EnerHarv 2024

PSMA International Workshop | 26-28 June, 2024 | Perugia, Italy

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EnerHarv 2024 Workshop

High Performing Anodes for Post-Lithium Ion Batteries

Stefano Marchionna, *Ph.D.*

Research team leader

RSE – Ricerca Sistema Energetico

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Thursday, June 27, 2024

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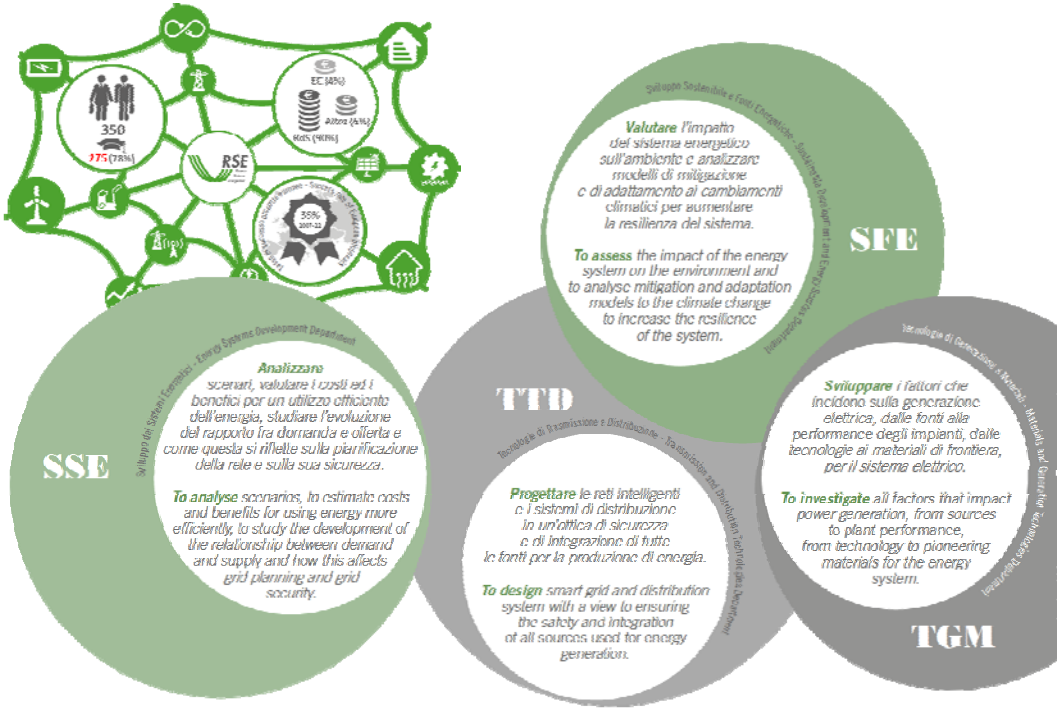
OVERVIEW

- Few words about *RSE* Spa and Our Mission
- Lithium batteries (LIBs) and their “Sustainability”
- LIBs vs Sodium ion Batteries (SIB/NIB)
- Anode for SIB: From MAX phases to MXenes …
- RSE’s approach to develop SIB based on direct use of MAX Phase
- Characterization of the self-assembled nano composites and storage mechanisms
- Conclusions and future works
- Q&A

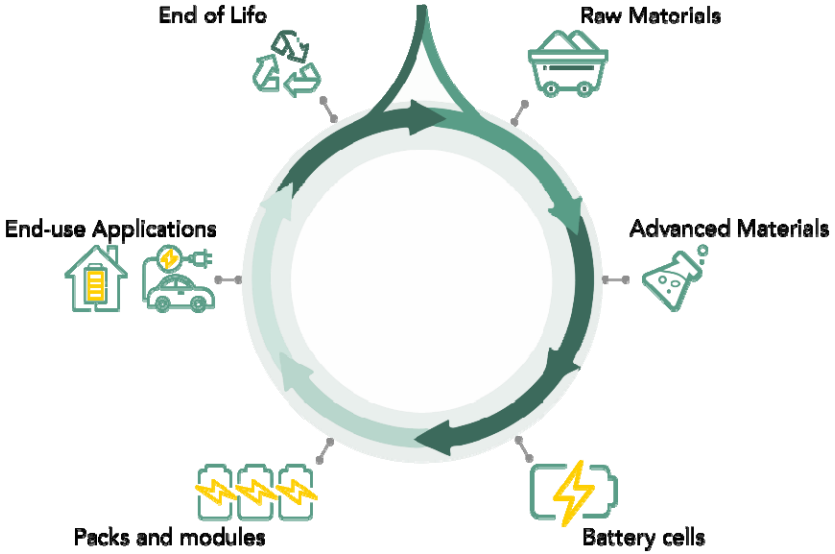
Let's know RSE - Ricerca sul Sistema Energetico S.p.A.



OUR MISSION: **Increase and share our scientific and technical knowledge** to be a strong player in national and international funded research programs **in ELECTRO-ENERGY FIELD** to make more and more innovative and competitive the Italian national electrical system for the benefit of final users and industrial operators. Supported by inner multi-disciplinary skills, strong emphasis is set on experimental applications up to pilot-plant design and testing.

Let's know RSE - Activities on electrochemical storage

The **ACTIVITIES ON ELECTROCHEMICAL STORAGE** aimed to **COVER THE WHOLE VALUE CHAIN**



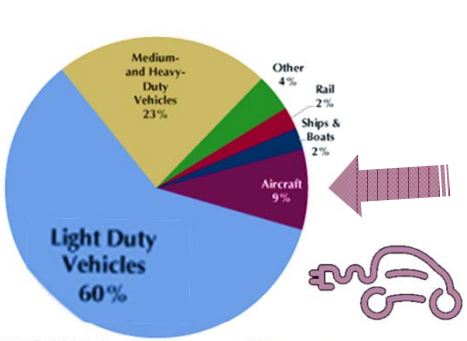
Ricerca di Sistema integrated project + ENEA +

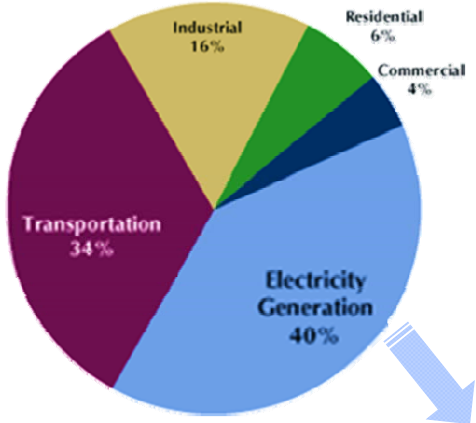
- Mining potential of **raw materials** and development of refining processes
- **Advanced materials** development (electrodes and electrolytes) for battery cells (Li-ion and *post lithium*)
- Multi-scale **computational tools** for screening of materials and system modelling
- Eco-design and **battery cell** realization (scale-up)
- Development of **diagnostic and control systems**
- **Re-use and recycling** technologies
- Evaluation of environmental (LCA), economic (LCC) and social **sustainability**

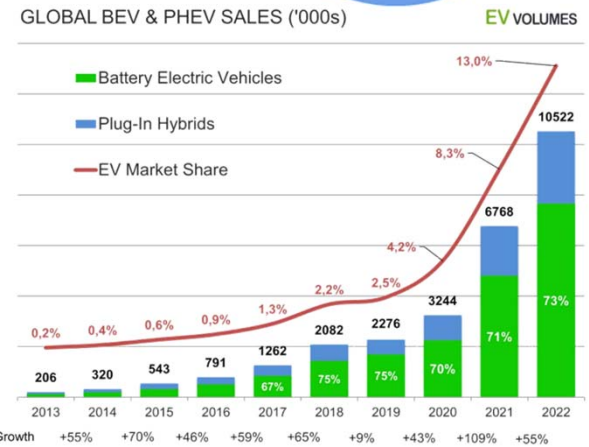
Energy storage for «sustainable» energy transition

CO_2 emissions for specific anthropogenic activities in USA (2018)

Environmental Protection Agency (EPA), Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2018

