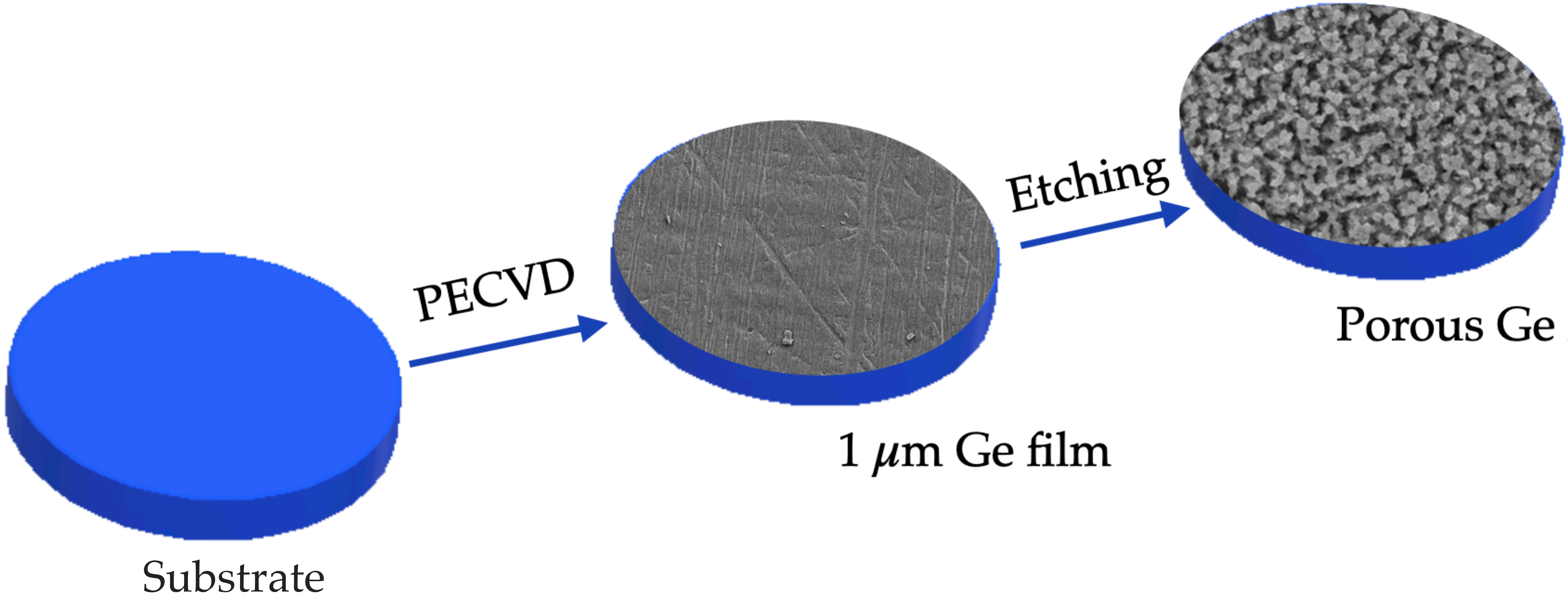
Data retrieved from the Materials Project for Li22Ge5 (mp-1204063) from database version v2022.10.28

Li Ge

TWO STEPS SAMPLE PREPARATION:

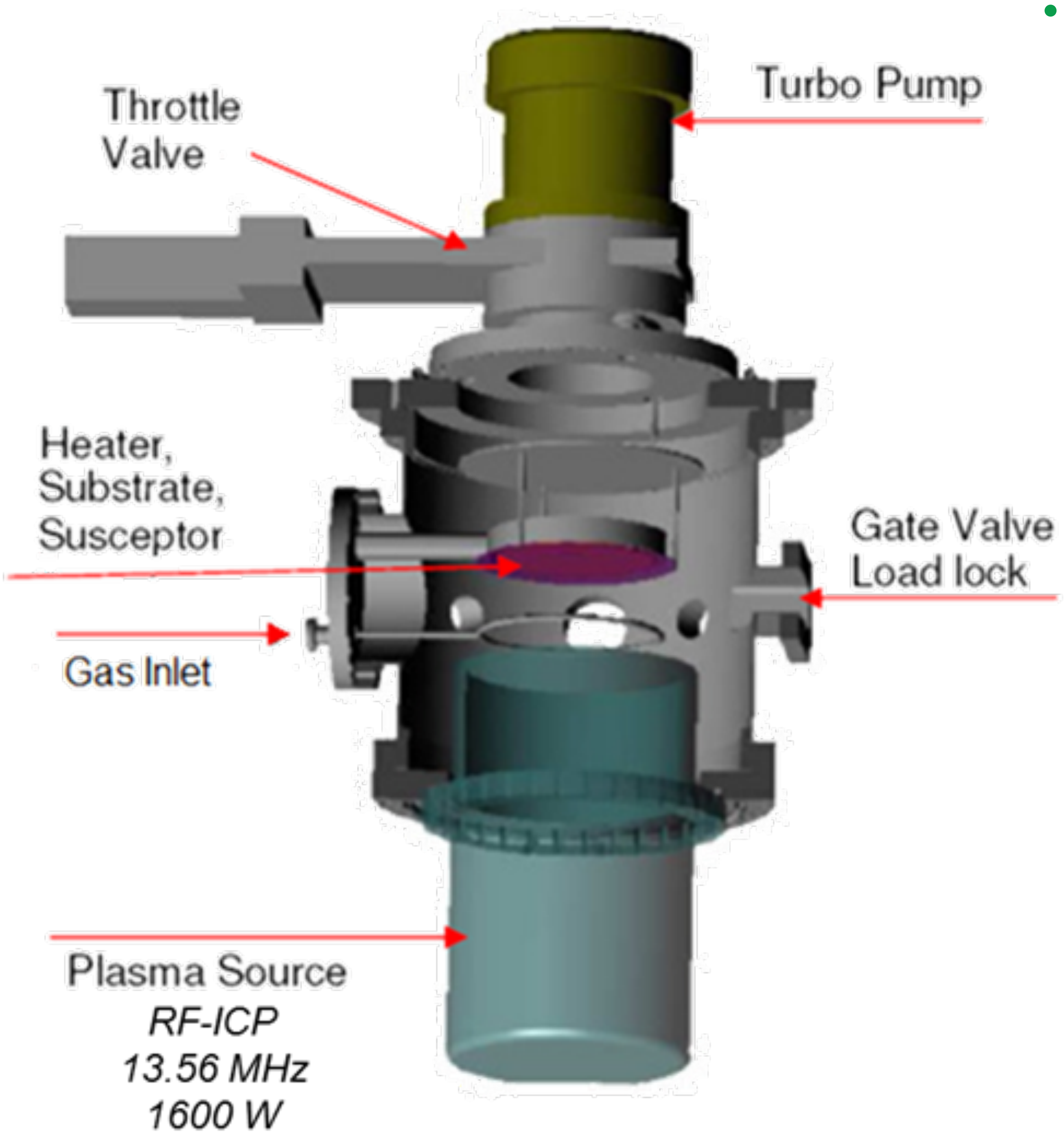
1. DEPOSITION
   via Chemical Vapor Deposition

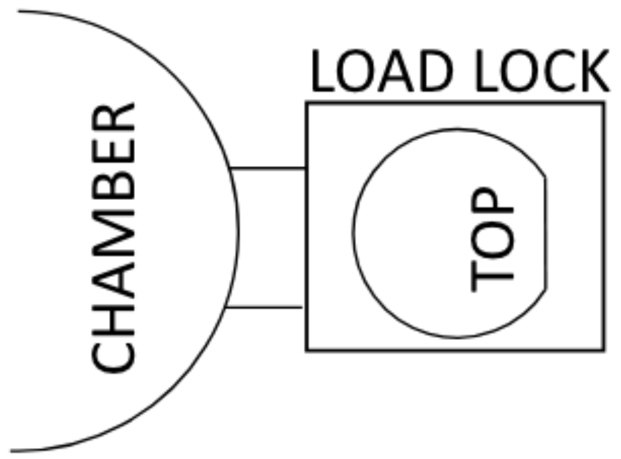
2. NANOSTRUCTURATION
   via Electrochemical Etching

