Programme & Book of abstracts for BATTERY 2030+ Annual Conference 2024





Annual Conference 2024 PROGRAMME May 28 – Day 1

08:00 - 09:00	Registration and Coffee + putting up posters	
Moderator:	Philippe Jacques, EMIRI	
09:00 - 09:10	Welcome by CEA and CNRS	Pascal Bayle-Guillemaud, CEA/DRF/Irig and Jean-Marc Bassat, CNRS Inst of Chem
09:10 - 09:20	Welcome by the European Commission	Johan Blondelle, DG RTD
09:20 - 09:30	The battery partnership – some reflections	Fabrice Stassin, BEPA
09:30 – 09:45	BATTERY 2030+ the previous phase and what now?	Kristina Edström, BATTERY 2030+, Uppsala University
09:45 – 10:30	Lithium-rich layered and disordered rock salt cathodes: the role of oxygen redox	Peter Bruce, University of Oxford
10:30 - 10:45	The global battery landscape	Monika Curto Fuentes, VDI/VDE
10:45 - 11:15	Coffee break	
Moderator:	Simon Perraud, CEA	
11:15 – 11:30	PEPR, a large French battery initiative	Helene Burlet, CEA
11:30 - 12:00	BIG-MAP	Tejs Vegge, DTU
12:00 - 12:15	Best practises – the next steps	Simon Clark, SINTEF
12:15 - 13:00	Oral presentations picked based on abstracts	Marta Mirolo, ESRF and Maria Arnaiz, CICe
13:00 - 14:30	Lunch break and poster session	





This project has received funding from the European Union's Horizon Europe research and innovation programme under grant number No. 101104022.



Annual Conference 2024 PROGRAMME May 28 – Day 1

Moderator:	Kristina Edström, Uppsala University		
14:30 - 16:00	Project presentations		
14:30 - 15:15	Healingbat, Phoenix, and Salamander		
	HealingBat's roadmap to self-healing	Stefan Palzer, University of Dortmund	
	Phoenix – Project overview	Joris de Hoog, VUB	
	Salamander – A smart, self-healing battery built for a sustainable economy	Samson Y. Lai, IFE, Inst. for Energy Techn.	
15:15 – 16:30	Opera, Opincharge, and Ultrabat		
	Opera – Development of operando techniques and multi-scale modelling to face the zero- excess solid-state battery challenge.	Qiong Cai, University of Surrey	
	Opincharge – Operando analysis and modelling of interface dynamics and charge transport in lithium-ion batteries	Philippe Moreau, CNRS	
	Ultrabat – Capturing ultrafast electron and ion dynamics in batteries	Hilton B. de Aguiar, CNRS	
16:00 - 16:30	Coffee break		
Moderator:	Montse Casas, CICe		
16:30 - 16:45	Batman – a French initiative for next generation batteries' digital twins' development	Marion Chandesris, CEA-Liten	
16:45 – 17:00	Openstorm – the French Battery Characterization Platform	Sandrine Lyonnard, CEA	
17:15 – 18:00	Introduction to poster pitches and evening beer session Actual Poster pitches	Marta Mirolo, ESRF and Maria Arnaiz, CICe	
18:00 - 18:15	Group photo		
18:15 - 21:00	Poster session and refreshments		







Annual Conference 2024 PROGRAMME May 29 – Day 2

07:30 - 08:00	Morning Coffee		
Moderator:	Kristina Edström, Uppsala University		
08:30 - 10:30	Project presentations		
08:30 - 09:15	ReUse	Marco Schott	
	Renovate – A circular and chemistry-neutral approach for recycling and recovery of battery waste feeds: the renovate project	Eliana Quartarone, University of Pavia and INSTM (Italy)	
	Revitalize – Recycling of low value components using high purity pre-treatment, direct recycling and green hydrometallurgical approaches for recycling of Lithium ion and Sodium ion batteries	Sulalit Bandyopadhyay, NTNU (Norway)	
09:15 – 10:30	BatCat – Integrating physics-based modelling with logics and data driven methods into actionable modelling and decision support for battery	Martin Thomas Horsch, Norwegian University of Life Sciences	
	BATTwin – Flexible and scalable digital-twin platform for enhanced production efficiency and yield in battery cell production line	Marcello Colledani, Politecnico di Milano	
	Cicero – MSA-based flowsheet to produce Made-in-Europe NMC cathodes	Brecht Dewulf, KU Leuven, Solvomet	
	Streams – Sustainable technologies for strengthening the European raw materials supply chain	Marcus Jahn, AIT	
10:30 - 11:00	Coffee break		





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Annual Conference 2024 PROGRAMME May 29 – Day 2

Moderator:	Mathieu Morcrette, CNRS	
11:00 - 11:10	Introduction of the battery valley in North of France	Mathieu Morcrette, CNRS
11:10 - 11:20	Tiamat	Asmae el Mejdoubi
11:20 - 11:30	Verkor	Gilles Moreau
11:30 - 11:40	Syensqo	Ludovic Odono
11:40 - 11:50	Revisiting the physical manufacturing space for battery cells	Frédéric Aguesse, CIDETEC
11:50 - 12:05	Skills and the BEPA/Batteries Europe position paper	Silvia Bodoardo, POLITO
Moderator:	Philippe Jacques, EMIRI	
12:10 - 12:30	Requirements in the Batteries Regulation with a focus on performance and safety	Andreas Pfrang, JRC
Moderator:	Thore Sekkeness, EBA 250	
12:30 - 13:00	Panel discussion on how to accelerate innovation from research to products	Reza Younesi, NoVo; Gilles Moreau, Verkor; Ludovic Odoni, Syensqo; Hervé Beuffe, Tiamat; Fanny Bardé, Solithor
13:00 - 14:30	Lunch break and poster session	
Moderator:	Marta Mirolo, ESRF and Maria Arnaiz, CICe	
14:30 - 14:45	Input from young scientists; What is the future – challenges and possibilities	Marta Mirolo, ESRF and Maria Arnaiz, CICe
14:45 – 15:30	Young Scientists - Oral presentations	
Moderator:	Philippe Jacques, EMIRI	
15:30 - 16:00	Reflecting comments and poster award	Bozorg Khanbaei (BEPA) & Halgard Staesche (Wiley) & Kristina Edström
16:00 - 16:30	Meeting point & transfer to the labs	Samson Y. Lai, IFE, Inst for Energy Techn.
16:30 - 17:30	Lab tours	





Invited speaker Abstracts



Integrating physics-based modelling with logics and data driven methods into actionable modelling and decision support for battery manufacturing

Martin Thomas Horsch^{1, 2}, L. Eduardo Córdova López¹, Aditya Dey¹, Dmytro Romanov¹, Elin Dypvik Sødahl¹, Gianluca Boccardo³, Silvia Chiacchiera², Mathijs A. Janssen¹, Peter Klein⁴, Kyandoghere Kyamakya⁵, Michael A. Seaton², Simon Stephan⁶, Ilian T. Todorov², Eirik Valseth^{1, 7}, Stephan Werth⁸, Martin Gebser⁵, Fadi Al Machot¹
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BatCAT (Battery Cell Assembly Twin) is one of the two projects, alongside BATTwin, that will realize the BATTERY 2030+ manufacturability programme from 2024 to 2027 by developing a digital twin platform and data space for battery manufacturing; BatCAT primarily considers vanadium-based redox-flow batteries as well as Li-ion and Na-ion coin cells. The present contribution summarizes the work plan, requirements analysis, and initial steps of work done within the project. Its main purpose, however, is to present pre-existing lines of work and ideas from a spectrum of fields that will be combined within BatCAT, specially in physics-based molecular and multiscale modelling, data-driven modelling, knowledge representation, and decision support systems.

The portfolio of physics-based simulation methods in BatCAT includes MD and MC simulation based on classical mechanical pair potentials, *e.g.*, using the DL_POLY and ms2 codes [1]. Mesoscopic DPD simulations will be carried out using DL_MESO, employing an *n*DPD potential as a basis for the conservative-force term [2]. The molecular and mesoscopic simulation results will feed into continuum simulations, including Poisson-Nernst-Planck equation solvers and equivalent-circuit models [3] as well as population balance models [4]. Surrogate models (*e.g.*, as in previous work, representing results from CFD simulation [5]) will include cellular neural networks [6] with the potential for exploitation by on-chip deployment [7] *e.g.* in battery management systems. For use in production, it is necessary to make the data and models XAIR, *i.e.*, explainable-AI-ready [8].

BatCAT will combine two approaches to decision support: First, logical reasoning by answer set programming (ASP) [9]; it was recently shown that ASP can increase the efficiency of neural-network surrogate modelling while also ensuring its interpretability [10]. Second, multicriteria optimization [11-13], integrating surrogate models into model parameterization [13], interoperating with the MolMod Database [14]. This line of work can build on business decision support systems from two previous Horizon projects: FORCE [15] and COMPOSELECTOR [11]. Model accuracy and reliability will be documented through epistemic metadata [16].

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Lithium-rich layered and disordered Rocksalt cathodes: the role of oxygen redox

Peter G Bruce, Robert A House, John-Joseph Marie, Miguel A Perez-Osorio, Gregory J Rees, Jun Chen

University of Oxford

Li-ion battery cathodes that can store more energy than those in use today are an important target for materials research. The challenge has proved formidable and demands a deeper understanding of the science underpinning intercalation cathodes.

For over 20 years it has been known that more Li⁺ (charge) can be removed from layered compounds such as Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ or Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ than is charge compensated by transition metal oxidation. Many excellent contributions have been made to the endeavour of understanding oxygen redox, what happens when electrons are removed from the O²⁻ ions (holes in the O valance band), the nature of the hole states and their link to the resulting structural changes.

We have shown that oxidation of O^{2-} forms O_2 that is either evolved from the surface or trapped in voids formed in the bulk by reorganisation of the Li vacancies on the transition metal sites within the structure. Although O_2 in these nano-voids can be reduced back to O^{2-} , the process is not energetically reversible, resulting in the 1st cycle voltage hysteresis (approx. 1eV). This mechanism also has implications which play out over extended cycling. The voids grow in size and O_2 cannot be fully reduced rationalising the well known problem of voltage fade in Li rich materials. It is possible to suppress O_2 formation, trapping hole states on O^{2-} and obtaining energetic (voltage) and structural reversibility. The electron holes are not localised on oxygen but itinerant. Such behaviour may point the way towards high energy density cathodes for Li-ion batteries.



Innovative MSA-based flowsheet to produce Made-in-Europe NMC cathodes

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The increasing electrification of the transportation sector and the need for fast energy storage in the electric grid has amplified the criticality of battery metals such as nickel, cobalt and manganese. Europe has to evolve in line with this trend, and hence, a domestic European materials value chain has to be created. To reduce Europe's dependency on third countries, both resource production and metal refining should be addressed. Primary European resources such as sulphidic ores from Nordic mines (e.g., Kevitsa, Luikonlahti) and limonitic and saprolitic laterites from the Balkan region should be considered, as well as post-mining materials from tailings and intermediate materials such as ferronickel (FeNi) and mixed hydroxide or sulphide precipitate (MHP/MSP). The processing of these resources needs to be competitive and have a low-carbon footprint. Hence, CICERO focusses on circular hydrometallurgical refining of nickel, cobalt and manganese, and uses methanesulphonic acid (MSA) as an alternative to sulfuric acid, the main acid currently being used in the highcarbon foot print HPAL process. MSA is a strong organic acid (pKa = -1.9) which is very stable against chemical oxidation or reduction, and does not hydrolyse in water.¹ It is a commercial, green, REACH-compliant and affordable organic acid. MSA salts are highly soluble in water and often exhibit higher solubilities than the corresponding sulfate salts. Moreover, MSA and MSA salts are compatible with electrowinning processes since the anode reaction involves the formation of oxygen gas (unlike chlorine gas formation in chloride electrolytes) and no cathodic reduction of the anion occurs (unlike nitrate reduction in nitrate electrolytes). The process developed in CICERO includes (1) MSA leaching and solution purification through solvent extraction, ion exchange, electrocoagulation and impregnated membrane separation; (2) obtain battery-grade MSA salts and perform NMC synthesis and (3) reagent regeneration and iron recovery in line with the Twelve Principles of Circular Hydrometallurgy.²

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- (2) Binnemans, K.; Jones, P. T. The Twelve Principles of Circular Hydrometallurgy. *J. Sustain. Metall.* **2022**, *9* (1), 1–25. https://doi.org/10.1007/s40831-022-00636-3.

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Innovative MSA-based flowsheet to produce Made-in-Europe NMC cathodes

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OPERA DEVELOPMENT OF OPERANDO TECHNIQUES AND MULTISCALE MODELLING TO FACE THE ZESSB CHALLENGE

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Anode-less or Zero-Excess Solid-State Batteries (ZESSB), where the anode is formed in situ, have emerged as a promising new generation of environmentally friendly batteries with high energy density, improved safety and higher cost-efficiency, but only after solutions for unstable anode formation are found. To develop these solutions, a deep understanding of the complex electro-chemo-mechanical processes within the battery is required, which is only accessible through advanced experimental and computational methods.

In OPERA we are developing **novel operando experimental techniques at the ALBA, ESRF and DESY synchrotrons and at the lab-scale and novel multiscale modelling approaches** to make progress the ZESSB technology. We aim to collect multiparameter data that will provide for the first-time unique time- and multiscale spatial-resolved information on the in-situ formation and subsequent stripping and plating of Li and Na anodes in terms of nucleation kinetics, microstructure, phase distribution, chemical composition, local impedance, stress fields and defect formation across electrodes and interfaces of model ZESSBs. The **conceptual understanding of the anode formation** will be used to develop innovative approaches to enable ZESSB energy storage technology. During the first year we have made progress mainly on the following project lines:

(i) Material screening for interlayers: We are developing interlayer materials at the anode side to enable stable plating/stripping during ZESSB operation. For this we have adopted a combination of Density Functional Theory (DFT) calculations and Molecular Dynamics (MD) coupled with trained Machine Learning (ML) potentials to screen nine different metals to be adopted as interlayer materials: Mg, Zn, Au, Ag, Pt, Al, Sn, Cu and Ni. We have performed an analysis of the adsorption, diffusion and dissolution energies of Li on the different metals to establish the best balance that promotes plating via 2D wetting. Guided by the simulation, we are testing the experimental behavior of the different metals to be used as interlayers by advanced electrochemical methods (dilatometry and ultra-fast transient methods), operando optical microscopy and Ion Beam Analysis (IBA).

(ii) Development of novel devices for operando studies: We are developing novel devices to perform operando plating and stripping experiments of the model cells under bending and stacking forces. First a novel set-up to perform time- and space-resolved high-energy X-Ray Diffraction (XRD) analysis has been performed and successfully applied for the microscale study of chemo-mechanically induced stresses within NCA/LSPS batteries during cycling in the P07 beamline of DESY. Then a prototype of a stacking pressure device has been developed and successfully tested in the ID13 beamline of the ESRF to investigate at the nanoscale the development of stress-fields at the battery interfaces by operando nano-XRD. Last, a bending strain device based on a piezoelectric PZT bimorph has been designed to control the position of the neutral plane and the curvature radius independently in orthogonal directions during electrochemical experiments.

(iii) Nucleation and growth kinetics during anode formation: We are studying the initial stages of plating by nanospectroscopy at the CIRCE beamline of ALBA. The growth kinetics of Na and Li anodes in ZESSB model cells have been investigated by a combination of Photoemission Electron Microscopy (PEEM) and Low-Energy Electron Microscopy (LEEM). The anode is grown in a virtual electrode approach which allows fine parameter control and high lateral resolution (20 nm). The initial stages of the anode formation are then analyzed in Ultraviolet (UV) and X-ray PEEM, using spatially resolved Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS). The method results in an ideal tool to investigate the crucial first steps of anode formation. (iv) Electrode-SSE mechanical coupling at the cell scale: To account for the presence of a Solid-State Electrolyte (SSE) in the cell that prevents the free expansion of the electrodes during cycling we have extended the standard mechanical sub-model of the overall pseudo-2D (i.e. Doyle-Fuller-Newman) electrochemical model by creating a more detailed 2D finite-element mechanical model. The new model is implemented in the same software environment as the electrochemical model, allowing for a full coupling between both. Our next step is to adapt our mechanical model for a Li anode configuration and integrate it in the whole cell model.

(v) Validation and transfer of strategies from model cell to practical ZESSBs: To validate the knowledge-based modification strategies gained during the project, a transfer from model half-cell to practically relevant ZESSB is necessary. Therefore, we are developing a reference full cell consisting of an LFP/PEO cathode, LLZO separator and anodic Cu current collector. An extensive electrochemical characterization of the cathode in half-cell configuration is being developed to ensure stable cycling behavior and consequently be able to deconvolute the influences of the anode modifications on the full cell performance.



A CIRCULAR AND CHEMISTRY-NEUTRAL APPROACH FOR RECYCLING AND RECOVERY OF BATTERY WASTE FEEDS: THE RENOVATE PROJECT

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RENOVATE aims at developing and demonstrating new circular economy solutions for the European battery value-chain, targeting the re-use of 95+% of in-specification cell fractions (e.g. metallic foil, graphite, electrolyte, fluorinated compounds and cathode active materials) within the battery production chain, fostering a closed-loop circular approach that would reduce battery material waste going to landfill, increase the availability of battery precursors in the European battery eco-system, and demonstrate new added-value business cases for recyclers and battery materials users. All recycled materials will be recovered over all potential streams (pre-customer scraps and EoL products). The RENOVATE closed-loop concept is holistic and flexible and will be validated at TRL4 for the recycling of EoL batteries based on both low (LFP) and high (e.g., NMC) energy density chemistries. It is designed to allow real and easily implementable "net zero carbon" process, with a specific focus on low impact and low energy aspects and the reduction of chemicals and resources. A specific aim will also be smart re-integration of the side streams (e.g.: scraps, waste chemicals/solvents) in the recycling processes, to minimize the residues coming from them.



ReUse – Efficient direct recycling for low-value LFP battery for circular and sustainable waste

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The development of sustainable, safe and efficient processes for battery recycling is crucial to improve the circularity and strategic autonomy of the European Li-ion battery (LiB) value chain, in line with the objectives of the Battery Partnership launched under Horizon Europe.

The objective of the ReUse project is to improve the circularity and sustainability of the entire low-value LFP battery waste stream - from production scrap to end-of-life LiB - by developing new recycling processes that maximize the recovery of input elements and components (Figure 1). Specific objectives include the development of automated sorting and disassemby strategies, the improvement of recycling efficiency and direct reuse of battery materials, and the assurance of sustainability through life cycle assessment, life cycle costing, and social impact studies. With a focus on maximizing material recovery, energy efficiency and purity, ReUse will develop a robust, flexible and sustainable direct recycling process for waste streams of varying composition and quality.

The project aims to increase the global competitiveness of the European battery ecosystem in line with the European Strategic Plan for a clean and sustainable transition towards climate neutrality. Building on the BATTERY 2030+ Roadmap and the European Partnership on Batteries, ReUse aims to contribute to the policy needs of the European Green Deal and efficient recycling technologies. The project will address the urgent need to address the shortcomings related to the technological, economic, and environmental sustainability of recycling end-of-life LiBs, especially LFP batteries, which are projected to make up 46% of the global LiB market by 2030.







REVITALISE: REcycling of low Value components using high purity pre-treatment, dlrecT recycling And green hydrometallurgical approaches for recycling of Lithium Ion and Sodium Ion BatteriEs

Sulalit Bandyopadhyay¹ and REVITALISE Team

¹ Particle Engineering Centre, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway.

As the need for effective battery waste management grows, NMC (Nickel Manganese Cobalt), LFP (Lithium Iron Phosphate), and Na-ion (Sodium- ion) batteries contribute significantly to this challenge, accounting for 85% of the problem. Traditional recycling methods prove inadequate, lacking efficiency and eco-friendliness. That's where the REVITALISE project, funded by the EU, steps in with an innovative solution.

Utilizing cutting-edge techniques like electrohydraulic fragmentation and ultrasonication for material purity, REVITALISE aims to revolutionize battery recycling. Furthermore, it introduces water remediation, extracting lithium from wastewater streams. Collaborating with industry leaders Verkor, Hydro, and Hydrovolt, the project ensures closed-loop recycling, optimizing recovery rates while minimizing environmental impact. Our goal is a commercially viable process with minimal environmental impact, incorporating hydrometallurgy. REVITALISE sets a new standard for green, cost-effective battery recycling, guiding us toward a sustainable future.

Overall recycling rates of 91%+ will be proven at TRL4 for waste processed from post-production scrap and end-of-life battery black mass. Our approach will enable direct recycling of 40% of the cathode and anode active parts, with direct characterization of the lithiation (or sodiation) being developed that will be used as a basis of a smart-reformation approach for reclaimed active materials. The remaining 60% being suitable for hydrometallurgical recycling based on leaching with green organic acids from food waste, such as vitamin C (ascorbates), vinegar (acetate) and citric acid (citrates) and inorganic acids produced from industrial wastes. A further innovation is the development of water remediation with Li recovery from all wastewater streams generated, through the implementation of polymeric nanocomposite membrane separation with direct Li recycling for Li in water concentrations down to 0.6mg/L. The recycled parts will be assessed for (closed-loop) battery and other secondary applications for precursors and semi-products by industrial partners, through reformulation and upcycling of battery materials and validation of remanufactured batteries. An optimized process flow will be determined to achieve commercially viable recycling with maximized recovery rates and minimal environmental impact.



SOLiTHOR's All Solid-State Li-Metal Battery pouch cells

Fanny Bardé¹

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SOLITHOR is developing a unique all-solid-state battery with a lithium-metal anode^[1-2] to enable safer, lighter, longer range, and faster electric vehicles' charging. Our technology is made up of a thin Lithium anode and our proprietary Solid Composite Electrolyte.

Prepared from liquid precursors, our Solid Composite Electrolyte can be incorporated into conventional porous cathode electrodes, bringing significant advantage in terms of upscaling and manufacturing. Unlike some of our competitors in the field ^[3, 5], SOLiTHOR's cell enables an All- Solid-State Battery that does not contain liquid, - hence offering the extra advantage of preventing any leakage risk. And, since the electrolyte is not sulfur-based (again unlike some of our competitors^[2,4]), risks related to the potential release of dangerous H₂S gas is totally mitigated.

This presentation will highlight the scientific and engineering challenges encountered when developing a thin Solid Composite Electrolyte and integrating it with Li-Metal anodes and conventional cathodes into pouch cells demonstrators. A snapshot of performance progress will be given - both at component and cell-level.

SOLITHOR was founded in 2021 with a mission to develop and commercialise next generation Solid-State Batteries to enable the transition to sustainable electromobility applications, on air, land and sea.



Figure 1. SOLiTHOR's pouch cell demonstrator

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The Global Battery Landscape: Current Activities of Batteries Europe in the Field of International Battery R&D&I Monitoring

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VDI/VDE Innovation + Technik GmbH (short: VDI/VDE-IT) is a project management company as well as a service and consultancy provider for various federal and state ministries, the European Commission as well as the financial sector and industry, primarily for small and medium-sized enterprises. Battery production is one of the major areas in focus of our current activities.

Batteries Europe is the platform bringing together all relevant stakeholders in the European battery research and innovation ecosystem in order to develop and support a competitive battery value chain in Europe. VDI/VDE-IT is a part of the Batteries Europe consortium and leads the task "Global Overview of Battery R&D&I, Funding and International Benchmark on KPIs".

International observation is crucial to understand the global innovation support structures for batteries as well as the policy goals and instruments for creating a successful battery ecosystem. Only by benchmarking the competitiveness of its battery innovation system, Europe can react to international developments, learn from international success stories and ensure its own leadership in battery technology.

In 2024, Batteries Europe is organising two fact-finding missions - to East Asia and North America. The first of them took place in Q1 2024 to Japan and South Korea, and the Battery2030+ Annual Conference is a great place to present the results and takeovers to the international research community.

The primary objective of both missions is to improve the mutual exchange of information and promote a better understanding of how battery innovation works in different regions, enabling all partners to gain first-hand knowledge of battery R&D&I and facilitating international cooperation.

The success of any country's battery strategy hinges upon several critical factors: access to battery raw materials like lithium, nickel, graphite, and cobalt; geopolitical composition and relationships with suppliers and competitors; commitment to sustainability; and financial resources for R&D and skilled workforce capable of driving innovation and technological advancement.

International collaboration is vital for success, enabling countries to pool strengths, share expertise, and navigate geopolitical complexities. By fostering partnerships and cooperation on a global scale, countries can leverage collective strengths, mitigate resource constraints, share technological expertise and pool financial resources. Through international collaboration, nations can navigate complex geopolitical dynamics, ensure sustainable practices across the battery value chain, and accelerate innovation to drive the transition towards a cleaner, more resilient energy future. In an increasingly interconnected world, collaboration serves as a cornerstone for unlocking the full potential of the battery industry, paving the way for shared prosperity and environmental stewardship across borders.

Please consult the website of Batteries Europe (<u>https://batterieseurope.eu/results/international-observation/</u>) to find a complex analysis of the national battery ecosystems in China, Japan, USA, Australia, South Korea, Canada, India, Indonesia, and the EU for further research. A comprehensive report with an overview of battery R&D&I, funding and international benchmarking on KPIs will be published soon.



Selected Oral Presentation Abstracts



Stable 4 V-class All-Solid-State Lithium Battery with Hydroborate Electrolyte and NMC811 Cathode

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Solid-state batteries are expected to extend the energy and power density beyond the limits of today's lithium-ion batteries, and to replace their flammable liquid electrolyte with safer alternatives. To date, there are only few solid electrolytes fulfilling simultaneously the high demands in terms of ionic conductivity, chemical and electrochemical stability, and mechanical properties. Hydroborates combine many attractive characteristics such as high ionic conductivity, compatibility with alkali metal anodes and soft mechanical properties, but are challenging to integrate into batteries with high-voltage cathodes. Here, we demonstrate stable dis-/charge cycling of solid-state lithium-ion batteries combining a Li₃(CB₁₁H₁₂)₂(CB₉H₁₀) hydroborate electrolyte with a 4 V-class LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathode, exploiting the enhanced kinetic stability of the LiCB₁₁H₁₂-rich and LiCB₉H₁₀-poor electrolyte composition.[1] Cells with lithium metal and indium/lithium anodes achieve a discharge capacity at C/10 of ~145 mAh g⁻¹ at room temperature and ~175 mAh g⁻¹ at 60 °C (Figure 1). Indium/lithium cells retain 98% of their initial discharge capacity after 100 cycles at C/5 (room temperature) and 70% after 1000 cycles at C/2 (60 °C). Capacity retention of 97% after 100 cycles at C/5 and 75% after 350 cycles at C/2 is also achieved with a graphite anode without any excess lithium. The energy density per cathode composite weight of 460 Wh kg⁻¹ is on par with the best solid-state batteries reported to date, demonstrating the potential of hydroborate electrolytes to deliver a competitive next-generation battery technology.