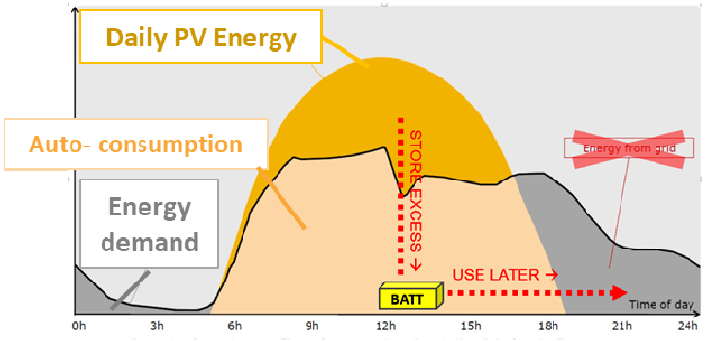






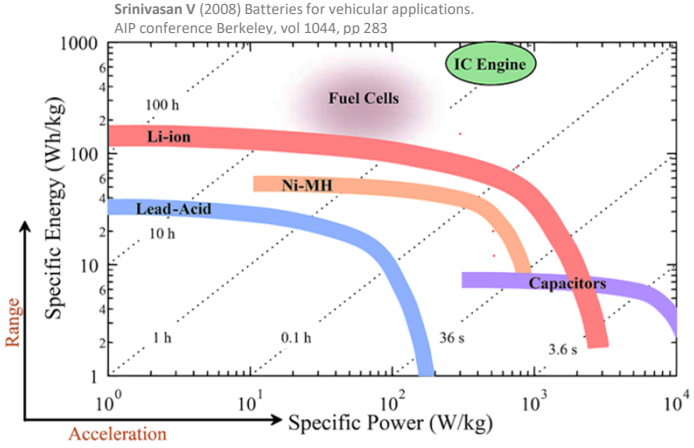
«Peak shaving»

Home battery systems



https://ev-volumes.com/news/ev/global-ev-sales-for-2022/

Energy storage for «*sustainable*» energy transition



State-Of-Art for LIB EV batteries

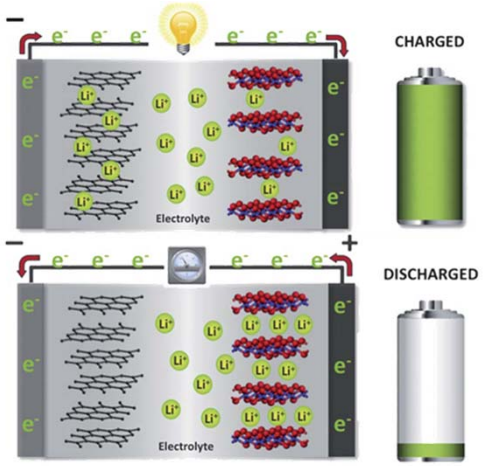
Specific energies near 250 Wh/kg

Main Challanges:

Safety

Sustainability (raw materials, recyclability, 2nd life)

Performance increase (new materials, full-cell design and treatment)



Electrolyte (Organic solvent + Li salt)

Negative electrode

- Graphite and other carbons
- Silicon anodes (blended)
- Lithium titanate

$$Li_xC_n \leftrightarrows xLi^+ + nC + xe^-$$

Positive electrode*

- Metal-oxides (e.g. LCO, NMC, NCA)
- Phosphates (e.g. LFP)

* **Different Li-ion cathodes for different applications**

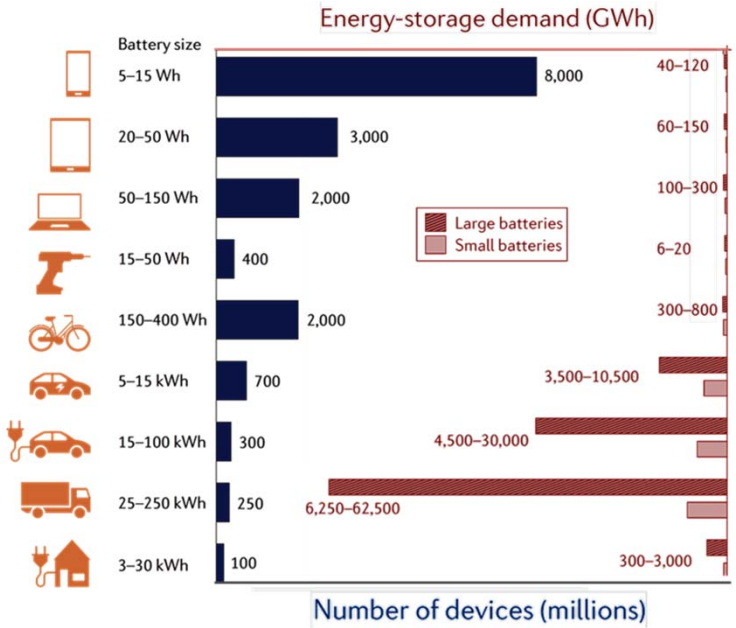
- EVs: NCA/NMC (nickel-based) for high energy density/long range
- Lithium iron phosphate (LFP) for buses, e-bike, stationary
- Lithium cobalt oxide (LCO) for mobile, consumer electronics

$$Li_{1-x}CoO_2 + xLi^+ + xe^- \leftrightarrows LiCoO_2$$

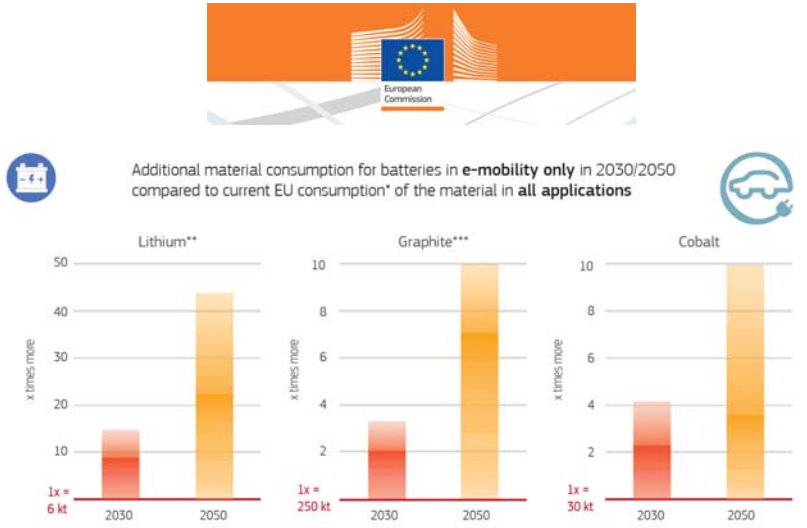
NCA: Nickel Cobalt Aluminum Oxide; NMC: Nickel Manganese Cobalt Oxide LFP: Lithium Iron Phosphate; LCO: Lithium Cobalt Oxide

LIBs: Let's check the 2050 global demand

Scenario 2050 Estimated number of devices and related energy demand for 2016–2050



Vaalma, D. et al., Nat. Rev. Mater. 3, 18013 (2018).

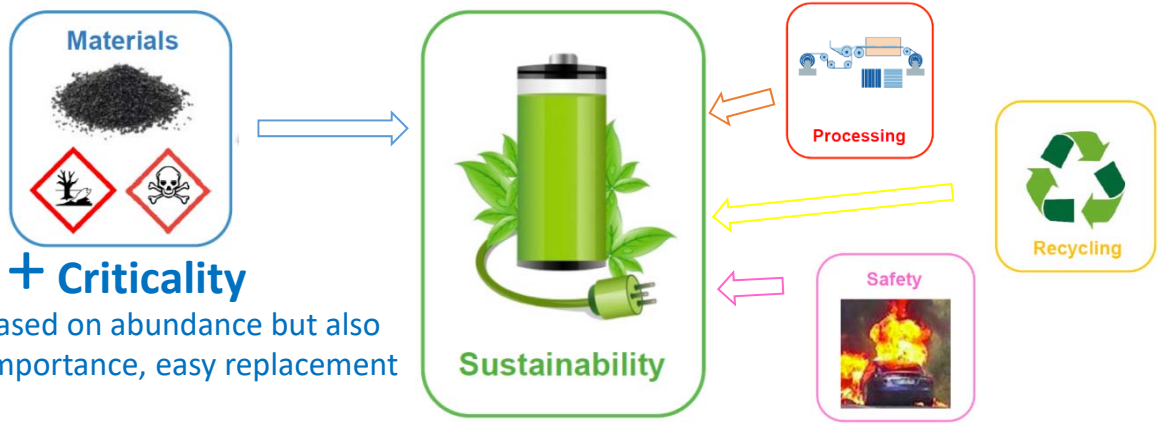


"European Commission, Critical materials for strategic technologies and sectors in the EU - a foresight study, 2020"

Cumulative capacity demand in 2050: ≈ **20-110 TWh**

Production 2016: **44GWh→** 2023: **2,8TWh → But.. about «SUSTAINABILITY?»**

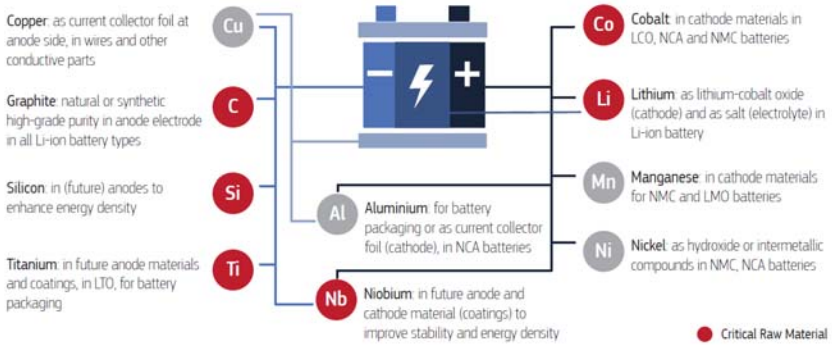
Sustainable energy storage for 2050 scenario