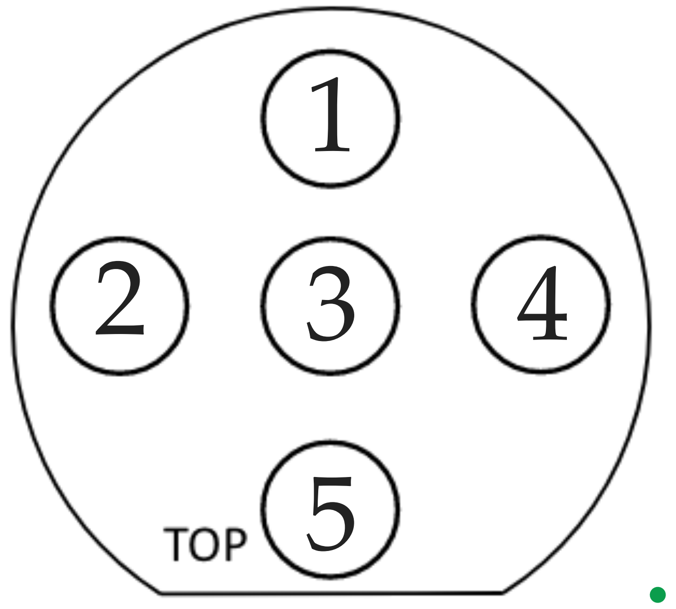


TOP-DOWN APPROACH

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**

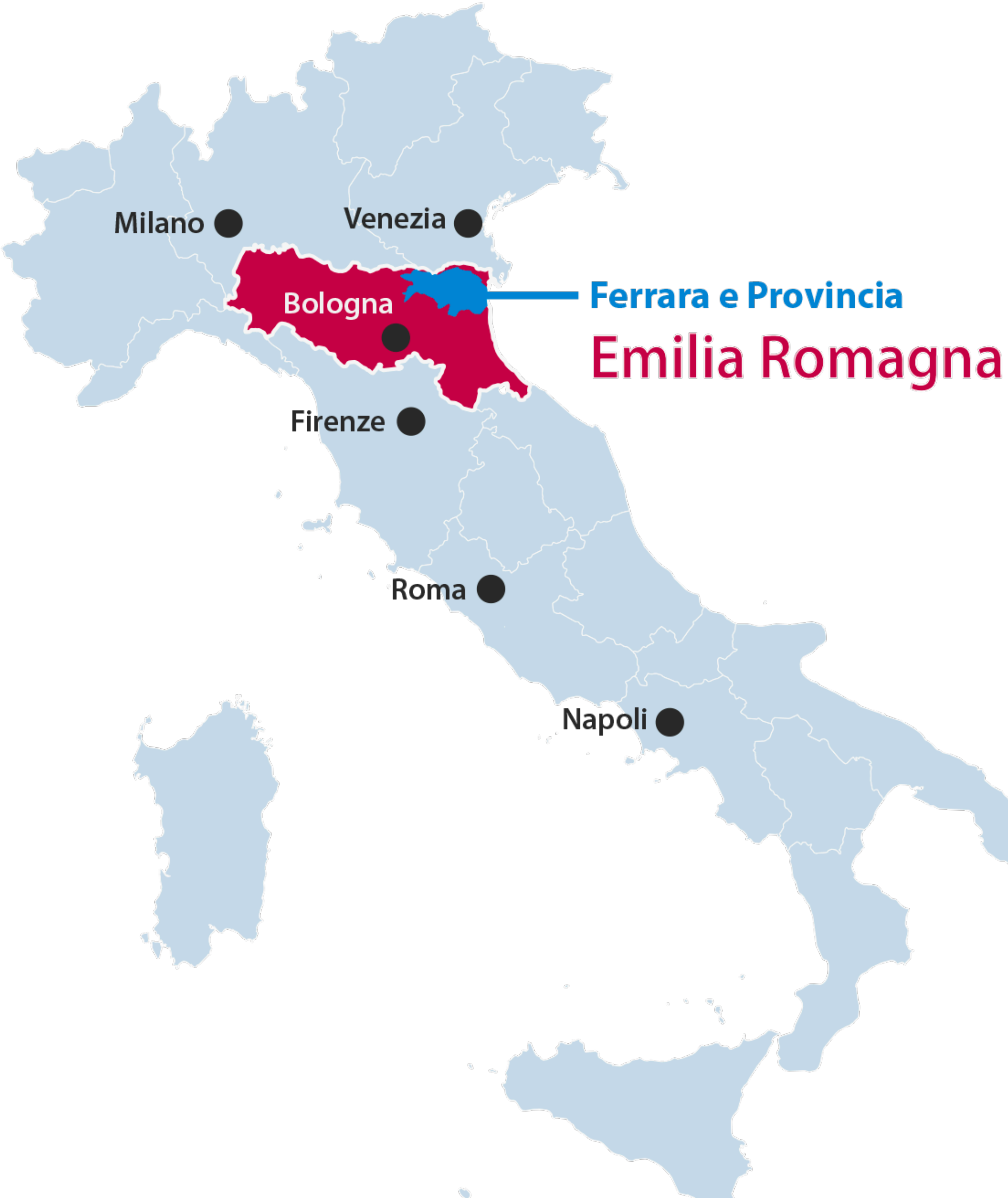
Growth rate: 1.265 nm/s

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**

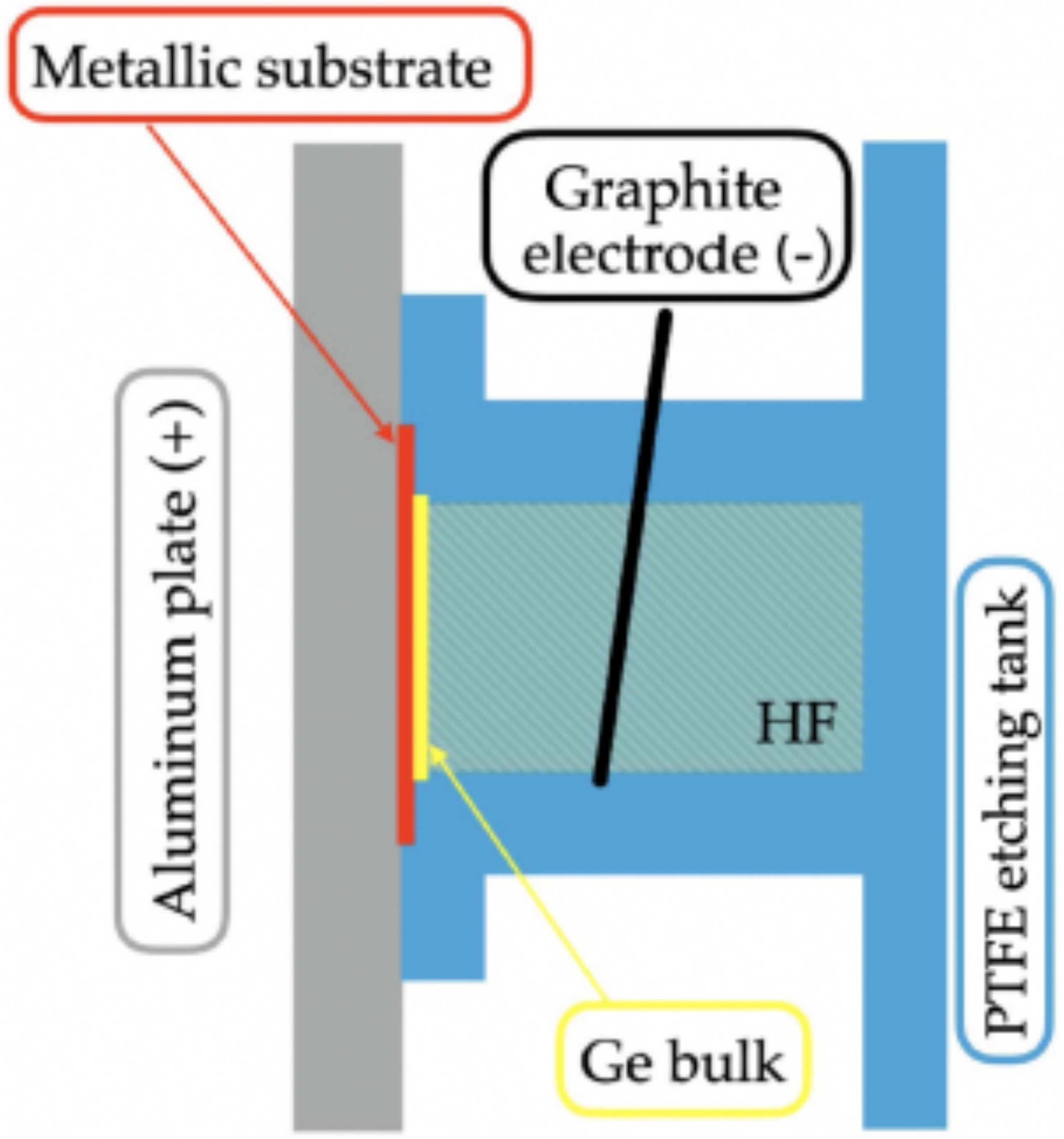


**Università
degli Studi
di Ferrara**

ELECTROCHEMICAL ETCHING

Electrochemical etching involves non-spontaneous reactions to

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



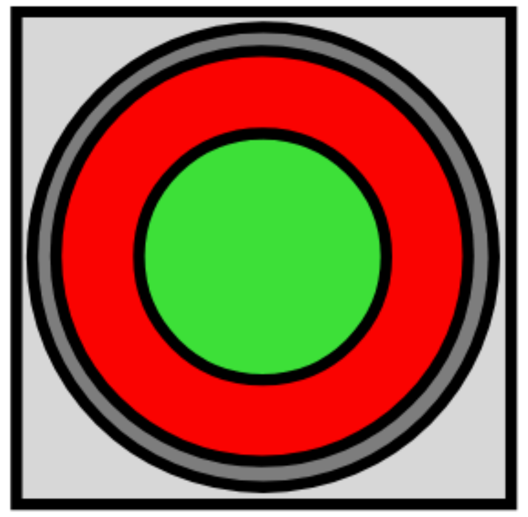
\+ connected to the Aluminum plate

\- clamped to a Graphite rod

Etching solution: HF - ethanol

V. Diolaiti, A. Andreoli et al, **IEEE TNANO Vol 22, (2023)** DOI: [10.1109/TNANO.2023.3311757](https://doi.org/10.1109/TNANO.2023.3311757)

*Comparison of Porous Germanium Thin Films on SS and Mo as Anode for High-Performance LIBs © 2023 by Valentina Diolaiti et al is licensed under CC BY-NC 4.0



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)