Figure 1. Discharge capacity over 100 cycles of the solid-state hydroborate battery at 60 °C, and SEM image of the NMC811 particles (grey) embedded in Li₃(CB₁₁H₁₂)₂(CB₉H₁₀) electrolyte (green).[1]

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Quasi-Solid Polymer Electrolyte with Autonomous Self-Healing Capabilities for Li-Ion Batteries

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Polymer electrolytes have attracted attention for their potential use in next generation LIBs due to their high energy density and safety, unlike liquid electrolytes which are prone to leakage and flammability.^{1,2} Quasi Solid Polymer Electrolytes (QSPEs) combine the advantages of liquid and solid components, with the liquid electrolyte immobilized in a polymer matrix. Capacity fading is a drawback associated with degradation and ageing of cell components. However, this problem can be overcome by using a self-healing PEG electrolyte based on hydrogen-bonded UPy moieties.

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) is considered one of the most important QSPEs due to its high dielectric constant, wider electrochemical window, high mechanical strength, shape and packaging flexibility, and good processability.^{3,4} However, the high crystallinity of PVdF-HFP results in low ion conductivity because of the limited free volume available for the mobile lithium-ion. To enhance the ionic conductivity, a blend was realized by combining a high molecular weight PEG-based self-healing polymer with LiTFSI salt. In addition, specific percentages of liquid electrolyte LiFSI 1M in EC:DMC were added.

The quasi-solid electrolyte membranes were prepared by solution casting using N-methylpyrrolidone (NMP) as solvent. The autonomous self-healing ability, morphology, and composition (SEM, IR), thermal and mechanical stability (TGA-DSC, DMA), ionic conductivity at different temperatures (via EIS), electrochemical stability window (LSV) and Li⁺ transfer number (BEV method) of the QSPE blends were investigated. The electrochemical tests were carried out at 40°C on symmetrical Li|QSPEs|Li cells at a current density of 0.2 mA cm⁻², which showed a cycle life of over 700 hours with low overpotential and excellent cyclability. The performance of the electrolyte was tested through galvanostatic cycling in half-cells with LFP as the cathode both in term of rate capability and stability over time with a C_{rate} of 1C for a large number of cycles. Accelerated rate calorimetry (ARC) analysis was finally performed to demonstrate the robustness of the realized QSPEs also in terms of cell thermal stability.

A polymer electrolyte with self-healing properties, good mechanical strength, and high potential stability was developed for use in LIBs. The autonomous self-healing ability was confirmed by tests before and after damage, which showed a good recovery of conductivity values. The electrolyte structure and composition effectively suppress dendrite growth and maintain good ionic conductivity even at room temperature.

The test results for a symmetrical and half-cell at a temperature of 40°C were promising in terms of stability and recovery capability over time, due to its self-healing properties.

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Comprehensive Safety Assessment of All-Solid-State Batteries: using X-ray Radiography, Calorimetry and Blast Testing Techniques.

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In the context of the energy transition, researches on batteries are devoted to improving their energy density, *i.e.* their autonomy and their safety, particularly to the risk of fire. Among the different types of battery, all-solid-state batteries are promising because of their high energy density. A ceramic or a glass electrolyte replaces some traditional components of lithium-ion batteries as the liquid electrolyte and the polymer separator.

However, safety concerns related to ASSBs have remained relatively unexplored. This investigation is focused on understanding the behaviour of all-solid-state batteries subjected to overheating abuse. Specifically, two batteries compositions: Gr|LLZO|NMC811 and Li|LLZO|NMC81 are studied. [1,2] The first cell aids in comprehending the impact of the electrolyte (liquid or solid) safety and the second enables to assess the safety of a reconstructed lithium-metal all-solid-state cell.

An innovative approach to assess the safety of all-solid-state cell in-development has been developed three distinct techniques: calorimetry, X-ray radiography and blast testing. This methodology could significantly contribute to the development of future battery technologies. Ensuring the integration of safety concerns right from the beginning is crucial, encompassing both cell performance and safety aspects.

Substituting liquid electrolyte with a solid electrolyte, the initiation and the maximal temperatures remain unchanged. It reduced by 10 % the heat released and reduced by 40 % the duration of thermal runaway. Using solid electrolyte no prevent from thermal runaway. Substituting liquid electrolyte with a solid electrolyte and substituting the lithiated graphite with a lithium-metal foil, the initiation temperature remains unchanged. The maximum temperature is at least increased by 40 %; the amount of gas and the duration of thermal runaway are decreased by 90 % and 95 %. Furthermore, the Li|LLZO|NMC811 cell is not an explosive but a 188 mbar aerial pressure has been measured. It corresponds to a 2.7 g mass equivalent TNT.

Furthermore, the characteristic parameters of thermal runaway are different. Therefore, the means to mitigate its thermal runaway are different and should be taken into account when all-solid-state batteries are developed. The impact of blast wave on the casing and battery pack integrity should be taken into when all-solid-state batteries are developed.

To conclude, all-solid-state batteries are neither safer nor less safe than lithium-ion batteries. However, their characteristic parameters of thermal runaway are different. This work underlines the importance of evaluating the safety of all-solid-state batteries with respect to users and the environment.



Figure 1: Experimental approach to characterize aerial overpressure using imaging and pressure sensor. [2]

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External Pressure Effects on the Performance and Ageing of High-Capacity NMC/G Lithium-Ion Cells for Automotive and Industrial Applications

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Lithium-ion batteries have become indispensable energy storage devices in our modern world, powering an array of applications from portable electronics to electric vehicles. Understanding and optimizing their performance is of paramount importance. This study investigates the influence of external pressure on high-capacity pouch and prismatic NMC/G lithium-ion cells, a configuration commonly used in automotive and industrial applications [1].

The research employs a comprehensive experimental approach to examine the impact of external pressure on various aspects of lithium-ion cell behavior, including electrical performance and ageing. The study considers different pressure levels, mimicking real-world conditions such as stacking in battery packs and mechanical stress during operation.

Results show that external pressure plays a crucial role in shaping the ageing of either pouch (Figure 1) and prismatic NMC/G lithium-ion cells. The first set-up involved maintaining a constant distance, simulating real-world conditions such as stacking in battery packs. The second set-up of external pressure was applied using a constant pressure. Notably, the constant pressure approach stands out as the superior choice, significantly enhancing the lifetime of these lithium-ion cells. Conversely, excessive pressure may compromise cell ageing and safety by increasing the risk of internal deformations [2].



Figure 1. Effect of pressure on capacity loss for a specific pouch cell



Figure 2. Different set-ups for testing prismatic cells under several pressure conditions

This study underscores the importance of considering external pressure effects in the design and application of pouch and prismatic lithium-ion cells. The findings offer valuable insights into optimizing battery pack design for electric vehicles, where pressures can vary dynamically, and provide a foundation for enhanced safety measures in critical energy storage applications. Ultimately, this research contributes to the advancement of lithium-ion technology, bringing us closer to more reliable and efficient energy storage solutions for our increasingly electrified world.

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Correlating Neutron and X-Ray Tomography to Resolve Critical Cylindrical Cell Damage

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Non-destructive methods like tomography offer many advantages for the study of cell damage in lithium-ion batteries (LIBs) as they preserve cell integrity. These techniques enable the application of multiple analysis modalities and even allow one to observe how zones of interest act during the operation of the cell in an *operando* setup. This is not possible in post-mortem methods where the cell is disassembled and subsequently destroyed. Further, by employing neutron techniques that are directly sensitive to lithium nuclei, in addition to X-Ray based ones, the results of both can be correlated and combined to reach new conclusions that would otherwise be inaccessible.

In this study we apply concurrent neutron and X-ray tomography at the NeXT instrument of the Institut Laue-Langevin (ILL) to study small silicon based cylindrical LIBs manufactured at industry level and investigate the distribution of lithium in aged and degraded cells. These cells contain a nanostructured silicon-graphite composite anode and were fabricated to optimize neutron and X-Ray tomography experiments, while still representing high-quality industrial manufacturing. We remeasured the same cells at the ID31 beamline of ESRF using Small- and Wide-Angle X-Ray Scattering Tomography and determined the measured position inside the cell using a Digital Volume Correlation based approach. This combination allowed us to characterize areas in the anode where the current collector was massively deformed with respect to lithium distribution and charging behavior via an *operando* experiment to resolve the origin of this type of cell damage. [1]



Figure 1. Left shows a rendering of the 3D NXCT data, combined with a SWAXS-CT slice rendered in the measured position. Right shows a matched and aligned position exhibiting physical deformations as seen with different modalities. Lithium deposits are visible with NXCT (top, red = X-ray attenuation, cyan = neutron attenuation), smaller silicon particles are visible with SAXS (middle), and lower lithiation of graphite is visible with WAXS (bottom, green = LiC6, blue = LiC12, red = graphite).

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Solid-state NMR investigations of boron-based self-healing binders for silicon anodes

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Self-healing binders have been proposed to improve the cycling stability of silicon electrodes by mitigating their degradation related to the large volume changes of silicon during battery cycling. One way to achieve self-healing behavior is the use of dynamic covalent bonds that break during the lithiation of silicon, allowing for volume expansion, and form again during delithiation when the silicon particles shrink.[1,2] However, it is challenging to confirm and track this mechanism experimentally, which hinders the further understanding and rational optimization of self-healing binders.

In this work, we present a novel self-healing binder system composed of the polymeric binder poly(vinyl alcohol) (PVA) and the self-healing additive 1,4-benzenediboronic acid (BDBA), in which PVA is cross-linked by BDBA through the formation of dynamic boronic ester bonds (Figure 1).[3] We introduce solid-state NMR spectroscopy as a powerful analytical technique to detect the presence of boronic ester bonds between PVA and BDBA, which is evident from ¹H-¹³C 2D correlation spectra and from ¹¹B Hahn echo spectra (Figure 1). In addition, the NMR experiments provide insights into the ratio of cross-linking and show that no significant amount of cross-linking with silicon occurs, but that borate species can be formed from BDBA in the presence of silicon. The NMR analysis can be performed even for low BDBA concentrations as found in an electrode, enabling future investigations of the evolution of dynamic covalent bonds in silicon electrodes during battery cycling.

Finally, we demonstrate that the novel binder system does improve the electrochemical cycling performance of silicon electrodes and that it shows less degradation than the PVA binder alone. In addition to electrochemical characterization, we present SEM and XPS measurements, which provide further insights into the effects of the self-healing additive on the silicon electrode.



Figure 1. Illustration of the self-healing binder system for silicon anodes and the detection of cross-linking with solid-state NMR spectroscopy.

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Theoretical Studies on LiF Formation at Graphite-Electrolyte Interfaces

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Rechargeable batteries play a pivotal role in numerous modern applications, ranging from portable electronic devices to electric vehicles.^[1] The efficiency and longevity of these batteries are significantly impacted by the formation and stability of the solid-electrolyte interphase (SEI) on the electrode surface.^[2] The SEI serves as a protective layer that separates the electrode from the electrolyte, thereby influencing the overall performance and lifespan of the battery.^[2] A deeper comprehension of SEI formation at the atomic level is imperative for advancing battery design and enhancing the electrochemical properties of rechargeable systems. The SEI is a dynamic and complex interface that evolves during the cycling of the battery, thus a mechanistic understanding towards SEI requires the careful design of simulation models with electrode-electrolyte interfaces.

Here, we employed ab initio molecular dynamics (AIMD) and density functional theory (DFT) calculations to examine interfacial behaviors and the LiF formation. Through molecular dynamics and structure sampling, we successfully construct a phase diagram as shown in Figure 1, correlating thermodynamic free energy with the potential, which is determined by the work function of electrode surfaces. By selecting the representative structure at the Li deposition potential (red dot marked in Figure 1), further DFT calculations are performed to reveal that LiF formation at graphite-electrolyte interfaces occurs easily via the intermediate LiHF complex, similar to observations on metal electrode surfaces in our previous work.^[3] Interestingly, LiF tends to be solvated by solvents rather than being directly deposited onto electrode surfaces (e.g., Au electrode), a phenomenon we identify as a critical determinant of the porous and uneven nature of the LiF layer observed on graphite electrodes. Moreover, we also consider the existence of defective graphite electrodes with pore structures, and very similar simulation results are obtained, demonstrating the high possibility of LiF formation via LiHF complex at interfaces.

Our systematic atomic-scale study via AIMD simulations and DFT calculations shows that the LiF formation is facile at graphite-electrolyte interfaces on both perfect and defective graphite electrodes. These different behaviors of LiF on graphite and metal electrodes explain the distinct morphologies of LiF films formed on electrodes as observed in atomic force microscope (AFM) experiments.^[4] Our finding offers new mechanistic insights into LiF formation at graphite-electrolyte interfaces.





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Operando monitoring at high resolution of the formation cycle of a composite Si/Gr optimized electrode by means of X-ray nano-tomography

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The recent rapid increase of the demand for higher energy density along with higher power density lithium-ion batteries (LiBs) requires the development of advanced cathode/anode materials with higher capacity. These challenges can be addressed providing that powerful characterization tools are able to probe the degradation phenomena occurring at multiple scales. Among these, X-ray tomography is a non-invasive 3D investigation tool suited to probe the microstructure of a wide range of functional materials at different length scales. (1) Moreover, phase contrast imaging has brought to light a practical way to enhance visibility between weak absorbing materials thanks to the interfaces between different refractive indexes within composite structures. It enables a contrasted and detailed overview of the 3D morphology of complex material, which is of particular interest in the frame of energy-related materials.

In order to address the irreversible capacity loss of composite silicon/graphite electrode, we have applied *in situ/operando*-interrupted characterizations at very high resolution for the first time to monitor its formation cycle. More specifically, we acquired images (voxel size of 50nm) by X-ray nano-tomography at the ID16B (2) beamline of the ESRF every hour during the first cycle at C/6. This allows us to identify distinct morphological evolution of the different phases (*e.g.* graphite particle, or nano-Si), gradients along the electrode thickness and anisotropy of microstructure changes.

These results were respectively obtained in the frame of the Battery Pilot HUB project at ESRF in Grenoble « Multi-scale Multi-techniques investigations of Li-ion batteries: towards a European Battery Hub » (MA4929). (3)

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Selected Poster Pitch Abstracts



Life Cycle Assessment of Anode Material for Lithium-Ion Batteries

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The High-performance Modular Battery Packs for Sustainable Urban Electromobility Services (HELIOS), co-funded by the European Union's H2020 Programme, aims to develop lighter and more efficient hybrid Li-ion battery packs for EVs. The HELIOS battery pack prototypes represent a significant advancement in battery technology, a unique combination of performance, flexibility, and cost-effectiveness combining same-size modules but different cell chemistries. Therefore, it is important to consider the potential environmental impacts associated with the manufacturing of hybrid chemistry battery modules. Moreover, intensive research is also being conducted to ensure more efficient, sustainable, and environmentally friendly battery chemistries for energy storage, leading to numerous studies related to Li-ion battery material technology. Consequently, along with developments related to cathode chemistries like nickel manganese cobalt (NMC), lithium iron phosphate (LFP) and lithium manganese oxide (LMO), newer anode chemistries - like lithium titanate oxide (LTO) - have been investigated due to their stability, safety, and rapid charging characteristics (1). Nevertheless, there remains uncertainty about LTO's environmental impacts (EI) and how these compare with more typical graphite-based anode materials. This research sets out to investigate the potential ecological effects of LTO via process simulation with HSC-SIM to determine a related life cycle assessment (LCA). OpenLCA (2) was utilized to generate an LCA to compare the EI for the production of 1 kg of LTO, 1 kg of graphite anode battery grade produced in China (CN) and 1 kg graphite anode battery grade produced in the rest of the world (RoW) (synthetic and nonsynthetic). Background data for the analysis was obtained through Ecoinvent 3.9 database and CML v4.8 2016, was utilized as the impact method to generate the life cycle inventory analysis (LCIA). The impact categories for this assessment were: global warming potential (GWP), acidification (ADP), energy resource nonrenewable (ER-NR), eutrophication (EPH), Human toxicity (HT), material resources (MR), and ozone depletion (ODP). Overall, the LCA results suggests that graphite manufactured in CN and RoW (synthetic and non-synthetic) has higher EI contributions than LTO except for EPH, MR and ODP. Overall, this study indicates further research related to LCA of battery cell manufacture and more appropriate Functional Units-based on KWh rather than kg-are needed to provide a more detailed assessment of the environmental aspects related to battery manufacture. Acknowledgements:

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WET-CHEMICAL AL₂O₃ COATING SYNTHESIS FOR CYCLE LIFE EXTENSION OF NCM CATHODES IN LI-ION BATTERIES

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The global need for Li ion batteries (LIBs) is increasing every year with the rise in the demand for electric vehicles and with the growing exploitation of mobile electronic devices. Along with the accelerated production of batteries, a concerning amount of battery waste is produced. One way to slow down the waste generation and control the expenditure of resources would be to produce longer-lasting batteries, thus postponing the need for battery replacement. Therefore, extension of LIB lifetime is an important research direction for the future of mobile electronics.

Battery ageing is caused by the degradation of the components within it. Since the components are all encased in the electrolyte together, the degradation processes of the anode, cathode, separator, and electrolyte are not isolated and can affect one another. Most often, depending on the electrodes used, the largest contribution to battery ageing stems from cathode degradation-related processes. In the state-of-art cathode material $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NCM) high capacities can be achieved if the nickel content is increased above 80% of the total transition metal content. However, along with higher nickel content comes more severe degradation. Main degradation pathways of NCM cathodes include surface phase transitions with associated oxygen release, particle cracking due to volume changes during charge-discharge cycling, transition metal (TM) dissolution, and cathodic solid-electrolyte interphase (CEI) growth[1].

Among other strategies, surface coatings have been extensively studied to mitigate NCM cathode degradation[2]. Coatings can be formed by various methods, like atomic layer deposition, chemical vapor deposition, and other coating methods, among which the wet-chemical method shows the most promise for relatively fast, cost-effective, and easy up-scaling.

In this work, a method is developed for an easily up-scalable wet-chemical synthesis of Al_2O_3 coating on $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM111) active material. The synthesis is based on a non-toxic coating precursor (aluminum isopropoxide – AIP) and solvent (ethanol). The coated material is characterized by various structural analysis methods (SEM, TEM, XRD, XPS), showing an aluminum-containing coating formed on top of NCM111 particle. LIB half cells containing the coated material are assembled for rate capability and cycling stability testing. A significant improvement in capacity retention is observed for the coated material. To exclude the effects of the coating procedure itself (without adding the AIP precursor) on the performance of the active material, a reference sample is prepared. The reference sample is prepared via the same wet-chemical procedure as the coated sample, except no AIP precursor is added. It is shown that even without the addition of the coating forming agent, the cycling stability is improved for the reference sample, although not to the same extent as for the coated sample. Additionally, the reference procedure is studied in more detail to understand which step of the reference procedure – washing or sintering – is responsible for the cycling stability improvement.

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Solid-state vs. Spray-drying synthesis for Mg-doped P2-Na_{0.67}Fe_{0.5}Mn_{0.5}O₂ as cathode material for Sodium-Ion Batteries

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Among the different cathodes studied for Sodium-Ion Batteries (SIBs), the P2-layered oxide structure has garnered significant attention for its electrochemical properties: they provide a stable host for sodium ions during the charge-discharge cycles, high specific capacities, and good structural stability. To increase the electrochemical performance of the P2-Na_{0.67}Fe_{0.5}Mn_{0.5}O₂ oxide^[1], we performed several substitutions by introducing Mg²⁺, an electrochemically inactive cation already known in the literature for its stabilizing properties during charge-discharge cycles^[2,3].

A series of P2-Na_{0.67}(Mn_{0.5}Fe_{0.5-x}Mg_x)O₂ (x = 0, 0.05, 0.1, 0.2, 0.3) was initially synthesized by solidstate synthesis, starting from commercial transition metals oxides and lithium carbonate. The x = 0.2 sample and the non-substituted oxide were also synthesized by Spray-Drying Synthesis followed by heat treatments, to evaluate how different synthesis routes and conditions can influence the morphology, the structural parameters and the electrochemical performances. The morphology and elementary composition of all materials were investigated through SEM-EDX, ICP-AES, and XRD analysis. All materials were characterized as cathode in coin cells using Na_(m) as counter-electrode between 1.5V and 4.2V and using different electrolytes. Operando XRD was also used to observe the structural modifications occurring during charge and discharge.

The solid-state syntheses performed resulted in the successful synthesis of the desired P2-layered structure with a small electrochemically inactive phase impurity. Structural analysis showed that the volume of the elemental cell (and particularly the parameter c) decreases as the amount of Mg increases, in contrast to what was expected based on literature reports for similar materials. In contrast, syntheses carried out by spray-drying followed by heat treatment resulted in the formation of purer P2 oxides than those obtained by the solid state. It was also confirmed that a small percentage of O3 (electrochemically active) phase is formed in addition to the main P2-phase as a consequence of Mg substitution. Moreover, with spray-drying synthesis, it was possible to considerably reduce the calcination temperature (800°C vs 1000°C) and increase the sustainability of the synthesis, as the first step was conducted in aqueous solution. From a functional point of view, the best-performing material was found to be Na_{0.67}Mn_{0.5}Fe_{0.3}Mg_{0.2}O₂. Compared with the unsubstituted oxide, the specific capacities achieved are significantly higher at each of the C-rates tested (about 110 mAh g⁻¹ vs. 70 mAh g⁻¹ at 0.5C, respectively). This material also proved to be significantly better than the pure oxide after a large number of cycles, as the capacity loss observed after 100 cycles is practically halved (29.1% vs. 54.7% at 1C). Comparing the performance recorded for the materials obtained through the two different syntheses carried out, it was found that those synthesized by spray-drying always showed better electrochemical performances.

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Promising Beginnings: A Preliminary Examination of CaB₁₂H₁₂ as New Electrolyte for Calcium-Based Energy Storage

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In this study we purpose a preliminary overview on the newly synthesized CaB₁₂H₁₂ salt for calciumbased batteries that exhibits chip and scalable synthesis, offering a first step for a potential breakthrough for the manufacture of safer and more cost-effective calcium-based batteries. The innovative electrolyte is based on CaB₁₂H₁₂ salts, designed to enhance the reversibility of Ca plating/stripping, addressing a critical challenge in calcium battery technology. This research purposes an optimized synthesis of this salt and explores his behavior in different solvent, revealing CaB₁₂H₁₂ 0.25M in NMP as an optimal formulation that allows reversible plating/stripping of calcium with overpotential below 0.5V vs calcium with current density of 0.1mAcm⁻².



*Figure a) galvanostatic cycling of symmetric cell Ca (CaB*₁₂*H*₁₂*0.25M in NMP (Ca with different current density b) Light optic microscope images of Ca deposit on gold using CaB12H12 0.5M in NMP as electrolyte*



Functional binders to tackle transition metal dissolution in LNMO cathode material.

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The high-voltage spinel oxide LiNi0.5Mn1.5O4 (LNMO) is a promising cathode material for next-generation high-energy lithium-ion batteries. With its high operating voltage of approximately 4.7 V vs. Li/Li⁺, it offers a high energy density of 650 Wh/kg together with a good rate performance. In addition, with little Ni and no Co LNMO also comes with the potential for low cost electrodes and improved sustainability to the currently used layered oxide cathodes. However, before full utilization of LNMO cathodes, there are still some challenges that must be overcome. One of these challenges is the oxidation of carbonate electrolytes at the high operating voltage, which in the presence of water generates HF that leads to the dissolution of Mn²⁺ ions from the LNMO particles. These dissolved Mn²⁺ ions then migrate to the anode where they are reduced to metallic Mn, causing increased resistance and capacity degradation over time.[1,2]

This study is a part of the ongoing European project IntelLiGent which focuses on developing nonfluorinated binders for LNMO cathodes with metal-ion scavengers to mitigate the issue of Mn-ion dissolution (Figure 1). This is done to trap harmful parasitic species before they reach the anode interface. Various binders have been investigated and compared to the state-of-art PVDF and CMC binder references. These include lithiated biopolymers with different molecular weights, and lithiated technical polymers at varying pH values, where the electrochemical cycling highlights a great dependence on the binders' functionality based on both Mw and pH levels. The findings also demonstrate stable cycling of aqueously processed LNMO cathodes.



Figure 1: a): Section of a regular LNMO cathode showing transition metal dissolution and crossover. b) The IntelLiGent self-mitigating cathode network.

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EXPLORATION OF AQUEOUS ELECTROLYTES WITH LARGE OPERATING VOLTAGE WINDOW FOR LOW COST M-ION CELLS

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Currently, Li-ion batteries are widely used in electric vehicles and in electronic devices, although other technologies such as Na-ion or K-ion are under investigations to overcome price issues and lithium scarcity. The electrolytes used in Li-ion batteries are composed of toxic and flammable organic solvents that raise the issues of safety and cost [1]. Therefore, water is a promising option as an electrolyte solvent in terms of manufacturing cost and safety of the electrochemical storage system using it [1,2]. However, aqueous electrolytes have one major disadvantage: their low electrochemical stability window (ESW) due to water oxidation and reduction reactions separated by 1.23 V, which prevents them from being used in high-energy batteries.

In order to have a wider operating voltage window, water electrolysis reactions must be shifted in potential. State-of-the-art suggests some ways to improve aqueous electrolyte's ESW such as the use of high salt concentration (water-in-salt [3,4] and water-in-bisalt [5]) and molecular crowding by addition of an inert solvent[6,7]. Both help to reduce the number of water molecules engaged in hydrogen bonding with other water molecules that leads to O_2 and H_2 production reactions. Another possibility to operate on wide potential windows is to use additives or coatings to protect the electrode surface. These solutions can be optimized and combined to produce a low-cost and safe battery cell.

In this work, initial tests were focused on Li-ion technology, by using aqueous electrolytes based on LiNO₃ and LiTFSI, respectively a low-cost salt and a salt commonly used in literature. Electrochemical measurements were performed to observe salt and concentration impacts on ionic conductivity and on ESW (Figure 1 (a) and (b)). Studying the environment of water molecules thanks to infrared spectroscopy (Figure 1 (c) and (d)) has enabled a better understanding of the salt impact on ESW. Indeed, anion structure and properties influence the ESW and the conductivity of the electrolyte. These results have highlighted the formulation parameters that need to be optimized to obtain a low-cost aqueous electrolyte with a wide ESW. More electrolyte characterizations are in progress for a better understanding of the electrolyte are to be with a wide the formulation (salt mix, diluent addition, etc) impact on ESW.