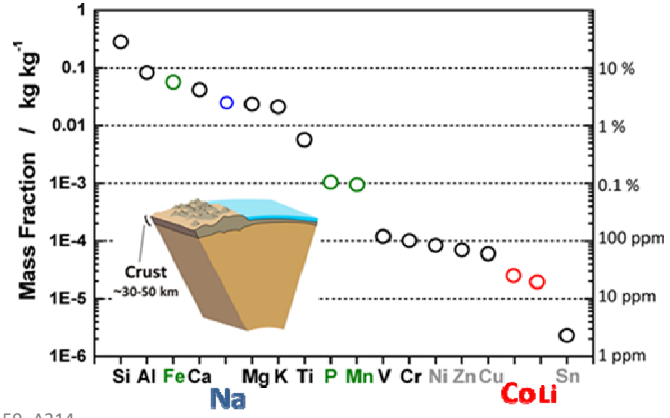


+ Criticality

not only based on abundance but also economic importance, easy replacement

Critical Raw Materials for Strategic Technologies and Sectors in the EU- 2020





N. Ogihara et. al, J. Electrochem. Soc., 2012, 159, A1034, G. Liu et. al, J. Electrochem. Soc., 2012, 159, A214
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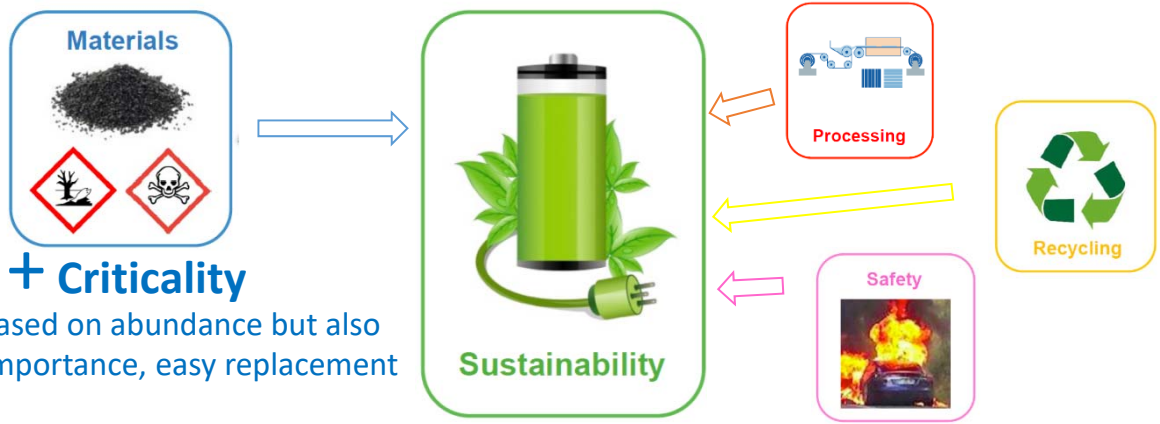

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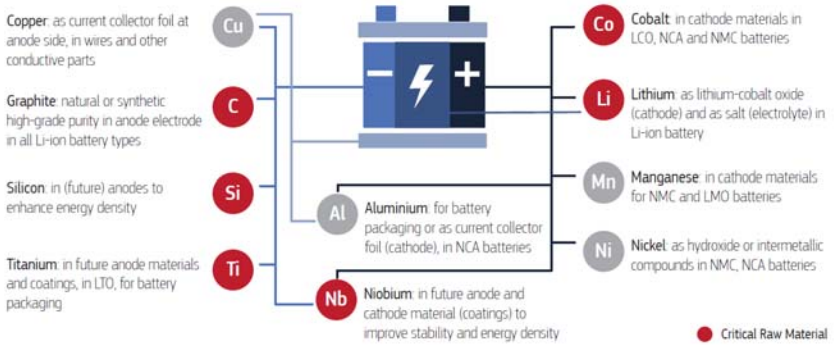
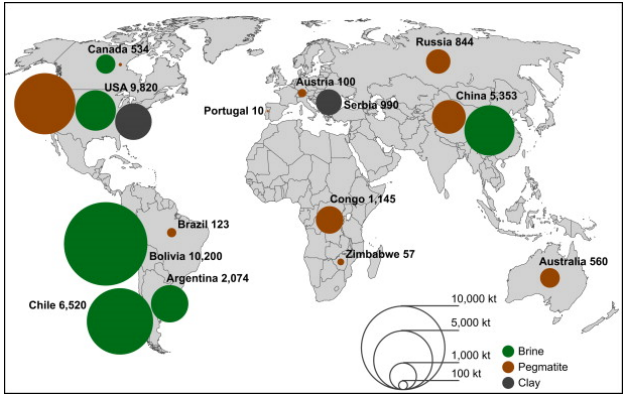


Lithium Deposits



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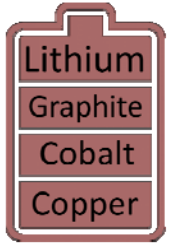
Sustainable energy storage for 2050 scenario

SIB-philosophy:

- Setup & working principle like LIBs
- reduced dependence on critical materials
- Low-cost & environmentally friendliness



LIBs

SIBs

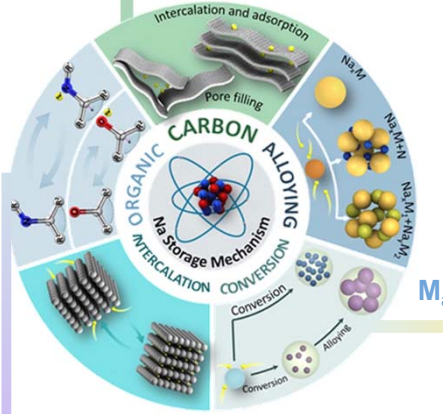
Characteristic	Lithium	Sodium
Crustal abundance (ppm)	20	23600
Distribution (reserves)	70% South America	Everywhere
Anode current collector	Cu	Al
Ionic radius (Å)	0.69	0.98
Molar mass (g mol-1)	6.94	22.99

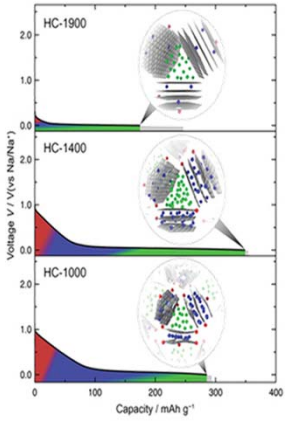
Keller, M.; Et al S. ChemElectroChem , 2016, 3 (7) 1124-1132

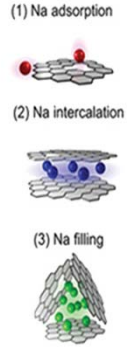
2 important advantages
- SIB are **Cu-Free** devices
- SiB can be shipped fully discharged at **0 Volt**

Hard Carbon

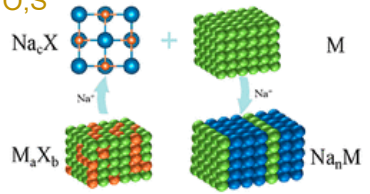
Carbonization of sucrose (or bio-waste) at 1000 -1900°C





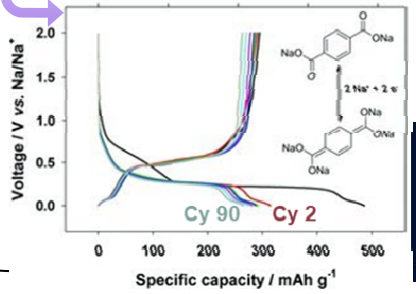


M_aX_b with M = Sn, Sb, Ge,etc X = O,S



Conversion- Alloying

Na salts of organic acids



RdS RICERCA DI SISTEMA

BANDO A
≈ 4.2 M€

ORANGEES

EnerHarv 2024

PSMA

RSE we move research

Sustainable energy storage for 2050 scenario

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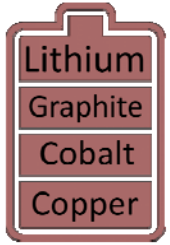

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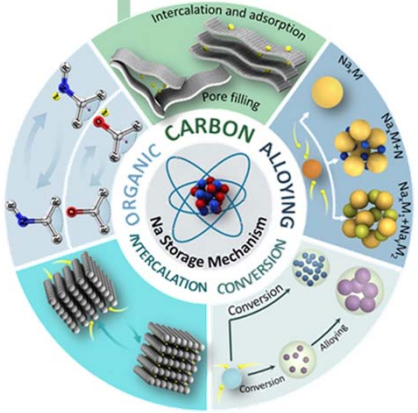

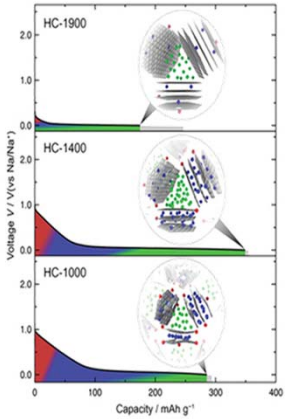

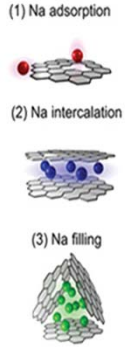

There are Alternative 2D materials can work as anode with high and stable capacitance values?