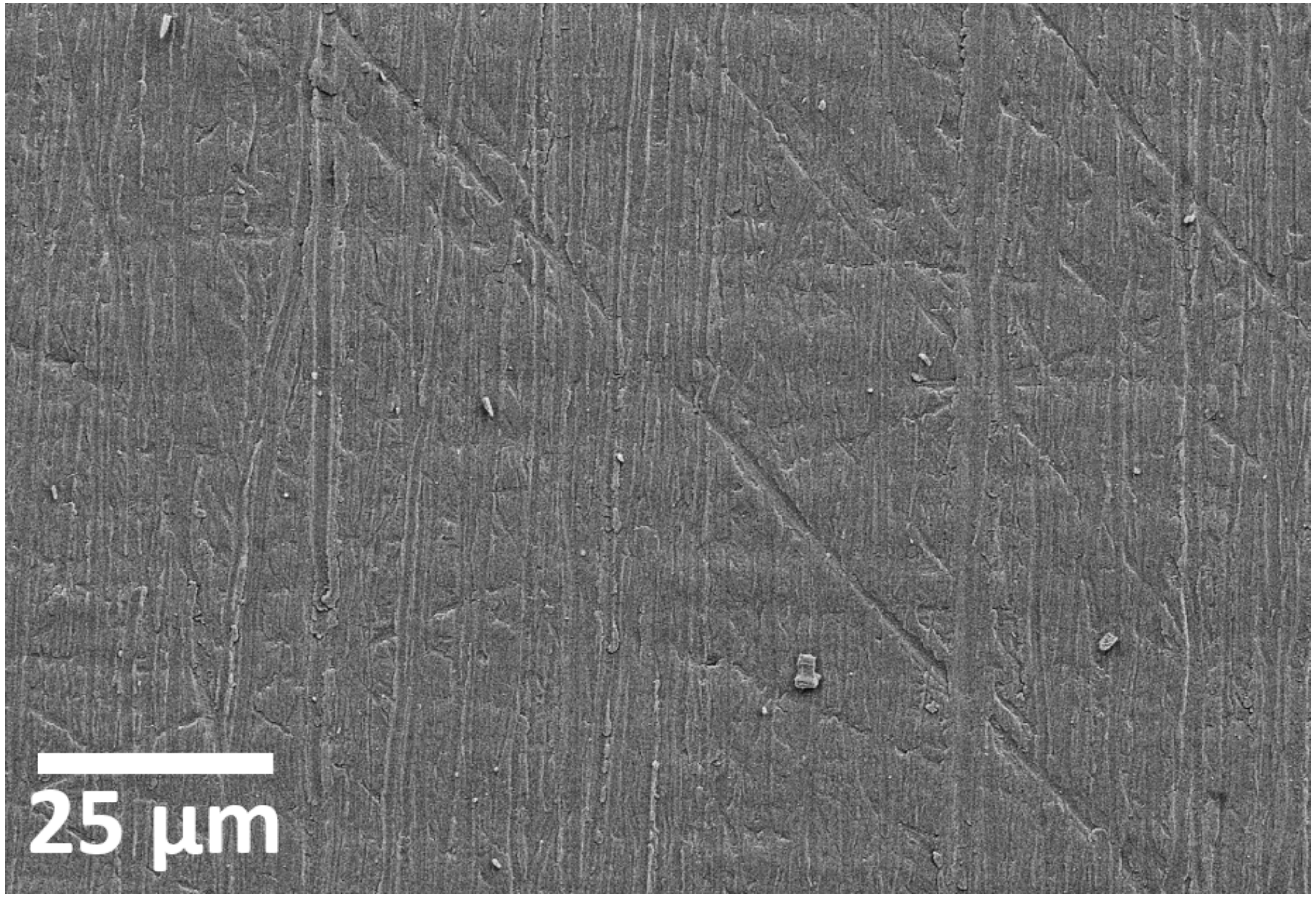
MORPHOLOGY

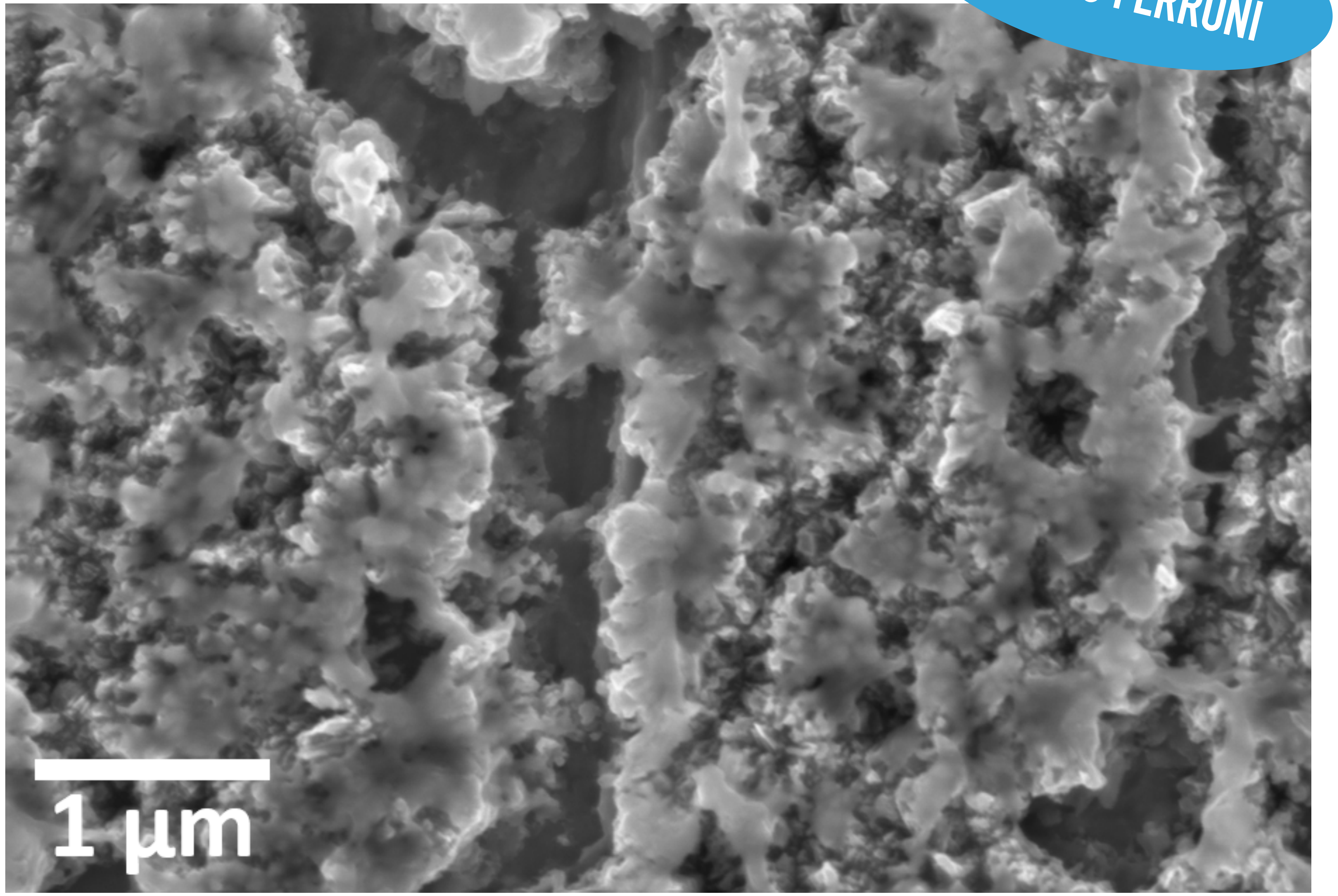
MO SAMPLE

GE BULK

GE NANO-STRUCTURED

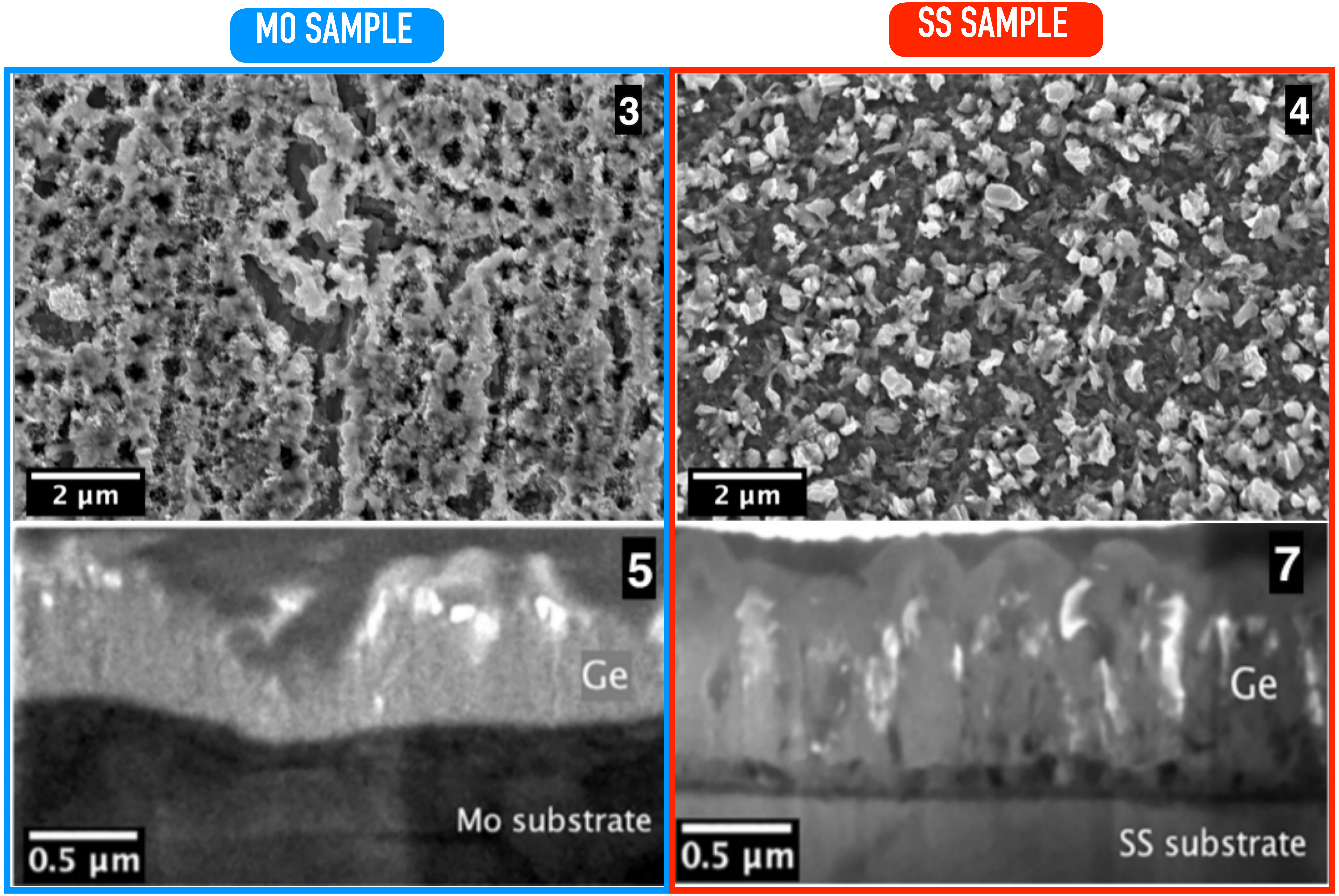
THANK TO MATTEO FERRONI





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

MO VS SS SUBSTRATE