Knowing the electrolyte properties (ESW, wettability, etc) will allow to wisely choose active and passive materials for the realization of an aqueous M-ion cell, with an ESW greater than 2.5V and an energy density of 140Wh/kg.



Figure 1: Ionic conductivity (a) and ESW on nickel (b) of $LiNO_3$ and LiTFSI at the same concentration ($\approx 5 \text{ mol/L}$) in water. Evolution of the water OH stretching band with concentration for $LiNO_3$ (c) and LiTFSI (d).

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Crosslinked ionogels containing active fillers for lithium-metal batteries

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The current climatic crisis highlights the importance of electrifying the transportation sector to reduce greenhouse gas emissions from anthropogenic sources. Lithium-ion batteries (LIBs), despite being a rather recent invention, gained a dominant role in the field of energy storage due to their high energy density, long cycle life and low self-discharge. LIBs experienced a dramatic improvement since the first studies in this field in the past century. However, the current technology still requires further improvement to meet the market needs, especially in the case of electric vehicles [1]. Concerning next-generation anodes, lithium metal is the most promising candidate, owing a specific capacity (3860 mAh g⁻¹), which is about ten times higher than the presently used graphite (372 mAh g⁻¹), and a very low redox potential (-3.04 V vs. SHE) [2]. Nonetheless, lithium metal electrodes are suffering a high reactivity with commonly used electrolytes and dendritic lithium deposition, causing severe safety issues [3]. Polymer electrolytes can be a suitable replacement for liquid electrolytes due to their ability to limit dendrite growth and the improved stability against lithium metal anode [4]. An increased electrochemical performance, high thermal stability and extended electrochemical stability window have been observed when introducing ionic liquids (ILs), i.e., room temperature organic molten salt, into the polymer matrix. These ionogels (IGs) are a promising class of polymer-based electrolytes for next-generation lithiummetal batteries. Unfortunately, fast Li⁺ kinetics are still a challenge due to the high viscosity and low transference number of ILs [5]. A possible solution is given by a hybrid approach as the insertion of active and passive filler can further boost the electrochemical performances of IGs.

Herein, we present composite IGs prepared via a one-pot preparation protocol by mixing the polymer precursors butyl methacrylate (BMA) and poly(ethylene glycol) diacrylate (PEGDA) with the IL PYR14FSI and, in addition, LLZTO nanoparticles. The inorganic filler is fully integrated in the polymer matrix by using an organosilane functionalization which allows for the formation of covalent bonds during the polymerization step. Three functionalized LLZTO nanoparticles were investigated, differing by the silane content, resulting in a maximum ionic conductivity of $6 \cdot 10^{-4} S cm^{-1}$ at 20 °C and an anodic electrochemical stability up to 5.3 V (vs. Li+/Li). Li|IG|LFP cells delivered a stable cycling with a specific capacity of 125 mAh g⁻¹ for hundreds of cycles owing to a high compatibility of the IG composite with lithium-metal anode.

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A STUDY ON SEPARATION KINETICS OF ANODE AND CATHODE MATERIALS SUPPORTED BY ACTIVE LEARNING TO OPTIMIZE DIRECT RECYCLING OF LITHIUM-ION BATTERIES

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Froth flotation is a widely employed physical separation process for the extraction of primary raw materials. However, flotation has recently gained attention for direct recycling of cathode and anode materials from end-of-life batteries. Due to the natural hydrophobicity of anodic graphite, froth flotation has proved to be effective for its removal from the battery active materials mixture. In this study, we aim to optimize froth flotation conditions using the separation kinetics of graphite and lithium metal oxides (anode and cathode materials, respectively) through a novel combination of design of experiments (DoE) and active learning aimed to analyze complex systems with multiple variables. We explored three significant factors affecting the kinetics of both materials: solids content, froth, and collector dosages. Through active-learning guided experimentation response surface areas for each operating condition were obtained. Our work introduces an innovative approach for improving the targeted objectives of recovery and kinetics, while also obtaining mathematical correlations that can help in the modelling of recycling processes using froth flotation.



Na-sulfide based Solid Electrolytes for battery applications

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The fast growth in electricity use increases the demand for all types of electrical supply equipment, as well as energy storage devices. Lithium-ion batteries already govern the energy market as rechargeable power sources for portable devices and electric vehicle applications [1]. Nevertheless, there are some challenges that Li-ion batteries face, including degradation during operation, Li supply chain issues, and environmental concerns connected to Li extraction [2]. Among them, safety issues linked to the flammability of liquid electrolytes represent significant challenges [3]. In this context, solid sodium electrolytes for Na-batteries are promising materials for overcoming these problems. They represent worthy alternatives for the increasing technology demand shifting towards sustainable energy solutions [3].

In this regard, Na₃PS₄ (NPS), Na_{2.85}P_{0.85}W_{0.15}S₄ (NPWS), Na₃SbS₄ (NSS), and Na_{2.85}Sb_{0.85}W_{0.15}S₄ (NSWS) solid electrolytes were obtained through a mechanochemical synthesis (left part of Figure 1). Subsequently, NPS and NPWS were characterized employing X-ray diffraction (XRD), Electrochemical impedance spectroscopy (EIS), Scanning electron microscope (SEM), and Energy Dispersive X-ray (EDX) techniques to investigate the structure, morphology, and conductivity of the formed electrolyte. Additionally, in situ XRD measurements (using wide-angle X-ray scattering) were conducted across varying temperatures on all Na-sulfur solid electrolytes. This study aimed to elucidate phase transitions and establish correlations between internal structure and ionic conductivity. All electrolytes exhibit two main phase transitions (right part of Figure 1). Only the NPS electrolyte was crystalline after the mechanochemical synthesis, while the other samples started with a semi-amorphous structure before transitioning to a fully crystalline phase. Finally, further analysis is needed to have a complete understanding of the thermal and conductivity properties of these electrolytes.



Figure 1. Left panel: representation of ball milling synthesis of NPS electrolyte. Imagen taken from [4]*. Right panel: phase transition of NPS while the temperature increases from RT to 300°C.*

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Degradation mechanisms of densified Li₃PS₄ sulfide-based solid electrolyte exposed to humid atmosphere: large-scale instruments investigation

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Solid-state lithium-ion batteries are promising candidates as next generation of energy storage devices. Unlike conventional lithium-ion batteries, they comprise a solid electrolyte (SE) instead of a liquid organic one. The use of SEs allow an increase in the battery energy density, which is required for automotive applications [1]. Among SE categories, sulfide based solid electrolytes (SSEs) have several advantages including a high ionic conductivity (up to 10^{-2} S/cm²) and good mechanical properties [2, 3]. However, they also have some limitations and one of the most critical being their high sensitivity towards humidity. In fact, when SSEs are exposed to a humid atmosphere, they are severely degraded and release toxic H₂S gas upon their reaction with water [4, 5]. This feature leads to significant process cost and potential safety issues associated with mass production of solid-state lithium-ion batteries with SSEs.

This study provides an exhaustive description of degradation processes occurring when Li_3PS_4 (LPS) SSE pellet is exposed to humid Argon (47% RH). A homemade flow-through setup was developed and used for precise quantification of H_2S evolved during Li_3PS_4 reaction with humidity. Two synchrotron radiation-based techniques, X-ray diffraction–computed tomography (XRD-CT) and X-ray nanotomography were used for evaluation of three-dimensional structural and morphological degradation of the pellets.

Constant in-situ and online H_2S measurements evidenced a two-stage reaction between LPS pellet and humid Argon: a fast surface reaction (peak) followed by a slower diffusion-controlled reaction (low plateau).

X-ray nanotomography revealed severe morphology degradation for humid Argon-exposed LPS pellet. Multiple cracks and pores were formed from surface towards the bulk of the pellet. The morphological mean degradation front after 120 min of humidity exposure reached 50 μ m.

XRD-CT allowed identification of main chemical degradation phases produced upon humid Argon exposure of LPS pellet. The spatial distribution of these degradation phases within the LPS pellet were also determined. XRD-CT also evidenced the presence of multiple strains within humidity –degraded LPS pellet that drive the morphology degradation.

X-ray nanotomography and XRD-CT ultimately allowed us to identify a cyclic and self-sustaining chemomorphological degradation mechanism for the degradation of LPS pellet exposed to humid Argon. This mechanism consists of an interplay between LPS hydrolysis and cracks and pores formation/growth following the hydrolysis.

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Investigations of Solid Electrolyte Interphase (SEI) Layer in 2D Silicon-based Anodes for Li-ion Batteries

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Silicon has attracted huge attention in the last decade because it has a theoretical capacity of 10 times that of graphite for Li-ion batteries [1]. However, the large volume expansion of the silicon anode, during the charge and discharge cycles, leads to the continuous formation of a solid electrolyte interphase layer (SEI) inducing the overconsumption of Li-ions [2]. Furthermore, silicon's poor electronic and ionic conductivity can cause sluggish electrochemical kinetics [2].

This work demonstrates the application of 2D silicon-based nanosheets with large lateral dimensions, leading to efficient limitation of SEI layer growth while significantly increasing the specific capacity of the battery. To achieve this, 2D siloxene nanosheets were successfully synthesized by the topochemical reaction of CaSi2 with HCl, resulting in both H- and OH-terminated sheets. To remove some functional groups, the siloxene was calcined at 300°C (SX300). To study the electrochemical performance, the half cells were fabricated using siloxene and SX300 and cycled at different charging rates. For the first time, and in comparison with previously published results [3]. The cells showed capacities of 1200 mAh/g and 1500 mAh/g for siloxene and SX300, respectively, which are more than 3 and 4 times higher compared to graphite. Using an additive in the electrolyte (FEC) also helped reduce capacity loss at higher charge rates and long cycling. XPS and cross-section SEM investigated the formation and evolution of the SEI layers. Some other cells were also prepared with commercial silicon nanoparticles to compare their SEI layer with the prepared siloxenes.



Figure 1. a) FE-SEM image of siloxene nanosheets, b) rate capability of siloxene and SX300 with and without FEC, c) cross-section SEM image of SX300 electrode.

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LIGNIN-BASED ELECTRODES FOR STABLE AND UPSCALABLE POTASSIUM BATTERIES

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The modern world requires energy conversion and storage technologies that are both environmentally friendly and reasonably priced. Currently, the most advanced technology available for reducing transportation-related CO2 emissions is lithium-ion batteries (LIBs) due to their numerous advantages, such as high voltage and reduced weight [1]. However, lithium is a scarce resource (0.0017 wt% in the Earth's crust) with its uneven distribution around the planet. In this context, potassium-ion batteries (KIBs) have emerged as a promising candidate. Potassium, with its abundant availability (2.09% in the Earth's crust) and uniform distribution, offers a compelling advantage. Furthermore, the low standard equilibrium potential of K+/K (-2.93 V vs. SHE) and its Lewis' acidity render it highly suitable for large-scale stationary storage systems [2]. Consequently, it is essential to design the battery electrodes according to this goal. In order to do this, our research teams have worked to develop, study, and optimize different anode electrodes using lignin, a readily available and sustainable biomass, as precursor.

In this work, different anodes were produced through the synthesis of two variations of lignin-based carbon materials derived from both softwood and hardwood sources. These biocarbon materials underwent activation via varying proportions of potassium hydroxide and were subjected to diverse physicochemical characterization, including SEM, XRD, and Raman spectroscopy. Additionally, electrochemical techniques were employed to assess their suitability as KIB anodes, with optimization of electrode and electrolyte compositions. Following this, a thorough electrochemical characterization involving techniques such as EIS, CV rate analysis, and C-rate testing was conducted on the cells exhibiting the most promising electrochemical performance. These electrochemical assessments revealed favorable reversibility and capacity retention, high efficiency, and excellent long-cycling performance.



Figure 1: a) XRD patterns of biocarbon powder materials. b) Lignin-based anodes cycling performance (0.05 A/g).

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Solid-Solid Phase Change Materials for the Thermal Management of Li-Ion Batteries

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Amidst the growing reliance on lithium-ion batteries for a range of applications, from mobile devices to electric vehicles, the imperative for robust thermal management strategies becomes evident. This study explores the efficacy of hybrid organic-inorganic layered 2D perovskites, a class of solid-solid phase change materials (SS-PCMs), in enhancing battery safety, longevity, and performance. These materials exhibit remarkable thermal stability, which curtails leakage risks, present a notable increase in energy density, extended battery cycle life, and improved heat management capabilities. Through an upscale synthesis and in-depth characterization, our findings elucidate the potential of these perovskites in thermal regulation, emphasizing their reversible phase transitions between crystalline and semi-crystalline or amorphous states, and minimal volumetric changes during heat absorption and release due to the absence of solid-liquid changes present in commercial PCMs [1]. In addition, compared to form-stable PCMs reported in literature, our materials offer a cheaper, less complex system, with comparable performances [2]. In this context, this research advances the possible successful design of the first thermally stable Li-ion battery employing SS-PCMs, offering a promising avenue for optimized thermal control and performance enhancement in energy storage systems. Despite being identified as promising materials for thermal management in the 1980s [3], employing 2D perovskites as hybrid SS-PCMs have received little attention until now [4]. In fact, hybrid SS-PCMs with a generic chemical formula $(C_nH_{2n+1}NH_3)_2M^{II}X_4$ (M = divalent metal; X = halogen) have demonstrated potential for heat transfer with tailorable phase change temperatures [5]. Herein, we present hybrid materials with high latent heat storage efficiency and thermal stability, even at temperatures double their transition temperature. Their unique thermal properties allow versatile shaping for optimized thermal exchanges. The employed advanced characterization techniques (synchrotron XRD-PDF, in-situ TEM, SAXS, STA, micro DSC, etc.) provided detailed insights into their structural and functional qualities. The aliphatic chain length and the type of cation influence the materials' energy capacity and transition temperatures, allowing for customization. Future research may focus on functionalizing these materials by diverse molecules, and advancing integration into diverse energy storage systems.



Final shape prospective

Figure 1. Work in progress covering the testing and shaping of materials for applying in a Li-ion battery system.

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Embedded detection of the state of temperature of Li-ion batteries by Intelligent Gray Box Model

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The development of embedded diagnosis tools for Li-ion batteries directly supports the Battery 2030+ roadmap's goal of improved performance, lifetime, and safety [1]. By monitoring internal parameters that define the State of Charge (SOC), State of Health (SOH), and State of Temperature (SOT) of the cells, these tools can significantly enhance battery management and redefine the secondary lives of the cells. To achieve this, the ULYSSE project, a French regional initiative supported by EIPHI Graduate school (contract "ANR-17-EURE-0002") and by the Bourgogne-Franche-Comté Region, is developing a gray box model with machine learning integration. This model, which acts as a digital twin (a virtual replica of the battery), aims to monitor key physical and chemical parameters within the cell. The project utilizes Embedded Electrochemical Impedance Spectroscopy (EEIS) for reliable, real-time monitoring. This data is then used to develop the battery digital twin through equivalent circuit modeling and train an intelligent feedforward neural network classifier, functioning as a Battery Thermal Supervising Systems algorithm. This combined approach allows for accurate, faster, and real-time SOT determination regardless of the battery's SOC level. Following an overview of the Intelligent gray box model (IGBM) development process, the presentation will focus on recent project results, particularly on sensorless SOT detection using the industry-standard STM32 microcontroller.

Keywords: State of temperature (SOT), Intelligent Gray Box Model (IGBM), Embedded Electrochemical Impedance spectroscopy (EEIS), Equivalent Circuit Model (ECM), Feedforward Neural Network Classifier (FNNC),



Figure 1. SOT detection by IGBM.

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Selected

Poster Abstracts



Dynamic Digital Twin Architecture for Accurate State Estimation in Battery Management Systems

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1. Introduction / Context

The rapid growth of the Electric Vehicle (EV) market highlights the importance of advancing battery technology. Supporting by Battery Management Systems (BMS) to ensure safe operation and optimize efficiency. However, challenges such as **low energy** and **power densities**, **long charging times**, and **degradation** still exist. **Digital Twins**, like Battery Digital Twins (DTs), are increasingly utilized for enhancing battery lifespan. They replicate battery behavior for smarter management, predictive maintenance, and 'what-if' analysis [1].

2. Goal / Objectives

This PhD thesis aims to provide a methodology for battery DTs, presenting a customized architecture for accurate estimation of **State of X** (where X stands for Charge, Health, and Energy) as key variables representing battery dynamics [2], proposing a novel partitioning of DT tasks between **the cloud and edge**, and demonstrating the effectiveness of the proposed solution using both synthetic and real datasets that can be accommodate by the BMS.

3. Methodology

a) Digital Twin Architecture

Digital twin is replication of the physical system digitally and the proposed DT for batteries are divided into three main layers [3]:

- I. <u>Hardware and Connectivity Layer</u>: Handles data collection, pre-processing, and offers edge or cloud data utilization.
- II. <u>Twin Layer</u>: Hosts the virtual battery replica in cloud, featuring a time-series database for battery data storage and State-of-Charge (SoX) estimation models.
- III. <u>Service Layer</u>: Shares data with third parties, offering services like visualization and predictive maintenance.
- b) Data-Driven Battery Modeling & Edge-Cloud Partitioning



The digital twin construct involves training SoX models with historical and new battery data

(data-driven). The EV collects measurements continuously, and the cloud updates SOH and **retrains** SOH and **retrains** SoC&SoE model, deploying them to the EV iteratively for accurate

estimation and model adaptation.

4. Result

Preliminary thesis results tested on three datasets: two public and one simulated. Various models, including **Gradient Boosting Models** (GBM) and **Neural Networks** (MLP, CNN, LSTM), were employed. Accuracy assessed using RMSE and MAE metrics. As seen from next figure, red solid line (**the retrained model**), closely matches actual discharge profiles and outperformed the outdated models by approx. **97x**, highlighting the need for periodic retraining. Validates recurrent adaptation and proposed architecture.



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Hybrid solid polymer electrolyte characterization by SAXS/WAXS analysis

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In an attempt to promote electromobility, the aim of the SAFELiMOVE-project is to meet the requirements of battery electric vehicles, such as fast charging capabilities and prolonged battery cycle life. In this context new solid-state batteries are developed using a hybrid solid polymer electrolyte (HSPE) consisting of Polyethylene oxide (PEO) semi-crystalline as primary polymer, which contains Lithiumbis(trifluormethylsulfonyl)amid (LiTFSI) as ion-conducting sel. By adding a specific amount of LATP particles the mechanical strength of these composite materials can be increased while maintaining the high ionic conductivity. As characterization technique, small and wide angle X-ray scattering techniques (SAXS/WAXS) are used to non-destructively analyse the nanostructural relationships inside this solid electrolyte. Primary scientific questions, which can be answered using this method, are addressed in this study. The initial structure of the single components of the HSPE is analysed and compared to the measured SAXS/WAXS signal of the composite material (see Figure 1). This allows for a better assessment of structural modifications, such as ordering, anisotropy of the polymer chains, and crystallographic arrangements. Since these materials are operated under slightly elevated temperature (60°C) to increase their electrochemical performance, analyses were carried out in situ at these temperatures to follow structural evolutions. Current investigations are focused on post-mortem analysis (after specific amount of cyles) and operando studies. We will highlight in this presentation first results and methodologic procedures.



Figure 1. (left) schematic overview of a battery with solid polymer electrolyte and structural information and (right) WAXS signal of the different elements and the composite material.

Acknowledgements:





MAGNETIC NANOPARTICLE EMBEDDED SELF HEALING POLYMER BINDER FOR SILICON ANODE OF LITHIUM-ION BATTERIES

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Silicon (Si) anodes have become popular in battery research due to its high theoretical capacity (3500 mAh/g) and storage capacity of a single silicon atom which is 4.4 Li atoms [1]. This phenomenon increases the volumetric energy density of the battery. However, Si atoms undergo too much volumetric change (%300 expansion) during Li intercalation/deintercalation (charge/discharge) that leads to unstable solid-electrolyte interface (SEI), and pulverization of Si atoms. These disadvantages cause rapid capacity fading. It has been observed that the self-healing polymer (SHP) has a positive effect on hindering the pulverization of Si nanoparticles [2]. To improve SHP performance, triggering systems as magnetic, thermal are used. Under the Battery 2030+ initiative, horizontal projects like PHOENIX, SALAMANDER and HEALINGBAT have been looking on how to integrate and optimize self-healing polymers and smart sensors & triggering systems into Li-ion batteries [3]. In this study as a part of PHOENIX project, poly (methacrylic acid-co-tetraethylene glycol monomethyl ether-co-dihydroxy stearic acid acrylate) is synthesized with free radical polymerization with Fe₃O₄ composite copolymer with free radical polymerization as magnetic triggerable SHP. When this polymer will be used in Si anode, it expects that decrease capacity fading and improve cycling stability. Synthesized polymers were characterized by using scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX), fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD).

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SYNERGIZING SYNTHETIC AND REAL DATA IN BATTERY HEALTH ASSESSMENT: NEURAL NETWORKS AND TRANSFER LEARNING

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Traditional SoH estimation methods, such as coulomb counting and voltage-based techniques, have limitations in terms of accuracy and adaptability [1, 2]. Neural networks offer a promising approach for SoH estimation due to their ability to model complex and non-linear relationships. However, training neural networks requires large amounts of data, which can be difficult to obtain for battery systems [3].

This research addresses the SoH estimation of batteries using neural networks and transfer learning. It leverages pre-trained models to speed up the learning process and reduce the amount of data required. Two datasets are used in the research: one from synthetic data generated from electrochemical models and the other from laboratory tests of real cells.

The article first discusses the datasets used, including synthetic data from electrochemical models and laboratory test data. The processing methods for extracting input features for the neural network are explained. The network architecture and hyperparameters used in the base model and transfer learning process are described.

The first algorithm is trained on the synthetic data and the hyperparameters are tuned to optimize its performance. Transfer learning is then applied to refine the base model using a limited amount of laboratory data.

In turn, two other models are created from scratch using only the laboratory data, one of which is trained with a small amount of data (the same training dataset as the TL model) and the other one includes more data in order to create a more complete and capable model.

The results show that the transfer learning model outperforms both a reduced model trained from scratch with limited data and a complete model trained with a large dataset. The transfer learning algorithm achieves higher SoH estimation accuracy and requires 75% less data and training time than the complete model. This approach improves the efficiency and robustness of neural network-based SoH estimation.

Overall, this research highlights the advantages of using neural networks and transfer learning for battery SoH estimation. It offers a more advanced and robust technique that can improve decision-making in battery management systems, proactive maintenance and prevention of premature failure in energy storage systems.

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VOLTAGE HYSTERESIS AS A FUNCTION OF STATE OF HEALTH IN COMMERCIAL CATHODE MATERIALS FOR LITHIUM-ION BATTERIES

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The timely replacement of an aging Li-ion battery can enhance users' quality of life, and for certain applications, it might be of paramount importance. Additionally, there is considerable interest in exploring possibilities of second-life applications for used batteries. However, due to the intricate nature of battery aging processes a universally accepted, standardized model for evaluating the state of health (SoH) of batteries doesn't exists for neither practical implementation nor scientific understanding.

In our research, we concentrate on two prevalent cathode materials and assess their SoH: commercially available lithium iron phosphate (LiFePO₄, LFP) and lithium nickel manganese cobalt oxide (LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂, NCM811). Samples underwent testing in a half-cell coin cell setup following a specific procedure, and the acquired data was utilized to compute the voltage hysteresis (see Figure 1). Subsequently, various potential correlations between SoH and voltage hysteresis were investigated. Our findings show a strong correlation between the SoH of a cathode and the observed voltage hysteresis in half-cells.



Figure 1. Schematic representation of experimental part.

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Cathodes incorporating Self-Healing polymers for Li-sulfur batteries

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The self-healing feature endows a material the ability to heal or repair itself spontaneously and finally increase the life expectancy of a material. Organic, cheap and easy to synthesize polymers with different functionalities capable of form supramolecular interactions (hydrogen bonds) offer rapid network remodeling earning the self-healing property.[1]

Energy storage devices are extremely desired to own the self-healing feature because the lifetimes of many rechargeable batteries are limited by the similar dilemma of mechanical fractures over cycling process. Specifically, lithium-sulfur (Li-S) batteries owing to their high theoretical energy density of 2500 W h kg⁻¹, abundant natural resources and environmental friendliness are regarded as one of the next-generation energy storage solutions. Nevertheless, Li-S batteries suffer from issues like the shuttle effect, poor conductivity, and huge volume expansion during cycling process, which hinder their practical development.[2]

Herein, a series of self-healing polymers were synthesized and characterized. Their self-healing behavior was tested (Figure 1) obtaining good self-healing responses in short times. The self-healing polymers were incorporated into the cathodes of coin cells. The cycling performance and charge-discharge curves were carried out to evaluate the performance of the cathodes with the self-healing functionality.



Figure 1. Illustration of the self-healing process.

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Advances on modelling Cobalt-Free and Graphite-Silicon cells

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The increasing demand for Li-ion batteries (LIB's) has led both the industry and the research community to look for materials with easy access, better capacities and lower degradation speeds. In terms of the positive electrode, there is a growing trend towards the reduction of cobalt content due to its price and extraction method. For the negative electrode, efforts are underway to combine graphite (Gr) with other elements such as Silicon (Si) or other Carbon-based materials [1][2]. Battery modeling is another line of research that is receiving significant attention, with the aim of understanding the main phenomena, enhancing performance and minimizing degradation. Physics Based Models, such as the Doyle-Fuller-Newman (DFN), enable to comprehend how lithium ions and electrons are distributed across different parts of the cell, during charge and discharge processes [3].

With the objective of contributing to these two lines of research, this study proposes a DFN model for the cell developed during COBRA project, that combines a cathode made of $Li_{1.1}Ni_{0.35}Mn_{0.54}Al_{0.01}O_2$ (LNMA) with an anode of Gr-Si 10% wt. Experimental investigations conducted at the coin cell level have provided most of the required parameters [3]. Some challenges were faced for appropriately parameterizing certain variables, due to the hysteresis and coulombic efficiency inherent in the materials as shown in Fig. 1 a) and b). Then, simulations were conducted at the half-cell level utilizing Pybamm to corroborate the obtained values and refine those with higher uncertainty, such as the exchange current density [4]. In addition, a full cell DFN model was created for simulating pouch cells with 30Ah capacity. The simulation achieved a Root Mean Square Error of 3.9% between the experimental and simulated voltages during a discharge at C/20.

