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

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EnerHarv 2024 Workshop

The use of recycled materials for producing more sustainable Li and Na batteries: the case study of PVB (and more)

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GAME Lab, Department of Applied Science and Technology (DISA), Polytechnic of Torino
National Reference Center for Electrochemical Energy Storage (GISEL) – INSTM

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Wednesday, June 26, 2024

OVERVIEW

- **Few words about the GAME Lab research group at the Polytechnic of Torino**
- **SUNRISE European project for the recycling of PVB**
- **The use of recycled PVB as binder for anodes**
- **Anodes materials from biomass waste**
- **The use of recycled PVB as electrolyte separator**
- **Conclusions**
- **Q&A**

Polytechnic of Torino

61 BSc/MSc courses in Engineering and Architecture

38700 students (20% foreigners)

1114 Professors/Researchers

300-600 M€/year income

40 ongoing Spin Offs

60 Start Ups

The **Department of Applied Science & Technology (DISAT)** is the second major Department at POLITO.

The Department covers different sectors, such as chemistry, physics, materials science and technology, metallurgy, nanotechnology, process engineering, **from the fundamental principals to their application on a laboratory scale and in pilot plants**.

The staff counts on more than 150 Professors/Researchers, 200 Post-Docs and PhD Students, and 60 Technical and Administrative Collaborators.

the Group for Applied Materials and Electrochemistry

GAME Lab research group is specialized in the field of **electrochemistry and materials science for energy devices**.

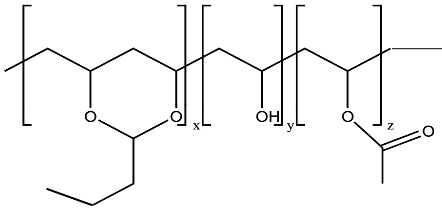
The focus is on the development of innovative, low cost and environmentally friendly materials for energy storage and conversion devices, and their structural, morphological and electrochemical characterisation.

GAME Lab is part of the consortium GISEL (the Italian Group for Electrochemical Energy Storage), which groups together all major Italian research centers and development stakeholders working in the field of the electrochemical energy storage technologies, promoting the discussion and cooperation among the researcher, either from academic or industrial sectors, supporting research projects and providing shared facilities and expertise.

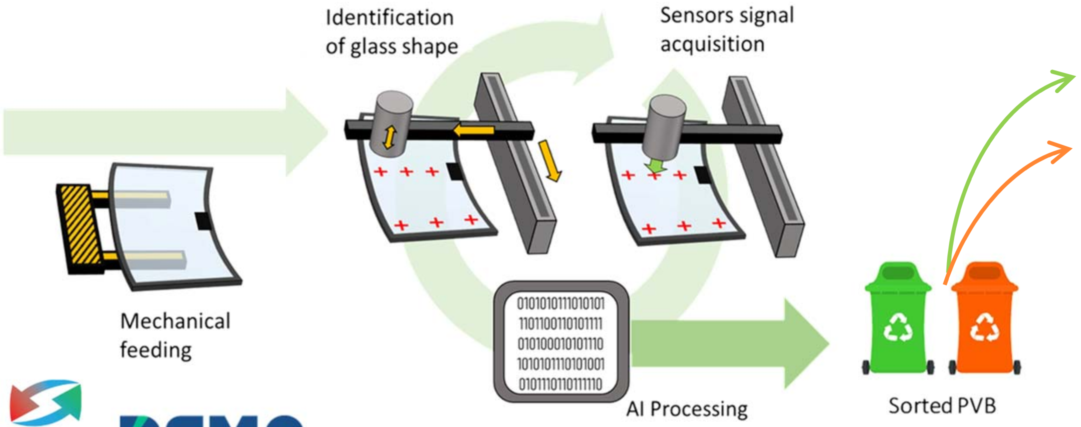
European project SUNRISE for the recycling of PVB

Polyvinyl Butyral (PVB) is used as the interlayer polymer in laminated glasses for construction, photovoltaic panels, and automotive.

PVB recycling presents several difficulties related to glass residues, humidity, heterogeneity, and optical degradation.



SUNRISE European Project is developing an innovative optical multi-sensor sorting tool controlled by an AI algorithm to collect post-consume PVB and classify it for composition and degradation.



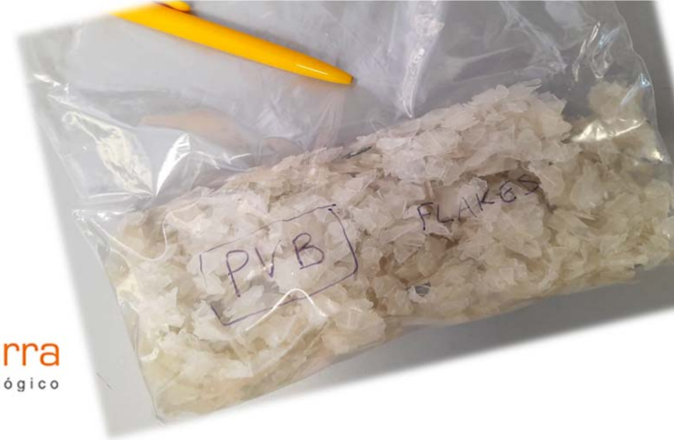
high-quality → reused in laminated glasses

low-quality → repurposed in secondary uses including batteries

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 958243 https://sunrise-project.eu/

Reusing the recycled PVB

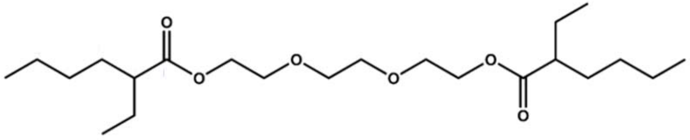
SUNRISE



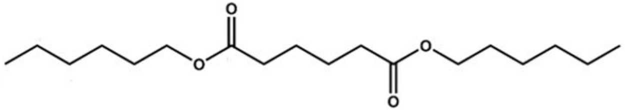
Recycled PVB was provided by Lurederra (Spain).

Recycled PVB was obtained through a **mechanochemical process**, involving shredding, filtering, acid cleaning (HCl), basic stabilization (NaOH), and water washing.

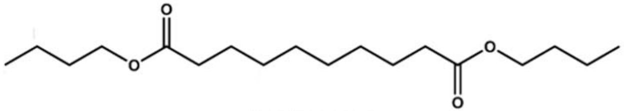
Lurederra
centro tecnológico



triethylene glycol bis(2-ethylhexanoate)
(3GO)



dihexyl adipate
(DHA)

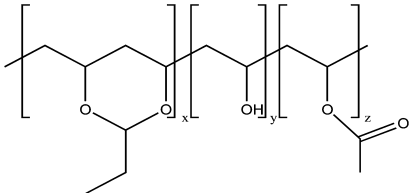


dibutyl sebacate
(DBS)

PVB used in laminated glasses for automotive contains three possible different plasticizers.