THANK TO MATTEO FERRONI

SEM and cross-sectional TEM bright field images:

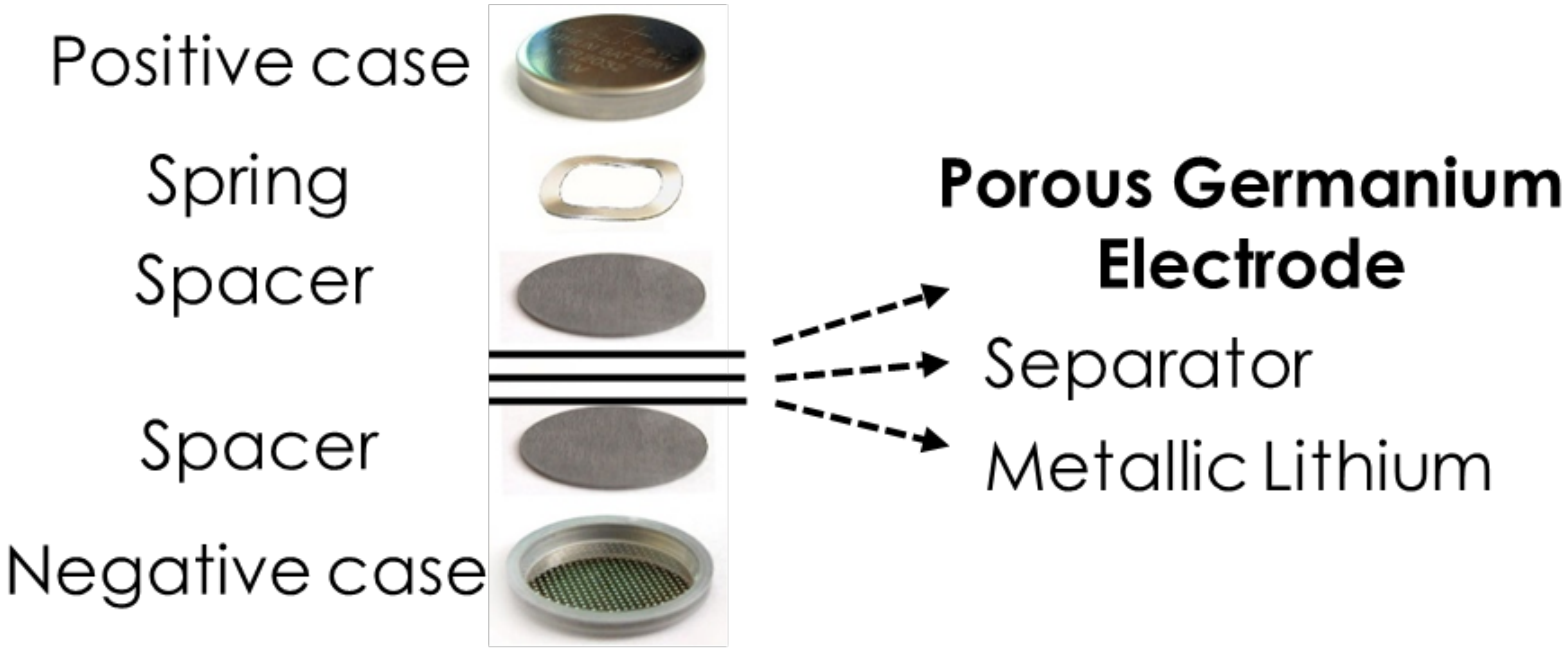
- Ge layer appears compact and uniform over the entire area
- Good adhesion of the film for both substrates
- Nanostrutures along all the deposition thickness