Sustainable energy storage for 2050 scenario

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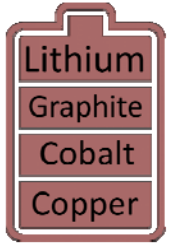

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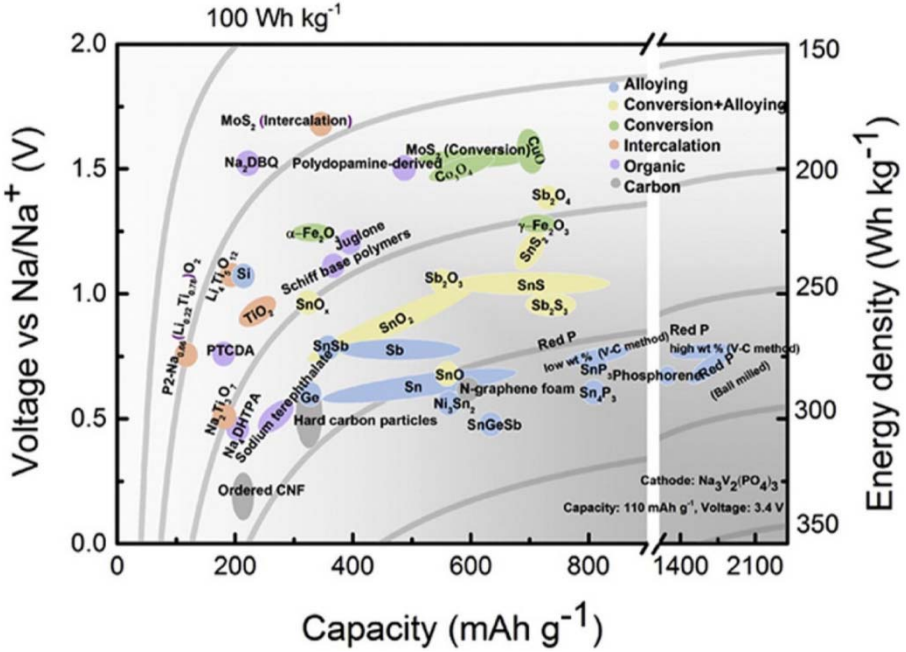
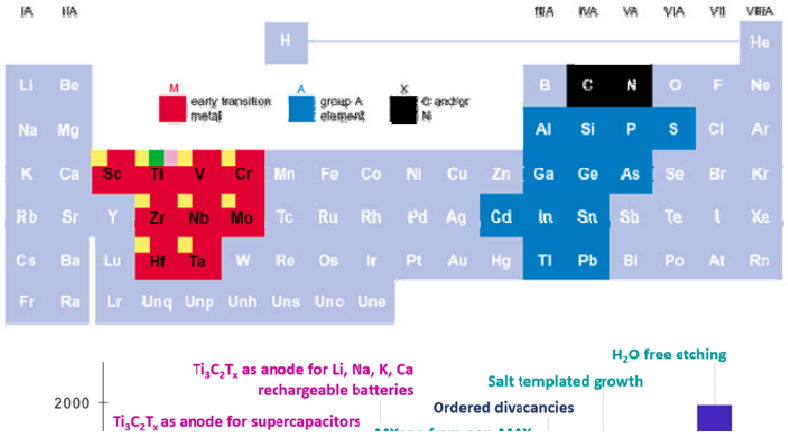
T. Perveen et al. Renewable and Sustainable Energy Reviews 119 (2020) 109549

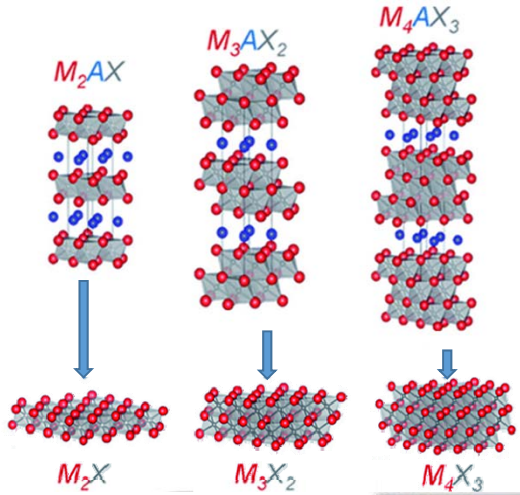


There are Alternative 2D materials can work as anode with high and stable capacitance values?

’s approach for innovative SIB anodes

From MAX phases to MXenes: a promising family …





… to MXenes

- More rigid Graphene-like materials
- Many applicative fields
- Strong potentialities in Energy storage

Publications

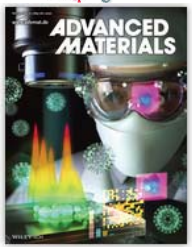
ADVANCED MATERIALS

Review

MXenes for Energy Harvesting

Yizhou Wang, Tianchao Guo, Zhengnan Tian, Khadija Bibi, Yi-Zhou Zhang, Husam N. Alshareef

First published: 20 January 2022 | https://doi.org/10.1002/adma.202108560 | Citations: 77



Volume 34, Issue 21
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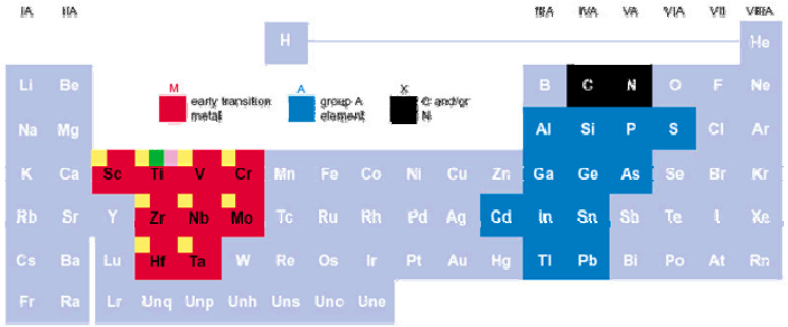
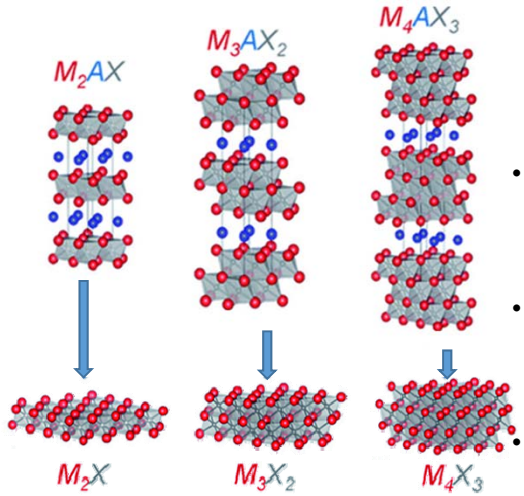
Advertisement

C. Ferrara, A. Gentile, S. Marchionna, R. Ruffo, Current Opinion in Electrochemistry, Volume 29, 2021,100764,

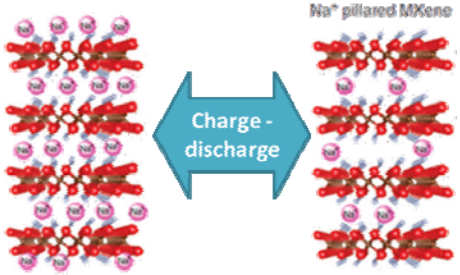
From MAX phases to MXenes: a promising family …

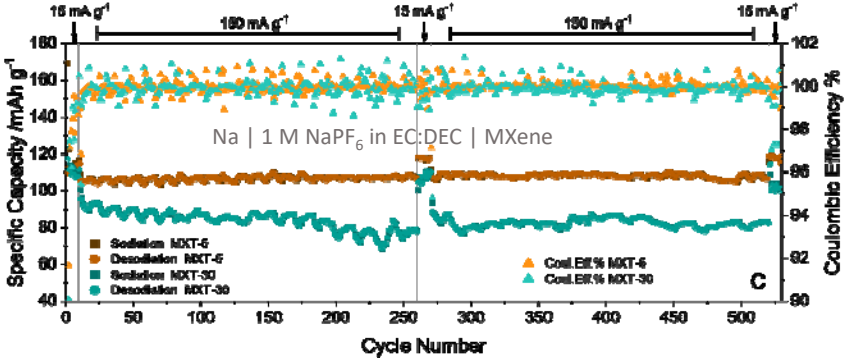




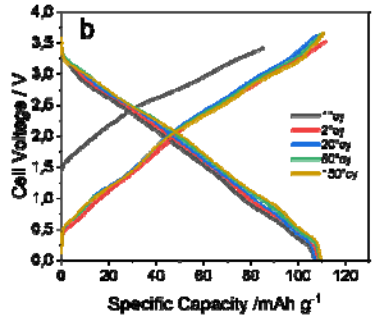
… to MXenes

- Suitable for intercalation of a wide variety of metallic ions
- High Coulombic Efficiency (99.74% at low current)
- Very high reversibility