In collaboration with CIDETEC, the parametrization was also analyzed using CideMOD, a new software based on the DFN model and the Finite Element method [5]. Various cases were investigated, subjecting discharges to different C-rates, at both software's Pybamm and CideMOD. At most scenarios, the results demonstrate negligible variability in the predicted voltage. However, slight differences were observed particularly at higher rates such as 2C, as Fig.1 c) shows. In this way, this research offers a DFN model of a 30Ah pouch cell, based on an innovative chemistry such as LNMA and an anode with Gr-Si 10% wt. Also, confirms CideMOD as a great tool for physics-based modelling, providing accurate results as well as one of the most used simulation tools. Further steps will be taken in this investigation to obtain better results regarding model accuracy and different scenarios, such as driving profiles, will be studied.



Figure 1: a) Open Circuit Potential (OCP) of cathode b) Open Circuit Potential (OCP) anode c) Comparison between Pybamm and cideMOD at 2C constant current discharge

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Diagnosing a Li-ion cell state of health by measuring its entropy

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The entropy of a physical system is a thermodynamic characteristic linked to the number of atomic configurations. When applied to a Li-ion cell, it means that the entropy value changes based on the state of charge (SOC) due to the movement of the Li⁺ ions, and also due to the phase changes of the electrode materials resulting from their crystallographic rearrangement. This implies that, like differential voltage analysis (DVA), entropy variation can be used to identify markers of cell aging for diagnostic purposes [1].

This thermodynamic signature can be extracted from the heat equation, which comprises three main factors: ohmic heat, entropic heat, and heat exchange with the environment. However, the traditional method of measuring entropy variation is very time-consuming, which is its main drawback. Entroview offers an accelerated entropy measurement solution [2], using voltage, current, and temperature to estimate entropy variation during cell cycling. This methodology enables the use of entropy variation as a new cell characteristic for cell state of health diagnostics in industrial applications.



Figure 1 : Entropy variation of a fresh and an aged cell

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Battery Heroes cluster

Several EU-funded projects focusing on cell manufacturing have been working together since beginning of 2023: <u>GIGAGREEN</u>, <u>NoVOC</u>, <u>greenSPEED</u> and <u>BatWoMan</u>. All these projects are working on the sustainable manufacturing of gen3b Li-ion cells.

Together these projects have established a clustering group that we have called Battery Heroes.

Battery Heroes is born to fuel collaboration between related projects towards the production of a new generation of batteries more efficient and with a lower carbon footprint. For this collaboration to become a reality, we will take conjunct actions both in communication and dissemination.

Some of the actions that are done or planned are creating a cluster brand identity (logo, colors, etc.), attending together with a booth at the Transport Research Arena (TRA), collaborating with the Horizon Results Booster to create some communication materials together (such as a video) or developing a common brochure that explains the four projects. Additional activities are on the way, as also the involvement of other EU projects working on cell manufacturing and A joint workshop with the LiPlanet network in September 2024.



The Battery Heroes booth at TRA 2024 in Dublin



Aerosol-based processes to produce battery materials

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Introduction

With the introduction of lithium battery in 1990 by Sony, the development of active materials has undergone a continuous process with the aim of increasing energy density. This is being realised through the development of new, nickel-rich and cobalt-free cathode materials, the production of silicon-carbon composite materials and the development of solid-state batteries.

The increasing demand for applications within electromobility or stationary energy storage requires the implementation of innovative, sustainable and continuous manufacturing processes as well as processes for coating active materials. Aerosol-based methods based on spray drying/spray calcination and spray granulation are presented using selected examples. Initial results on electrochemical characterisation will be presented.

Materials and methods

Preparation of cathode active materials

The development of new cathode materials based on the layered oxide $LiCoO_2$ led to lithium-nickel-manganese oxides NMC and lithium-nickel-aluminium oxides NCA, among others, by substituting cobalt with other elements. In addition to these materials, which are mainly used for electromobility, there are also oxides of the olivine structure, e.g., lithium iron phosphate LiFePO₄, and materials of the spinel structure LiMn_{2-x}Ni_xO₄. The production of these active materials involves a variety of methods, some of which require several process steps. These include precipitation and solid-state reactions, hydrothermal processes and sol-gel processes. By using aerosol-based spray drying and spray calcination processes, the process steps can be reduced, and continuous production can be realised.

Preparation of anodic active materials

Graphite is a common anode material. The theoretical capacity of this material is limited to a theoretical capacity of 372 mAh/g due to the formation of the compound LiC₆. The drive towards higher energy densities has led to a focus on other elements. Silicon offers an alternative solution due to its good availability and a much higher theoretical capacity of 3600 mAh/g. A volume change of 320% during the charging and discharging cycle leads to particle breakage, loss of contact with the current arrester and continuous erosion of the protective boundary layer between the silicon and the electrolyte. The production of silicon-carbon composite materials offers a promising approach to compensate for the volume change. Production can be carried out using continuously guided aerosol-based processes based on spray drying and spray granulation.

Production of solid electrolytes

Another method of increasing energy density is the development of solid-state batteries in which the liquid electrolyte is replaced by a lithium-conducting material, for example lithium lanthanum zirconium oxide LLZO. This allows metallic lithium to be used as the anode material (theoretical capacity of 3860 mAh/g). The challenge here lies in the synthesis of the solid electrolyte. The reaction time can be shortened by producing it using aerosol-based processes.

Coating of cathode materials

Another representative of solid-state electrolytes is lithium phosphorus sulphide LPS. The material is characterised by a high ionic conductivity. However, the material is chemically less stable against oxidic cathode materials, so that a coating of the active materials is necessary. Lithium phosphate Li₃PO₄, lithium niobate LiNbO₃, lithium borate Li_xB_yO_z and lithium titanium oxide LTO are being discussed. Processes based on spray drying and spray calcination can also be used for this in order to realise continuous processing.



Hot-press manufacturing of ceramic solid electrolytes

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In recent years, the interest in solid electrolytes as a as a post-lithium-ion alternative technology has increased sharply, due to the numerous new chemistries which allow high performances and improved safety following the absence of flammable organic liquids¹. In this sense, inorganic ceramic materials, such as NASICONs and garnets, are a particularly interesting choice because of their high room temperature conductivity and chemical stability towards metallic lithium.

However, the synthesis of oxide-based ceramics is usually carried out with high-temperature solid-state methods, featuring long reaction times and high sintering temperatures, which can be detrimental to the final product². The improvement of the manufacturing process requires significant efforts, directed mainly at the decrease of the processing temperature with appropriate adjustment of the precursors and the use of additives. Improvements in densification also reflect positively on the mechanical and electrochemical properties of the materials.

This research aimed for the modification of the synthesis conditions for ceramic oxides $Li_5La_3Bi_2O_{12}$ (LLBO)³ and $Li_7La_3Zr_2O_{12}$ (LLZO)⁴, using different approaches including elemental substitution and addition of agents to vary the formation temperatures of the target phase. Sintering by hot-pressing was employed to enhance the densification. The evolution mechanism was investigated via *in situ* XRD and a thorough structural characterization was carried out.

The results of the investigation show that the addition of external agents has a positive impact on the evolution and the sintering of pellets. Carbon introduction into the precursor mix allows for a visible decrement in the formation temperature for the final phase. The additive helps in the densification step, leading to better final performances in cell. Aliovalent doping of the structure displays analogous effects in stabilizing the final phase at room temperature. The investigated materials exhibit high conductivities considering the low-temperature thermal treatment.

The improved electrochemical outputs show the advantages of hot-pressing to produce more performant solid electrolytes and confirms the effectiveness of the modifications investigated in this research.



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Thermal Runaway Propagation Behavior of Lithium-Ion Cells: A Transient 3D Modeling Approach

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Improvements in the safety systems of electric vehicles (EVs) are on the rise, with lithium-ion batteries (LIBs) emerging as their primary power source. Mechanical, electrical, or thermal stresses on LIBs can lead to internal short circuits, potentially causing a thermal runaway (TR) of the cell, resulting in the release of significant energy. This energy release comprises three main components: heat generation inside the cell due to exothermic reactions, combustion of gases vented by the cell, and ejection of particles through the cell's cap. This study aims to investigate the thermal runaway propagation behavior of Li-ion cells by developing a transient 3D model. The model integrates internal exothermic reactions within the cell with gas and particle venting processes. A Reynolds-Averaged Navier-Stokes (RANS) approach was utilized to describe the turbulent flow of the gases released by the cell, while a finite rate/Eddy dissipation model was employed for the combustion process. Various phenomena such as Lagrangian particle transport and combustion modeling were explored. Thermal abuse conditions were applied to the cell. Preliminary simulations were conducted on two geometries: the first being an adiabatic small-enclosed vessel with a volume of 0.54L, aimed at determining the energy released by the cell during TR; the second, the same vessel with a small opening, aimed at determining the velocity of the flame and the particles ejected by the cell. Results demonstrate the significant effect of hot particle injection on the energy released by the cell during TR, emphasizing its importance. Finally, the model's validity and reliability are confirmed through experimental data validation.



Figure 1. Illustration showing different thermal runaway propagation mechanisms from heat dissipation within 18650 battery modules.



Machine learning modeling of solid electrolyte interphase growth at Li6PS5Cl/Li-metal contacts

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The structure and growth of the solid electrolyte interphase (SEI) region between an electrolyte and an electrode is one of the most fundamental, yet less-well understood phenomena in solid-state batteries. The initial stages of this growth are currently inaccessible to experiments, and previous parameterized models have suggested mutually contradicting hypotheses about the physics and chemistry at play [1]. I will present a parameter-free atomistic simulation of the SEI growth for one of the currently promising solid electrolytes (Li6PS5CI). We employ moment tensor potentials [2,3], trained on ab initio simulations. Whereas ab initio molecular dynamics (MD) can only tackle a few hundred atoms for 100 ps [4], our machine-learned MD simulation comprises over 30,000 atoms for 10 ns. Thanks to this expanded range of space and timescales, we unveil a growth mechanism in two steps: a rapid initial influx of Li rapidly reduces the electrolyte into an amorphous phase; this is followed by a kinetically slower crystalization of the reduced phase into a Li2(SxPyCl1-x-y) solid solution. I will present numerical data and clarify the physics underlying the qualitatively different functional forms of the two-phase growth.

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SODIUM STORAGE MECHANISM IN NON POROUS HARD CARBON

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Hard carbon (HC) is a promising anode material for commercializing sodium-ion batteries (SIBs) due to its abundant resource, low-potential region, and high reversible capacity, whereas the intrinsic complex microstructure and nanostructure of hard carbon, the general sodium storage mechanism, remains controversial.^[1] The sodium storage mechanism in the pore structure is associated with: 1) the specific surface area, 2) the microstructure, and 3) the graphitization structure.^[2] Here, we precisely synthesize the N, O co-doped hard carbon nanosheet (NOC-10) without >1 nm pores and low specific surface area (7.2 mg/cm²) as the baseline, establishing the relationship between disordered isolated graphene sheets and the electrochemical behavior for sodium storage. Combining synchrotron small-angle X-ray scattering, wide-angle X-ray scattering, N₂ adsorption-desorption isotherms, *operando* X-ray diffraction, in-situ Raman spectroscopy, and galvanostatic measurements, the optimized sample demonstrates a high capacity at low plateau region, whereas scarcely any micropore and mesopore (1–100 nm). Based on these results, an interlayer-filling mechanism is proposed to overall comprehend the electrochemical behavior of sodium storage in the plateau region, which may provide a reverse perspective deep insight into the microstructure will greatly forward the rational design of complex carbon structure as the high-performance anode materials for advanced sodium-ion batteries.

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2BoSS project: Sulfur-based sustainable batteries

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This poster will present the European ERA-MIN3 funded 2BoSS project [1]. In 2BoSS, we aim at validating a silicon-sulfur lithium-ion battery compatible with the circular economy, designed to minimize the use of CRMs while keeping reliable performances and enabling a circular use of material resources. We work out effective recycling strategies for the separation and reuse of raw materials from the 2BoSS battery, and implement eco-design in the choice of metal additives in the active materials in this aim. Finally, the consortium assesses cost, life cycle and environmental, health and safety impact in the perspective of a scaled-up manufacturing.

It is important to assess all impacts to help guiding sustainable and circular design of technologies in the early stages of development. The tool used to analyse environmental and social impacts here is Life Cycle Assessment (LCA). Life Cycle Inventories representative of future possible industrial production are being built starting from data collected at the laboratory scale in the consortium. These datasets are to be shared with the scientific community through the Life Cycle Data Network of the EU Platform on Life Cycle Assessment.

To host the sulfur within a carbon framework in the cathode of the 2BoSS battery, we use a porous carbon matrix derived from the calcination of agricultural biomass waste. Sulfur is loaded in the porous carbon by ball milling, a scalable and solvent-free process. The matrix is optimized for high electrical conductivity, high porosity and surface area. It is also loaded with a polysulfide-reduction catalyst to avoid sulfide shuttling in the battery. The anode active material is a silicon-carbon composite obtained by growing silicon nanowires either onto porous carbon from biomass or onto recycled graphite from used batteries. A high loading of silicon (>15%) ensures a high energy density [2]. The poster will discuss how to optimize lithium availability in the battery by prelithiation, and how to assemble the cell with an electrolyte compatible with both sulfur- and silicon-based electrodes, as these active materials are highly demanding towards electrolyte composition.

In 2BoSS, circularity is a key aspect of the project. Recycling lithium-sulfur batteries represents a significant step forward in the field of energy sustainability. While the recycling of lithium-ion batteries is commonplace, that of lithium-sulfur batteries remains a challenge. Unlike other battery types, they do not contain precious materials such as cobalt, which can limit the perceived benefits of recycling. However, the importance of considering recycling from the battery design and production phase is undeniable to ensure a complete and sustainable life cycle. The high content in silicon is also a challenge for lixiviation methods.

Aiming at circularity, we also focus on responsible sourcing of key inputs to fabricate the battery. We maximize the use of recycled materials such as recycled graphite, organic waste from winery, sulfur from oil refining processes, silicon as a byproduct of alloys production, copper, steel, and aluminum foil from suppliers employing a high percentage of secondary raw materials in a commitment to decarbonize their smelting processes. The value chain of 2BoSS diversifies raw materials sourcing and improves resource efficiency (including recycling), while reducing dependency, thereby promoting the production and export of a post lithium battery cell with a value chain made in Europe.

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Innovative High voltage electrodes based on LNMO/LFP blended materials for Li-Ion batteries

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Electrochemical energy storage solutions, like lithium-ion batteries (LiBs), have emerged as the dominant technology for a broad spectrum of applications, ranging from portable electronics to stationary storage and electric vehicles. Nonetheless, to cater to the continuously growing market demands, there is a pressing need for the development of batteries that offer enhanced power and energy density. In this context, cathode materials that are entirely free of cobalt and operate at high voltages (for example, 4.75 V), such as LNMO (lithium nickel manganese oxide - LiNi0.5Mn1.5O4), stand out as particularly promising for boosting the electrochemical capabilities of future high-energy-density LiBs. Regrettably, LNMO is plagued by certain issues, including the tendency for easy cation leaching during cycling, especially at high C-rates, and electrolyte decomposition at elevated voltages. A viable strategy to alleviate these problems, thereby improving the system's safety, lifespan, and cost-effectiveness, involves the use of mixed electrodes composed of various active materials. In the ongoing HYDRA H2020 project, this study investigates the effects of blending LFP (lithium iron phosphate - LiFePO4) with LMNO, examining the resultant morphological and electrochemical characteristics. LFP was selected for its exceptional thermal and electrochemical stability, along with its impact on the cathode's electrochemical performance, including cycling stability, lifespan, and safety. The proportion of LFP in the cathode mixture was varied to examine its role, and the electrochemical properties were assessed in both halfcell and full-cell setups. Specifically, the straightforward and scalable method of physical mixing through resonant acoustic mixing (RAM) ensured a uniform distribution of LFP and LNMO particles, leading to an improvement in electrochemical performance. The mixed LNMO/LFP cathode achieved a specific capacity exceeding 125 mAh g-1 at C/10 and maintained over 80% capacity after 1000 cycles at 1C against lithium. Similarly, in full-cell tests against graphite, the mixed electrode demonstrated nearly 30% higher capacity retention, close to 74%, after 100 cycles compared to the pure LNMO cathode.

Resonant acoustic mixing



Figure 1. The figure summarizes the approach of blending LNMO and LFP with RAM technique and the electrochemical results obtained in full-cell configuration.

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Techno-economic and social factors assessment for distributed hybrid energy system-based EV charging station: comparison of Li and Na based battery storage systems

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Abstract:

Global population growth and increasing living standards has rapidly increased the worldwide demand for personal vehicles' demand, which will be doubled by 2050 [1]. The environmental pollution through the widely used combustion engine vehicles is critical and causes immense environmental and social impacts. Maintaining global economic development by continuously meeting the needs of the present and future generations with simultaneous preservation of the environment is the key target of sustainable development goals (SDGs). Among several sustainable goals supplying affordable, clean and reliable electricity to all is the (SDG 7) is one of the major targets of the countries [2]. To achieve this SDG 7 transportation sector must follow the trajectory of emerging energy generation systems [3]. Transition towards electric vehicles is a potential option for sustainable transportations, because the energy is used in a very efficient way and causes potentially less environmental impacts. The growing numbers of electric vehicles increases the energy consumption rate for charging purposes. Integrating electric vehicles into the national grid systems may create a disturbance in grid stability or local transmission line congestion, if it is not managed in an intelligent manner. It poses significant challenges to grid operation and planning. It may also increase the electricity cost, due to unreliable electric supply. Therefore, shifting towards renewable resources for charging the electric vehicle is a feasible option. The utilization and development of renewable resources is an urgent requirement to deal with energy security crises and environmental issues. Integrating renewable resources in central grid may create disturbances in reliable energy supply. Thus, the technical barrier demands to implement decentralized options. The limitations and fluctuation provision of renewable resources can be solved by designing off-grid hybrid energy systems. For designing distributed renewable energy system, energy storage plays a key role. Today lithium-ion battery systems represent the most dominant technology used for such energy systems but raise concern in terms of sustainability. However, many new energy storage systems are emerging, which could be also used for such applications and could provide benefits in terms of sustainability [4]. Therefore, for decentralized hybrid energy systems market prevalent Lithium-ion and emerging Sodium-ion battery systems are investigated [5], [6]. The study proposes a methodology to assess techno-economic and social factors for designing an overall sustainable off-grid hybrid energy system for an EV charging station. The generation of excess electricity, renewable share and the amount of unmet load are considered under technical factors. As an economic factor the levelized cost of electricity and net present cost of the system are evaluated. Human development index, job creation and local transport employment are the major social factors that are assessed in this study. The proposed methodology aimed to determine an acceptable overall sustainable off-grid energy system for EV charging stations. The methodology is validated with the Indian and European data. The inclusion of environmental impact assessment based on [5] will be assessed in future work. The developed methodology is shown in Fig. 1.



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Fig. 1: Overall methodology

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PHASE ENGINEERING IMPROVES THE ELECTROCHEMICAL STABILITY OF LITHIUM-RICH COBALT-FREE LAYERED OXIDES FOR LITHIUM-ION BATTERIES

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The expanding electric vehicle market is largely dependent on $LiNi_xMn_yCo_zO_2$ (NMC) as positive electrode material for lithium-ion batteries (LIBs). The resulting increased demand for cobalt is a pressing concern, since 65% of its global mining is concentrated in a single region. Also driven by its high cost and toxicity, there is a consensus to diminish cobalt usage in LIBs. This has led academia and industry to prioritize developing innovative positive electrode materials with reduced cobalt content or cobalt-free alternatives, such as lithium-rich cobalt-free layered oxides (xLiMO₂*(1-x)Li₂MO₃ (M = Mn, Ni, etc.)). With both rhombohedral and monoclinic crystal phases, this materials class has theoretical capacities around 250 mAh g⁻¹, has improved thermal stability, and is cost-effective because of the manganese-rich composition. Still, the practical application of these materials is hindered because of the pronounced voltage decay during electrochemical cycling, which is caused by the transition from a layered to a disordered spinel-type structure. Research efforts have focused on mitigating this voltage fade, for instance by including dopants to stabilize the crystal structure. For further optimization, it is crucial to quantify the degree in which doping affects the change in crystal structure during electrochemical cycling.

In this study, various post-mortem characterization techniques were used to investigate the impact of aluminum doping on the electrochemical stability of lithium-rich, cobalt-free Li_{1.26}Ni_{0.15}Mn_{0.61}O₂. Using statistical analysis based on spectroscopic data, the extent to which Al doping reduces disordered spinel phase formation was quantitatively investigated. The active materials were synthesized via spray pyrolysis followed by calcination. Aluminum doping effectively mitigated voltage fade, enhancing capacity retention from 46% to 67% over 250 cycles at 0.2 C. Structural analysis revealed that doping has a significant effect on the crystalline properties of the materials: the undoped material has a monoclinic crystal structure, but doping increases the rhombohedral character of the layered oxides. As shown by electron microscopy, the more stable rhombohedral phase is present as a shell around monoclinic core particles. This effectively shields the monoclinic phase from the electrolyte, avoiding irreversible oxygen redox, the formation of Mn³⁺, and the degradation into a disordered spinel phase. As such, the doping procedure results in the formation of a stabilizing rhombohedral interface. Over the course of galvanostatic cycling, the rhombohedral content of the doped materials increases, further contributing to the overall electrochemical stability. As such, this study provides insight into the role that aluminum doping plays in phase engineering and in the improvement of the electrochemical stability of lithium-rich cobalt-free layered oxides.

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RECOVERY AND REGENERATION PROCESS OF GRAPHITE FROM EOL LI-ION BATTERIES BLACK MASS

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The rapid growth in demand for lithium-ion batteries (LIBs) is posing challenges in the management of end-oflife (EoL) systems and the supply of critical raw materials (CRMs), especially Lithium, Cobalt, and Nickel. Such challenges can be addressed by collecting and recycling spent LIBs through economically and environmentally sustainable processes and by enabling the transition to a circular economy vision based on the use of secondary raw materials. These processes involve not only the metallurgic approaches to recover the critical metals, but also the pre-treatment strategies that are crucial to enhance the recovery efficiency of other valuable materials (e.g., graphite, fluorinated compounds, binders, electrolyte). Despite its strategic importance in the battery supply chain, the recycling of Graphite still remains poorly explored. The SoA technologies based on pyrolysis in high-T environment lose such material producing CO₂ emissions. Graphite recycling not only alleviates the environmental strain but also facilitates the conservation of precious resources [1].

As task of the RENOVATE WP3 "*Recovery of organic components and Carbon materials*", here, we introduce a method for the recovery and regeneration of spent graphite from a real black mass produced by means of mechanical pre-treatments on EoL EV modules. The proposed recovery approach is based on a more sustainable froth floatation process [2,3] including green chemicals. The regenerated graphite is characterized by a multi-technique characterization approach (e.g. XRD, Raman Spectroscopy, SEM-EDX, ICP-OES) and used to assemble new cells as secondary material for the anode. The electrochemical investigation, specially the long-term cycling, is used to evaluate the effective feasibility of the whole recycling process.

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Vanadium-free oxide glasses: Promising positive electrode material for Li-Ion and Na-Ion Technologies

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The development of new materials for battery positive electrodes is required to increase the batteries performances. Currently, best commercial positive electrode materials are crystalline oxides, and reach 150 to 190 mAh/g (so less than 700 Wh/kg at material level) for Li-ion technology (LCO, NCA or NMC material), and 120 mAh/g (or less than 450 Wh/kg at material level) for Na-ion technologies (NVPF or Lamellar Oxide materials). Nevertheless, glasses are promising materials as their vitreous structure can undergo structural changes like alkaline insertion/disinsertion mechanisms. Furthermore, depending on their composition, they can be easy to processed and produced on an industrial scale.

Most of the papers on glass positive electrodes reported in the literature focus on Vanadium-containing glass. Furthermore being a glass forming element that helps the glass network formation, Vanadium presents multiple oxidation states that can lead to high electrochemical performances through the exchange of several electrons per Vanadium. The reported glasses are generally elaborated in reducing conditions and reach specific capacities around 300 mAh/g (i.e. 1000 Wh/kg) for Li-ion cells [1]. Such performances in energy density make glass a highly interesting material family for positive electrode. Nevertheless, Vanadium is considered by European Union as a critical raw materials. So there is a strong interest in developing Vanadium-free glasses for positive electrode. These materials are less investigated in the literature, reaching around 60 mAh/g for iron silicates glasses in Li-ion technology [2]. Similarly, glasses for Na-ion battery positive electrode remain poorly studied. Specific capacity of 115 mAh/g was reported by Nakata *et al.* [3] for sodium iron phosphate glass.

The present work investigates new oxide glass compositions for Li-ion and Na-ion technologies. The glasses were synthetized and characterized to investigate their structures (SEM, EDS, Raman spectroscopy, UV-vis, XRD, ...). Positive electrodes were prepared with ball milling technique, assembled in coin cells using either Li-metal or Na-metal configuration. Then the positive electrodes were electrochemically evaluated by galvanostatic cycling. The electrode were characterized *post-mortem*. Data collection from structural, chemical and electrochemical characterizations are used to develop a database to predict best promising new compositions by using machine learning techniques. This work will also give first insights relative to the links between glass composition, elaboration conditions, structural properties, and electrochemical performances.



Figure 1: Methodology employed in our study

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Development of a Data-Driven Method for Diagnosing the State of Health of Battery Cells, Based on the Use of an Electrochemical Aging Model

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Accurate estimation of the remaining useful life of lithium-ion batteries for electronic devices is crucial. Data-driven methodologies encounter challenges related to data volume and acquisition protocols, particularly in capturing a comprehensive range of aging indicators. To address these limitations, we propose a hybrid approach that integrates an electrochemical model with data analysis techniques, yielding a comprehensive database.

Our methodology involves infusing aging phenomenon into a Newman model. From this model, we build by simulating a dataset of Check-up signals by initializing the model at various aged states. This lead to the creation of an extensive database capturing various aging states based on non-destructive parameters. This database serves as a robust foundation for subsequent analysis. Leveraging data analysis techniques, notably principal component analysis and t-Distributed Stochastic Neighbour Embedding, we extract primordial information from the data. This information is harnessed to construct a regression function using either Random forest or Support vector machine algorithms. The resulting predictor demonstrates a 5% error margin in estimating remaining battery life, providing actionable insights for optimizing usage. This comprehensive approach ensures a thorough exploration of battery aging dynamics, enhancing the accuracy and reliability of our predictive model.

Furthermore, the calibration of the Newman model for aging and performance using data from a European project called Teesmat with optimisation algorithms. This allows us to see different ageing phenomenon and compare with real data in several ways of ageing.

Of particular importance is our reliance on the database generated through the integration of the electrochemical model. This database serves as a crucial asset in advancing our understanding of aging states. Indeed, with our method we do not estimate the remaining useful life based only on macroscopic information but an approximation of internal states. Beyond its capability for precise remaining life predictions, this database-driven approach offers valuable insights for optimizing battery usage and adapting the predictor to various scenarios. This underscores the practical significance of our method in facilitating better decision-making regarding lithium-ion battery management.