V. Diolaiti, A. Andreoli et al, **IEEE TNANO Vol 22, (2023)** DOI: [10.1109/TNANO.2023.3311757](https://doi.org/10.1109/TNANO.2023.3311757)

CELL ASSEMBLY

Ar-filled MBraun glovebox

HALF CELL CONFIGURATION FOR A CR2032 CELL



Positive case
Spring
Spacer
Spacer
Negative case

Porous Germanium Electrode
Separator
Metallic Lithium

ISTITUTO ITALIANO
DI TECNOLOGIA

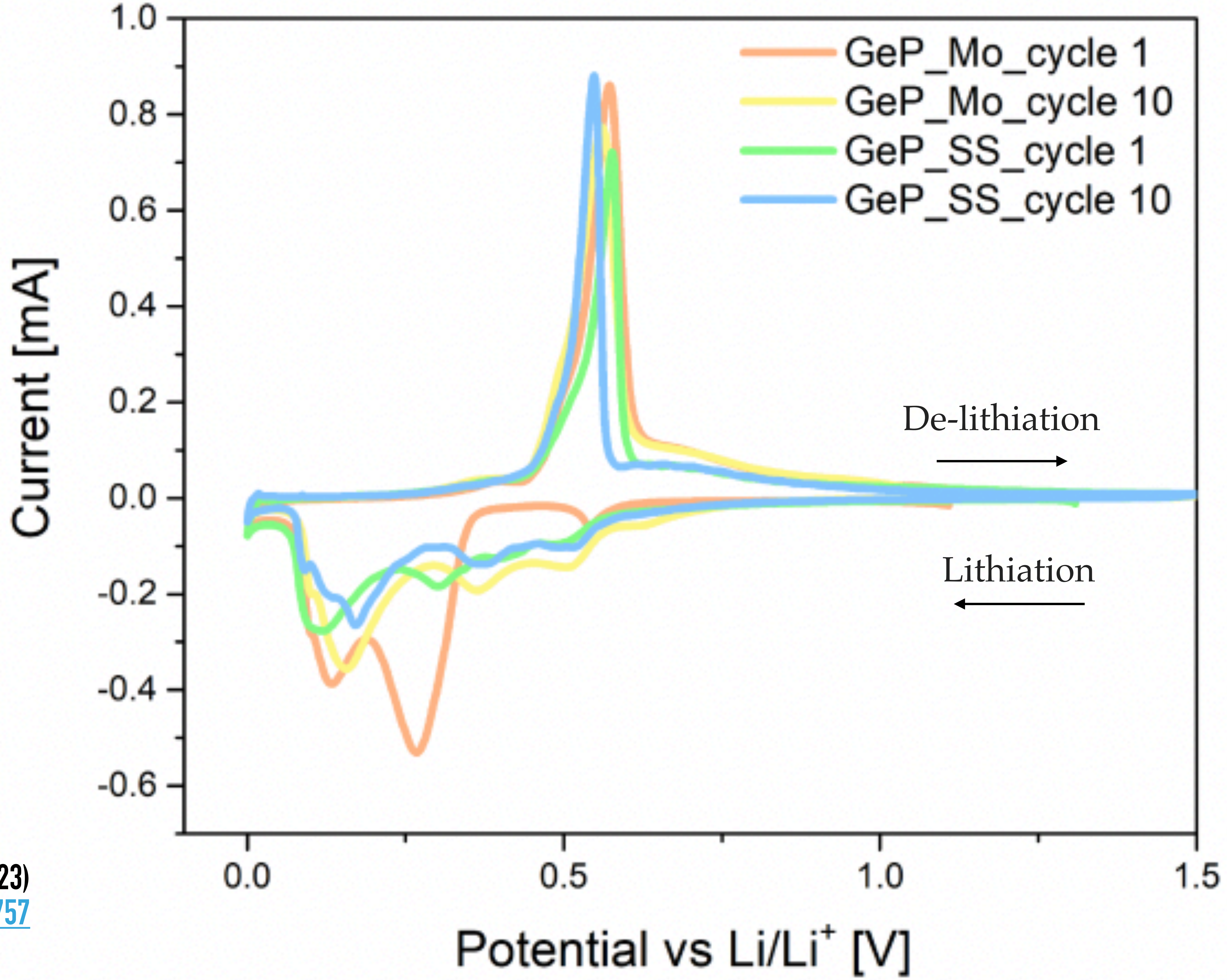
LP30
1M **$LiPF_6$** in EC:DMC=1:1 vol
+
FEC additive
(fluoroethylene carbonate)