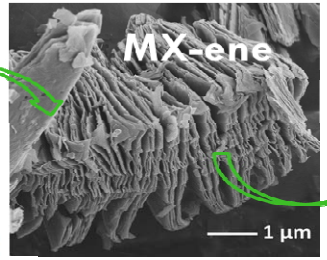
MXene | 1 M $NaPF_6$ in EC:DEC | NMO

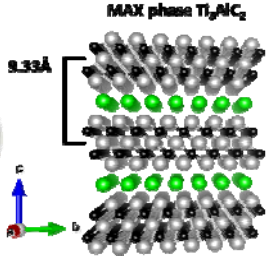


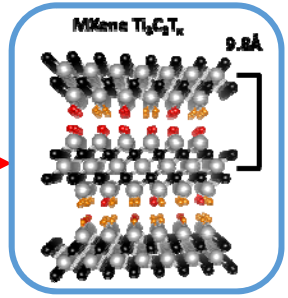
Nature Communications (2021), **6**, 6544 Nano Letters (2021), 21, 8290

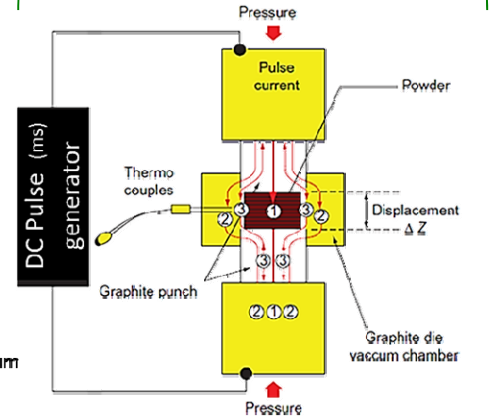
From MAX phases to MXenes: ...with «problems» of SUSTAINABILITY

MAX phase via Direct
Spark Plasma Sintering (SPS):
- High purity
- Scale-up
- Fast process



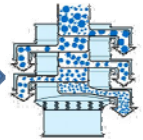


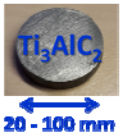


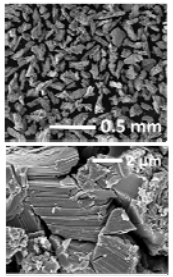


SPS

FUJI- Dr. Sinter
Model 925
Max Current : 10kA
Max Strength: 250 kN
In Gas (Es:Ar) or Vacuum





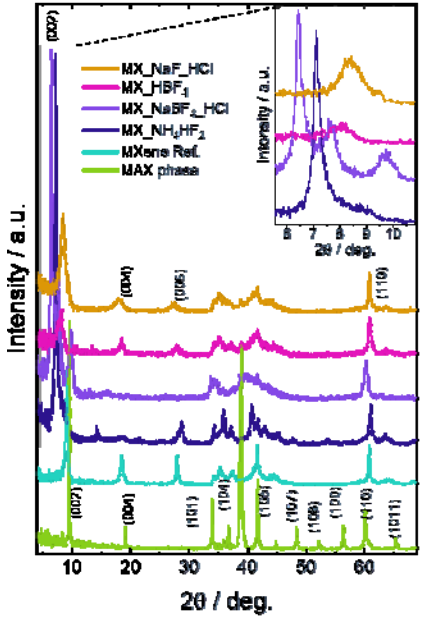


Problem: **HF** is *the* etching agent

HOW TO BE MORE «SUSTAINABLE»?

From MAX phases to MXenes: …MORE SUSTAINABLE CHEMISTRY?

1st Approach → Check more sustainable etching solution



Sample	2θ /deg.	d(002) /nm	Unit cell c /nm	Crystallite size /nm
MAX phase	9.55	0.93	1.85	58
MXene Ref[1]	9.10	0.97	1.94	21
MX_NH_4HF_2	7.16	1.23	2.47	28
MX_NaF_HCl	8.40	1.05	2.10	6.4
MX_HBF_4	8.06	1.10	2.19	7.2
MX_$NaBF_4$_HCl	6.43*	1.37	2.75	29

Pure HF

Pure HF[2]

$Ti_3AlC_2 + 3HF \rightleftarrows AlF_3 + Ti_3C_2 + 1.5H_2$

$Ti_3C_2 + 2H_2O \rightleftarrows Ti_3C_2(OH)_2 + H_2$

$Ti_3C_2 + 2HF \rightleftarrows Ti_3C_2F_2 + H_2$

MX_NH_4HF_2

Etching solution 1[3]

$NH_4HF_2 \rightleftarrows NH_4^+ + HF + F^-$

$HF + H_2O \rightleftarrows F^- + H_3O^+$

MX_$NaBF_4$_HCl

Etching solution 2[4]

$NaBF_4 + HCl \rightarrow HBF_4 + Na^+ + Cl^-$

$HBF_4 \rightleftarrows HF + BF_3$

$BF_3 + 3H_2O \rightleftarrows 3HF + H_3BO_3$

$HF + H_2O \rightleftarrows F^- + H_3O^+$

MX_HBF_4

Etching solution 3[4]

$HBF_4 \rightleftarrows HF + BF_3$

$BF_3 + 3H_2O \rightleftarrows 3HF + H_3BO_3$

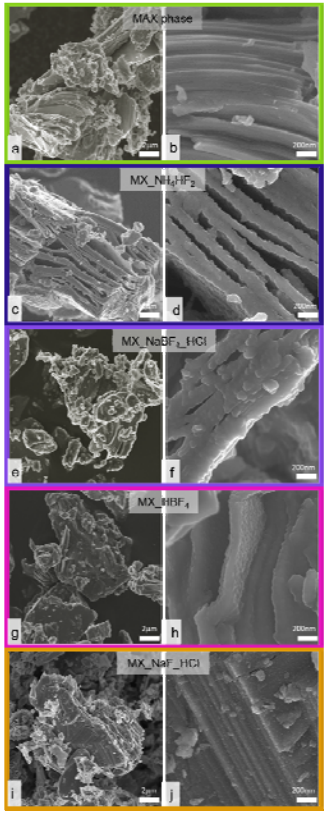
$HF + H_2O \rightleftarrows F^- + H_3O^+$

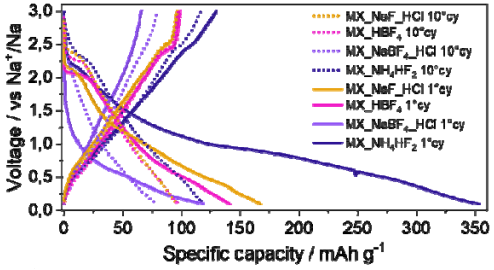
MX_NaF_HCl

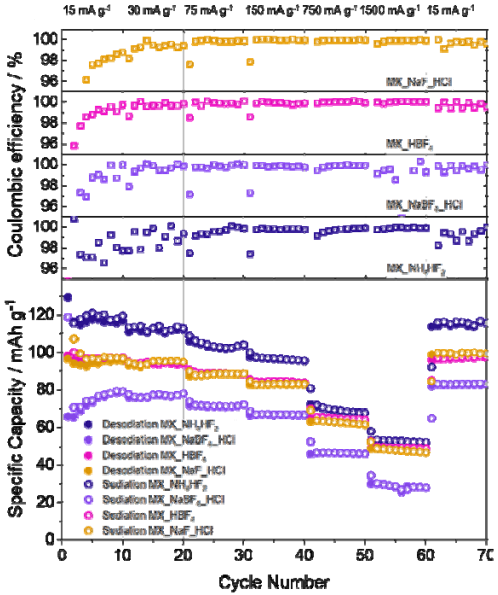
Etching solution 4[4]

$NaF + HCl \rightarrow HF + Na^+ + Cl^-$

$HF + H_2O \rightleftarrows F^- + H_3O^+$







A. Gentile, S. Marchionna, M. Balordi, G. Pagot, C. Ferrara, V. Di Noto, R. Ruffo, ChemElectroChem 2022, 9, e202201064.

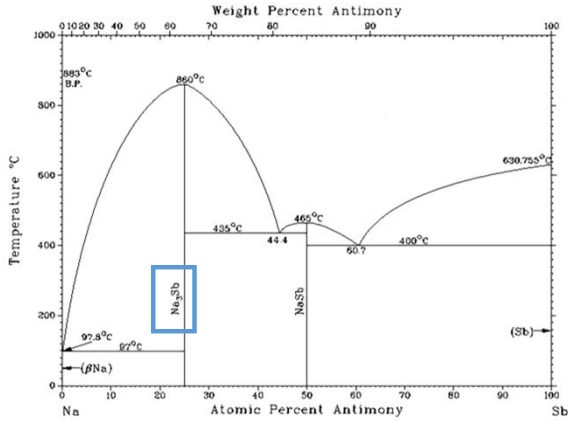
From MAX phases to MXenes: IMPROVE STORAGE PERFORMANCE?