The content of plasticizers and the proportion among the different PVB components were evaluated by NMR, IR, TGA and GPC.

M_w (g/mol)	PVB/OH (molar ratio)	PVB/plasticizer (weight ratio)
135 000	5.0 – 7.7	1.08 – 2.07



Polymers 2024, 16(1), 10

National Technical University of Athens

UNIVERSITÀ DI TORINO

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Recycled PVB in batteries

SUNRISE

Binder

The **targeted cost < 10$/kg**
(with respect to commercial PAA and PVDF binders)

To provide good contact among the components and with the current collector

Separator

The **targeted cost < 60$/kg**
(with respect to commercial PP Celgard® separator)

To allow the conduction of electrolyte ions between anode and cathode, but inhibiting electrical short-circuit

Preliminary tests with pure PVB purchased from Sigma-Aldrich.

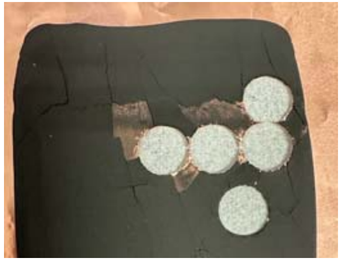
Lurederra centro tecnológico

Final tests with the flakes of recycled PVB provided by LUREDERRA.

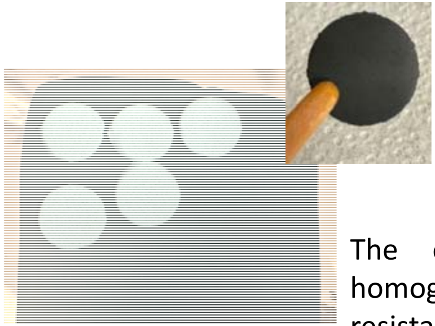
Preparation of hard carbon (HC) anodes with PVB

Electrode composition
- 90% active material (HC) *
- 5% conductive carbon black
- **5% binder**

*** KURANODE™ type 2**
- average particle size: 5 μm
- specific surface area: 6 m^2/g
- interlayer d_{002} spacing: 0.38 nm



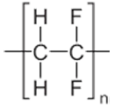
PVB cannot be used as binder alone because the adhesion of the electrode laminate onto the metal current collector is not efficient.



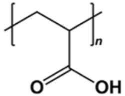
The electrode laminates are homogeneous and mechanically resistant.

New HC electrodes were prepared with a mix of PVB and standard polymers as binder:

- PVDF/PVB (80:20), using NMP as solvent
- PAA/PVB (80:20 or 50:50), using ethanol as solvent



Poly(vinylidene difluoride)

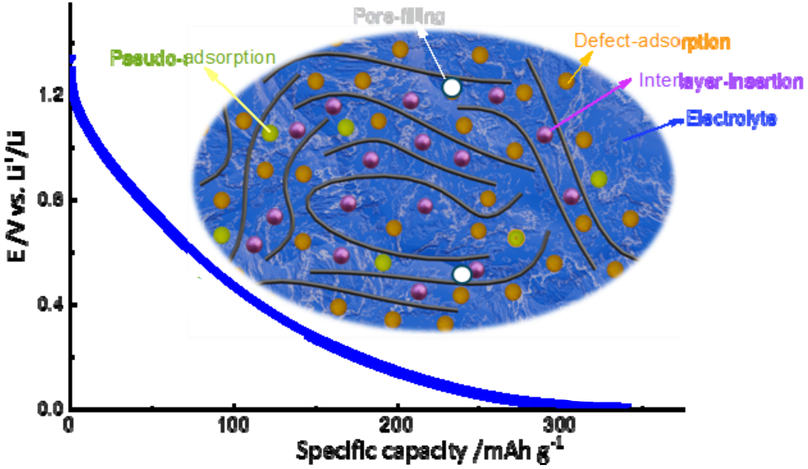


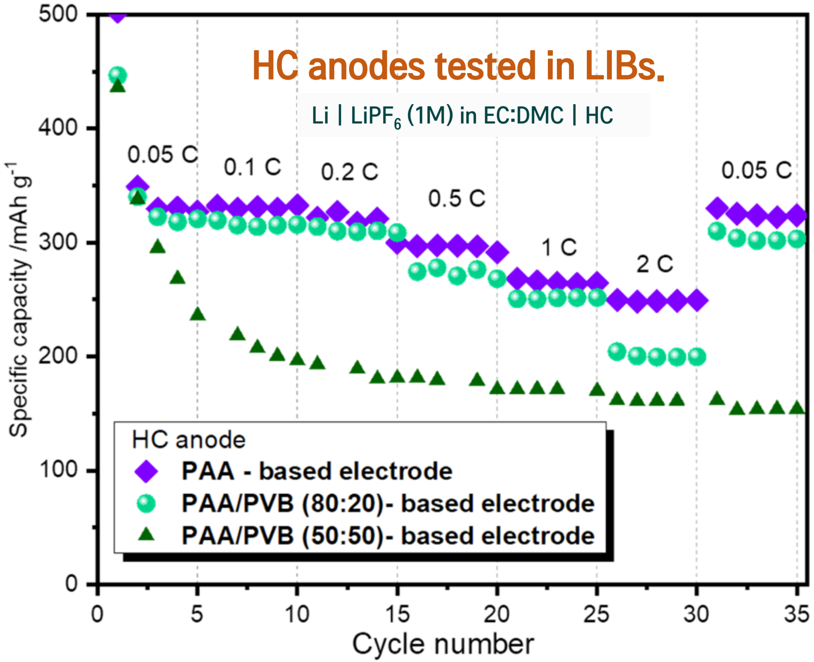
Polyacrylic acid

HC anodes performance in Li-based batteries

Many processes are involved upon Li storage in HC to give the total capacity.