Mass loadings ~ 0.3 mg
for 1 μm Ge film

ELECTROCHEMICAL ANALYSIS

Cyclic voltammetry on SS and Mo

$V \in [0.01 - 1.5]$ V

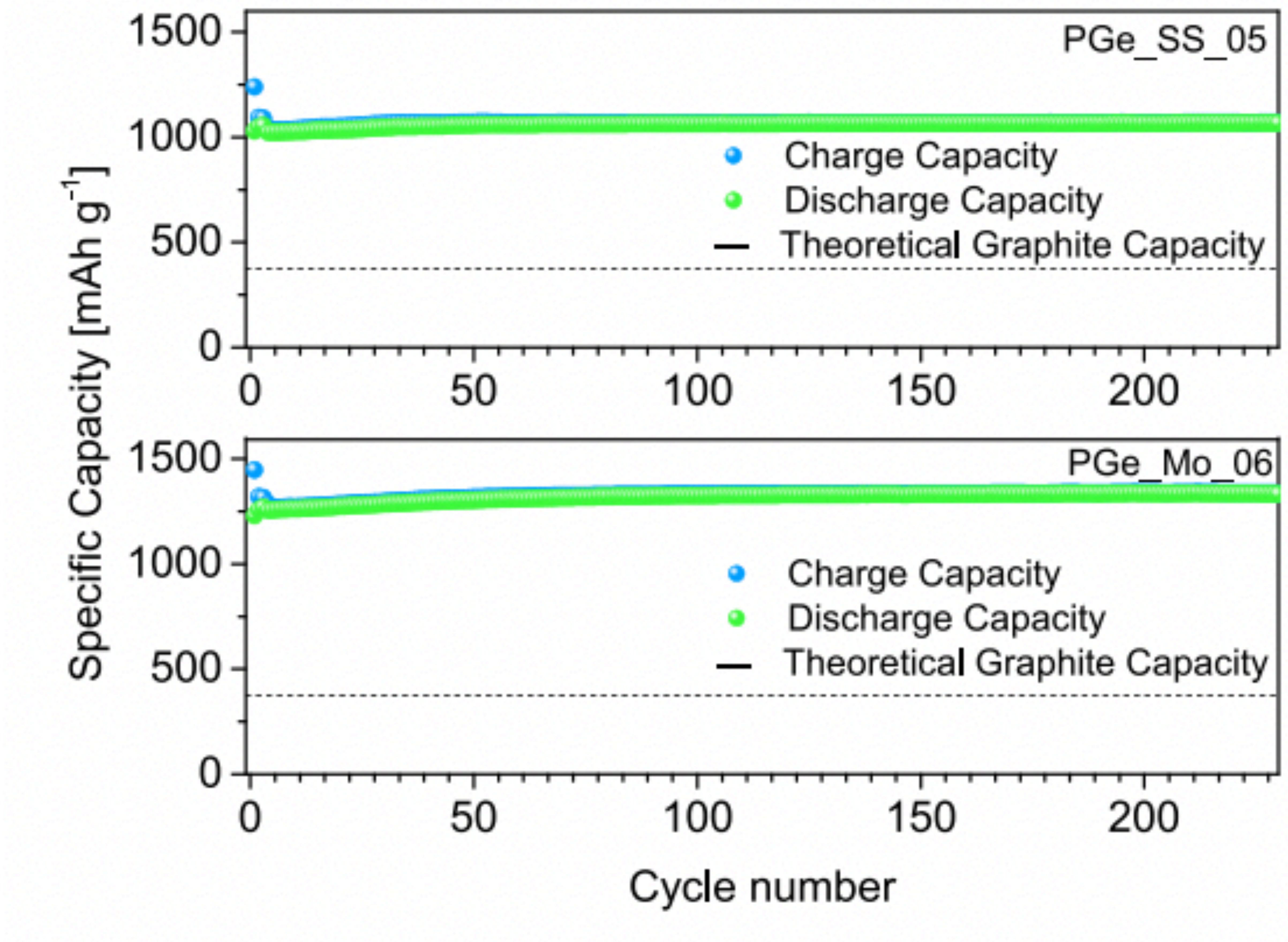


V. Diolaiti, A. Andreoli et al, **IEEE TNANO Vol 22, (2023)**
DOI: 10.1109/TNANO.2023.3311757

ELECTROCHEMICAL ANALYSIS

THANK TO SILVIO FUGATTINI FOR THIS MEASUREMENT

Capacity @ 1C on SS and Mo



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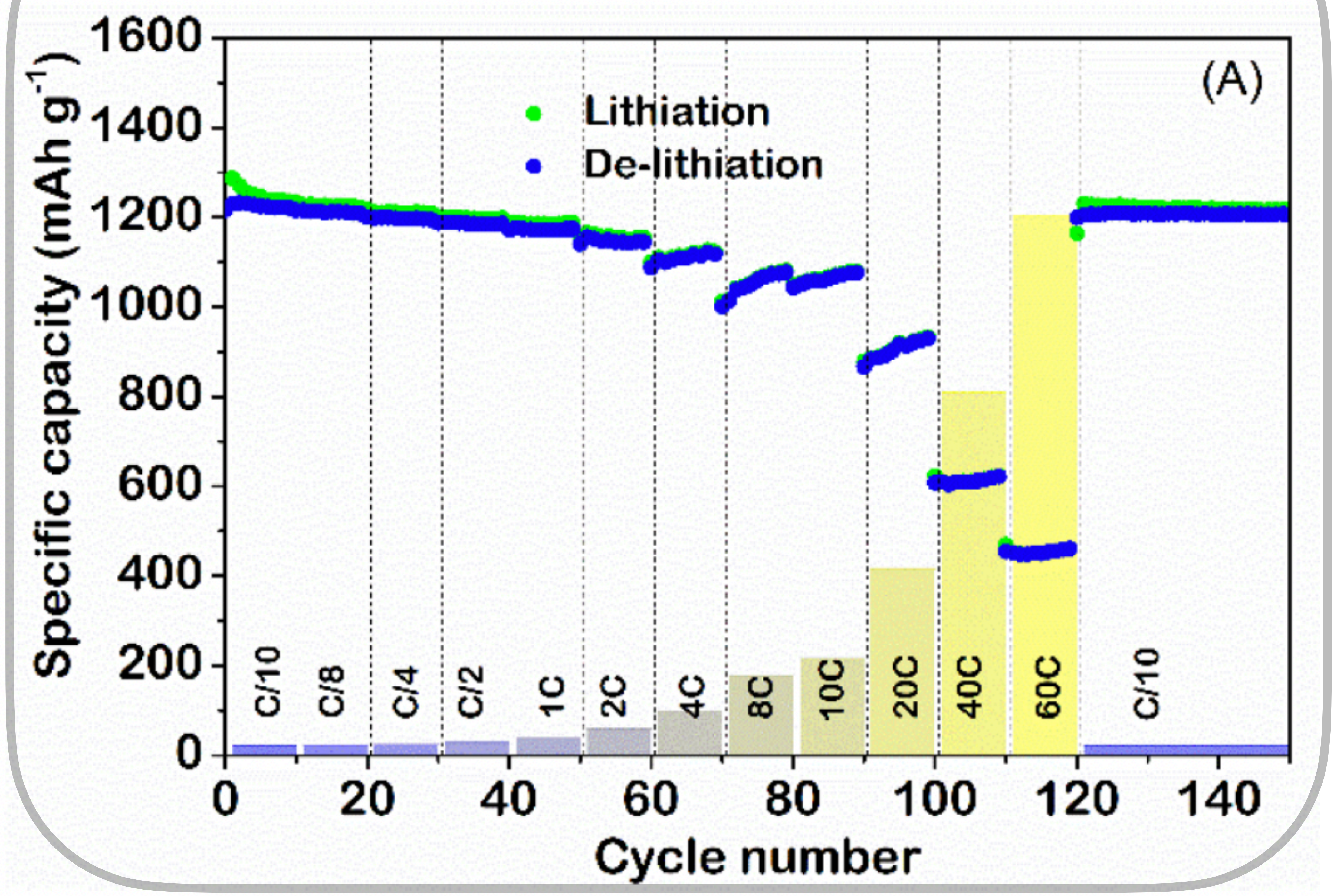
*Comparison of Porous Germanium Thin Films on SS and Mo as Anode for High-Performance LIBs © 2023 by Valentina Diolaiti et al is licensed under CC BY-NC 4.0