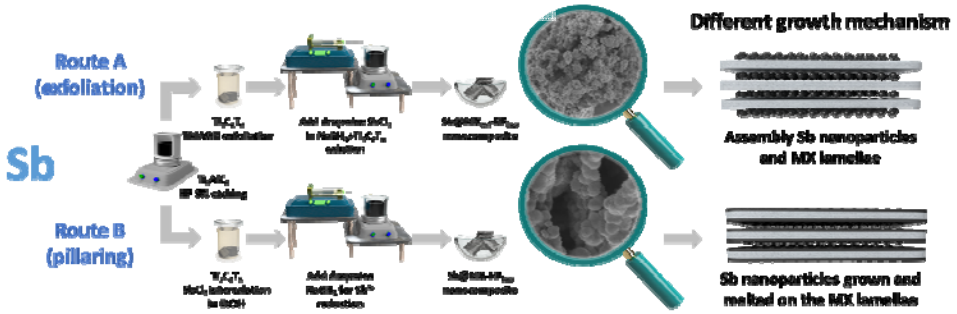
2nd Approach → MXene based composites

$$Sb + xe^- + xNa^+ \rightarrow Na_xSb$$

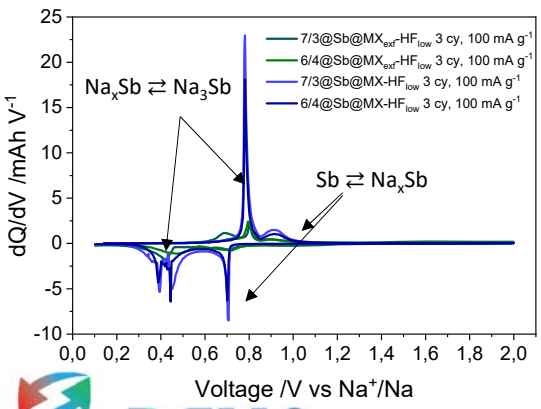
$$Na_xSb + (3-x)Na^+ + (3-x)e^- \rightarrow Na_3Sb$$

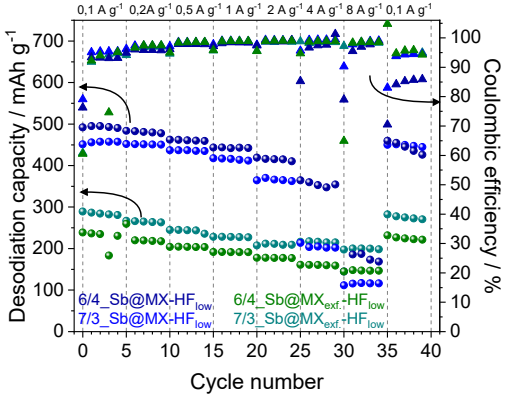
Specific Capacity = 660 mAh g^{-1}

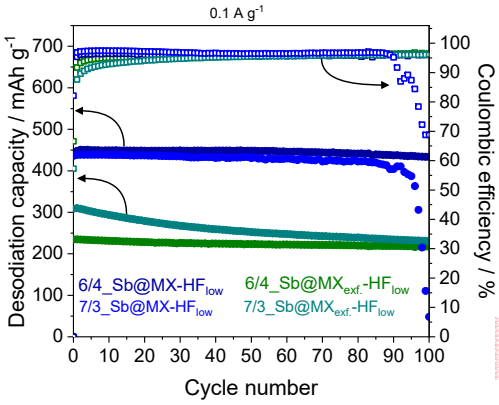




Na | (1M) $NaClO_4$, EC:DMC:$FEC_{5\%}$ | **Sb@MX** | Al







Two steps formation process
- Sb ⇄ Na_xSb
- NaSb ⇄ Na_3Sb

6/4 Sb@MX-HF$_{low}$ is the optimal ratio for some stable material in electrochemical tests. Higher Sb quantity produces capacity loses or cell death

≈ 450 mAh/g

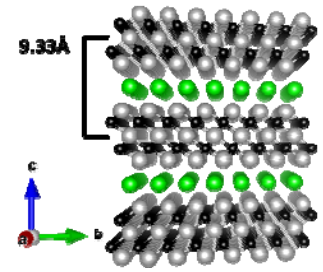
Coul. Eff. ≈ 95%

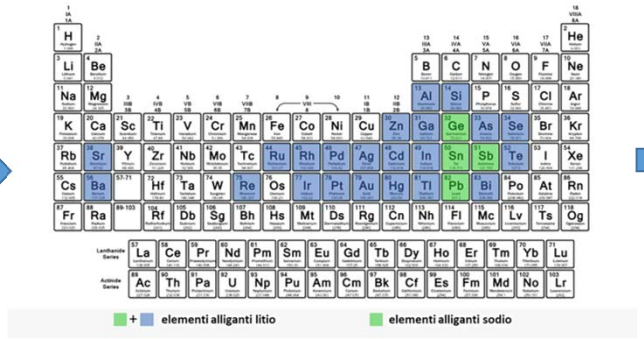
H. Hou et al., Electrochim. Acta 2014, 146, 328–334

From MAX phases to SELF NANO-STRUCTURED OXIDES

3th Approach → MAX phase doping with alloying element

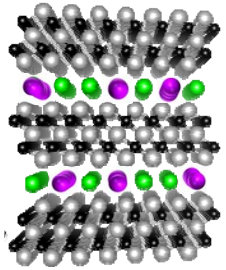
Ti_3AlC_2 MAX phase





Substitution of precursors before SPS synthesis

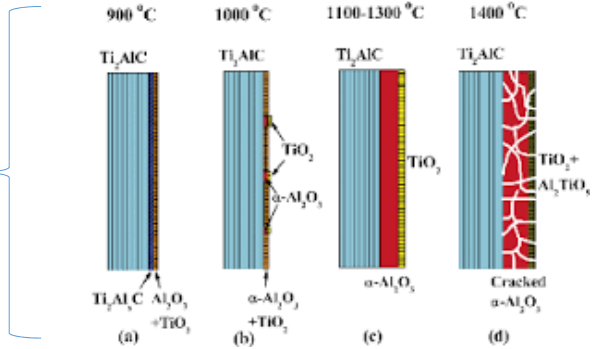
$Ti_3Al_{(1-x)}Sn_xC_2$ MAX phase

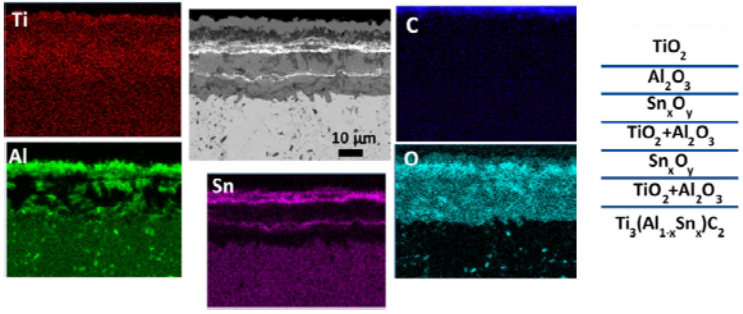


MAX Phase DIRECT USE

OXIDIZED MAX Phase

Oxide scale formation after Post-synthesis oxidation → ΔT°





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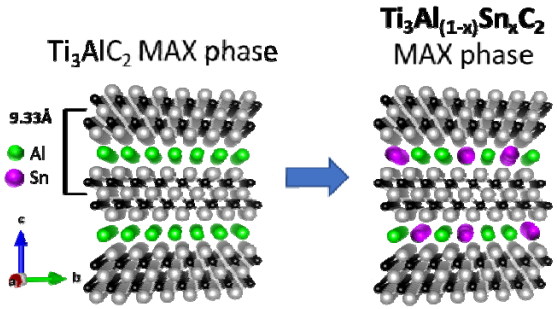
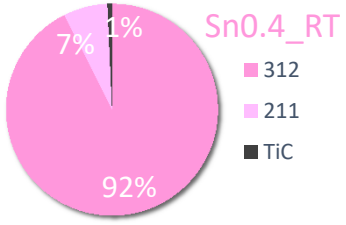
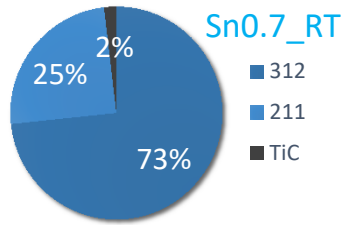
RSE we move research