J. Mater. Chem. A 2023, 11, 19669-19684



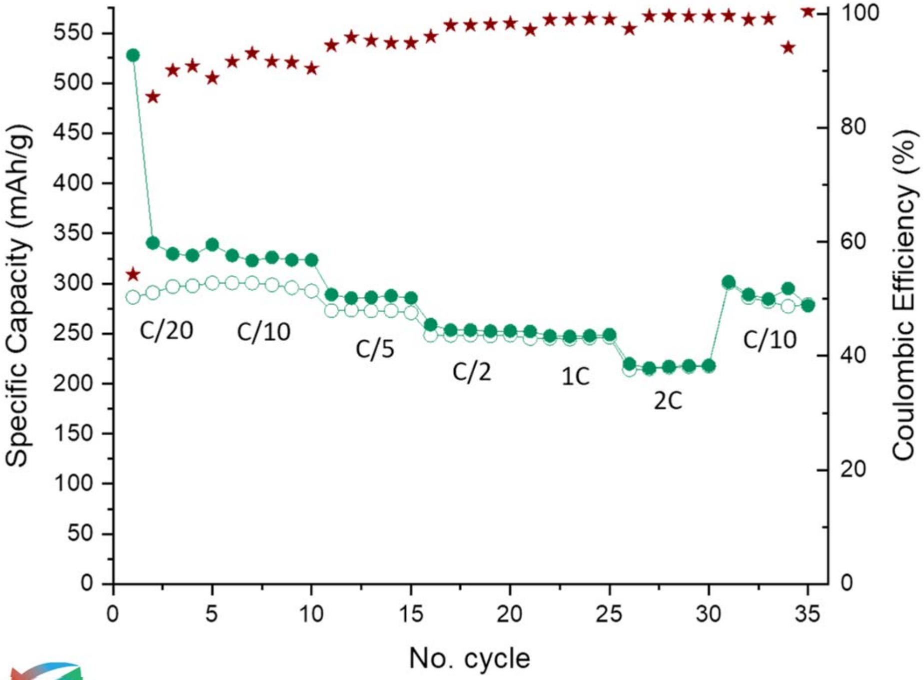


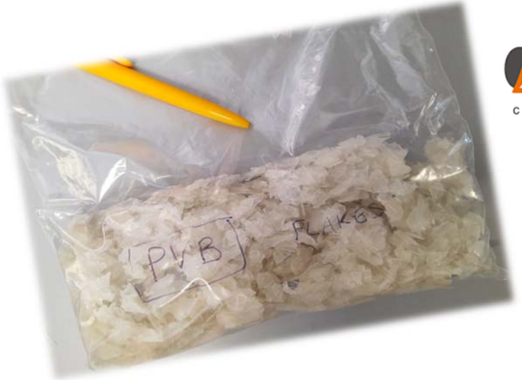
PAA and PAA/PVB (80:20) based electrodes show similar C-rate capability profiles.

Higher percentage of PVB (50%) causes a drop of capacity.

Preparation and use of HC anodes with re-PVB

HC anodes were prepared using the recycled PVB provided by Lurederra (Spain) within the framework of SUNRISE project.





Lurederra centro tecnológico

SUNRISE

HC anode prepared with PAA/rePVB (80:20) displayed good rate capability even at high current.

Low initial Coulombic Efficiency due to high polarization, likely because of secondary reactions by polymer "additives" (plasticizers, contaminants, degradation products, etc).

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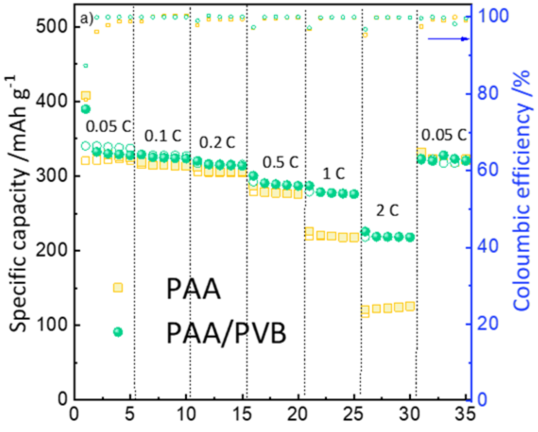
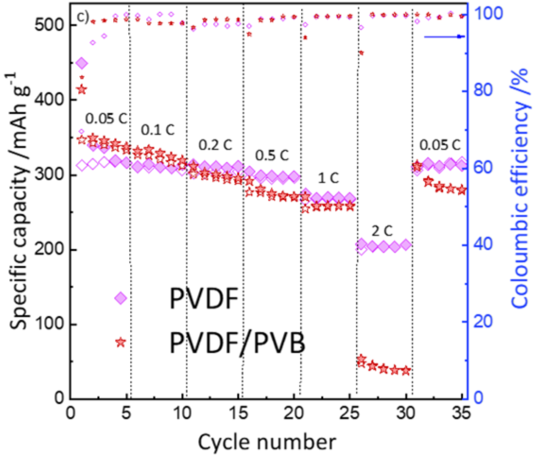
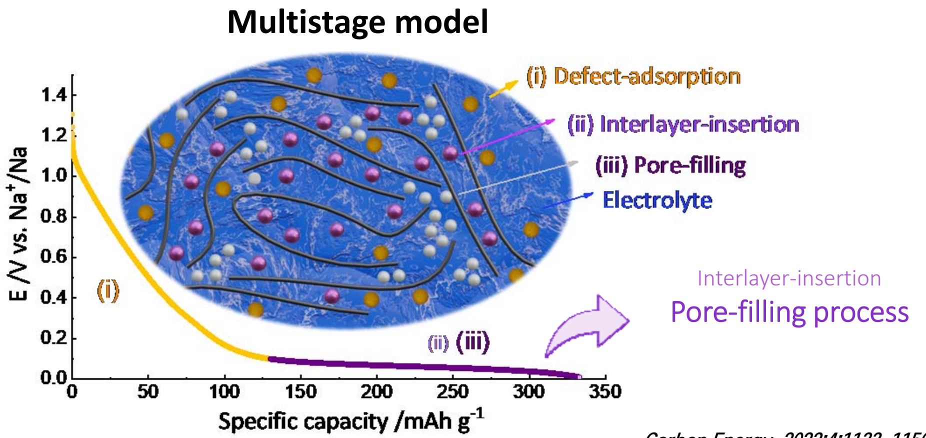
Use of PVB-based anodes in Na-based batteries