2BoSS project: Synthesis of silicon nanowire-graphite composites for Li-Sulfur batteries

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This poster will present the European ERA-MIN3 funded 2BoSS project [1]. In 2BoSS, we aim at validating a silicon-sulfur lithium-ion battery compatible with the circular economy, designed to minimize the use of CRMs while keeping reliable performances and enabling a circular use of material resources. We work out effective recycling strategies for the separation and reuse of raw materials from the 2BoSS battery, and implement eco-design in the choice of metal additives in the active materials in this aim.

As the demand for high energy density storage increases, lithium-sulfur batteries (LSBs) are being considered as a promising solution. However, before commercialization, they must overcome several limitations, including instability of sulfur cathodes and lithium metal anodes. Considering this, silicon nanowires (SiNWs), with a high theoretical capacity and low discharge potential, represent an interesting alternative anode material capable of meeting this demand. Nonetheless, their synthesis requires a cost reduction to achieve industrial relevance. Our study introduces low-cost catalysts, tin sulfide/or oxide, that allow growing silicon nanowire directly on recycled graphite (from Ecograf), producing Si-rich anode composites (over 23%wt of Si) [2]. The non-uniform distribution of self-confined conductive silicon nanowires on the surface of recycled graphite (rGt) takes advantage of their matrix to effectively pad volume changes and significantly reduce the phenomenon of sputtering and capacity fading during lithium insertion and extraction, as well as maintaining the SiNWs' integrity.

Within the ERA-MIN3 project "2BoSS" (2boss.eu) [1], we recently inquired how to improve this process towards a more sustainable material to be included in lithium-sulfur batteries. First we developed a post-synthesis treatment to remove the tin growth catalyst from the composite. Second, we turned to recycled graphite to include this material in a circular strategy in the battery sector. Third, we used porous carbon obtained from biowaste to synthesize composites with very high silicon content (over 40%wt).

In order to achieve optimal compatibility with both the anode and cathode, and also because the etherbased electrolyte is unstable with Si-based anodes, carbonate electrolyte with additives in Si anode will be used to prelithiate the anode electrode and test it with an ether electrolyte in a full cell. Assembly of full cells is under way.



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Extending the Electrochemical Window of Aqueous Zn-MnO₂ Batteries through pH Gradient Dual-Electrolyte

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Over the past decade, research interest in zinc-manganese dioxide (Zn-MnO₂) batteries has increased substantially due to green policy implementation efforts. These batteries are a potential addition or replacement for Li-ion batteries where their use is too costly or not desirable due to safety concerns. Commercially available alkaline Zn-MnO₂ batteries have a low potential of 1.5 V and are generally non-rechargeable. Many studies have addressed rechargeability problems by modifying the MnO₂ cathode and controlling the depth of discharge. However, the issue of low potential and thus undesirable energy density still needs to be addressed [1,2].

Herein we have addressed these issues and developed high-potential rechargeable aqueous $Zn-MnO_2$ batteries by employing novel polymer hydrogels. The developed dual-electrolyte battery (Fig. 1.) consisted of Zn foil as an anode, MnO_2 /carbon black mixture as a cathode, and acidic and alkaline polyacrylamide hydrogels with incorporated immobilines as electrolytes. No membranes or separators were used in the battery construction. On the acidic hydrogel side, *acrylamide* monomer was polymerized with *2-Acrylamido-2-methyl-1-propanesulfonic* acid, thus achieving a pH of ~2. On the alkaline hydrogel side, *acrylamide* monomer was polymerized with (*3-Acrylamidopropyl*)trimethylammonium hydroxide, achieving a pH of ~12. By ensuring an equal number of ions on each side of the hydrogel, it is possible to fix the pH gradient for up to a week. Previously, by employing Pluronic F-127 hydrogels incorporated with 0.5M H₂SO₄ and 1M KOH, it was possible to maintain the pH gradient only for 25 hours [3].

Using this unique dual electrolyte increased the open circuit potential of the battery and prevented the formation of an insoluble $ZnMn_2O_4$ compound, allowing the battery to be repeatedly charged and discharged. The constructed pH gradient dual-electrolyte hydrogel $Zn-MnO_2$ battery provided an open circuit potential of 2.4 V and maintained a discharge voltage above 2 V throughout a week of charge-discharge cycles.



Figure 1. Schematic illustration of the acid-alkali dual-electrolyte battery.

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Nanostructured diatom-SiO₂: A sustainable option for enhancing Li-ion battery anode performance

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The main component in today's Li-ion battery anodes is graphite, which have high stability and durability. However, it has a relatively low storage capacity which may limit the overall battery performance. Silicon displays a high theoretical storage capacity but despite substantial research efforts it is still challenging to use due to the massive volume expansion at Li insertion, and consequent deterioration of the particle microstructure. SiO₂ has a lower theoretical storage capacity than Si but still several times higher than graphite. Theoretical studies indicate that SiO₂ would react irreversibly with Li ions as an in situ convertible oxide, producing electroactive Si domains dispersed in a matrix of electrochemically inactive species. The on-site produced Si would then react reversibly with Li, being the main contributor to the storage capacity, whereas the inactive phases would buffer Si volume variations, yielding an anode with higher stability. Notably, nanostructures of SiO₂ have been shown to achieve cycling capacities around 1300 mAh g^{-1} [1]. However, the production of nanostructures often requires complicated methods as well as the use of hazardous chemicals. A more sustainable way to achieve similar structures may be to benefit from the fact that SiO₂ is one of the biominerals that can be produced by organisms (biosilica). This is for example widely observed in diatoms, a type of unicellular photosynthetic microalgae. There are more than 100,000 estimated diatom species of varying size (from 2 µm to 2 mm) and shape, each of them with a complex hierarchical architecture from nano- to macroscale. Due to the above-mentioned challenge with volume expansion of lithiated Si, one could hypothesize that when using diatoms in Li-ion batteries the size and structure of the diatoms could have a major influence on the electrochemical performance. Single-cultured diatoms gives insight into which parameters that are the most crucial for optimized battery performance.

In this poster we will present initial work on Li-ion battery anodes based on single-cultured diatom SiO_2 material with focus on X-ray photoelectron spectroscopy (XPS) characterization. We will also discuss the methodology and challenges to obtain reliable XPS data in these kinds of systems.



Figure 1. (a) Si K-edge fluorescence yield absorption spectra for SPA (single-cultured diatom type 1) and material references. (b) O 1s X-ray photoelectron spectra and (c) Si 2p spectra for SPA, SPB (single-cultured diatom type 2), DE (diatomaceous earth) and SiO₂ reference (normalized and energy shifted with reference to O 1s main peak).

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Investigating the pH buffering effects of PAA as a binder for the aqueous processing of LNMO

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Due to high energy densities and the absence of cobalt within its structure lithium nickel manganese oxide (LNMO) makes for an interesting alternative cathode material for electric vehicle applications of the future. While the production of LNMO electrodes typically involves the use of a polyvinylidene fluoride (PVDF) binder along with n-methyl-2-pyrrolidone (NMP) solvent, the ability to aqueously prepare LNMO would reduce battery processing costs and improve sustainability. However, the aqueous processing of oxide based Li-ion cathodes remains challenging due to Li⁺/H⁺ proton exchange which results in pH increases (> 10) and corrosion of the aluminium current collector. The resulting electrodes see reduced capacities and a worsened electrochemical performance. In this study, we investigate the stability of LNMO in water processible polyacrylic acid (PAA)-based binders as a function of pH. Starting from the free-acid, the pH of the PAA is controlled by reacting it with either sodium or lithium salts to form NaPAA and LiPAA in pHs ranging from 5 to 8. The binders are evaluated on their ability to buffer, and hence control, the pH during aqueous processing of LNMO. Furthermore, ICP-MS was used to characterize the amount of transition metal leaching of LNMO at the different binder pHs. Finally, the electrochemical performance of the prepared electrodes was evaluated in full-cells and benchmarked against PVDF prepared samples.



CARBONATE-BASED SINGLE-ION POLYMER ELECTROLYTES FOR LITHIUM BATTERIES

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Lithium-ion batteries (LIBs) stand as the predominant technology in electric vehicle power units due to their superior energy densities and extended lifespans relative to alternative battery technologies. Despite their advantages, LIBs face safety concerns due to the high flammability of the liquid electrolyte and the growth of lithium dendrites, which can lead to short circuits.^[1]

One of the most promising strategies to overcome these issues is the replacement of liquid electrolytes by solid-state materials. Within this context, **solid-state polymer electrolytes (SPEs)** have garnered significant interest over the last two decades. SPEs are characterized by their low flammability, enhanced thermal stability and are not prone to leakage. ^[2] Their distinct processability and advantageous interface properties also make them compelling candidates for solid electrolytes. Moreover, transitioning to all-solid-state batteries would elevate Li-ion battery energy densities by using **Li-metal as a negative electrode**, while avoiding dendrite formation. ^[1]

State-of-the-art SPEs primarily utilize polyethylene oxide (PEO) and its derivatives. However, these systems face limitations due to their low Li⁺ conductivities at ambient temperatures and their compromised electrochemical stability at high voltages (> 4.6 V). ^[3] To overcome these limitations, research has extended to other polymer families. Notably, **polycarbonate-based electrolytes** have demonstrated **stabilities up to 5V** ^[4] and efficient Li⁺ mobility ($t_{Li+} \approx 0.8$) ^[5]. To further improve the transport number (t_{Li+}), the **single-ion strategy** involves grafting the Li⁺ counter-ion to the polymer chains through covalent bonds. This approach aims to reduce or eliminate the mobility of anions, which can lead to cell polarization and, consequently, the dendritic growth of Li-metal. ^[6]

Our research aims to develop high-voltage SPEs that enable operating with NMC cathodes, preventing lithium dendrite formation, and achieving satisfactory ionic conductivities. We are investigating the synthesis of single-ion carbonate monomers and their ring-opening polymerization (ROP) to forge an **innovative single-ion polymer electrolyte** (SIPE) architecture (Figure 1). This SIPE design allows carbonate functions, responsible for Li+ conduction, and single-ion functions, with weakly coordinating lithium salts, to be very close. It could therefore achieve promising conductivity.



Figure 1. From carbonate-based single-ion polymer electrolyte to functional Li-ion battery

In this poster presentation, we will present our latest results on the synthesis and the polymerization of organic carbonate units functionalized with a **novel fluorine-free cyano-based lithium salt**, as unprecedented monomers for the design of SIPEs.

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Solid state fluorine-free polymer electrolytes for lithium-metal batteries

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Fluorine-free salts may be an alternative to common fluorinated salts that negatively affect the cost, electrolyte safety by the formation of corrosive and toxic compounds and environmental friendliness in lithium metal batteries.¹

Aromatic anions with cyanide substituents are known as a possible alternative to common Li salts due to its high capacity to delocalize negative charges, high ionic conductivity, high thermal stability, and broad electrochemical stability window.²

Moreover, it is crucial that new generation batteries meet the requirements of today's industry in terms of energy density. One promising alternative is the use of lithium metal as anode material owing to its high specific capacity (3860 mAh·g⁻¹). Nevertheless, the use of lithium metal as anode material requires moving to solid state electrolytes, such as polymer electrolytes, due to their incompatibility with highly flammable commercial liquid electrolytes.³

This work shows that blends of fluorine-free salts and poly(ethylene oxide), PEO, may be a viable alternative to solid-state fluorine-based electrolytes due to their good electrochemical and mechanical properties. Three salts were characterized for this purpose; lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolate (LiPDI), lithium 4,5-dicyano-2-(trifluoromethyl)imidazolate (LiTDI) and lithium 2,4,5-tricyanoimidazol-1-ide (LiTIM). The first two, fluorinated, were analyzed in order to compare them with the LiTIM salt, fluorine-free, to see the impact of fluorine on the prepared electrolytes.



Figure 1. Chemical structure of the lithium salts used for polymer electrolytes; lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolate (LiPDI), lithium 4,5-dicyano-2-(trifluoromethyl)imidazolate (LiTDI) and lithium 2,4,5-tricyanoimidazol-1-ide (LiTIM)

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BASE – the Swedish Battery Excellence Competence Center

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Batteries Sweden, BASE¹, formed in 2020, is the Swedish academia-industry competence center that focus on excellent research to support the rapidly growing battery-relevant industry, across the entire battery value chain. The long-term vision of BASE is to address the energy storage challenges associated with the transition to a fossil-free society. At the core of this endeavor is the creation of new knowledge and development of new technology. The center is financed by three academic partners (Uppsala University, Royal Institute of Technology and Chalmers University of Technology), the Research Institutes of Sweden (RISE) and the Swedish Agency for Innovation (Vinnova) – alongside no less than 18 industrial partners. Through innovation-driven research projects that foster collaboration between academia and companies, BASE establishes a stable platform for highly relevant battery research in Sweden. The center aims to develop materials, components, and full-scale devices for future generations of ultra-high-performance batteries. BASE covers the full value chain of batteries: raw materials, materials refinement, cell production, component development, modelling and battery control, application of batteries and recycling.

Today the BASE activities revolve around three thematic areas: "New and emerging cell concepts", "Modelling and Characterization hand-in-hand" and "The smart battery cell". Additionally, three cross-cutting activities (Gender, Education, and Sustainability) are central to BASE. We here highlight two collaboration projects and one cross-cutting activity.

Non-flammable liquid electrolytes for safer batteries²

Laptops, cell phones and electric vehicles catching fire have been reported several times in the past, and therefore industry has spent a lot of effort to improve the safety of batteries. While solid electrolytes have attracted attention in recent years, partly for safety promises, they have other limitations. In contrast, we here aim to develop non-flammable liquid electrolytes for lithium and sodium batteries. The project targets electrolytes based on binary solvent systems that do not mix. The BASE industrial partner Altris explore these systems – and other liquid electrolytes – for sodium-ion batteries.

Mechanical modelling and characterization of batteries^{3,4}

There exists an interplay between the mechanical properties of different battery components and the resulting cell performance, which has so far not been extensively explored. Targeting these issues by modelling tools – combining mechanical and electrochemical modelling – is highly relevant for materials, component and cell developers, and for industries with key competences in modelling. This project aims to gain a better understanding of the impact of mechanical instabilities and microstructural heterogeneities in electrode materials on battery performance. To achieve this, a numerical 3D framework is developed that considers the coupling between multi-physics battery phenomena and can simulate stress and fracture in battery materials under varying operating conditions.

Gender perspectives in BASE⁵

People will do the work - work that leads to the production of new knowledge, provides technical solutions, and involves continuous work with problem solving. For BASE to be as successful as it can be people will need to collaborate and interact, and their competences and skills must be valued and used in the best possible way. In that respect, gender issues are, and will be, of importance. In this project, the focus is not on representation, instead, the ambition is to create awareness of the processes that lead to imbalance and which often can be found in unawareness, attitudes and culture.

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COLLABAT: COLLAborative BATtery Cluster

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COLLABAT cluster (Collaborative Battery) aims at virtually clustering independent R&D projects on electric battery system developments jointly addressing the technical scope areas of the LC-BAT-10 topic. Through the cluster, the main objective of COLLABAT is to achieve a higher level of impact beyond project level, contributing more strongly to the adoption of the next generation of electro mobility in Europe by 2030, in alignment with the targets and timeline defined in the ERTRAC electrification roadmap.

The COLLABAT cluster's project coordinators and dissemination managers trust that together, they will boost awareness regarding the research outcomes and promote technology transfer across relevant stakeholders, such as academia, vehicle OEMs and the entire Electric Vehicle's battery supply chain.

Cluster objectives:

- Engage with a larger EV stakeholder community in EU and abroad to present joint ideas developed.
- Independent platform for industry to discuss & propose common producers, standards and methods for testing and evaluation of EV battery packs.
- Explore synergies between cluster projects for common dissemination in external events.
- Collaborate in organising project events on specific topics related to battery packs for BEV and PHEV.
- Maximise dissemination via combining efforts for joint publications in journals and magazines, as well as creating dedicated material at cluster level.

Cluster projects:

- ALBATROSS (Advanced Light-weight BATteRy systems Optimized for fast charging, Safety, and Second-life): Development of an integrated approach based on smart batteries combined with lightweight designs. Using innovative cooling technologies, we will achieve pack temperature range 5-40°C. The project is addressing the needs of European Electric and Hybrid-Electric passenger vehicle market by overcoming driver concerns relating to battery range and anxiety, cost, long-term reliability and excessive charging times. [1]
- HELIOS (High-pErformance moduLar battery packs for sustalnable urban electrOmobility Services): Integration of innovative circular designs, materials and technologies in the field of Li-ion batteries to improve the charging capabilities, overall performance and cost-effectiveness of electric battery packs used in electric vehicles. The HELIOS project aims at assessing the effectiveness, circularity and sustainability of urban mobility models that are based on the use of EV fleets, such as car-sharing and e-busses fleet. [2]
- LIBERTY (Lightweight Battery System for Extended Range at Improved Safety): overall target is upgrading EV battery performance, safety and lifetime from a lifecycle and sustainability point of view. The key objectives of LIBERTY are to achieve a range of at least 500 km on a fully charged battery pack, halved charging times, an ultimate safe battery system, a long battery lifetime of over 300,000 km for first life, the ability to reuse the battery pack for second life applications and sustainability over the battery pack's entire life cycle. [3]
- MARBEL (Manufacturing and assembly of modular and reusable EVbattery for environment-friendly and lightweight mobility): Developing an innovative and competitive lightweight battery with the objective to accelerate the mass market take-up of electric and hybrid vehicles. The MARBEL project focuses on the need for fast charging and long-lasting batteries to boost end-user demands, while applying high modularity and easy assembly and developing novel testing methodologies. [4]

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Salt Effects on the Mechanical Properties of Ionic Conductive Polymer: A Molecular Dynamics Study

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Self-healing polymers have caught much attention for potential applications in electrochemical energy storage systems because of their superior mechanical properties. However, unlike ion transport properties where much has been understood recently with the aid of atomistic simulations [1-3], the understanding of salt effects on mechanical properties of polymer electrolytes at the atomistic level remains elusive. A model ionic conductive polymer system, i.e., poly(ethylene oxide)-LiTFSI, was used to study the impact of salt concentrations on mechanical properties, including different types of elastic moduli and the viscoelasticity with both nonequilibrium and equilibrium molecular dynamics simulations. We found an encouragingly good agreement between experiments and simulations regarding Young's modulus, bulk modulus, and viscosity. To characterize the self-healing capabilities of ionic conductive polymer, the elastic restoration time is defined as time required for the system to restore its equilibrium density after expansion under a tensile strain and shown to correlate positively with the mechanical properties (Figure 1). We identified an intermediate salt concentration at which the system shows high ionic conductivity, high Young's modulus, and short elastic restoration time. In addition, we applied this protocol to study the mechanical deterioration of the h-bonded UPy end group PCL-PTMC polymers with addition of different salts. This study laid the groundwork for investigating ionic conductive polymer binders with self-healing functionality from molecular dynamics simulations [4].



Figure 1. Correlations between the elastic restoration time at the near zero strain rate and the near zero-strain rate Young's modulus. The dashed line with arrow heads indicate the direction where the salt concentration increases.

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Aero-fit Structural Batteries: Advantages and Challenges

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More-electric, hybrid-electric and all-electric aircraft concepts are key enablers in tackling the challenge of reducing greenhouse gas emissions from aviation making use of electrical energy to enable highly energy-efficient electric drive trains and distributed electric propulsion concepts. However, the limited energy and power density of current battery technologies, leading to a substantial weight penalty is a major limiting factor for the large-scale introduction of electrified aircraft. LiB currently is reaching its theoretical limits and will remain the dominant technology in the upcoming years. One possible alternative to conventional battery systems installed in aircraft are multifunctional load-bearing structures capable of storing electrical energy, also known as structural batteries (SBs), as they offer highest degree of integration enabling effective energy densities (at integration level) that double or triple the cell level GED.

AIT is developing structural battery technology specifically for aeronautical applications in the EU-funded CS2 SOLIFLY and HE MATISSE projects. A structural electrochemistry with non-flammable thermoplast-ionic liquid structural electrolyte and high-energy composite electrodes was developed that is scalable from small lab to pilot line [1]. Two SB cell concepts were developed, AIT's thin multilayer laminate SB cells [1] and UNIVIE's coated carbon fibre concept [2]. Their integration into solid laminate carbon-fibre composite structures was studied to maintain the high mechanical strength of the monofunctional baseline structure [3].

In the SOLIFLY project, the AIT SB technology was successfully demonstrated in the first high-strength aeronautic-grade multifunctional stiffened panel. The panel integrated 20 AIT SB cells in its skin with minimum weight impact without change of its global rigidity under high compression loading of up to 18 tons. 80% of the SB cells were functional after autoclave curing and none of the controlled cells failed during the testing.

One important factor for future introduction of SB technology is its scalability. SOLIFLY has assessed the manufacturability of the two SB cell concepts against SotA battery cell production [4], see Fig. 1, identifying the process steps in conventional battery cell production that are already available with high transferability (green), low to mid transferability (yellow) and processes that not yet available (red), proving the scalability of the AIT SB approach.



Figure 1. Manufacturability Assessment [4].

This poster discusses the progress made in structural batteries for aviation in current EU projects, their potential and challenges for their maturation.

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Non-Flammable, Fluorine-Free Sodium-Ion Batteries Through Electrolyte Engineering

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An ever-growing demand for energy storage within the transport and electricity sectors has highlighted potential resource constraints for Li-ion batteries (LIBs), in particular with respect to Li.^{[1]-[3]} Sodium-ion batteries (SIBs) hold promise as a complementary technology to LIBs, particularly for stationary energy storage.^[4] To be competitive with LIBs, SIBs need to reach parity in cost and in capacity density.^{[5]-[7]} SIBs can however offer more than simply a cost competitive option to LIBs, with other potential strengths being found with respect to both safety and sustainability. For example, Prussian white cathodes are based on abundant elements and can sidestep sustainability concerns associated with state-of-the-art LIB cathodes.^[3] However, to address safety concerns of LIBs it is impossible to ignore the electrolyte. State of the art electrolyte in LIBs is both toxic and flammable, and if the Na analogue is used in SIBs these undesirable traits are also brought to SIBs.

Recently Mogensen et al.^[8] proposed sodium bis(oxalato)borate (NaBOB) in trimethyl phosphate (TMP) electrolyte that overcame the flammability concerns of NaPF₆ in carbonate electrolytes. In addition to non-flammability, the use of NaBOB instead of NaPF₆ (along with CMC binder rather than PVDF) meant the battery system was halogen free. Switching from TMP to triethyl phosphate (TEP) allowed for a relatively less-toxic electrolyte (NaBOB and TEP are listed by the European Chemical Agency as 'harmful if swallowed' in comparison to 'harmful if swallowed, in contact with skin or inhaled' for NaPF₆ in carbonates, although limited research has been conducted on the toxicity of NaBOB and so this should be received with limited certainty) without sacrificing cell performance.^[9]

Despite promise, hurdles remain for NaBOB in organophosphate electrolytes. Principal amongst these has been: (i) the poor solubility of NaBOB in most solvents, and (ii) the difficulties transferring promising low mass-loading full cell results to higher mass-loading full cells. This work looks at a range of approaches in tackling these challenges, delving into the underlying cause of cell failure in NaBOB in TEP and attempting to remedy these problems through two electrolyte engineering approaches. Firstly, cosolvents have been investigated as a means to increase the solubility on NaBOB, and secondly, formation protocols have been refined for NaBOB in TEP. Such interventions allow for an almost doubling of the concentration of NaBOB at the point of saturation without sacrificing flammability, and provide an industry-applicable route to alleviating poor cycling performance.



Figure 1. Prospective cosolvents for NaBOB with their saturation point and corresponding ionic conductivities (left), and refined formation protocols (middle, right) for NaBOB + TEP.

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HIGH ENTROPY PHOSPHIDES AS BIFUNCTIONAL OXYGEN ELECTROCATALYSTS FOR RECHARGEABLE ZN-AIR BATTERIES

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Rationally designed high-entropy materials (HEMs) that fully utilize multi-metals as active sites are regarded as potential efficient bifunctional oxygen redox catalysts for zinc air batteries^[1-3]. Herein, FeCoNiPdWP high entropy phosphides (HEPs) nanoparticles are synthesized through a low-temperature colloidal method. Such HEPs show high entropy properties, synergistic effect, and electronic modulation, leading to superior oxygen evolution/reduction reactions (OER/ORR) performance. The individual elements roles and switchable active sites in HEPs for OER/ORR are detailed. HEPs exhibit an extremely low OER overpotential of 227 mV at 10 mA/cm², attributed to the reconstructed FeCoNiPdW high entropy oxyhydroxide with high metal oxidation states of Fe/Co/Ni as the active sites, together with an electronic modulation by Pd and W to optimize the adsorption of the oxygen intermediates and decrease the reaction energy barriers. Besides, Pd is found to be the most active element among the five metals in ORR. The strong d-d orbital coupling of different elements, especially Pd, Co, and W, in the reconstructed catalyst fine-tunes ORR electron transfer pathways, delivering a ORR half-wave potential of 0.81 V with a pure four-electron reduction mechanism. Aqueous zinc-air battery based on HEPs exhibits a superior specific capacity of 886 mAh/g_{Zn}, and excellent stability for over 700 h of continuous operation. This work provides a platform to understand the role of each element in HEMs, which will guide the design and engineering of the next generation of bifunctional oxygen catalysis.