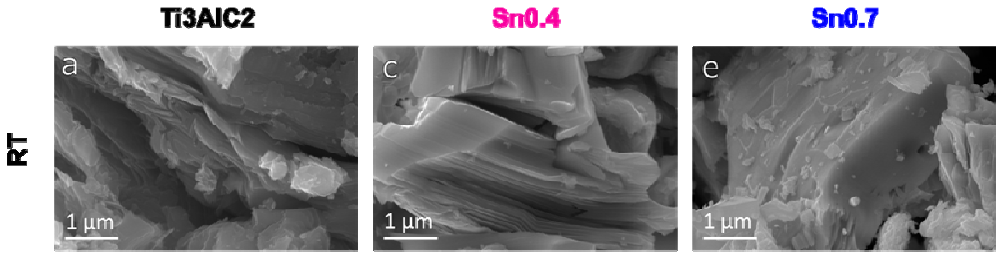
Pure and Oxidized $Ti_3Al_{(1-x)}Sn_xC_2$ MAX phase



Campioni	Sn 0%	Sn 40%	Sn 70 %
Post sintesi SPS (RT)	Ti3AlC2_RT	Sn0.4_RT	Sn0.7_RT

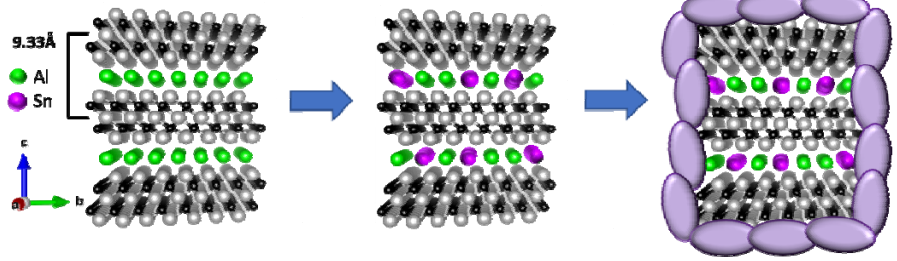




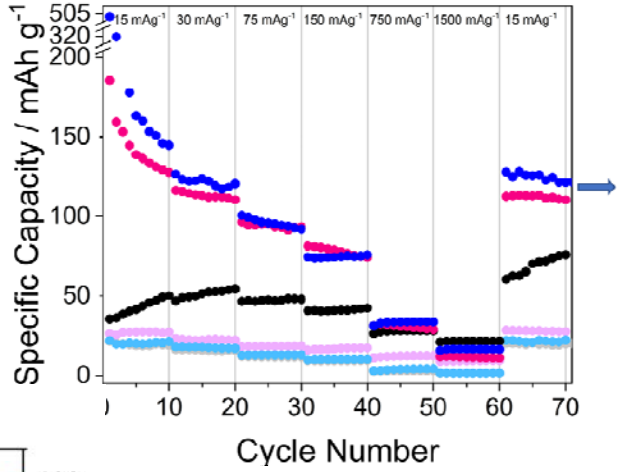


Ostroman, I., Ferrara, C., Marchionna, S., Gentile, A., Vallana, N., Sheptyakov, D., Lorenzi, R., Ruffo, R. Small Methods 2023, 2300503..

Pure and Oxidized $Ti_3Al_{(1-x)}Sn_xC_2$ MAX phase

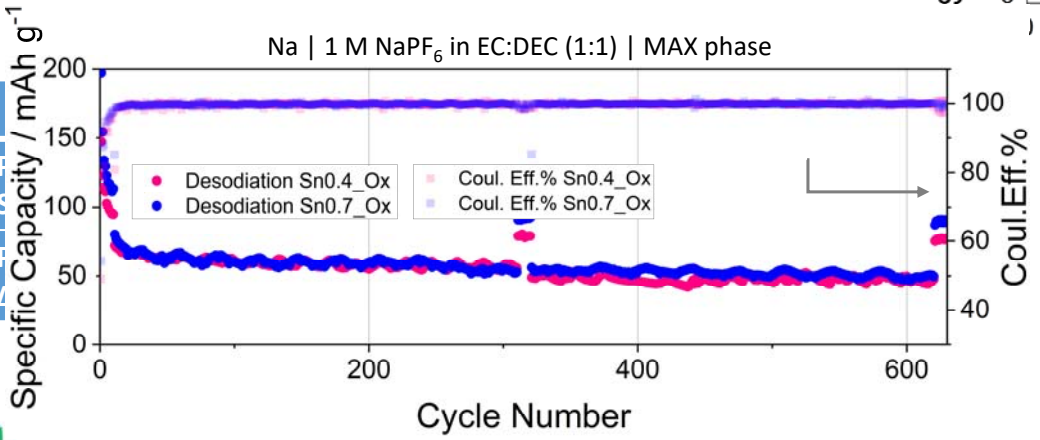


Na | 1 M $NaPF_6$ in EC:DEC (1:1) | MAX phase OX



Same Specific Capacity as Mxenes !!

Na | 1 M $NaPF_6$ in EC:DEC (1:1) | MAX phase



Coulombic Efficiency (at 1 C)

Sn0.4_Ox vs Na: **99.78** ± 0.28 %

Sn0.7_Ox vs Na: **99.77** ± 0.25 %

Capacity loss (after 630 cycles)

Sn0.4_Ox vs Na: **25 %**

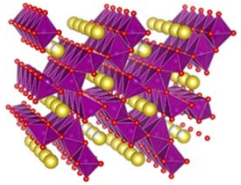
Sn0.7_Ox vs Na: **23 %**

Ostroman, I., Ferrara, C., Marchionna, S., Gentile, A., Vallana, N., Sheptyakov, D., Lorenzi, R., Ruffo, R. Small Methods 2023, 2300503..

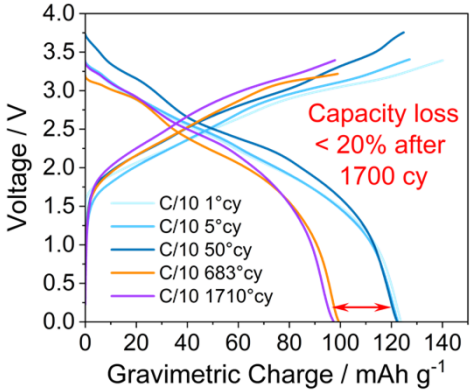
Pure and Oxidized $Ti_3Al_{(1-x)}Sn_xC_2$ MAX phase: Full-cell test

Electrodes		Electrolyte	Full-Cell structure tested in 3-electrodes "*Hohsen*" cell geometry	Potential Limits *(GCPL2- EC-Lab®)*	
Anode	Cathode			Anode	Cathode
MAXphase Sn70% _OX	$Na_{0.44}Mn_{0.9}Cu_{0.1}O_2$	$NaPF_6$ EC : DEC 1:1%$_{vol}$	MAXphase Sn40% OX_1 |$NaPF_6$ EC:DEC| $Na_{0.44}Mn_{0.9}Cu_{0.1}O_2$ with Na/Na+ as Ref	0,01V-3V	2V-3,8V

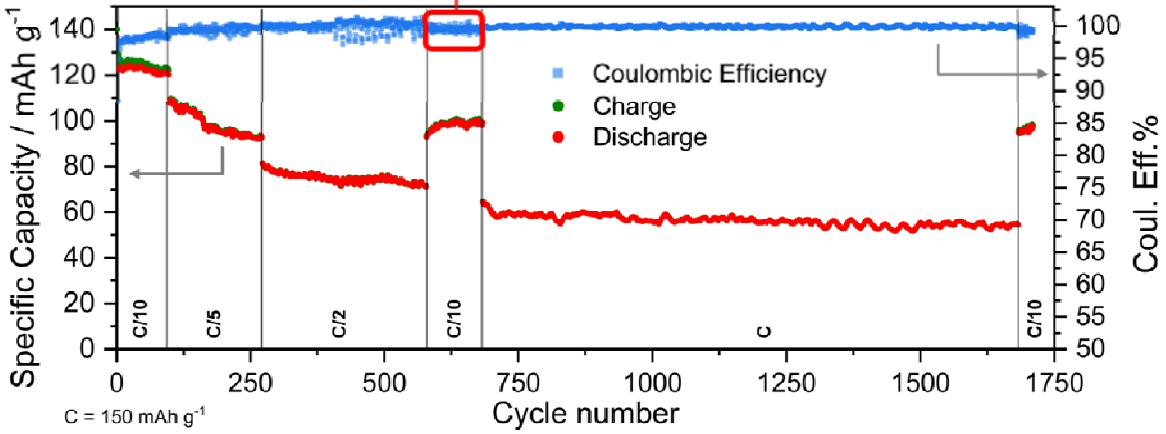
Coulombic Efficiency at low current (C/10): **99.57 ± 0.38 %**