Na | NaFSI (1M) in EC:DMC | HC





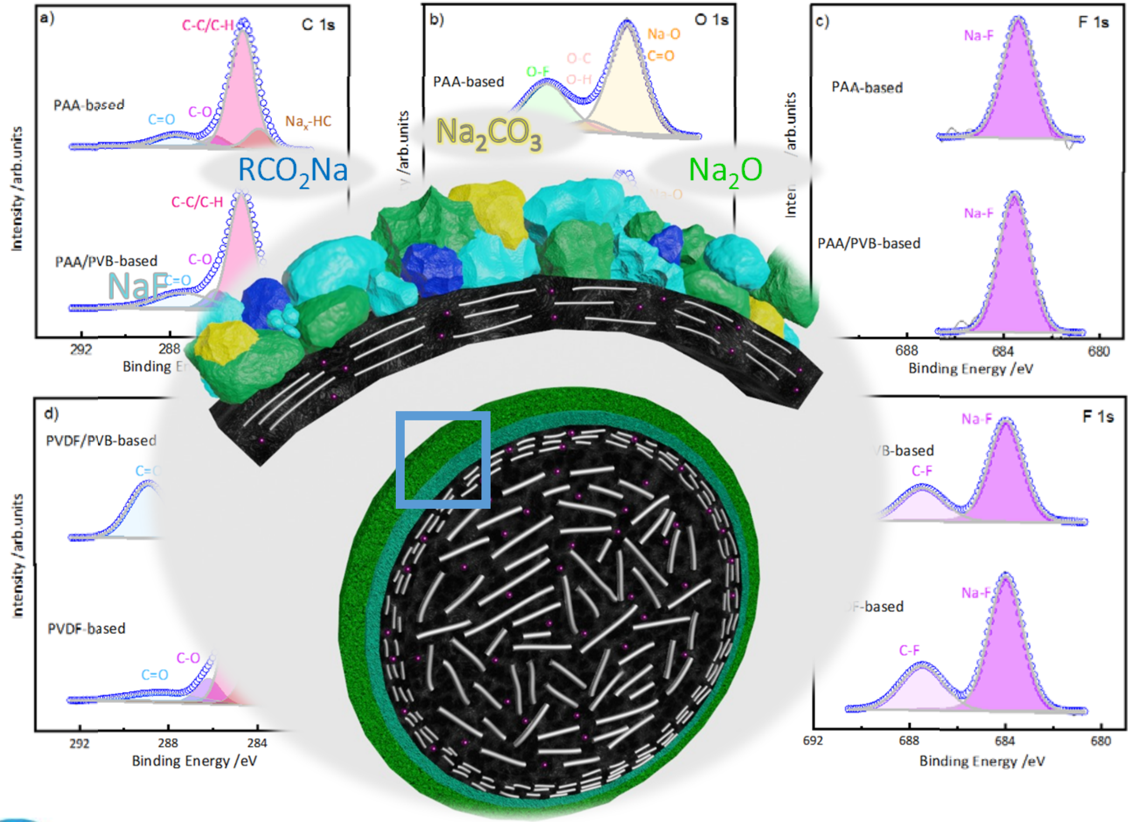
Carbon Energy. 2022;4:1133–1150

- PAA/PVB binder displays the best performances, especially at high currents.
  - strong network between COOH groups of PAA and OH groups of PVB
  - good compatibility between butyral group and carbons

- PVDF/PVB has lower performances with respect to PVDF alone, likely because the poor compatibility between the two polymers.

NIBs: Chemical characterization of the SEI

XPS analysis was performed on cycled electrodes to characterized the SEI composition.



Na | NaFSI (1M) EC:DMC | HC   *(after 10 cycles at 1C)*

PAA/PVB-based electrode:

- A slightly higher % at of NaF and Na_2O.
- Dense and thin inorganic SEI.

PVDF/PVB-based electrode:

- thicker SEI layer.
- Na_2CO_3 is more prevalent at the surface.

Adv. Funct. Mater. 2021, 31, 2100278

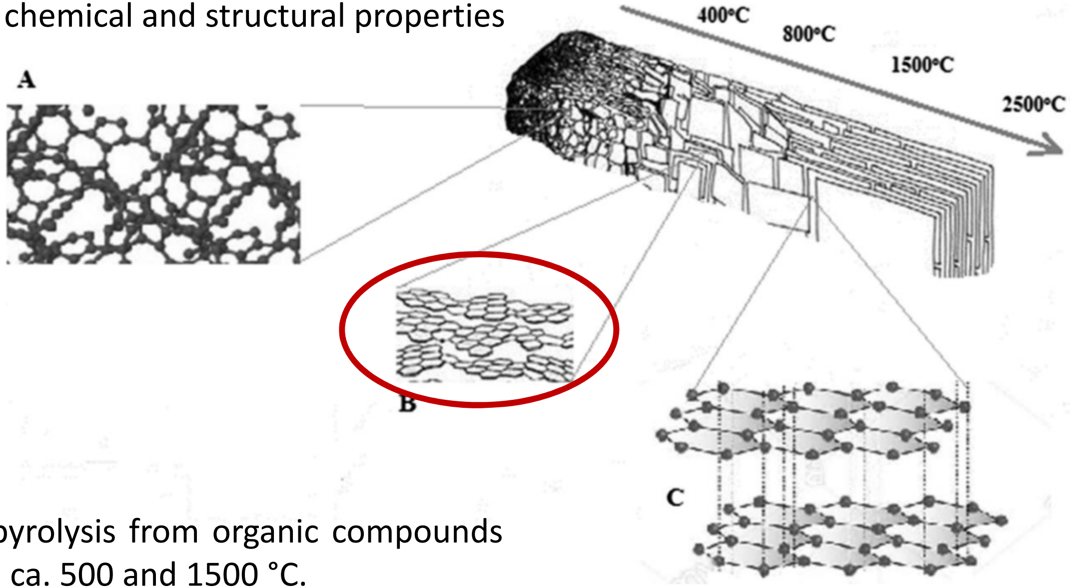
Journal of The Electrochemical Society, 2020, 167, 070526

Energy Environ. Sci., 2024, https://doi.org/10.1039/D3EE03141A

Hard Carbon: from commercial materials to waste recovery

Hard Carbons are among the most promising anodic material for Na-ion batteries:

- ✓ High specific capacity
- ✓ Low operating potential (E vs. Na^+/Na)
- ✓ Low cost
- ✓ Wide availability from different sources
- ✓ Possibility of tuning the chemical and structural properties



Hard carbons are obtained by pyrolysis from organic compounds in a temperature range between ca. 500 and 1500 °C.