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The circular economic system for critical raw materials: a pathway towards a sustainable energy future

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The average global temperature on Earth has increased significantly in the past decades [1]. Responsible for the temperature rise is human activity and especially caused greenhouse gas emissions [2]. Globally, one-quarter of total greenhouse gas emissions are generated by road transportations, which use fossil fuels as an energy source [3]. Efforts and activities are being carried out to combat the negative consequences of global warming and climate change. Battery electric vehicles (BEVs) and solar and wind energy, using potentially renewable energy, have drawn much attention from industries and companies toward a more sustainable energy future [4]. This cause a huge demand in minerals and metals for batteries in mobile and stationary and energy transition [5,6]. But, critical raw material (CRM) mined and applied in batteries have significant environmental, economic, social, and ethical impacts, especially for the extraction stage. For example, approximately 1.5 million tons of carbon dioxide equivalent (CO₂e) can be attributed to the mining of Cobalt. For lithium extracted from hard rock mines it is estimated that for every ton of lithium extracted from hard rock mines, 15 tons of CO₂ are emitted into the air. In the case of ethical and social challenges, human rights violations are a major concern. Around 70% of Cobalt, a key component in lithium-ion batteries, is mined in the Democratic Republic of Congo (DRC). The mining workforce there often includes children and families, and the conditions are frequently unsafe. Malpede (2022), for example, investigated the "dark side" of mining raw materials for batteries in the Democratic Republic of Congo (DRC), which provides 70% of Cobalt globally [7]. Cobalt is an essential part of a battery's electrode for most of the presently used lithium-ion batteries, e.g. NMC, NCA Only one important Li based battery system use no Co (and Ni), which is called lithium -iron- phosphate (LFP). Malpede also concluded that children illegally employed in cobalt mining suffered from lower cognitive and physical development than their peers in areas that do not mine cobalt [7]. More notably, since several raw materials are found in a particular country, several governments and BEV companies have expressed concern regarding the geopolitical consequences associated with the supply chain of battery components. To address these problems related to the chain supply, a circular economy can keep the raw materials within a closed loop economy and potentially reduce carbon footprint and external costs. The circular economy is a system of production and consumption where products and materials are designed and managed with a focus on reducing, reusing, recycling, and recovering them [8]. By 2040, the amount of copper, lithium, nickel, and cobalt recovered from waste batteries can reduce minerals' comprehensive primary supply demand by about 8 % [9]. The spent LIBs recycling is vital for environmental protection and the reuse of valuable resources. Considering the previously mentioned significance of the circular economy, this approach could lead to some issues. The sustainability assessment methodology, including life cycle assessment (LCA), Ethical frameworks, and life cycle social assessment (LCSA), can contribute to analyze and potentially minimizing the impacts of products considering a circular economy by identifying hotspots and dilemmas. Therefore, this content concludes although a various effort has been made regarding the sustainability of CRM utilized in energy systems, there needs to be more value chain sustainability, such as ethical issues, e.g., environmental pollution, forced child labor, and human rights issues. The conclusion is drawn that sustainable energyhas been realized, considering all facets of sustainability.

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Innovative Anode Solutions to Enhance Sodium-Ion Battery Performance

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In this work, we propose strategies that include 2D heterostructures, strain, surface modifications, and optimized electrode geometry to improve the anode's mechanical stability and electrochemical performance and decrease the time to charge sodium-ion battery technology (SIB). The results of my innovative strained heterostructure based on graphene demonstrate significant improvements in the rate performance of graphene anodes using the proposed heterostructure and surface modification strategies and further enhancement of their electrochemical properties. The theoretical calculations demonstrated a considerably low energy barrier of 0.019 eV, which facilitated a more rapid diffusion of the sodium-ion as well as more efficient charge transport kinetics during the charging process. Our results also show that this heterogeneous structure can provide a higher theoretical storage capacity (590 mA/g) than phosphorene (433 mAh/g) and graphite (375 mAh/g)¹. Our study offers new insights into the design of high-performance energy storage devices, and the research highlights the importance of engineered materials and a well-thought-out design of heterostructures to enhance the performance of batteries. [1].



Figure 1. Innovative sodium-ion battery.

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DEVELOPMENT OF THIN-LAYERED GAS SENSORS FOR BATTERY CELL MONITORING

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Formation of gaseous side products caused on cell degradation in LIBs has been significantly responsible for the performance decay and safety issues and thus, has been intensively studied in recent years [1,2]. The degradation leading to gas generation during battery operation is related to the side reactions between electrode material and electrolyte and thus, strongly dependent on the type of anode, cathode and electrolyte used to manufacture the battery [1]. According to the experimental studies CO and CO₂ gases are released on cathode side during the cycling of lithium-ion batteries, while C_2H_2 , CO and H_2 gases production occurs on anode side [3]. In general, four main sources for the release of gaseous substances inside the electrochemical cell can be distinguished: (1) CO and CO₂ evolution due to the oxidation of the organic electrolyte; (2) CO and O₂ formation as a result of electrochemical decomposition of residual carbonate species (particularly in the case of Ni-rich NMC cathode powders in the initial charge cycle); (3) O₂ release due to the structural instability of NMC cathode at high states of charge; (4) H₂ formation due to reduction of residual moisture in the cell and electrochemical decomposition of the carbonate electrolyte [2,3].

The investigations of the present work are done in the frame of PHOENIX project (Horizon Europe under the grant agreement No. 101103702) aiming to develop initially highly sensitive thin-layered metal oxide-based sensors for hydrogen detection and for integration inside the battery cell. For this purpose, sensors consisting of top-bottom electrode (TBE) configuration and a Cr-doped TiO₂ sensing layer were fabricated in three steps: (1) deposition of bottom Pt electrodes on flexible PI film substrate via sputter coater (BALTEC, Hallbergmoos, Germany); (2) sputtering of Cr-TiO₂ sensing layer using Z400 magnetron-sputtering equipment (SVS, Gilching, Germany); (3) deposition of top Pt electrodes as cross-bar batter to the bottom Pt electrodes (Fig.1a). Gas sensing tests were performed with the sensor and catalyst characterization unit SESAM, which contains 8-channel flow controller from MKS Instruments GmbH, a Quartz inlay gas mixing and heating chamber in CARBOLITE tube furnace, and Keithley 2635A Source meter DC-measurement unit. All setup instruments were controlled with LabVIEW program. Gas sensing measurements were performed towards different H₂ concentration (600-1000 ppm) at different temperature (RT, 40°C, 60°C) with a constant 1 V bias. Almost no response was seen at room temperature in all range of H₂ concentration, while the increase of working temperature to 40°C led to a good sensor response towards the lowest measured H₂ concentration of 600 ppm (Fig. 1b).



Figure 1. (a) TBE sensor on flexible PI film substrate; (b) Dynamic sensor responses towards different H₂ concentrations at different temperatures.

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Development and characterization of new families of organic alkaline salts for Charge Transfer Complexes in battery applications

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In the current climate context, different strategies were set-up to generate and store energy in a more responsible way, specifically in our transition away from thermic vehicles. To this day, the golden standard in the industry for alternative solutions of electricity storage for transportation remains lithium-ion batteries.^[1] However, the rising demand for the mass production of portable electronic devices and electric vehicles now leads to new expectations.^[2] Research is now focusing on the development of All-Solid-Sate Batteries expected to improve safety^[3] while ensuring higher energy densities.^[4]

Polymer-based electrolytes have gathered great attention since the first report of lithium ion conductivity in poly(ethylene oxide) in the 1970s. More recently, organic charge-transfer complexes (CTCs) have been reported with promising super-ionic conductivity in the solid-state at room temperature by associating a donor/acceptor organic couple with a lithium salt.^[5] These specific chemical structures hold a great potential to tune their electrochemical properties by changing the different partners (acceptor, donor and Li salt) and their molar ratios in the CTC.



Example of the composition of the CTCs presented in this work, a picture of the CTC electrolyte and Nyquist plot at RT and 80°C of one of the most promising CTC

In this work, we synthesized two new families of organic alkaline salts (Li, Na, K) derived from the aromatic unit of chloranil, frequently used as an acceptor in CTC species. One family holds anionic trifluoromethanesulfonamide moieties, used as mimics of the LiTFSI salt. The other family is functionalized by malononitrile functional groups to obtain fluorine-free compounds as an answer for European governmental restrictions on the use of polyfluoroalkyl substances (PFAS).

lonic conduction properties of these CTCs were measured in standard battery applications, including in liquid, gel and solid electrolytes. Finally, we used them to develop charge-transfer complexes with different donor partners and compared their ionic conductivities to the state-of the art CTC electrolytes.

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An affordable redox flow battery based on zinc-air chemistry

As societies around the world are increasing their renewable energy production, the intermittent nature of renewable electricity becomes an increasing problem for grid operators. Chemical batteries are the preferred technology for short- and medium term storage of renewable electricity. Since batteries do not inherently add value to electricity, the price of storage needs to be as low as possible (under €0.25 per kWh). Current matured battery chemistries are to expensive for grid-scale applications. Therefore, the Rezilient program is developing a zinc-air redox flow battery. This battery will consist only of cheap and non-critical elements. In our research we tackle several problems, with the goal of producing a prototype. We investigate methods to increase the stability of metallic zinc that hinder the formation of dendrites and hydrogen. Also, the oxygen reduction/evolution will need to be catalysed by cheap materials. Other aspects, like flow dynamics and reaction kinetics are studied.



ELMO-LION: Educational Learning Modules on Li-ion Batteries. Li-ion battery course and summer school for PhD students

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ELMO-LION is a new European battery technology and innovation 6 ETCS PhD course and a Summer School co-funded by EIT RawMaterials. Course contains three modules: the first module "Online Lectures" includes 8 lectures for 2 hours each provided by famous experts of battery area. Lectures are related to synthesis of the battery materials, spectroscopic study, first principles modelling, diagnostic and operation, reuse and recycling, battery market. For the second module "Project Work", 10 topics for projects are chosen from actual needs of industrial partners. Students should prepare ideas how to solve provided cases analyzing available literature sources and own ideas. Work will be carried out under supervision of mentors and proceeded in remote format. Discussion about given case should be written as a report. The third module "Summer school" will take place in Padova, Italy for 5 days from Monday 29th of July to Friday 2nd of August. Students will participate in lectures and seminars from industrial and academy partners, study how to apply proposal for Startup funding. Also, students should develop projects under industrial and academic supervising. Price for module "Online Lectures" is $50 \notin$ and it bring 2 credits. Price for module "Project Work" is $50 \notin$ and it bring 2 credits. Price for module "Summer School" is 300 € and it bring 2 credits. It includes all summer school activities (lectures, seminars, project work, ELMO-LION dinner), accommodation for 4 nights and catering. Price for the whole course is 350 € and it bring 6 credits.

ELMO-LION partners are Aalto University, EMPA, Politechnico di Milano, University of Padova, Delft University of Technology, University of Eastern Finland, University of Helsinki, University of Oulu, Centro Ricerche Fiat, Metso Outotec, LUT University. More information: https://elmo-lion.com/



Figure 1. ELMO-LION logo (left) and QR code (right).



Elucidating the performance of non-flammable and non-fluorinated electrolytes for Na-ion batteries

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Safety of ion batteries, Li-ion, Na-ion and other chemistries, is a topic concerning closely both the producers and the consumers. One of the biggest contributors to the battery safety is the electrolyte. In Li-ion batteries, flammable carbonate-based electrolyte solutions are generally used, and due to the similar operating principle of Na and Li-ion batteries, carbonate solutions have also been utilized in Na-ion batteries. When that is combined with fluorine-containing salts (e.g. PF₆-anion), the safety risk and the environmental impact of these electrolyte solutions are considerable. While these systems are already very established for Li-ion, for Na-ion batteries it is not yet as clear whether this is the optimal electrolyte composition as there has been less research on them. In this work, the electrolyte investigation is focused on trying to find both non-flammable and non-fluorinated electrolyte combinations. Based on the work by Colbin [1] and Welch [2] et. al, new additives are tested in an electrolyte containing sodium bis(oxalate)borate (NaBOB) salt dissolved in triethyl phosphate (TEP) that has shown promising properties, e.g. the ionic conductivity of 5 mS/cm at room temperature. The electrochemical properties of the electrolytes are tested and compared to their structural changes to understand the irreversible reactions and capacity losses in the system.

The initial cycling results of 0.35M NaBOB-TEP solution with different additives are presented in Figure 1. Phosphorous-containing additives were selected as a focus group due to the previous initial good results of some phosphorous containing additives in the work by Welch et. al. [2] The purpose was to see how different phosphorus compounds affect the cycling performance and what kind of effects the valence state of phosphorus and sub groups bonded to it have. The results indicate that both the previously reported Prop-1-ene-1,3-sultone (PES) and 1,3,2-dioxathiolane-2,2-dioxide (DTD) improve the performance of NaBOB-TEP electrolyte. In addition, Butyl sultone (BS) seems to have a similar effect while methylene methanedisulfonate (MMDS) seems to quickly decrease the performance. The poor performance of MMDS additive is related to the two phosphorous atoms in its structure, leading to different decomposition products during cycling. The results also indicate that the additives with only one single-bonded oxygen attached to the phosphorous (PES and BS) form more stable decomposition products than additives with two.



Figure 1. a) Structures of the additives: 1. PES, 2. DTD, 3. BS, 4. MMDS. b) The cycling stability of several NaBOB-TEP electrolytes with different additives. Prussian white is used as a positive electrode and hard carbon as a negative electrode in the cell. The cycling is done in pouch cells in the voltage range of 1.3–3.8 V.

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Surface Modification of LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC 811) electrode to form a stable conductive interface

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In the present day, the predominant battery technologies still rely on conventional liquid electrolyte systems, presenting notable safety challenges due to the chemical instability and flammability inherent in these liquids. Solid-state batteries promise a more robust alternative, effectively mitigating the risks associated with flammability and leakage, thus markedly enhancing the safety profile of battery cells. All solid-state batteries (ASSBs) are recognized as the future of battery technology, as they address many of the existing problems and constraints of conventional Li-ion technology. In this context, the objective of the AM4BAT EU project is to develop an all-solid-state Li/NMC cell. To accomplish this goal, it is essential to develop stable interfaces between the solid materials. In this study, we tested several routes to protect the surface of NMC to stabilize its interface with electrolyte. The reported study deals with NMC testing in conventional liquid electrolyte.

One of tested coating methods proved to significantly improve the rate performance and cycling stability. To reveal the structure of coating and mechanisms of its protection, NMC 811 cathode materials with and without coating layer, before and after cycling were analyzed using transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). The analyses revealed a thinner cathode electrolyte interphase (CEI) layer in the modified NMC electrode, elucidating its superior electrochemical performance.

The protected NMC 811 material will be scaled up and used in the AM4BAT final process for solid cells development.

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A post-mortem inspection of aged solid polymer NMC811/Lithium metal cells

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All solid state batteries are currently presented as future technology to replace conventional lithium ion cells as they could outperform them in term of energy density and downsizing. Nevertheless, in depth understanding of the formation and evolution of the solid interphases upon cycling is still needed to optimize these systems [1]. Aged single-layer solid polymer NMC811/Lithium cells were further analyzed by a post mortem inspection to identify their main degradation mechanisms. Neat cross-sections of solid stacks were successfully obtained, which enables the direct observation and localized fine characterization of the interphases (SEM-EDX, Raman) [2]. This post-mortem analysis, coupled with operando EIS, provides new insights on the electrochemical deterioration of solid polymer NMC811/Lithium metal batteries.



Post-mortem analysis on cycled solid stacks

c)



Figure 1. Electrochemical characterization and post-mortem analysis of a solid polymer NMC811/Li battery (2.85 mAh/cm², 2.54 g/cm³): a) Capacity and b) cell resistance (at OCV) evolutions depending on the state of health (SoH), c) SEM observation (x500) of the cathode/solid electrolyte interphase

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Modeling Li-ion battery electrodes accounting for microstructure properties: The Newman's model revisited

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Volume-averaged treatment of microscopic transport and reaction equations can be performed to obtain a model in which the solid and fluid phases are conceived as a pseudo-continuum. The most established lithium-ion battery (LIB) porous-based model is the Newman's pseudo-two-dimensional (P2D) model used as a good trade-off between numerical computational cost and physics precision. However, this model does not resolve the local fluctuations of physical quantities on the microstructure and can give inaccurate results especially at high C-rate. In this work, we revisit the P2D model by applying the method of volume averaging [1] to mass and charge transport equations of LIB microstructure models. The outcome is a non-classical homogenized model where the effective properties do not only depend on geometry, but are shown to be functions of the local current density [2]. In this way, the concept of tortuosity is discussed and revisited. The model reduces to the classical P2D at low C-rate, but extents the validity range of the P2D at high C-rate for complex microstructures. Moreover, the new model allows to reconstruct the local fluctuations from the averaged variables, whereas this information is not available from the classical P2D model.



Figure 1. (a) Lithium concentration in the electrolyte during lithiation from a simulation on a real 2D microstructure of NMC. The simulations results at various C-rate are compared to the classical P2D (b) and revisited P2D (c).

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Understanding fluoride ion diffusion in BaSnF₄

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Fluoride ion batteries (FIBs) present a promising post Li-ion battery technology, but identifying solid electrolytes with high room temperature fluoride ion mobility remains a significant hurdle, hindered by a limited understanding of the fluoride ion conduction mechanism. BaSnF₄ exhibits a high ionic conductivity of 1×10^{-4} S/cm at ambient temperature, rendering it a potential solid electrolyte for FIBs. The underlying ionic conduction mechanism for BaSnF₄ and the involvements of Sn²⁺ lone pairs (LPs) in this process remain obscure. Using machine learning molecular dynamics with *ab initio* accuracy, we investigated how the Sn²⁺ ions translational motion lowers the diffusion energy landscape, enlarges the ionic conduction channel, and alters the LPs orientational dynamics, thereby increasing BaSnF₄ ionic conductivity. We demonstrated that the LPs' rotational flexibility necessitates the Sn²⁺ ions translational motion. Furthermore, we comprehensively examined the fluoride ion diffusion behavior in BaSnF₄ and found two-dimensional diffusion at Ba-Sn layers, with F⁻ ions rapidly crossing Sn-Sn layer enabled by Sn²⁺ translational motions, creating Frenkel defects in the structure. Our work elucidates the atomistic origin governing the fluoride ion conduction in fast ionic conductors and will contribute to the rational design of solid electrolytes for FIBs.



France

Surface Engineering to Stabilize High-Voltage Ni-Rich Cathodes

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Layered Ni-rich LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathode materials are increasingly recognized for their high capacity and relatively low cost in the development of next-generation lithium-ion batteries (LIBs). Notably, it is desirable to access the theoretical capacity valves through high-voltage operation to further increase the energy density of LIBs. However, the fast capacity drop is becoming the plague for its practical application due to the structural/interfacial instabilities during cycling, such as crack formation, especially when charged at high cut-off voltages (\geq 4.5 V vs. Li/Li⁺). Crucially, developing micron-sized single-crystalline Ni-rich material is an effective strategy to solve these problems owing to the intrinsic mechanical stability and good structural integrity without microcracking compared with their polycrystalline counterparts.

In order to maintain stable cathode–electrolyte interface and bulk structural integrity for the singlecrystalline NMC811 (SC-NMC811) cathode material, surface modification has been adopted as a promising way to overcome these challenges and improve the electrochemical performance of high-voltage SC-NMC cathode materials. In this study, it is demonstrated that stable cycling of the SC-NMC811 cathode materials at high voltages up to 4.7 V can be realized by tailoring a homogeneous ultrathin surface coating layer. This surface layer acts as a protective barrier, preventing direct contact between the electrolyte and active NMC811 particles, thereby mitigating undesirable side reactions and enhancing the overall electrochemical performance, especially leads to a higher reversible capacity as well as a remarkable improvement of the capacity retentions at high voltages. We will present a thorough analysis of the influence of the surface layer on the structural, interfacial, and electrochemical properties of the SC-NMC811 cathodes. Furthermore, the stabilization mechanism of the established surface layer will be explored in depth, offering critical insights into how surface modifications contribute to the advancement of high-voltage cathodes. This understanding provides valuable insights into the development of advanced LIBs with improved energy density and long cycle life.

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Developing high-performance and safe electrolyte for silicon and lithium metal batteries

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Compared with the state-of-the-art graphite anodes, silicon and lithium metal are considered as the most promising alternatives for higher energy density lithium batteries owning to their high theoretical capacity. However, significant challenges such as low coulombic efficiency, short cycle life and safety concern have seriously hindered their practical applications. [1,2] To enable the use of silicon anode, we are developing a polymer electrolyte with self-healing properties to stabilize the electrode interphase and restrain the huge volume change of silicon material. When compared with commercial carbonate liquid electrolyte with or without additives, our designed polymer electrolyte enables the NMC622//Si full cell with improved capacity retention and combustion resistance. Meanwhile, for rechargeable lithium metal batteries, our designed nonflammable electrolyte also enables the LFP//ultra-thin lithium metal ($\leq 25 \ \mu m$) with greatly extended cycling life, which delivers more than 88% capacity retention after 400 cycles. Our research paves the way for safer and more efficient lithium-ion batteries with silicon or lithium metal-based anodes, which will help to realize higher energy density and longer-lasting battery technologies.

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MODELING THE EFFECT OF SULFUR DISSOLUTION ON ELECTROLYTE RESISTANCE IN LITHIUM SULFUR BATTERIES

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Lithium-sulfur (Li-S) batteries have only recently gained interest as a promising alternative for next-generation electrochemical storage solutions, thanks to their high theoretical energy density and high specific capacity, coupled with the low cost of sulfur¹, however to fully realize this potential a profound understanding of the underlying chemistry is crucial, together with their major degradation mechanisms. Li-S batteries have intricate reaction pathways involving multiple reduction steps, as the battery during charge and discharge cycles undergoes significant volumetric and chemical transformations, posing a challenge in isolating the contribution of each individual step. Modeling is a powerful approach to accelerate the advancement of Li-S batteries on multiple fronts, providing information on their chemistry in a controlled environment and at the same time reducing both time and cost². While existing models provide qualitative descriptions of discharge voltage profiles, there are critical shortcomings that necessitate further development. As highlighted by T. Zhang et al³. in his lumped model, these models often fail to capture the evolution of electrolyte resistance and consequently underestimate its effect on the supersaturation point, which is corroborated by electrochemical impedance spectroscopy (EIS) data. During discharge, the concentration of dissolved ionic species, particularly long-chain polysulfides with high solubility in conventional electrolytes, significantly influences electrolyte viscosity. As their concentration rises, conductivity declines, leading to a more pronounced ohmic drop at the supersaturation point. Furthermore, the model developed by Zhang neglects the dissolution kinetics of sulfur from the liquid to solid phase. This omission can have a notable impact on the high-voltage plateau and the evolution of the electrolyte volume fraction, which in turn affects electrolyte conductivity. The mathematical model employs a five reaction steps for sulfur reduction and for the voltage loss both cathode and electrolyte resistance are considered, this approach makes possible to catch the voltage profile during discharge at different C-rates and to properly simulate the electrolyte resistance, in agreement with the values measured by electric impedance spectroscopy.



Figure 1. Discharge profiles at 0.08C compared to voltage drop caused by electrolyte resistance.

Acknowledgements

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³ Zhang et al., «Modeling the Voltage Loss Mechanisms in Lithium–Sulfur Cells».



¹ Manthiram, Chung, e Zu, «Lithium–Sulfur Batteries».

² Parke et al., «Progress on Continuum Modeling of Lithium–Sulfur Batteries».

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The low maturity of solid-state technology to replace flammable and toxic SoA liquid electrolytes and the need of tailor-made cell manufacturing lines hampers its commercialization. The development of cost-effective and sustainable material will draw the roadmap for solid-state batteries (SSBs). On this regard, polymer electrolytes are considered as competitive materials [1].

Poly(ethylene oxide), is the reference polymer matrix. However, the high tendency of ethylene oxidebased polymers to crystalize and their narrow electrochemical stability window (3.9 V vs. Li/Li⁺), limits their compatibility even with the standard low voltage LiFePO₄-based cathode at high temperature (>60 °C). At this temperature, the polymer is molten, and the poor mechanical integrity may suffer from several side reactions, such as lithium dendrites growth. The strategy developed in the framework of the HEU SAFELiMOVE project (Grant Agreement no. 875184) to manufacture multilayer 1 Ah solid-state batteries based on Li/NMC811 chemistry will be presented (Figure 1a), focusing on the progress made during the preparation and electrochemical properties of the ethyl oxide-based hybrid composite polymer electrolyte (HCPE) to boost the ionic conductivity without compromising the mechanical properties Figure 1b, c [2,3].



Figure 1. a) 1 Ah cell configuration and cell chemistry; b) ionic conductivity between 20 and 80 °C, as a function of the inverse of the temperature (temperature in °C in the top axis); c) stress-strain curves from tensile tests in longitudinal and transversal direction, with respect to the stretching direction of the supporting separator.

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[3] *Submitted. 2024.* N. Boaretto et al. Hybrid Ceramic Polymer Electrolytes Enabling Long Cycling in Practical 1 Ah-Class High-Voltage Solid-State Batteries with Li Metal Anode



Unveiling Ga-Based Electrodes for Next-Generation Li-ion Batteries

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The rapid advancement of energy storage technologies has made Lithium-Ion Batteries (LIBs) the top choice in commercial rechargeable systems. However, their current limitations in volume energy density and mass energy densities fail to meet the demand for storing large amounts of electric energy. Therefore, intensive research is focused on developing new battery concepts to overcome this challenge. Solid-State Batteries (SSBs) have emerged as a promising alternative to conventional LIBs due to their superior safety, energy density, and longevity.

2D materials provide numerous benefits as electrode materials for LIBs, including their large surface area, mechanical flexibility, and the ability to accommodate the insertion and extraction of Li ions during charging and discharging cycles. Among these 2D materials, Ga-based options like gallium selenide, gallium sulfide, gallium oxide, pure gallium, and its alloys stand out as promising choices for enhancing battery performance. They are redox-active and utilize a dual charge storage mechanism involving conversion reactions and alloying, leading to high theoretical capacity. Liquid Ga promotes enhanced ion diffusion [1], alleviates volume changes, and can recover contacts between electrode components during cycling, thereby guaranteeing superior cycling stability [2]. In this work, GaSe and Ga₂S₃ were used as active material in electrodes for conventional LIBs and SSBs, respectively. Their properties resulted in good electrochemical performance, high capacity and cyclic stability for the assembled batteries.

In conventional LIBs (liquid electrolyte), GaSe was combined with carbon nanotubes (CNTs) to create a high-performing free-standing composite electrode, GaSe@CNTs. The interlaminar distance of GaSe allowed excellent ionic mobility, leading to high capacities (430 mAh/g after 50 cycles at 500 mA/g). Meanwhile, the presence of CNTs provided increased flexibility, conductivity, and stability throughout cycling. To further enhance the composite's performance, a bilayer configuration GaSe@CNTs/CNTs was proposed through material engineering. This bilayer design notably improved capacity reaching to 770 mAh/g at the 50th cycle and maintaining excellent performance even after extended cycling (830 mAh/g after 200 cycles). Post-mortem analysis using Ion Beam Analysis (IBA) techniques such as Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA) confirmed enhanced Li diffusion in the electrode, supporting the improvements achieved with the new configuration (Figure 1).

Our research on SSBs focused on the fundamental electrochemical characterization of Ga_2S_3 as a redoxactive material at temperatures of 25 °C and 35 °C. Also, we investigated various strategies utilizing stack pressure to mitigate capacity fading. The most promising approach involved the formation of pure Ga within the electrode mixture at low current densities and lower stack pressure during the initial three cycles. Subsequently, the stack pressure was gradually increased from 40 MPa to 80 MPa. This strategy demonstrably preserved a capacity of around 350 mAh/g at a current density of 0.43 mA/cm².