Capacity @ different C-rates on Mo



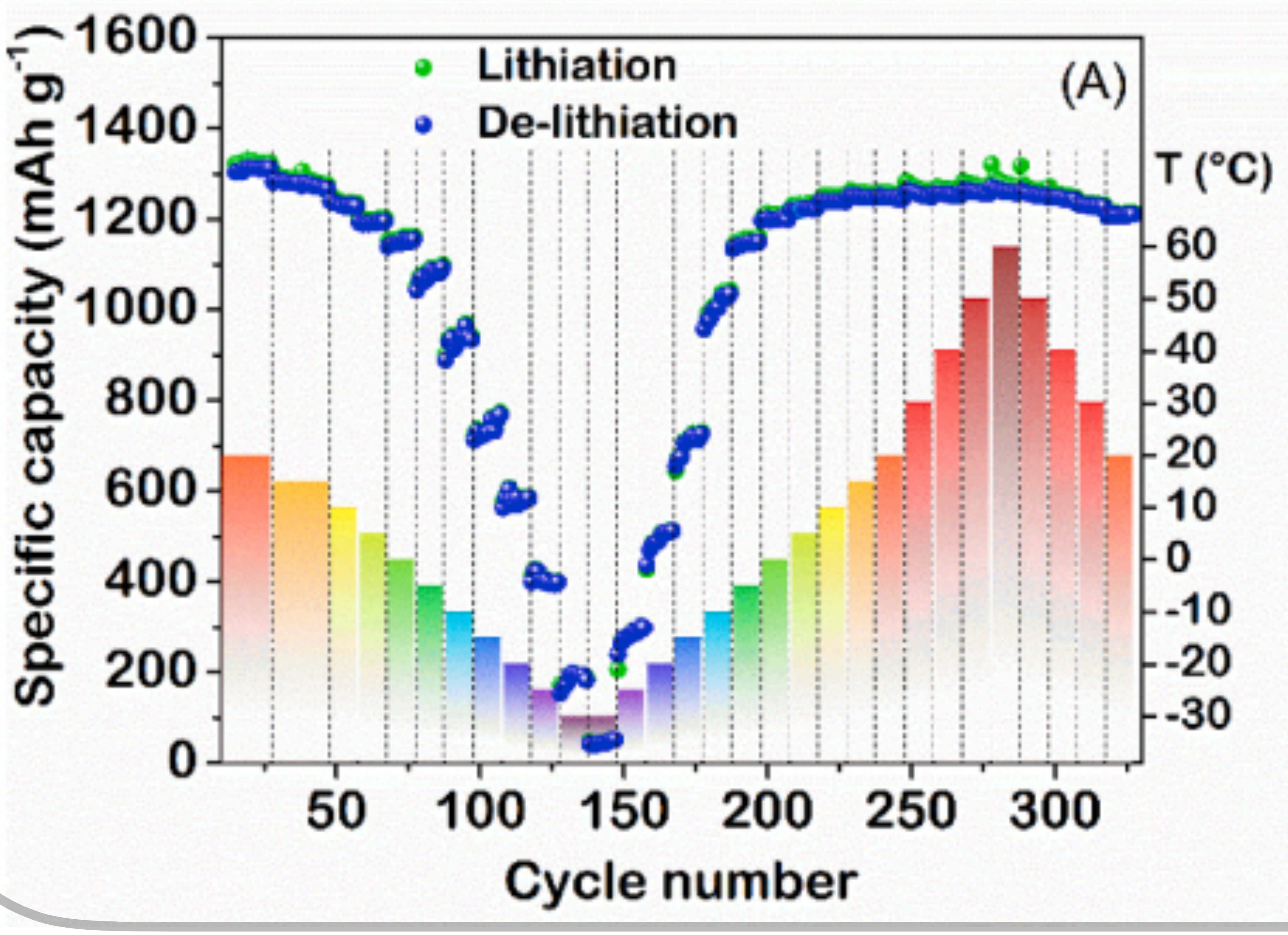
S. Fugattini, A. Andreoli et al, **Electrochimica Acta, Volume 411 (2022) 139832, ISSN 0013-4686** https://doi.org/10.1016/j.electacta.2022.139832

ELECTROCHEMICAL ANALYSIS

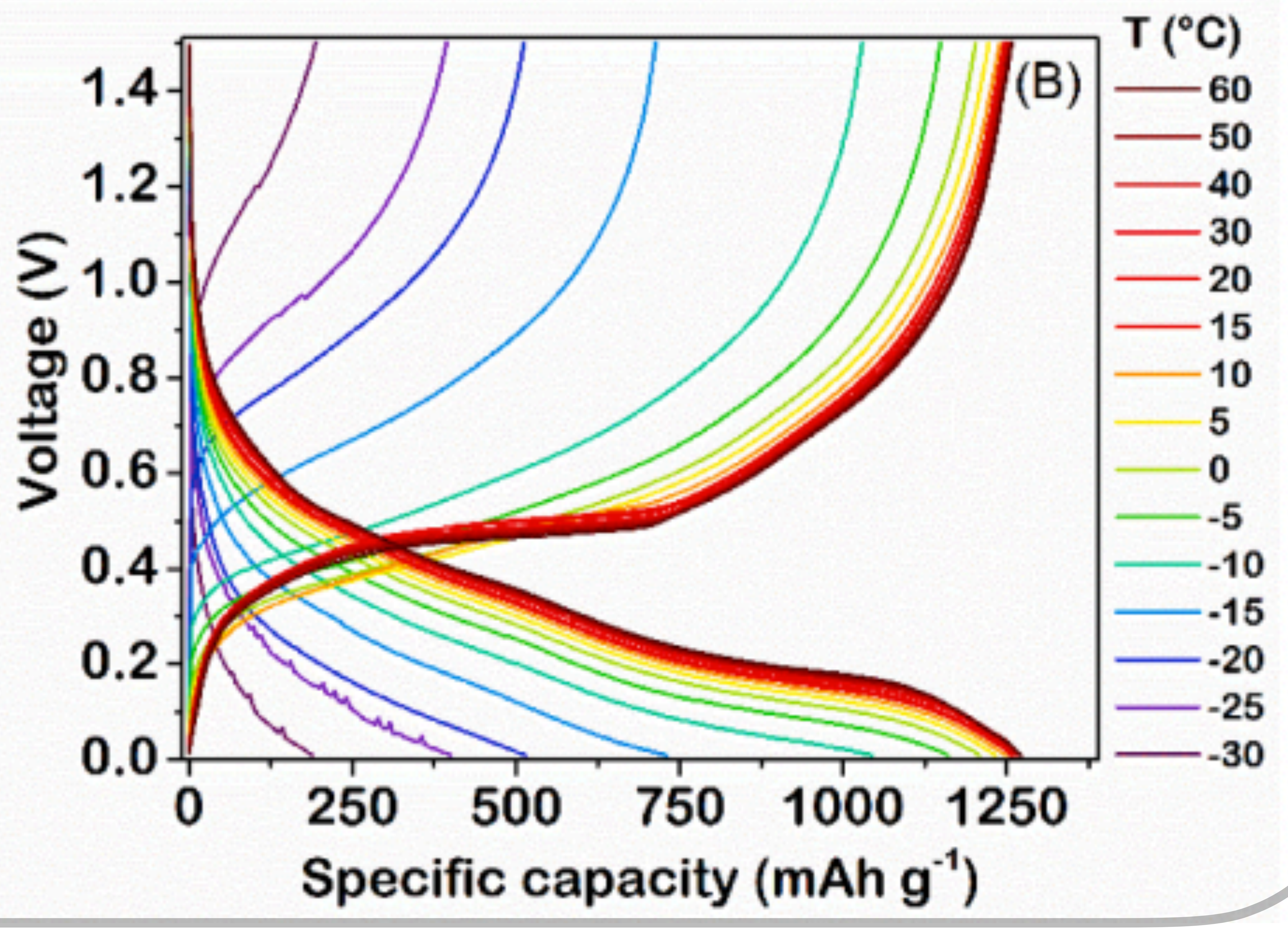
THANK TO SILVIO FUGATTINI FOR THESE MEASUREMENTS

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

Capacity vs Cycle number



Charge/discharge profiles



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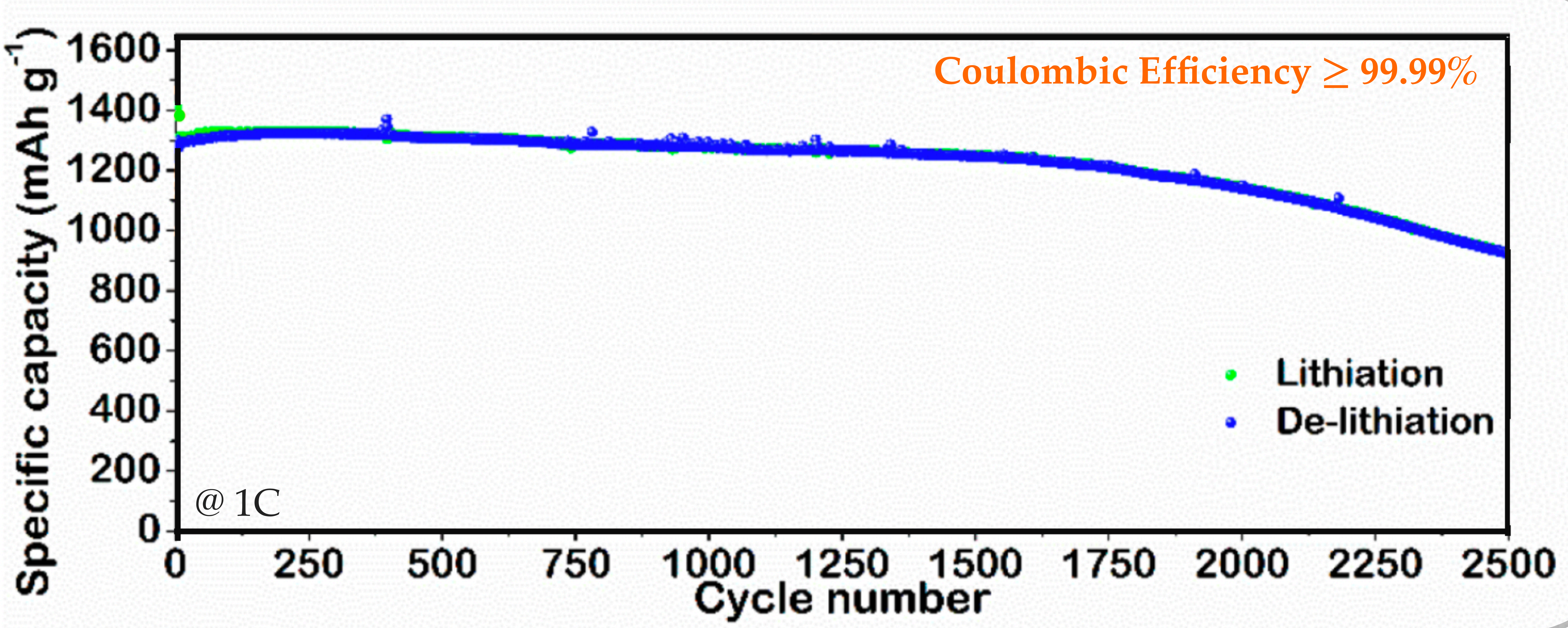
ELECTROCHEMICAL ANALYSIS