A. Tomczyk et al., *Rev. Environ. Sci. Biotechnol.* **2020**, 19, 191-215
"Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects"

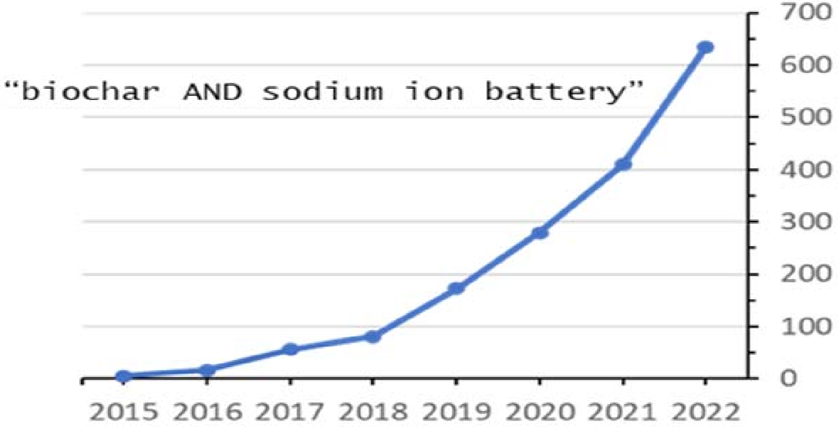
Anode materials from agricultural wastes

Biomass-derived biochar is one of the most relevant classes of hard carbons.

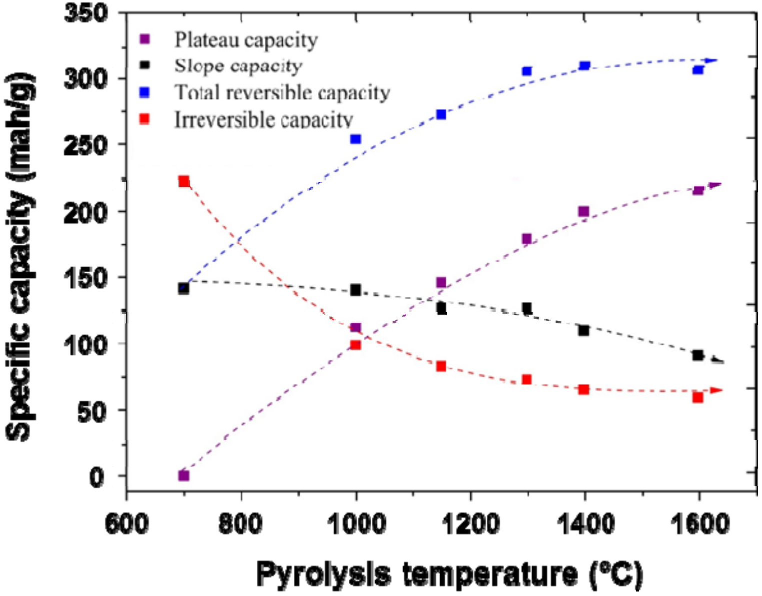
Many different agricultural wastes have been explored as feedstock for the sustainable production of anode materials for Na-based batteries.

Difficulty in comparing together all the obtained results because of the **different procedures of preparation and conditions of electrochemical testing.**

Feedstock	Pyrolysis Temp (°C)	Capacity (mA g^{-1})	Current density (mA g^{-1})
Lignin	1300	183	300
Olive stones	1400	291	20
Saccharides	1300	353	25
Sucrose	1600	270	6000
Cellulose	1600	310	37



M. Bartoli et al., *Renew. Sust. Energ. Rev.* 2024, 194, 114304



V. Simone et al., "Hard carbon derived from cellulose as anode for sodium ion batteries: dependence of electrochemical properties on structure", *Journal of Energy Chemistry* **2016**, 25, 761-8.

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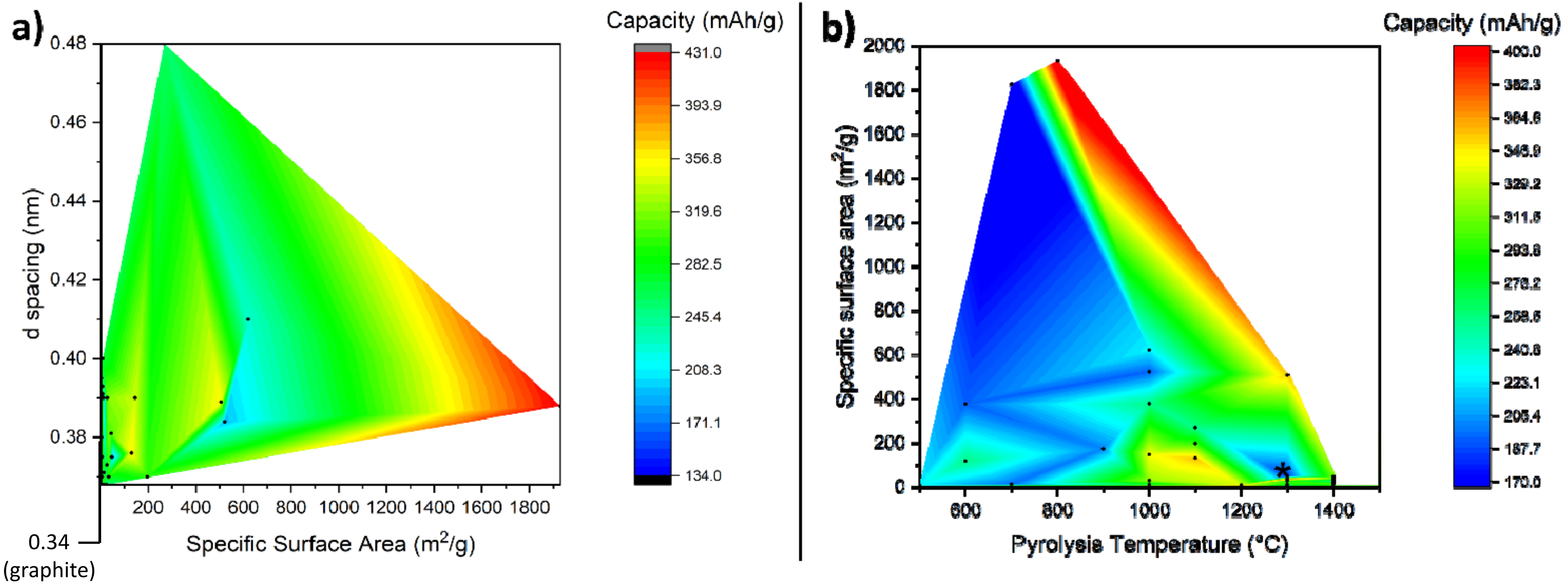
ALL INFORMATION SHALL BE CONSIDERED S

Anode materials from agricultural wastes

Attempt to rationalize the results reported in the literature:

M. Bartoli et al., *Renew. Sust. Energ. Rev.* **2024**, 194, 114304



Optimal d-spacing range between 0.38 and 0.43 nm

High surface area can be beneficial, but it risks to promote secondary reactions (low Coumbic efficiency)