Figure 1. Schematics of the LIB electrode configurations (composite and bilayer) with their cross-section SEM images. Galvanostatic cycling curves and RBS & NRA (inset) spectra.

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Electrochemical Impedance Spectroscopy for SoX estimation: the zBMS integration framework

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Abstract: : CSEM developed a cell management system with Electrochemical Impedance Spectroscopy (EIS) measurement capabilities for individual cells, where EIS is performed at regular time intervals. The BMS master with embedded software layer performs state estimations, as well as patented balancing functionalities [1] and periodically sends the EIS data to the cloud for state inference and model recalibration. In this poster we demonstrate the added value of EIS for State-of-Charge (SoC) [2], State-of-Health (SoH) [3] and State-of-Safety (SoS) estimation.



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Influence of Experimental Setup in the Determination of Thermal Runaway Parameters of a Li-ion Cell.

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Li-ion batteries offer many advantages, including high energy and power density, high efficiency, and a long lifetime. As a result, they are widely used in many domains such as electric transportation, portable devices, and energy storage station that stabilize renewable energy production. Despite these advantages, Li-ion batteries are not without drawbacks, and several incidents of fire have been reported in various fields, notably in energy transport and storage. These batteries can therefore be dangerous when exposed to aggressive external factors or due to manufacturing defect. All these constraints, can lead to an internal exothermic reaction between the anode, the cathode and the electrolyte, which can lead to a thermal runaway. This results a sudden energy release, flammable gases and particles release, and eventually explosion of the cell. Ultimately, thermal runaway can spread to the surrounding cells of the module or battery pack. Therefore, the safety of batteries is an essential concern for users and manufacturers. The literature review shows that numerous studies have examined the energy and mass released during thermal runaway with different test setups and operating conditions. In addition, the thermal runaway energy of Li-ion cell depends not only on the cathode chemistry or the cell characteristics, but also on the experimental setup [1]. Nevertheless, the determination of potential risks remains complex due to the diversity of data. It is important to note that, to our knowledge, no scientific paper has considered the same type of cell tested with different devices, so the impact of the test setup is unclear. This is the aim of our experimental study. A new methodology was developed to compare the influence of the experimental setup on the determination of the fundamental parameters characterizing mass and energy transfers during thermal runaway of a Li-ion cell. This work focuses on two closed-system setups: a small-scale tube calorimeter ($V \approx 0.5L$) and a large-scale vessel called volume calorimeter ($V \approx 250 L$). For both setups, the temperatures, gas volume, particle mass and energy releases obtained under different environmental conditions will be compared to understand the impact of the setup on the thermal runaway of a Li-ion cell.

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The correlation between oxygen stoichiometry and phase stability in Ni-rich layered cathodes

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In this talk, I will present the pivotal role of oxygen stoichiometry in Li1Ni0.9Mn0.05Co0.05O3 and its influence on the electronic structure and stability of the material, a key factor in advancing the functionality of Li-ion batteries for electric vehicles [1]. Focusing our discussion on Ni-rich layered cathode materials, we explore how the manipulation of oxygen vacancies facilitates Li/Ni intermixing, significantly impacting battery performance. By using sophisticated techniques such as operando X-ray diffraction, cutting-edge hard X-ray absorption spectroscopy, X-ray emission measurements, and corroborative first-principles calculations, we shed light on the atomic-level mechanisms that enhance electrochemical properties. Our results demonstrate the real-time structural transformations occurring within cathode materials during battery operation, specifically during charging and discharging cycles. This real-time insight reveals the direct impact of oxygen vacancy variations on cathode particle behavior. Through our findings, we propose that understanding the interplay between oxygen vacancies and the dynamic phase stability of Ni-rich cathodes could pave the way for designing structurally optimized Li-ion batteries for electric vehicles [2].

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Exploring the Predictive Ability of the Doyle-Fuller-Newman Model

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The Doyle-Fuller-Newman (DFN) model has emerged as the industrial and academic standard for physics-based modelling of lithium-ion battery cells, and has prevailed for roughly 50 years. Numerous studies can be found where the DFN model is validated against experimental data for cell voltage. From here, two questions arise: firstly, how well is the DFN model able to describe other variables, such as the evolution of concentration and potential profiles in active material and electrolyte? Since this data is extremely difficult to measure experimentally, this question remains relatively unanswered. In light of the absence of experimental data for these variables, some work has used the next-best substitute - direct numerical simulations (DNS) on electrode microstructures - to address this question. However, these studies have often been limited to unrealistic electrode geometries, due to their simple periodic structure or their unrepresentative size. The second question which arises is on the predictive ability of the DFN model: how well can the model predict cell behaviour, without having to rely on experimental cell-voltage data (or DNS data) for parameterisation? This is crucial question for cell design, as if the DFN model requires experimental discharge data or a detailed DNS simulation to be accurate, then one of most attractive benefits of modelling (the ability to rapidly and inexpensively screen cell configurations) has been lost. Schmidt et al. explored the predictive ability of the model, by defining parameters solely from knowledge of the electrode geometry and materials; however, this work only considered relatively thin electrodes, and a single discharge rate [1]. Tredenick et al. made an in-depth comparison of the DFN model to DNS results for thick electrodes, at multiple discharge rates [2]. But the DFN model in this work was parameterised using the DNS results, and thus the objective of the paper is not to comment on the predictive ability of the model defined a priori. The work presented here aims to address these questions, and explore how well the DFN model can predict DNS results across multiple discharge rates and temperatures for realistic electrode geometries, by using thicknesses typical for a commercial cell and including carbon binder domain (CBD) in the structure. Finally, as a perspective, the use of volume-averaging theory to derive alternative approaches to the DFN model will be discussed.

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Scalable pretreatment of Li metal anode for polymer based lithium-ion batteries

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Solid-state lithium metal batteries are promising candidates for high-energy, next-generation commercial batteries. Heterogeneous deposition and reactivity at the lithium anode and electrolyte interface limit their cyclability [1]. Adding a protection layer on top of lithium metal is an efficient way to mitigate this limitation [2]. To ensure its efficiency, a mechanical pretreatment is needed prior the protection to remove the native passivation film [3]. Hand scraping of lithium metal's native film and treatment in a glovebox under argon are the most often used process to do so, but they are not transferable to a larger scale. To enable the scaleup of lithium anode metal production, we used a scalable native film removal process in a dry room: roll pressing between two plastic liners. The obtained lithium anodes were characterized by potentiostatic electrochemical impedance spectroscopy (PEIS), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX). Their performance were tested in Li symmetric cells based on a polymer-based separator using galvanostatic cycling. Despite the reactive atmosphere of the dry room, roll pressing reduces Li symmetric cell resistance and increases their lifetime. Further work will focus on adding a tailored protection layer using liquid reactivity and upscaling the roll pressing process to a pilot scale equipment available at CEA.



Figure 1: Potentiostastic electrochemical impedance spectroscopy of Li symmetric cell composed of Li metal electrodes taken from strip prepared using different process : (blue) 300 μm thick native Li strip, (orange) and (green) Li strip roll pressed to 290 and 150 μm, (red) Li roll pressed to 150 μm with liner change at each steps and (purple), Li strip scrapped then roll pressed to 290 μm

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An Ethylene Carbonate/Propylene Carbonate Electrolyte for Silicon-Graphite/NMC811 High-Energy Lithium-Ion Battery Cells with Improved Safety and Cycle Life

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Li-ion batteries (LIBs) based on silicon-carbon composite (Si-C) and Ni-rich (NMC811) layered material have demonstrated a potential to reach high energy density requirements for energy storage tools for electric vehicles [1]. However, several challenges limit their wide commercialization. Long term cycling remains a major issue related to instability of solid electrolyte interphase (SEI) layer on the electrodes. An increased the energy density also interrogates about the safety of Si-C/NMC system. This highlights the importance of proper electrolyte formulation to improve performance and safety level of this technology, which was the goal of the present study. A possibility of using a propylene carbonate (PC)/ ethylene carbonate (EC)- based electrolyte with low vapor pressure and high flash point to improve safety performance of Si-C/NMC811 cells is reported in the present work.

A range of electrolyte compositions and additives was screened for Si-C/NMC811 system in coin cells to evaluate the electrochemical performance. The best performing electrolytes were validated in pouch cell tests. It was found that the EC/PC- based electrolyte (El-3) presents a much longer cycle life (+64%) compared to the reference EC/DEC/DMC-based electrolyte (El-0) and reaches higher accumulated discharge capacities of respectively 15164 mAh.g⁻¹ vs 10505 mAh.g⁻¹. Operando gas analysis was conducted using online electrochemical mass spectrometry (OEMS) method. The optimized electrolyte (El-3) was compared to the reference El-0 to evaluate the impact of the electrolyte composition on the gassing behavior of Si-C/NMC cell. Three cycles with different cut-off voltages were applied (two cycles in nominal conditions between 2.5V and 4.3V, one cycle in abusive conditions between 2.5V and 5V vs Li⁺/Li). The results show a significant decrease of hydrogen (-73%) and CO₂ (-19%) generation during 3 cycles for the EC/PC based electrolyte (El-3) compared to El-0 in the Figure 1 below.



Figure 1. Volume of gases H_2 (m/z=2), C_2H_4 (m/z = 26), CO (m/z = 28) and CO_2 (m/z = 44) per cycle for the reference electrolyte El-0 (a) and the optimised electrolyte El-3 (b) obtained using OEMS method.

This work demonstrates that EC/PC-based electrolyte with proper additives can be a safer alternative to classical electrolytes containing linear organic carbonates for Si-C/NMC cells. This conclusion is reinforced with accelerated rate calorimetry measurements.

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European-wide harmonized, commonly accepted and applied single life cycle assessment (LCA) approach for a zero-emission road transport system - Pre-standardizing results of the TransensusLCA project

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Zero tailpipe emissions vehicles (ZEVs) are a promising option for more sustainable mobility services. Action needs to be taken in Europe and globally to foster less polluting road transportation prioritizing climate-neutrality targets throughout the whole value chain and not only in the use phase. To this end, decision-making processes need to be informed via robust methodologies to evaluate and monitor sustainability performance. Life cycle-based methodologies, such as LCA and Life Cycle Sustainability Assessment (LCSA), are the logical choice as these can provide a holistic sustainability perspective. They are increasingly used within policy-making, industry, and science to obtain sustainability information on products, services, or technologies. Their scope even extends to large-scale systems, including ZEVs covering the whole value chain from extraction to end-of-life. However, all the methods are not equally mature and include a number of choices that can lead to variations in results. Currently, harmonization is lacking on these choices, which leads to discrepancies in results for the same product, hinders the comparability of studies, and limits the usefulness of the methods for guiding decision makers.

TranSensus LCA **[1]** aims at developing a baseline for a European-wide harmonized, commonly accepted and applied single LCA approach for a "zero-emission" road transport system. The project's ambitions are to enhance comparability between LCAs and represent reality as closely as possible. Bringing together relevant stakeholders from industry and research, an evidence- and real-life data-based LCA approach is being conceptualized and harmonized. By consensus, TranSensus LCA will enable industry, mobility providers and planners to provide sustainable products and optimize mobility solutions as needed to combat climate change. Since 2023, the conducted work in the project continuously delivers and improves a description of the building blocks of a recommended approach to enable fair comparison of LCAs of ZEVs.

The development of these building blocks relies on a scientific and consensus-driven approach within the project following the ISO 14040 LCA framework [2]. Based on the state of the art and the analysis of needs and gaps, discussions on regulations, practices, scientific alternatives, methodologies and other similar initiatives enabled providing recommendations, or, a limited number of alternatives to address each treated topic. After two internal votes, already 73 recommendations integrated the building blocks of the Environmental, Economic and Social LCA approach for retrospective vehicle LCA. Following a brief description of the project, this contribution will share the process used to reach such results and will focus on an essential topic, electricity modelling. This topic is of paramount importance when performing an LCA, as it can lead to huge impacts, and especially so for companies using Energy Attribute Certificates. Thus, the status of the discussions on electricity modelling in the ZEV production phase will be presented along with the different approaches possible, namely location-based and market-based. Main polemic points and the pros and cons of each approach will be described.



Figure 1. Retrospective LCA-Building blocks of TranSensus LCA methodology in 2024.

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STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF NOVEL HIGH ENTROPY OXIDES

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Recently, high entropy oxides (HEO) have been reported as a new class of materials. In this context, HEO, which are solid solutions that consist of five or more elements [1], show wide application, including in renewable energy sources. Their high stability, together with their high theoretical capacity, provides a possibility to use in green energy [2]. However, the detailed study of the electrochemical properties of the HEO materials is at early stages. This work presents a novel HEO, i.e. (Zn_{0.25}Mg_{0.25}Co_{0.25}Cu_{0.25})Al₂O₄, with spinel structure prepared via one-step mechanochemical route. In addition, their lithiated derivates were prepared for the first time with the following composition: $Li_{0.5}Zn_{0.125}Mg_{0.125}Co_{0.125}Cu_{0.125}Al_2O_{3.5}F_{0.5}, \quad \text{and} \quad$ Li_{0.5}Zn_{0.125}Mg_{0.125}Co_{0.125}Cu_{0.125}Al₂O_{3.5}Cl_{0.5}. The mechanochemical reaction between oxide precursors and LiF/LiCl was used. The phase evolution of spinel structure was controlled by X-Ray powder diffraction. The microstructure and morphology of the sample were investigated by TEM together with STEM, SAED, and HR-TEM analyses. The STEM micrographs demonstrated a nanocrystalline character of the as-prepared samples, with an average crystalline size in the range of 6 to 17 nm. The elemental distribution of powders was evaluated by EDS analysis. The oxidation states of each element were studied by XPS method. Electrochemical properties were investigated by cyclic voltammetry of Li insertion in the potential window of 0.01 - 3.0 V vs Li⁺/Li at a scan rate of 0.1 mV s⁻¹ (Figure 1). The specific capacity of (Zn_{0.25}Mg_{0.25}Co_{0.25}Cu_{0.25})Al₂O₄ oxide show a value of 54 mAh g⁻¹. The charge capacity of the tested anode Li_{0.5}Zn_{0.125}Mg_{0.125}Co_{0.125}Cl_{0.125}Al₂O_{3.5}F_{0.5} was found to be 71 mAh g^{-1} and for $Li_{0.5}Zn_{0.125}Mg_{0.125}Co_{0.125}Cl_{0.125}Al_2O_{3.5}Cl_{0.5} - 52$ mAh g^{-1} . Based on the obtained results, the mechanochemical method shows a novel way for synthesis and development of unique high entropy oxides, and this research provides extraordinary ideas for discovering new anode materials for lithium ion batteries.





 $\label{eq:Li0.5} Li_{0.5} Zn_{0.125} Mg_{0.125} Co_{0.125} Cu_{0.125} Al_2 O_{3.5} F_{0.5}, \mbox{ and } Li_{0.5} Zn_{0.125} Mg_{0.125} Co_{0.125} Cu_{0.125} Al_2 O_{3.5} Cl_{0.5} \mbox{ samples at a scan rate of } 0.1 \ mV \ s^{-1}.$

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Life Cycle Sustainability Assessment of an Innovative Closed-Loop Chemistry-Neutral Approach for Recycling and Recovery of Battery Waste Feeds

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Background: As the global push for sustainable mobility and renewable energy storage intensifies, the demand for lithium-ion batteries (LiBs) is expected to increase 5-fold by 2033 at 15% compound annual growth rate (CAGR), which will cause a high demand for battery materials^{1,2,3}. Additionally, batteries installed in the last decade will step by step coming to their end of life in the upcoming years and will pose significant challenges to the environment if not properly managed^{4,5}. Thus, recycling and recovery of battery waste feeds will play an important role in not only providing secondary resources to address this growing demand but also providing supply security for regions with low primary battery material production and enhancing the sustainability of the overall battery supply chain^{1,4}.

Innovation: Existing state-of-the-art recycling technologies (physical treatment combined with pyrometallurgical and/or hydrometallurgical processes) allow only a recycling with low efficiency and potentially not all materials can be recovered^{6,7,8}. In order to recover >95% of the battery cell materials and fractions (e.g., metallic foil, graphite, electrolyte, fluorinated compounds, and cathode active materials), a novel recycling approach, pretreatment by high-voltage fragmentation and subsequent recycling technologies such as direct recycling or solvo-hydrometallurgy, is identified at TRL 4 in the framework of the <u>Battery2030+</u> project <u>RENOVATE</u>. The recovered battery cell materials are characterized and used in the manufacturing of new cells, and waste streams generated along the process chain are further processed to obtain valuable materials such as surfactants, making the whole recycling process waste-free and circular.

Objectives: Life Cycle Sustainability Assessment (LCSA) of emerging technologies at low TRL allows technology developers to adapt technologies towards more sustainability at a relatively low cost and effort compared to a more mature stage of the considered technology⁹. A specific work-package in RENOVATE project addresses the quantification of economic, environmental, and societal impacts of this novel recycling technology in accordance with ILCD Handbooks and PEF^{10,11}. The main goals are to identify the most promising recycling technology and recycling process chain for different battery chemistry types with significantly different composition shares (and potentially low value content) from a sustainability perspective. Additionally, the aim is to investigate the quality of the recycled products and the cost associated with using them directly in the battery supply chain or in other industries. Furthermore, a theoretical scale-up of life cycle inventory (LCI) data from TRL 4 to the industrial scale will be performed in a prospective manner to compare competitiveness with state-of-the-art or alternative emerging recycling technologies.

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ECOLOGICAL VANADIUM REDOX FLOW BATTERY FOR CARBON MITIGATION

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The "Ecological Vanadium Redox Flow Battery for Carbon Mitigation" is strategically designed to stimulate the adoption of innovative renewable energy and energy storage technologies within European Union (EU) countries. By harnessing the potential of Vanadium Redox Flow Battery (VRFB) systems, the research aims to address renewable energy intermittency and contribute to the EU's carbon reduction goals. With a core focus on promoting sustainability, to underscores the importance of responsible materials sourcing, efficient manufacturing processes, and comprehensive life-cycle management as seen in Figure 1. This aligns perfectly with the EU's commitment to environmentally conscious practices. The unique regulatory and environmental conditions of EU countries provide an optimal backdrop for the research goals. Stricter emissions regulations and a growing emphasis on clean energy create a receptive environment for implementing VRFB technology to store surplus renewable energy. This, in turn, aids in achieving the EU's renewable energy integration targets. By developing and deploying VRFB systems, the research aims to demonstrate tangible results. These include enhanced grid stability, increased renewable energy utilization, and reduced carbon emissions. Furthermore, the research dissemination of findings and best practices holds the potential to accelerate similar sustainable energy initiatives across the EU. Through its focus on sustainability, innovative technology adoption, and alignment with EU environmental commitments, this research endeavors to not only address renewable energy intermittency but also contribute significantly to the EU's carbon reduction goals, fostering a greener and more sustainable future.



Figure 1. Research study flow



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Nowadays, lithium-ion batteries (LIBs) are playing a crucial role in the field of sustainable renewable energy sources. However, the limitations related to the supply of critical raw materials (CRMs) and the practical specific capacity of commercial LIBs, are leading to research on new energy storage systems, such as lithium-sulfur (LiS) batteries. This chemistry have great advantages in respect to lithium-ion batteries, such as high energy density, low cost, high availability of active material and they are more sustainable.

However, LiS systems suffer from two main limitations: the migration of long-chain polysulfides to the anode surface and the precipitation of the final products of charge and discharge processes , both leading to loss of active material. Both phenomena can be contained working on the cathode formulation by changing different features, such as the physico-chemical nature of the carbonaceous matrix and/or the addition of different catalyst materials. The optimization process generally required several time-consuming and resource-demanding experiments. For this purpose, the employment of a computational model, able to describe the electrochemical behaviour of the cell, can be a suitable option to predict the effect of different operating conditions on the cell performances.

The developed model is a continuum physics-based model that describes the battery at the pore-scale level (i.e. the scale of the electrode active material), focusing on the cathode side of the cell. It can predict the discharge behaviour of the cells, providing important insights on the shuttling phenomena and the sulfide precipitation.

This computational work is accompanied by an experimental simulation campaign, dealing with different important aspects, evaluated in their impact on electrochemical performance (in the sense of the mentioned phenomena of shuttling and lithium sulfides precipitation).

First, the influence of different components employed in the cathode formulation is investigated: namely, the choice of carbonaceous matrix nature (e.g.: mesoporous or nanofiber carbon). Then the effect of varying the preparation procedure is studied, both in the procedure to mix the components, and in the preparation of electrodes of different thickness.

The impact of the mentioned features is established by performing several electrochemical tests, such as galvanostatic cycling, cyclic voltammetry and intermittent current interruption. These experiments can also be used to validate and inform the model.

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METAL ORGANIC FRAMEWORKS-INTEGRATED SEPARATORS FOR INTERNAL GAS ABSORPTION IN LITHIUM-ION BATTERIES

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Nowadays, lithium ion batteries (LIBs) are respected as the most promising and essential energy storage systems in electrification of transportation, portable electronics, etc. [1]. Currently recognized cathode and anode materials are layered lithium transition metal oxides (TMOs) such as $Li_{1+x}(Ni_{1-y-2}Mn_yCo_2)_{1-x}O_2$ (NMC) and graphite, respectively. Among the various strategies to increase the specific capacity ($\geq 200 \text{ mAh/g}$) and cycle life (>1200 cycles) over a wide voltage range, increasing the fraction of highly redox-active Ni in NMC cathode materials (Nirich NMC) appears to be very effective. However, operation of NMC cathode LIBs in liquid electrolyte results in the evolution of several gases; mainly being H₂, O₂, CO, CO₂ and RH, which pose problems causing battery performance loss, volume expansion, degradation and safety issues [2]. The particular gas evolution causes are electrochemical oxidation of organic electrolyte, electrochemical decomposition of residual Li_2CO_3 species formed on the surface of Ni-rich NMC cathodes and structural instability of NMC cathode at high states of charge (SOC) [3].

In the EU-funded project PHOENIX (grant agreement No. 101103702), with the purpose of scavenge of the abovementioned gases, the aim is to design and develop various metal organic frameworks (MOFs) integrated separators to be integrated in LIBs to minimize significant volume changes and electrode degradation during long cycles [4]. MOFs composed of metal ions and organic ligands are considered as idealized materials for gas absorption and storage in LIB due to their highly ordered pore structure and tunable size. This work describes, the initial developments on the nanosized zirconium (Zr) metal organic frameworks (Zr-MOFs-808) which are synthesized by using the easy and scalable solvothermal method. The synthesized Zr-MOFs-808 has been intensively characterized by XRD, SEM (Figure 1), EDAX etc. for their further optimization. Finally, Zr-MOFs-808integrated poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) thin film solid polymer separators (Figure 1) have been fabricated for efficient hydrogen (H₂) storage application in LIBs.



Figure 1. SEM image of Zr-MOFs-808 nanoparticle and Zr-MOFs-808-integrated thin film polymer separator.

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Building an ideal interphase for lithium metal

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Li-metal batteries are expected to be the next generation of Li-ion technology because of their higher energy density. Indeed, the Li-metal anode has one of the highest specific capacities (3860 mAh.g⁻¹). Hence, Limetal could be a key material to match the fast-growing demand for safe, cost-efficient, and high-energy-density batteries for greener transportation [1]. However, lithium metal high reactivity and propensity to dendritic growth strongly hinder its commercialization [2]. The passivation layer that naturally forms on the surface of lithium metal is a contributing factor to the formation of dendrites in lithium metal batteries since it plays a major role on the uniformity of the lithium nucleation during the charging process [3]. We propose using vacuum thermal evaporation to produce a high performance ultra-thin lithium metal anode ($\leq 25 \mu$ m) with a native layer one order of magnitude thinner than in commonly used extruded lithium. This high purity and controllable surface state provides excellent electrochemical properties, but also allows the design of a lithium metal coating with a passivation-free interphase, which is of paramount interest for designing artificial SEI and prevent dendrite formation.



Figure 1. Comparison between evaporated and extruded lithium metal of the discharge capacity and coulombic efficiency at a current density of 1 mA.cm⁻² using 2.0 mAh.cm⁻² NMC622 cathode in carbonate electrolyte (a). Calculated atomic concentration of the carbonate, hydroxide, oxide, and metal from the Li 1s XPS spectra as a function of the depth for the evaporated and extruded Li metal anodes (b).

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How to use DoE to describe the health loss of Li batteries

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Here we focus on the study of state of health monitoring of secondary batteries with advanced "green" formulations. European recycle map on battery energy storage plans to replace positive electrodes consisting of cobalt (Co) and fluorinated (F) graphite-based negative electrodes constituents with environmentally sustainable alternatives. Recently, "green formulations" was validated; in particular, recent trends suggest the use of highcapacity negative electrodes (e.g. Si or Li), Co-free positive electrodes, aqueous soluble binders and fluorine-free electrolytes [1]. Our aims are to describe the health and the degradation of the cells with electrochemical techniques and to describe the chemical and morphological changes occurring during the battery cycling, through spectroscopies (Raman and IR) operating in parallel with impedance analysis. These experimental data will be integrated together in a multiblock dataset, which will constitute the basis for chemometric processing. The purpose of this chemometric modelling is to correlate SOH evolution to the chemical and physical state of the battery [1]. Here we illustrate the analysis of SOH of two different pouch cell formulation constituted by LTO (Lithium-Titanate) as anode, LFP (Lithium-Iron-Phosphate) as cathode and the LP30 electrolyte (EC:DMC 1:1 and LiPF₆ 1M); the second formulation is constituted by a thin lithium foil of commercial Li metal (purity of 99.7%) as anode, LFP as cathode and an ethers based formulation as electrolyte. After formation cycles (CC-CV), the cells have been submitted to aging tests. The different operating conditions are chosen with an Experimental Design (ED) and supported by a PCA (Principal Component Analysis). The PCA analysis was used to choose the operating parameters for the subsequent aging experiments. Is illustrated also the analysis of SOH of a coin cell formulation consisted by a LRLO (Lithium Rich Layer Oxide) as anode, commercial Li metal layer as cathode and LP30 additive with a ionic liquid (IL) as electrolyte. of which the OCV (Open Circuit Voltage) was correlated with the health of the devices themselves. Turning to the chemometric modelling, as a starting point we verified the ability of PLS regression applied to the voltage profiles during charge cycles to estimate the SOH of a benchmark dataset by Lin et al. [1]



Figure 1: a) SOH trend of Li-ion battery during the aging test; b) SOH trend of Li metal battery during the aging

test.