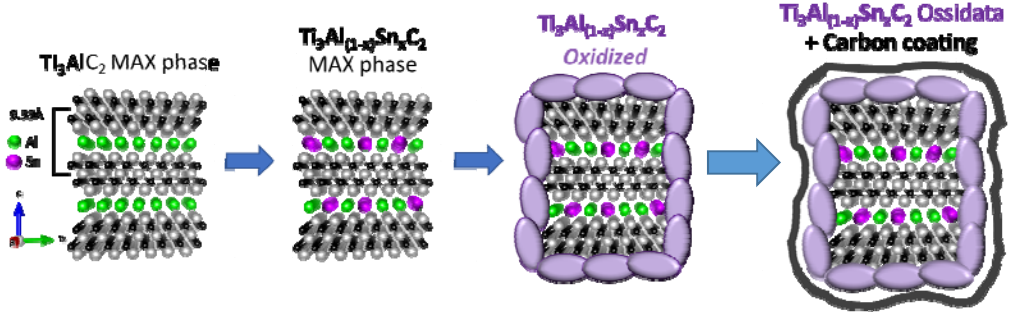
Cathode (by RSE)
$Na_{0.44}Mn_{0.9}Cu_{0.1}O_2$

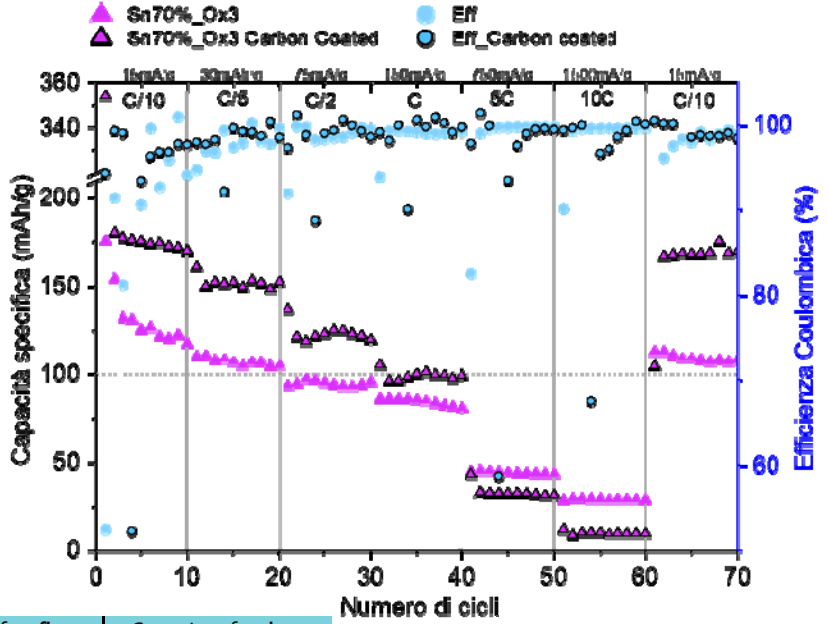


Sn0.7_Ox MAX phase | 1 M $NaPF_6$ in EC:DEC (1:1) | NMO
(MAX phase was presodiated)



Pure and Oxidized $Ti_3Al_{(1-x)}Sn_xC_2$ MAX phase: carbon coating





To improve the electrical conductivity of the oxidized MAXphase, the powder have been **CARBON COATED VIA HYDROTHERMAL PROCESS**

$Ti_3Al_{1-x}Sn_xC_2$	Thermal treatm.	Reversibility 1°Cycle (%)	Retention capability after C-rate test (%)	Coulombic Efficiency (%)	Capacity after **first** 10 cycles C/10 (mAh/g)	Capacity after **last** 10 cycles C/10 (mAh/g)
Sn = 70%	**RT**	44.7	93.5 ± 0.7	98.6 ± 0.8	**35.7 ± 0.7**	33.4 ± 0.5
		52.5	93.0 ± 2.1	99.1 ± 0.4	**122,6 ± 2.3**	114.0 ± 0.8
+ Carbon coating	Ox	**50.8**	**97.2 ± 2.4**	**98.9 ± 1.5**	**173.6 ± 2.4**	**168.9 ± 2.4**

WORK IN PROGRESS

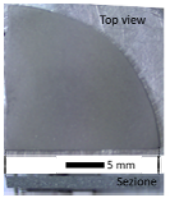
FUTURE WORKS:

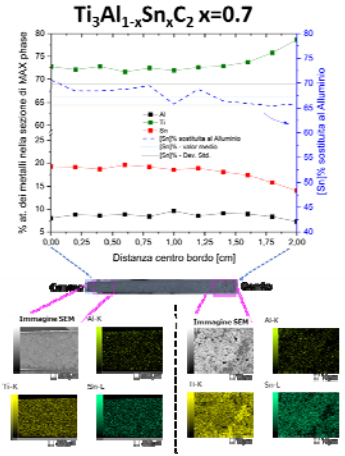
Storage performance (LIB and NIB) *vs :*

- thermal oxidation profile

Nome trattamento termico	Step 1			Step 2			Step 3		
	Temp (°C)	Rampa (°C/h)	Attesa (min)	Temp (°C)	Rampa (°C/h)	Attesa (min)	Temp (°C)	Rampa (°C/h)	Attesa (min)
Ox1	450	900	180						
Ox2	600	450	40						
Ox3	400	900	3	700	120	40			
Ox4	400	900	3	700	120	40	850	120	180

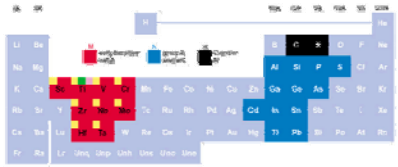
- SPS synthesis of **$Ti_3Al_{(1-x)}Sn_xC_2$ with x=1 (Ti_3SnC_2)**

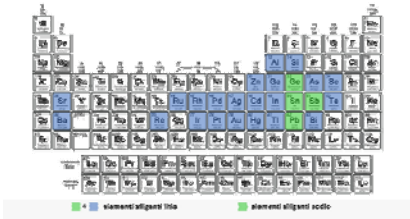




- **$Ti_3Al_{(1-x)}Sn_xC_2$** powder granulometry vs Storage performances (d_{50} < 50 µm)

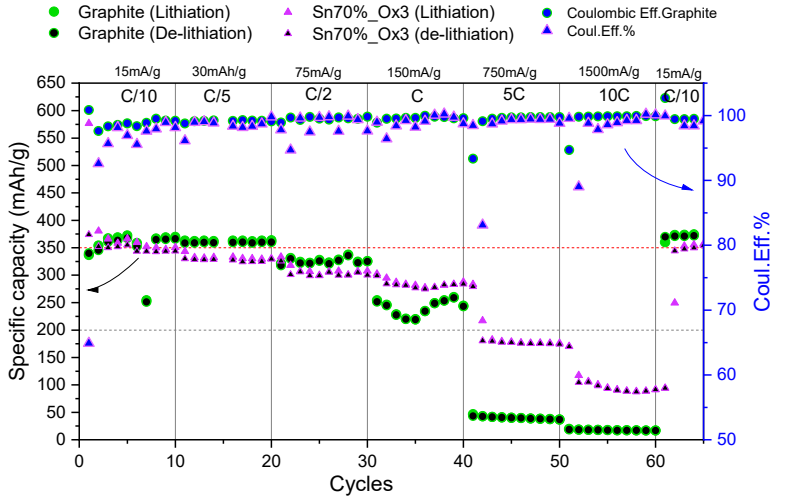
- exploit SPS versatility to test New **A** elements in MAX phase chemistry to exploit the same approach: oxidation→ conversion/alloying storage





Conclusions

- SIB is a crucial technology to facilitate in a more sustainable way the penetration of BESS to support the energy transition
- RSE has chosen to approach at the development of SIB covering all the value chain of these devices and exploiting its experience as test facility of commercial LIB
- MXenes, obtained exfoliating Ti3AlC2 MAX phase has been tested as anode for SIB showing good performances if combined with alloying elements (es: composite MX/Sb → 450 mAh/g)
- For the first time, RSE has demonstrated the potentialities of the direct use of MAXphase as anode for SIB showing good capacity values and stable performances for more than 1500 Cycles in a full cell SIB
- Carbon coating treatment can push the capacity value (vs Na/Na^+) of oxidized $Ti_3Al_{(1-x)}Sn_xC_2$ MAXphase up to Hard Carbon storage performance (200-300 mAh/g)
- More parameters need to be investigated (composition, thermal treatment in air, granulometry) to explore the real potentialities of MAXphase as anode for SIB and also for LIB like alternative to graphite



ACKNOWLEDGEMENT

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Thanks very much for your time and attention!

And now ..Questions/comments???

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