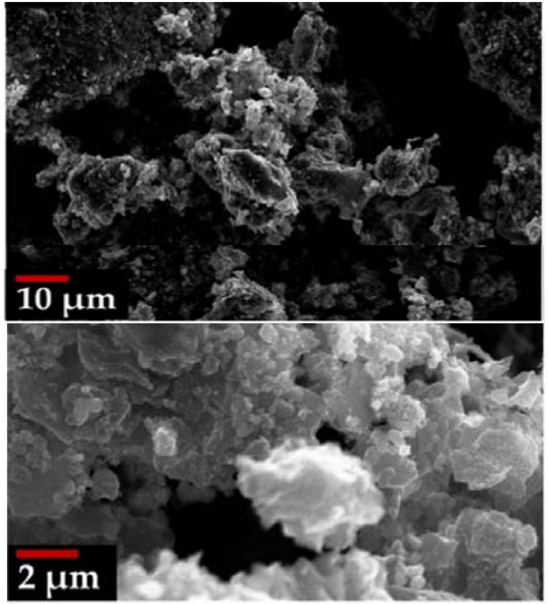
Positive effect by increasing the pyrolysis temperature

Anode materials from facemask wastes

Nowadays, the disposal of used facemasks is strictly demanding, considering the **huge amount of facemasks** that were employed **to limit the diffusion of coronavirus pandemic**.

Thus, we have explored the conversion of facemasks into hard carbons by **pyrolysis in mild conditions**.

Pyrolysis at 800 °C

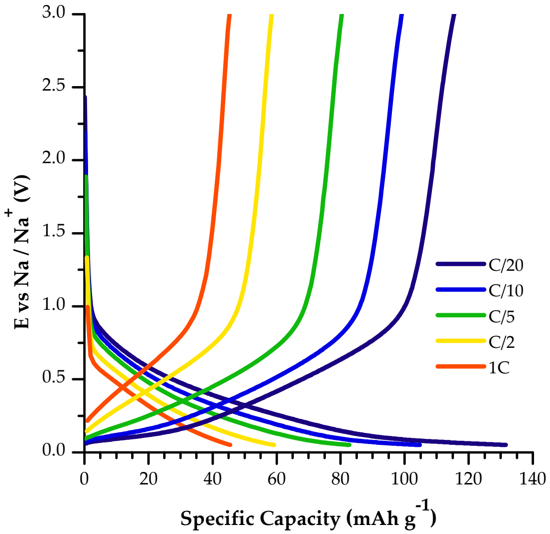


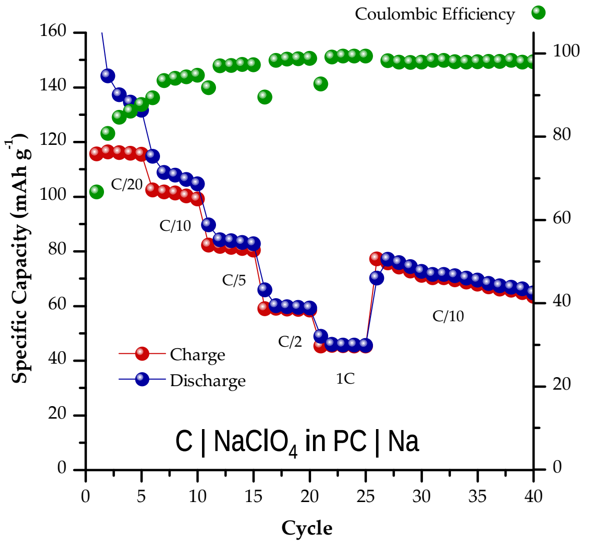
Highly amorphous carbon

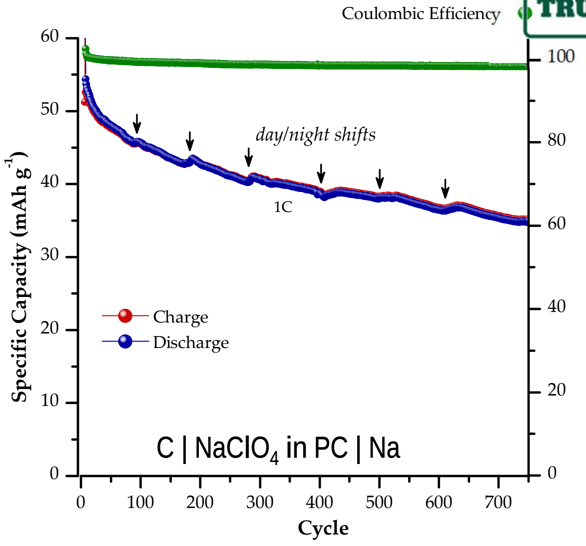
S. Porporato et al., "Repurposing Face Masks after Use: From Wastes to Anode Materials for Na-Ion Batteries", *Batteries* 2022, 8, 10, 183

Electrochemical performances of HC from facemasks

The **galvanostatic cycling** of C-facemasks displays the typical **capacitive** behavior of Hard Carbon materials, with two slopes for the two steps of **adsorption and insertion of Na^+ ions**.







Specific capacity is 175 mAh/g at the 1st cycle at C/20, settling down at 135 mAh/g at the 5th cycle.

A gradual capacity drop occurs upon increasing the current rate, up to 46 mAh/g at 1C.

Another cell was tested under prolonged cycling at 1C (after 5 activation cycles at C/10), maintaining a good stability (with a drop of ca. 30% after 750 cycles) and a Coulombic efficiency stable at 98%.

S. Porporato et al., *Batteries* 2022, 8, 10, 183

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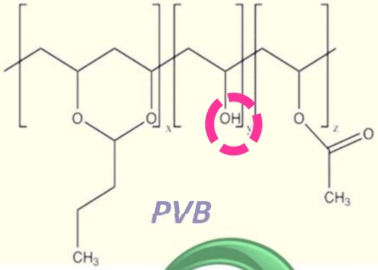
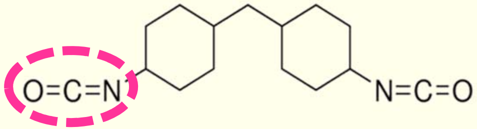
Preparation of PVB-based membranes