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Understanding interface and redox mechanisms in gelled NMC622 based electrode

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Next generation of lithium-ion batteries promise enhanced energy density, capacity retention, safety and streamlined manufacturing processes. As a plausible solution to challenges faced with liquid organic electrolyte systems and Solid-state batteries an innovative lithium battery technology is presented. In this novel approach, a hybrid polymer membrane serves as the electrolytic component, while both electrodes are gel-based. This design eliminates the need for traditional electrolyte filling and impregnation steps in manufacturing. Throughout its development, the hybrid polymer technology has demonstrated superior performance, including enhanced capacity retention and prolonged cycle life (extending to several thousand cycles). Understanding the intricate mechanisms occurring at the interfaces within this hybrid polymer technology is pivotal for its industrial scalability. A current focal challenge lies in accessing and characterizing the embedded interfaces using nondestructive methods like XPS or Raman. Stabilizing the interface is crucial to understand the influence of gel electrode configuration on its formation and changes over time. Subsequently, the correlation between redox processes occurring on the surface and in the bulk are evaluated by analyzing the surface chemistry at different redox potentials corresponding to specific phase transitions in the LiNi0.6Mn0.6Co0.6O2 (NMC 622) system. This methodology highlights the evolution of metal oxidation states and electronic structure of NMC622 at different depths. Further analysis using XPS, Raman, and SAXS-WAXS techniques are performed to elucidate the mechanisms underlying reversible cationic and anionic redox processes and to compare them with those observed in conventional NMC-based systems. This comprehensive approach enhances our understanding of the intricate processes occurring at the interfaces within the hybrid electrode system.



Keywords: Gel electrode, anionic-cationic processes, CEI analysis, phase transitions, oxidation state

Fig: Single Diamond Model for studying the interfaces using Surface analysis technique: XPS



Thermal Degradation Mechanisms triggered by Water in Lithiumion Batteries

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The mitigation of water impurities is one of the key challenges during the production of modern batteries. Moisture levels depend on parameters like dryness of the used materials and humidity during assembly. Previous investigation showed that water can lead to severe degradation of the conductive salt [1] and a lower stable operation window of the positive electrode [2]. This can lead to increased and lower temperatures of gassing onset Additionally, the products formed during the degradation can be toxic or explosive and cause additional safety risks. [3] Most studies focus on the impact of water during battery operation within the operational temperature window; however, only by including thermal degradation, a holistic picture of battery safety can be drawn. First simulations indicate a negative effect of water on thermal runaway. [4]

Here we utilize a High-Temperature Online Electrochemical Mass Spectrometry Setup (HT-OEMS), which was presented recently by Bläubaum et al. [5], coupled with post-mortem analysis tools. With isotope-labeling of water during HT-OEMS we investigated the degradation of lithium-ion batteries up to a temperature of 132°C. We were able to track the degradation caused by water in different concentrations (Fig. 1). Lower onset temperature for gassing as well as higher volumes of gas produced were identified for increasing water contents. Using Scanning Electron Microscopy, we identified surface film formation for both negative and positive electrodes in presence of water. The products formed on the positive electrode were identified to be multiple types of carboxylic acids.

We were able to show that HT-OEMS is an effective method to evaluate the degradation caused by impurities during thermal abuse. Post-mortem analysis was effectively used to identify the location of processes as well as products formed. The insights found by this investigation confirm experimentally that higher water contents pose a safety risk. Production conditions are expected to impact battery safety, and the recent trend towards water-based electrode production needs to take this into account.



Figure 1. Gas evolution during temperature increase of a lithium-io battery with a) 0ppm and b) 1500 ppm added heavy water.

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Graduate School Electrochemical Energy Storage

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The Graduate School Electrochemical Energy Storage (GS-EES) supports almost 90 doctoral researchers at Karlsruhe Institute of Technology (KIT), Ulm University and Justus-Liebig-University Giessen and is the largest graduate school in Germany in the field of electrochemical energy storage.

The GS-EES addresses the full interdisciplinary spectrum of electrochemical energy storage and conversion, from fundamental science to processing and application. Among our topics are Lithium-ion batteries, post Lithium batteries and fuel cells.



Figure 1. Main components of the GS-EES qualification program.

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- Annual Summer School

Both the Block Course and the Summer School are open to open to all interested PhD, master students and post-docs, no matter at which institution they are enrolled.

The GS-EES participates in the work package "European curricula in future battery technologies" of the coordinating support action of Battery 2030+.


Real-time structural and chemical imaging of degradation processes in battery interface

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Lithium-ion batteries have become the most preferred energy storage solution for modern electronic devices and the growing electric vehicle industry. With their increasing popularity and demand, the focus is now on enhancing the performance and safety of these batteries. To achieve this, a deeper understanding of the structural and chemical degradation processes occurring at the electrode-electrolyte interfaces during battery operation are necessary. Traditional ex-situ and in-situ analyses are not sufficient in capturing the dynamic changes at these interfaces. As a result, operando techniques, which enable real-time analysis, have become crucial for understanding these intricate processes. Operando scanning electron microscopy (SEM) has been previously used for imaging the structural changes at battery interfaces during electrochemical cycling [1]. But conventional chemical analysis techniques associated with SEM, such as Energy Dispersive X-ray spectroscopy, struggle to detect lithium, a vital component of lithium-ion batteries. Thus, techniques that allow simultaneous structural and chemical imaging in operando conditions are scarce. In this context, secondary ion mass spectrometry (SIMS) emerges as a valuable tool due to its capability of imaging light elements like hydrogen and lithium even at very low concentrations. SIMS has been used for both ex-situ and in-situ chemical imaging of battery materials in recent years [2,3]. However, operando SIMS analysis methods are not widely available. In our poster, we will present the advances we have made in developing a new operando technique that allows simultaneous SEM-SIMS imaging of the structural and chemical changes at battery interface at sub-20 nm resolution.

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3D PRINTING OF NASICON-TYPE ELECTROLYTES FOR ALL-SOLID-STATE BATTERIES

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In the last years the efforts for approaching the next generation of all solid-state lithium batteries (ASSLBs) are focusing on the production of 3D complex structures to increase the active interface between the electrodes and the electrolytes, improve the mechanical resistance and limit the dendrite formation, increase the critical current density or allowing high cathode loadings. Among different techniques, additive manufacturing strongly attracted the attention of the scientific community, however most of the reports focuses on the 3D printing of electrodes or polymer containing electrolytes, while only few focused on the production of a full ceramic electrolyte by these techniques [1-3].

The present work explores the potential of stereolithography (SLA) printing in fabricating 3D structured solid electrolytes with tailored design for high performances batteries for Internet of things applications [3]. The design and production by 3D printing of Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) and Li_{1.3}Al_{0.3}Ge_{1.7}(PO₄)₃ (LAGP) electrolytes will be presented. We achieved good densifications by carefully designing paste formulation, printing, and post-printing processes. We successfully designed and fabricated structures with various shapes, with a total thickness of 500 μ m (see Fig. 1b). The ionic conductivity of the printed and sintered parts was measured by electrochemical impedance spectroscopy and resulted to be 5 x 10⁻⁴ S·cm⁻¹ at 25 °C very similar to the sintered LATP pellets with relative densification ~94%.

Our findings highlight the potential of 3D printing to accelerate the development of ASSBs based on NASICON-type electrolytes with custom designs and improved performances thanks to complex 3D architectures which play a crucial role in enhancing battery performance. These benefits are essential for advancing the capabilities and reliability of solid-state battery technology.



Figure 1. a) as-printed "green" LATP membrane; b) SEM image of cross-section of LATP flat membrane after sintering at 800 °C for 6 h; c) Arrhenius plot of 2 samples of LATP: printed and sintered flat membrane and a sintered pellet produced by conventional dry pressing manufacturing, in the inset the Nyquist plot of both samples recorded at 25 °C.

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Towards autonomous robotic battery materials research & innovation – the Aurora platform

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Today, only short individual segments of the experimental battery research & innovation cycle are automated, often requiring man-power-intensive intermediate process steps to complete the cycle. In addition, the outcome of lab-level battery research is often dependent on the researcher's skill level compromising reproducibility. Extending lab automation by combining multiple segments into automated application-relevant closed-loop sequences enables rapid testing of scientific hypotheses and validation of physical models. Besides reducing human error and improving reproducibility, this approach also frees the experimentalist from repetitive tasks providing more time for creative tasks.

In a joint collaborative effort, the Swiss company Chemspeed Technologies and Empa developed and validated an automated coin cell assembly robot integrated into an argon glove box. The robot assembles 32 coin cells per batch with individual sets of prefabricated electrodes. Anode/cathode capacity balancing, critical for cell cycling stability, is fully automated to a precision of 0.01 mg. The robot is capable of formulating up to 32 individual liquid electrolytes with up to 8 different liquid ingredients, which are then dispensed at a precision of 1 mg employing a patented gravimetric viscous fluid dispensing unit, avoiding error-prone density and volume measurements. Cells are then cycled on a 256 channel potentiostat interfaced with an open-source Python package developed within the Battery2030+ BIG-MAP Aurora project [1,2]. Each cell is traced and monitored as a digital twin within the open-source workflow management platform AiiDA developed at EPFL/PSI [3,4].



Figure 1: a) Cell assembly robot assembling CR2023 coin cells with graphite anode and NMC622 cathode, b) Discharge capacity of the 32 cells cycled in sets of 8 cells to different upper cut-off voltages at a dis-/charge rate of C/3. The discharge capacity after every tenth cycle is shown. An outlier cell with more pronounced capacity fading is observed in the set of cells cycled to an upper cut-off voltage of 4.6 V.

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Shining light on the link between structure and sodium storage mechanisms in hard carbons: a systematic synchrotron WAXS study

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Non-graphitisable carbons (NGCs) or hard carbons are promising candidate materials for deployment in the anodes of sodium-ion batteries (SIBs), owing to low volumetric changes, low working potential (below 1 V vs. Na⁺/Na), reasonable specific capacities (beyond 300 mAhg⁻¹), cyclic stability and low cost. [1] NGCs lack threedimensional long-range order, consisting of loosely stacked graphitic nanosheets, extensive microporosity and defects. This structural complexity implies that, despite extensive work synthesising NGCs with excellent Na ion storage capacities, there is a clear information gap on the precise structural details of these materials.

Consequently, the exact mechanism of sodium storage in NGCs, inextricably linked to their structure, is poorly understood and lacks consensus. Several conflicting models have been proposed, however, the following structural aspects have been identified as crucial to the corresponding mechanisms: porosity (pore filling), stacking (intercalation) and the lateral extent of the graphene sheets (adsorption). [2] Moreover, given the non-crystalline nature of NGCs (broadening, peak asymmetry), 'classical' treatment in laboratory X-ray Diffraction (XRD) using the Bragg and Scherrer equations is problematic and often insufficient, since identification of the relevant reflections is not trivial.

In this work, we propose to follow the full-scattering model developed by Ruland and Smarsly [3], implemented through the CarbX software [4]. This model provides a wealth of structural parameters of NGCs (around 17), far beyond what is typically reported in the literature, allowing for a near-complete description of the material, including the aspects identified as crucial to sodium storage. Using synchrotron wide-angle X-ray scattering (WAXS) at the ID31 beamline of the ESRF, we plan to establish a novel, comprehensive database of these parameters for hard carbons from various providers (academic partners, in-house synthesis, industry).

Using these parameters coupled with electrochemical testing (coin cells) and *operando* synchrotron WAXS, we envisage developing a correlation between structure of the NGCs and sodium storage mechanisms. Once established, this will allow for rapid screening of candidate NGCs through quantifiable numerical parameters, greatly bolstering the development of anode materials for SIBs.



Figure 1. Schematic of the current study. Structure of NGC figure adapted from [5].

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Enhanced Electrochemical Performance of Metallic CoS-Based Supercapacitor by Cathodic Exfoliation

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Two-dimensional nanomaterials hold great promise as electrode materials for the construction of excellent electrochemical energy storage and transformation apparatuses. In the study, metallic layered cobalt sulfide was explored in the area of energy storage as a supercapacitor electrode. By a facile and scalable method for cathodic electrochemical exfoliation, metallic layered cobalt sulfide bulk can be exfoliated into high-quality and few-layered nanosheets with size distributions in the micrometer scale range and thickness in the order of several nanometers. With a two-dimensional thin sheet structure of metallic cobalt sulfide nanosheets, not only was a larger active surface area created, but also the insertion/extraction of ions in the procedure of charge and discharge were enhanced. The exfoliated cobalt sulfide was applied as a supercapacitor electrode with obvious improvement compared with the original sample, and the specific capacitance increased from 307 F·g⁻¹ to 450 F·g⁻¹ at the current density of 1 A·g⁻¹. The capacitance retention rate of exfoliated cobalt sulfide increased to 84.7 % from the original 81.9 % of unexfoliated samples while the current density was a factor 5 higher. Moreover, a button-type asymmetric supercapacitor assembled using exfoliated cobalt sulfide as the positive electrode exhibits a maximum specific energy of 9.4 Wh·kg⁻¹ at the specific power of 1520 W·kg⁻¹.



BATTERY 2030+ Knowledge Base – Ontologized Standards and Protocols in Battery Research and Development

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The establishment and adherence to standardized protocols and procedures within the realm of research and development constitute a fundamental pillar for fostering enhanced collaboration, adhering to the principles of Findable, Accessible, Interoperable, and Reusable (FAIR) data. Within the framework of the BATTERY 2030+ initiative, our endeavors encompass the formulation and aggregation of standards and protocols to both experimental and theoretical investigations of batteries, as delineated in the BATTERY 2030+ Roadmap [1]. These resources were subsequently made accessible to the battery R&D community in 2023 through an online repository [2]. Central to our methodology is the establishment of a network comprising key performance indicators (KPIs) and process parameters (PPs) (Figure 1, left). This network elucidates the manner in which KPIs of process steps exert influence on subsequent downstream processes. Commencing with the synthesis of active materials and traversing through the domains of coating, electrode fabrication, cell assembly, and formation, our analysis extends to encompass final electrochemical testing. For each individual KPI, we delineate recommended measurement methodologies, extant standards and protocols, as well as the downstream processes influenced thereby. Dynamic in nature, our online repository (Figure 1, right) is continually augmented to encapsulate the intricate interrelations and dependencies among procedural steps and measurement outcomes vis-à-vis specific KPIs and PPs. Ultimately, our aspiration is to curate an online knowledge repository that amalgamates the collective expertise and knowledge accrued by prominent battery research entities across Europe, thereby serving as a valuable educational resource for burgeoning battery scientists and engineers. Our ongoing efforts are migrating the Knowledge Base to OpenSemanticLab to make it open for the whole European battery community to contribute and linking it to the BattINFO Ontology.



KPI website with easy GUI linked to data base

Figure 1. BATTERY 2030+ Knowledge Base Website.

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A distributed MAP for autonomous battery research

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We present a Materials Acceleration Platform (MAP) powered by a new implementation of the Fast INtention-Agnostic LEarning Server (FINALES) [1] framework. This MAP not only connects experimental and computational methods across geographically distributed partners, but also bridges scales from investigations on the material level to such on the coin cell level. We demonstrate two independent optimization tasks run by two optimizer instances simultaneously operating on the same MAP infrastructure. The optimizers tune the electrolyte formulation for maximum ionic conductivity and maximum end of life (EOL), respectively. To shorten the time of an iteration in the EOL optimization task, this demonstration includes a multi-step process involving several hardware and software tenants (which is how we refer to the clients in our MAP). We use this increased complexity to showcase the use of a tenant to handle workflows while maintaining the centralized communication design of FINALES. We also show the integration of the BIG-MAP Archive [3] with FINALES via an Archiving tenant and subsequently render the entries in the BIG-MAP Archive semantically searchable by mapping our data to the BattINFO [4, 5] ontology. All this is enabled by improvements in the FINALES framework mainly concerning the structure of the database, the extensive use of unique identifiers and defined data structures for communication.

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Ab initio and AI atomistic elucidation of the Solid Electrolyte Interphase growth mechanisms in solid state batteries

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A fundamental issue in the development of all solid Li-ion batteries is the current lack of understanding of the interface between the solid electrolyte and the cathode or anode electrode. When an electrode, such as Li metal, gets in contact with an electrolyte, chemical reactions take place to form the so-called Solid Electrolyte Interphase or SEI. This is a layer composed of different phases and one of the first targets of this research is to determine phases in time and space, automatically out of the large collection of atomic coordinates provided by molecular dynamics (MD) simulations¹. Our proposed approach is to use the same atomic environment descriptors (an array of numbers) that we employ in the training of machine learning (ML) moment tensor potentials^{2,3}. With the use of principal component analysis (PCA), Support Vector Machine (SVM)⁴ and atomic environments of each of the different perfect phases we were able to distinguish Li2S, Li3P, Li6PS5Cl and LiCl in the interphase as shown on the figure 1.



Figure 1. Side view of the Interphase, red color is Li₂S, blue Li₆PS₅Cl, lemon is Li3P, orange is LiCl and pink is Li in the electrode.

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Atomistic modelling of the anode-electrolyte interface for zero-excess solid-state batteries

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The all-solid-state Li metal batteries, which utilize Li metal anode and ceramic solid-state electrolyte, are considered the "holy grail" of next-generation batteries, with potential for high energy density and high safety.[1,2] Recently, the concept of anode-less or zero-excess solid-state batteries (ZESSBs), which removes the Li metal anode at the battery fabrication stage, has attracted a lot of interest as it simplifies the battery manufacturing process, improves safety, and could bring significant cost reduction. However, the absence of excess Li and the Li plating/stripping occurring on the surface of the commonly adopted Cu current collector, which has a natural structure mismatch with Li, are the main disadvantages of ZESSBs. Therefore, the design of interlayer materials, used in the interface between the solid electrolyte and the current collector, is crucial to determine the initial Li nucleation and induce subsequent uniform growth.[3]

In the Horizon Europe OPERA project (https://horizon-opera.eu), we will develop efficient interlayer materials at the anode side and interface engineering strategies to enable the stable plating/stripping process of Li during the operation of ZESSBs. We adopted a combination of Density Functional Theory (DFT) calculations and molecular dynamics (MD) coupled with trained machine learning (ML) potentials to investigate various metals as possible interlayer materials and their interface with the solid-state-electrolyte. We screened nine different metals to be adopted as interlayer materials based on their reactivity with Li: Mg, Zn, Au, Ag, Pt, and Al form a solid solution with Li metal, while Sn only forms intermetallic alloys through phase transition changes. Cu and Ni do not have solubility with Li and are commonly used as current collectors. We investigated the adsorption and diffusion of Li on the surface of interlayer materials, as well as the dissolution of Li into the lattice of the interlayer metal. We observed that after the formation of the Li-Zn and Li-Mg solid-solution, Li binds strongly to the surface of the alloy, and the Li migration to the lithiated site remains fast. On the other hand, Li is less favorable to adsorb on the lithiated sites of the Li-Au, Li-Ag, Li-Pt, and Li-Al solid-solution layer, and the migration of Li to these sites is kinetically hindered. We used the aforementioned properties to compare the performance of Li deposition on different high Li-concentration solid-solution alloys and on an extended model of the Li-Mg solid-solution alloy. For the latter, approximately 60 models were proposed, comprising the entire concentration range between Li and Mg. We estimate that the best balance between binding and diffusion of Li to promote plating via a 2D wetting is found in the low Li concentration range of Li-Mg solid solution alloys. We performed a similar analysis for the Li-Sn alloys, in which, due to phase transition changes, new lattice configurations and defects (e.g. steps) are introduced on the surface, leading to high variation in adsorption energies. The diffusion of Li on the surface of Li-Sn alloys are currently under investigation.

We have conducted molecular dynamics (MD) simulations employing machine learning (ML) potentials, finetuned with DFT-based data, to model the interface between Li metal and the interlayer material. We have successfully estimated the diffusion coefficients of Li on the surface and into the interlayer metals. Our findings confirm the tendency of Li atoms to diffuse into the lattice of Zn and Mg. Additionally, our simulations reveal the preferential formation of Li clusters on the Cu surface. We are currently expanding our simulations to include other interlayer metals considered in this study and the solid-state electrolyte, with the aim of providing insights to guide the future design of ZESSBs.

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Prussian blue analogs (PBAs) are promising candidates for commercial sodium-ion battery cathodes for their low cost and high power and energy densities. Current studies mainly focus on the reaction mechanism of PBA at the atomic scale, and there's little information about the material behavior at the electrode scale, which is crucial to enhance the rate capability and mitigate material degradation. In this study, we performed an operando wide-angle micro X-ray scattering measurement with a 40 μ m spatial resolution on a manganese-iron-based PBA (NaxMn[Fe(CN)6]) pouch cell, which contains an infrared (IR) optical fiber (d = 150 μ m) enabling operando IR measurement (Fig. a). The measurement revealed the rhombohedral to tetragonal biphasic reaction mechanism during desodiation and the in-plane sodiation heterogeneity of the whole electrode and the region around the fiber at a 1/15 C rate (Fig. c). We observed the delay in (de)sodiation caused by the fiber, and we managed to correlate the electrode heterogeneity to its biphasic reaction mechanism and the plateau in the potential profile, and the decay in capacity. Our findings shed light on previously unexplored electrode-scale behaviors of PBAs and demonstrate the feasibility and the necessary precautions when conducting operando IR on pouch cells.



(a) The schematic shows the pouch cell with an optical fiber and the measuring area of the big map and small map scan. (b) The potential profile of the pouch cell during the operando WAXS measurement. The red dots correspond to the selected maps shown below. (c) The selected big maps and small maps. The region in red/blue represents the PBA is more/less sodiated.



SUSTAINABLE RECYCLING TECHNOLOGIES FOR LITHIUM-ION BATTERIES

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Recycling of lithium-ion batteries has become a point of concern as the waste streams originating from end-of-life batteries are expected to grow exponentially in the coming years. Besides environmental considerations, the recovery of materials from the batteries also carries geopolitical and economical value, as materials present in the lithium-ion batteries such as lithium, cobalt, nickel and copper are critical and/or strategic raw materials for EU. (Figure 1) Our team in TNO EMSA focuses on development of sustainable recycling technologies for lithium-ion batteries. In this presentation an overview of our studies on hydrometallurgical methods for metal recovery from lithium-ion batteries will be presented. Furthermore our insights on efficiency of black mass production and minimization of material losses during battery shredding and physical separation processes will be discussed.



Figure 1. Schematics visualizing the urge for Li-ion battery recycling and our approach to develop sustainable recycling technologies for efficient material recovery.



Oxygen vacancies boost Zn-ion diffusion in Mn₂O₃

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Manganese-based aqueous rechargeable zinc-ion batteries (ARZBs) are gradually becoming promising large-scale energy storage systems due to their high energy density, low manufacturing cost and inherent high safety. However, the sudden decrease in capacity due to the structural instability caused by the J-T effect and the limited diffusion of zinc ions are still the main bottlenecks constraining their further development ^[1-3]. In this paper, Oxygen vacancy-rich Mn₂O₃ (V_o-Mn₂O₃) is obtained by MOF-derivation and secondary annealing treatment, which effectively optimizes the diffusion path of Zn²⁺ and improves the reaction kinetics. The appearance of oxygen vacancies distorts the structure around the vacancies and provides a path for the diffusion of Zn²⁺, which greatly improves the charge transfer efficiency, promotes the electron rearrangement, enhances the electrical conductivity, and ultimately improves the reaction kinetics and electrochemical properties of Vo-Mn₂O₃. In addition, a charging and discharging mechanism based on the simultaneous insertion and conversion of H⁺ and Zn²⁺ was demonstrated. As a result, the stable Zn/V₀-Mn₂O₃ battery shows a high specific capacity of 351 mAh.g⁻ ¹ at a current density of 0.3 A.g⁻¹, particularly good rate performance, with a discharge specific capacity of 206 mAh.g⁻¹ at a current density of 6A.g⁻¹, and Capacity retention of 74.3% after 10,000 cycles even at a current density of 12 A.g⁻¹(only 150s pre-cycle). This excellent electrochemical performance suggests that oxygen vacancies may contribute to the development of future cathode materials for advanced aqueous zinc ion batteries.

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STABILITY AND ION CONDUCTIVITY OF NOVEL LI6PIO6: A DFT STUDY

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In this study, we employ a computational search utilizing DFT (Density Functional Theory) to uncover promising solid-state electrolytes for advanced energy storage devices. Focusing on oxide materials, we investigate the potential of Li6PIO6 as a stable and high-conductivity electrolyte. Motivated by recent findings highlighting the superior ion conductivity of Li6PBrO6 [1], we propose the substitution of bromine with iodine in Li6PIO6, anticipating similar favorable properties. Through thorough computational simulations, including substitution and structural relaxation within the framework of density functional theory, we demonstrate the stability of Li6PIO6 by placing it on the stability convex hull diagram. Furthermore, phonon dispersion calculations validate the stability of the material by confirming all positive frequencies. Expanding our exploration, we explore other compositions within the Li-P-I-O system, unveiling novel metastable structures such as Li7PO6 and Li7P3O11. Employing a Machine Learned Interatomic Potential (MLIP), we calculate ion conductivity, revealing a high value of approximately 1 mS/cm for disordered Li6PIO6 materials. Distortion studies were achieved through controlled alteration of one iodine atom position, from 4a to 4c Wyckoff position [2]. Additionally, an assessment of the electrochemical stability window reveals a high value of approximately 4 eV, further establishing the viability of Li6PIO6 as a prospective solid-state electrolyte. In Summary, our findings substantiate the candidacy of Li6PIO6 as a promising electrolyte material, offering potential advancements in energy storage technology.

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Humanity, with the changing understanding of the ways of energy production, is moving towards the implementation and use of green energy systems on a daily basis. An integral part of this change is the development of energy storage devices such as batteries. In parallel with market-dominated lithium-ion battery technologies, research is also being carried out in other alternative directions, such as Na⁺, Zn²⁺, Ca²⁺, etc. ion battery technologies **[1,2,3,4]**. As the understanding of the processes in batteries improves among scientists, new opportunities are opening up in the development of battery technology. Rechargeable zinc-ion aqueous batteries have regained their attention due to perspective utilization in large-scale storage devices. In this study, we have modified the Zn electrode surface through laser irradiation. Two different laser wavelengths (266 nm and 1064 nm) and irradiation mediums (air or water atmospheres) were used to prepare the described anode surfaces. Samples characterization was done by Raman spectroscopy, scanning electron microscopy (SEM), cyclic voltammetry, and impedance measurements. Observations show that by modifying the surface with laser processing, the specific surface capacitance of the sample can be increased up to 30%. A brief overview of results is visualized in Figure 1. From the measurements, we concluded that the laser-modified sample electrode cycling (ZnO growth and Zn plating) is more efficient, and the electrode capacity increases compared to the unmodified Zn sample.



Figure 1. Laser irradiated Zn anode a) SEM images, b) Raman measurement results of samples obtained in air atmosphere before and c) after electrochemical measurements, d) cyclic voltammetry measurements at the same scan rate (30C) and e) calculated specific capacitance values

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