THANK TO SILVIO FUGATTINI FOR THIS MEASUREMENT

BEST RESULT ACHIEVED SO FAR!



Coulombic Efficiency ≥ 99.99%

@ 1C

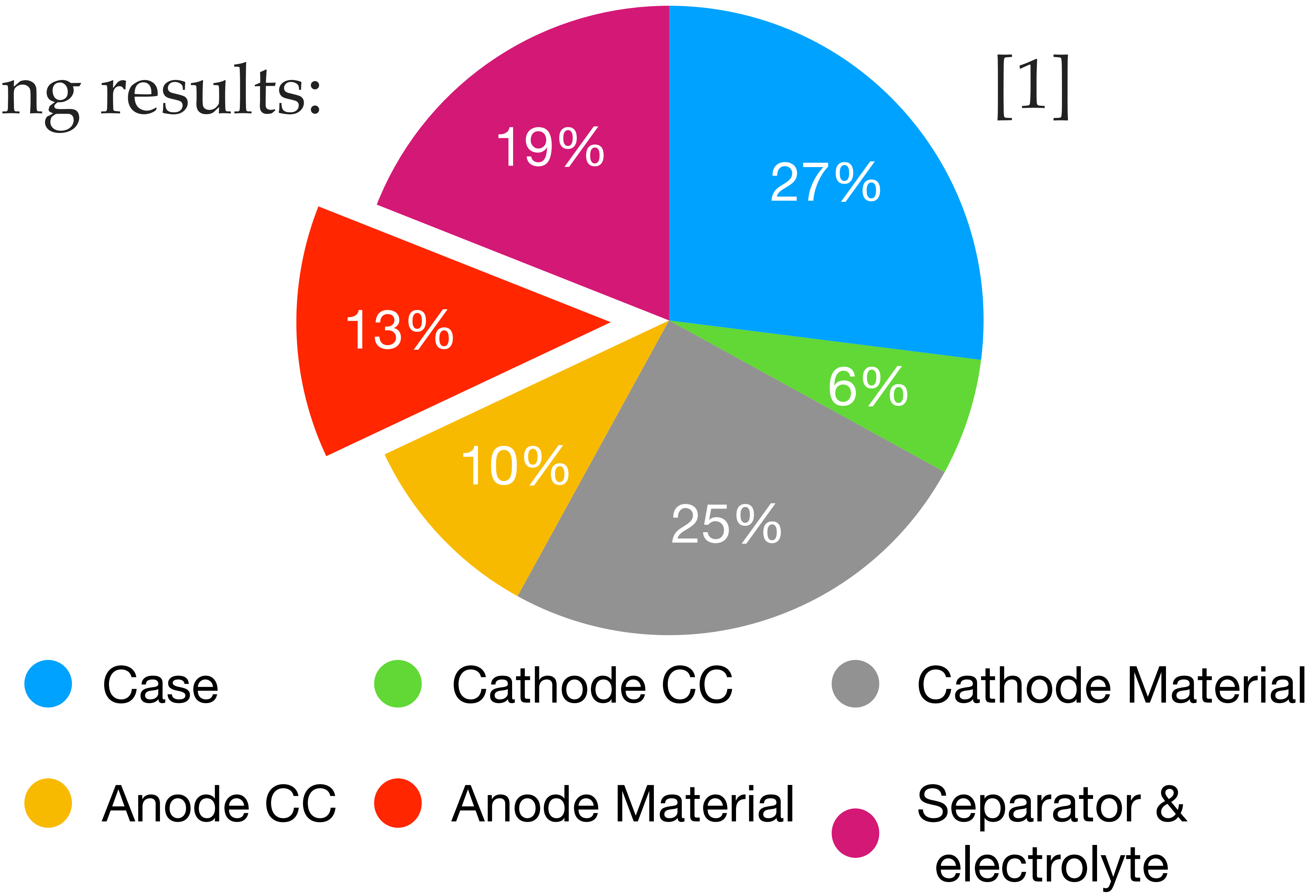
S. Fugattini, A. Andreoli et Al, Electrochimica Acta, Volume 411 (2022) 139832, ISSN 0013-4686 https://doi.org/10.1016/j.electacta.2022.139832

CONCLUSIONS

The here proposed Porous Germanium anode shows promising results:

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

only 1/3 of the active material is needed



[1]

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

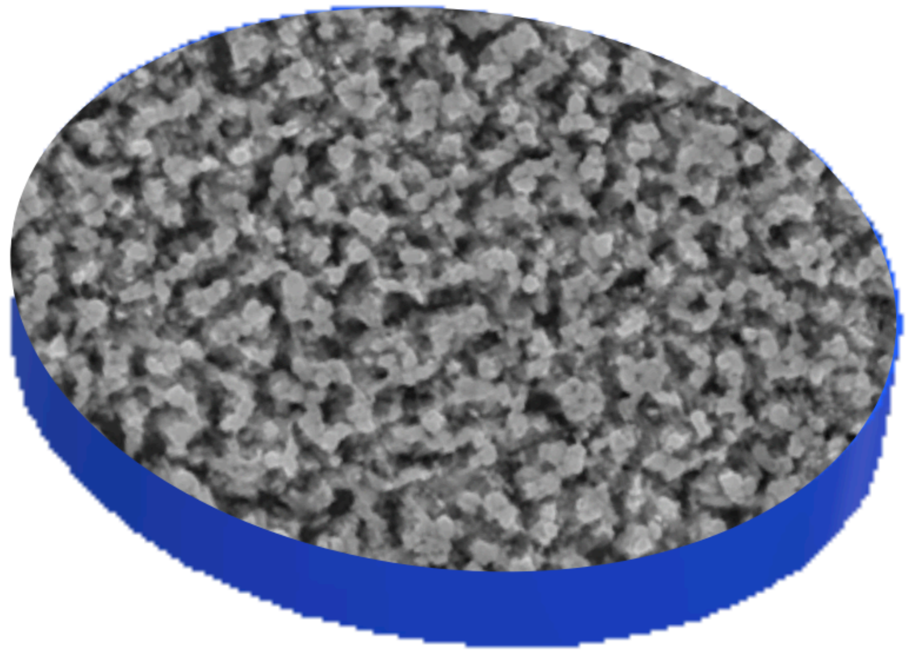
The here proposed Porous Germanium anode shows promising results:

- 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



GLITTERY
BATTERIE SPAZIALI

Università degli Studi di Ferrara

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).

OUR TEAM

GLITTERY
BATTERIE SPAZIALI

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THANK YOU FOR YOUR ATTENTION!