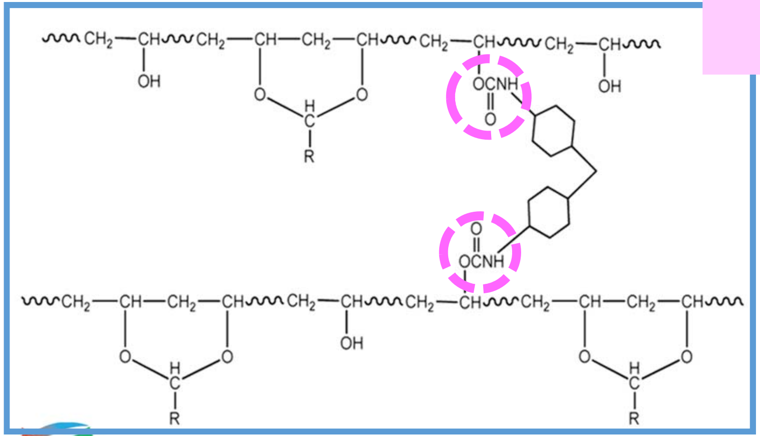
PVB

+



4,4'-methylenebis(cyclohexyl isocyanate) $H_{12}MDI$

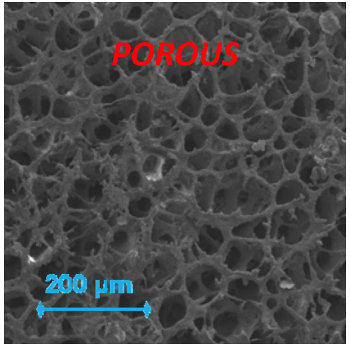
Solvent: NMP
Temperature: 70 °C
Time: 30 min



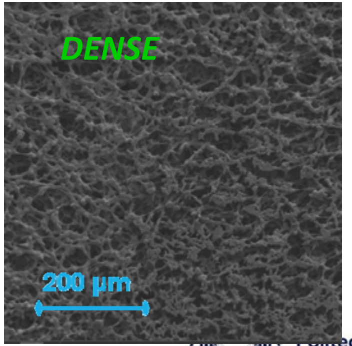
Urethane bond formation proved by IR spectroscopy!

coagulation bath

H_2O



NMP + H_2O (1:15 w/w)



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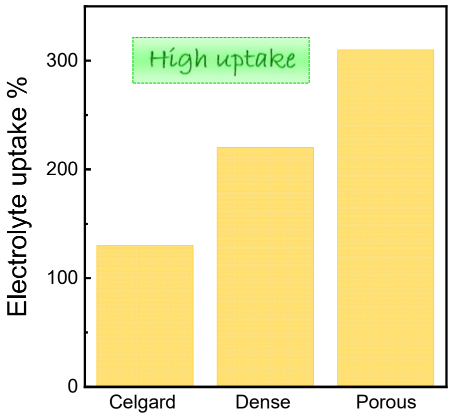
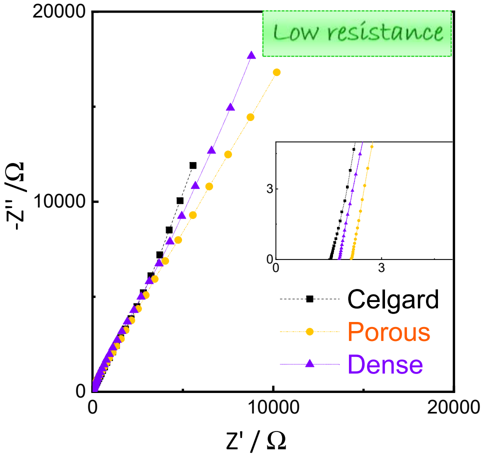
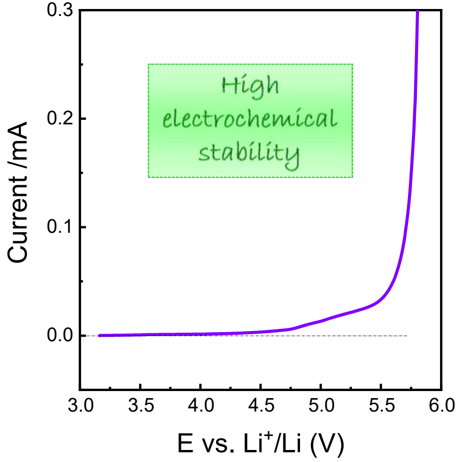
Characterization of PVB-based membranes

The electrochemical properties of PVB-membranes were evaluated in comparison with **standard separator Celgard® (PP)**.

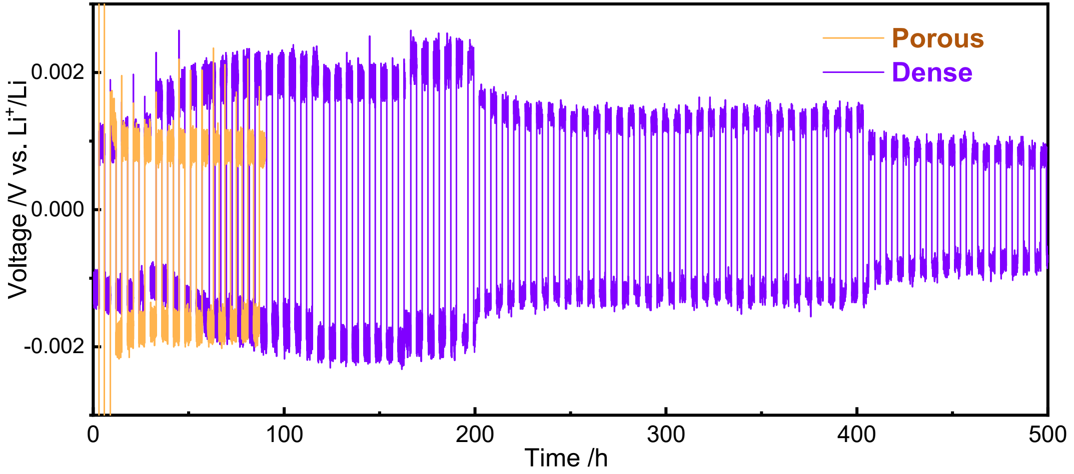






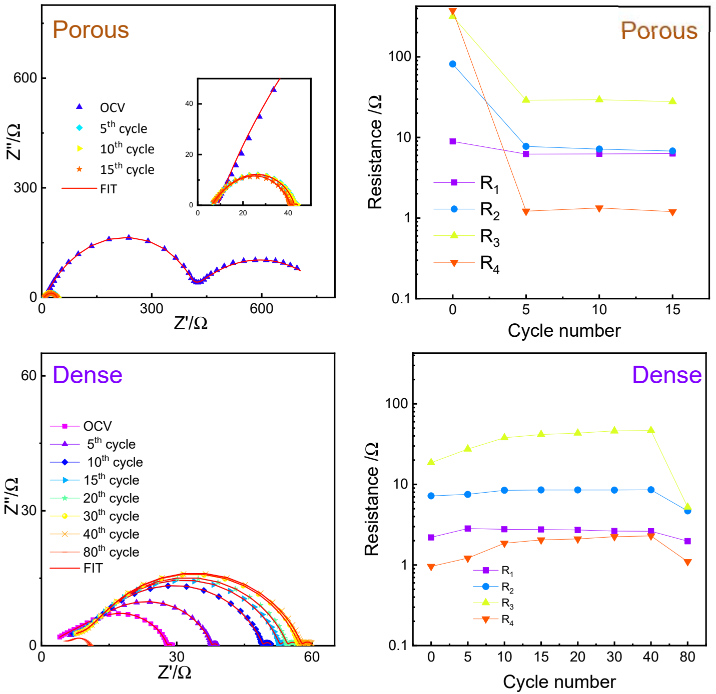
- The **soaking properties** were evaluated by measuring the weight of each membrane before (dry weight) and after 6 hours of immersion in electrolyte (wet weight), displaying **high electrolyte uptake**.
- **EIS** was employed to evaluate the bulk resistance of the membrane: PVB-based membranes displayed **low resistance**, comparable with Celgard. The calculated ionic conductivities are 0.29 and 0.32 mS/cm for the porous and dense separators, respectively (Celgard conductivity is 0.36 mS/cm).

Li plating and stripping through PVB membranes



Symmetric lithium-metal cells with $LiPF_6$ in EC-DC as electrolyte.

Current value of 0.05 mA cm^{-2} for 3 h per step.



EIS each 5 cycles.

- Porous membrane: high initial overpotential (visible also in EIS)

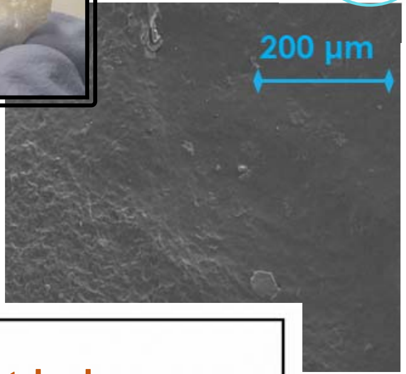
  short circuit after ca. 100 hours because of dendrites

- Dense membrane: low overpotential

  stable behaviour upon long cycling

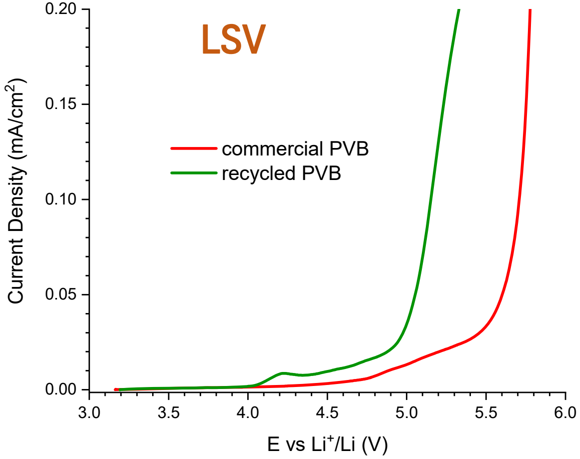
  resistance value decreased upon cycling

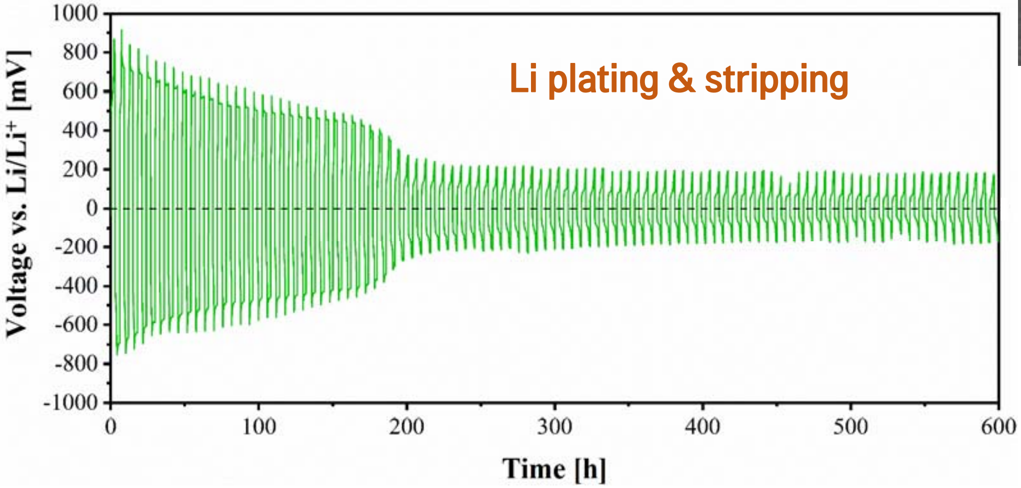
Membrane from recycled PVB



Synthetic protocol adjusted because of the presence of plasticizers: rePVB:H_{12}MDI ratio reduced to 20:1

No differences in morphology depending on the coagulation bath: dense and packed morphology, with elastic behavior.





The **presence of plasticizers** reduces the window of electrochemical stability **starting the degradation at lower voltage**.

High overpotential but **stable upon cycling**, revealing good compatibility with metal Li.

Conclusions

PVB as sustainable Polymeric Binders

- ❖ The substitution of a fraction of standard polymer binders with PVB can improve the mechanical adhesion of the system and promote the formation of a stable and efficient SEI.
- ❖ Recycled PVB can be used following the same procedure adopted for commercial PVB, the presence of plasticizers and contaminants causes a low coulombic efficiency only at the first cycles, then the system stabilizes.

PVB as sustainable Polymeric Separators

- ❖ Light and thin PVB-based membranes were prepared by cross-linking reaction with a diisocyanate compound.
- ❖ The membranes were successfully tested as electrolyte separators in Li-ion batteries (electrolyte uptake as high as 221%, electrochemical stability up to 4.7 V).
- ❖ Dense elastomeric membrane can be formed from recycled PVB, compatible with metal Li and stable upon cycling.

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Thanks very much for your time and attention!

And now ..Questions/comments???

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Published papers

- https://sunrise-project.eu/
- **Nikitakos et al., Polymers 2024, 16(1), 10** – PVB characterization
- **Bartoli et al., Renew. Sust. Energ. Rev. 2024, 194, 114304** – biochar as anode
- **Porporato et al., Batteries 2022, 8, 10, 183** – hard carbons from facemasks as anodes
- **Bonomo et al., Frontiers in Chemistry 2023, 11, 1352000** – polymers for energy storage
- **Jagdale et al., Electrochimica Acta, 2021, 368, 137644** – carbon fibers from waste as anodes
- **Falco et al., Materials Today Sustainability, 2023, 21, 100299** – electrolytes with ionic liquids