Ref. Ares(2025)6409335 - 06/08/2025

AM4BAT PROJECT

Deliverable 3.4

Report on Hybrid Solid Electrolyte Paste for Rapid Prototyping and Separator

- Collaborative project
- Grant agreement No. 101069756
- Topic: HORIZON-CL5-2021-D2-01-03
- Start date of the project: 01-07-2022
- Duration – 48 months

WP	3	Hybrid Solid Electrolyte

Dissemination level	PU	**Due delivery date**	June 2025
Nature	R	**Actual delivery date**	July 2025

Lead beneficiary	LEITAT Technological Center
Contributing beneficiaries	PHOTOCETRIC (PHO), TORRECID (TOR), CEA

[1] Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU) **SEN**= Sensitive, limited under the conditions of the Grant Agreement.

[2] Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** = Other

[3] Creation, modification, final version for evaluation, revised version following evaluation, final.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

Document history

Issue date	Version	Changes made / Reason for this issue	Author
25-07-2025	1	Creation	Milad Madinehei (LEITAT)

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

Contents

LIST OF ABBREVIATIONS

HSE: Hybrid solid electrolyte (polymer + ceramic)

SE: solid electrolyte (polymeric)

DoA: Description of Action

EC: European Commission

EIS: Electrochemical Impedance Spectroscopy

E&IM: Exploitation and Innovation Manager

FTIR: Fourier transform infrared spectroscopy

GA: Grant Agreement

IPR: Intellectual Property Rights

LCA: Life Cycle Assessment

LLZO: Lithium lanthanum zirconium oxide

PC: Project Coordinator

PMC: Management Committee

PSC: Scientific Committee

TGA: Thermogravimetric analysis

TM: Technical Manager

TMPTA: trimethylolpropane triacrylate

WP: Work Package

WPLs: Work Package Leaders

1. Executive summary

This deliverable presents the final results of WP3 concerning the development and electrochemical evaluation of a UV-curable hybrid solid electrolyte (HSE) for use in the AM4BAT cell. The focus was on achieving a processable solid-state electrolyte with high ionic conductivity, good stability, and compatibility with lithium and cathode materials.

The developed electrolyte is based on a photopolymer formulation of Monomer-1 (AN), Monomer-2 (GN), and trimethylolpropane triacrylate (TMPTA), combined with lithium salt and LLZO filler. The use of UV-curing enables low-temperature, scalable processing compared to conventional heat-curing systems. The selected composition demonstrated ionic conductivity values in the 10^{-4} S/cm range and a lithium-ion transference number of 0.84, significantly higher than conventional liquid electrolytes. Thermal analysis and FTIR aging studies confirmed the chemical and thermal stability of the films over time.

Different processing strategies were evaluated, including free-standing electrolyte films and films cured directly on the electrode surface. The latter approach showed reduced interfacial resistance and improved electrochemical performance. Symmetric Li|HSE|Li cells demonstrated stable cycling and interface stability, confirming the mechanical and electrochemical robustness of the electrolyte.

The results of WP3 establish a fully formulated and processable HSE system that will serve as input for the prototyping activities in WP6 and WP7. These findings support the integration of photopolymer-based electrolytes in solid-state battery manufacturing workflows and demonstrate their potential for safe and efficient all-solid-state lithium batteries.

2. Introduction

This deliverable (D3.4) reports the final development stage of the HSE formulated within WP3 of the AM4BAT project, focused on enabling safe, high-performance solid-state lithium batteries. The electrolyte system under investigation is based on a photocurable polymer matrix incorporating lithium salt (LiTFSI) and garnet-type ceramic filler (LLZO), designed to deliver high ionic conductivity, wide electrochemical stability, and processability suitable for integration in multilayer cell manufacturing.

Compared to conventional thermally cured polymer electrolytes, the UV-curable formulation developed here allows photoinitiated crosslinking at room temperature, which provides significant advantages in terms of processing speed, energy efficiency, and compatibility with thermally sensitive cathode chemistries. The base monomer system (AN:GN:TMPTA) was optimized through iterative screening with and without LLZO filler, focusing on ionic conductivity, film integrity, lithium transference number, and electrochemical stability.

In previous deliverables (D3.1 to D3.3), individual components were characterized in detail: (i) LLZO was synthesized both via electrospinning (LEITAT) and solid-state routes (TOR), with the latter selected for further use based on LCA and scalability studies in WP8; (ii) various photopolymer combinations and salt concentrations were studied to tune viscosity, ionic mobility, and polymer–salt interaction; and (iii) the HSE system was benchmarked in free-standing form, achieving ionic conductivities up to 10^{-3} S/cm at room temperature and t^+ values around 0.84, well above standard polymer electrolyte baselines.

This final stage of WP3 focuses on assessing the functional performance of the HSE in realistic cell formats. Key activities included the use of free-standing electrolyte films and in situ photopolymerization directly on the cathode surface to evaluate the impact of interface contact and processing route. Full and half cells were assembled with lithium metal anodes and commercial NMC cathodes, as well as AM4BAT WP4 cathode developments. Electrochemical impedance spectroscopy (EIS) and galvanostatic cycling were employed to assess interfacial resistance evolution, ionic transport characteristics, and cycling stability.

The results demonstrate that curing the electrolyte directly on the electrode surface significantly reduces interfacial resistance and enhances cycling stability compared to laminated configurations. Capacity retention and voltage stability profiles further support the mechanical and electrochemical integrity of the HSE. These insights provide the technical basis for transitioning the material to prototype development under WP6 and WP7, marking a key milestone in solid-state cell integration.

3. Objectives

The main objective of this deliverable (D3.4) is to complete the development and functional evaluation of the photocurable HSE and validate its integration into realistic battery cell configurations within the AM4BAT project. This work marks the transition from material-level formulation and screening (addressed in previous deliverables D3.1 to D3.3) to cell-level electrochemical testing and process optimization.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

In this final phase, the focus is placed on understanding the electrochemical behavior, interface quality, and processing scalability of the optimized electrolyte formulation under conditions relevant to prototype integration. The specific goals of this stage are to:

1. **Evaluate the electrochemical performance of the optimized HSE formulation** in symmetric cells and in lithium half-cells using commercial NMC cathodes, under galvanostatic cycling that reflect practical use.
2. **Assess compatibility between the HSE and electrode interfaces**, particularly lithium metal anodes and Ni-rich layered oxide cathodes, by analyzing interfacial resistance evolution, polarization behavior, and capacity retention.
3. **Investigate the influence of electrolyte processing strategies**, comparing free-standing membranes with in-situ photocured films applied directly onto the electrode surface, to understand how curing conditions and interface formation affect cell performance.
4. **Establish the technical readiness of the HSE formulation for integration into prototype cells** in subsequent work packages (WP6 and WP7), confirming its compatibility with scalable processing techniques, stable cycling performance, and reproducible fabrication protocols.

Through these objectives, this deliverable aims to consolidate the functional role of the HSE developed in WP3, define practical processing windows, and provide critical input for the prototyping and device-scale assembly tasks to follow.

4. Methodology

The detailed methodologies for the formulation, material characterization, and initial electrochemical evaluation of the HSE were thoroughly described in previous deliverables (D3.1–D3.3). Therefore, these steps will not be repeated here in full. However, for context, a brief summary is provided below.

In earlier phases of the AM4BAT project, the photocurable electrolyte was developed through a systematic investigation of various monomer systems, cross-linkers, curing agents, and lithium salts, with and without LLZO ceramic filler. The focus was on achieving high ionic conductivity, mechanical integrity, and electrochemical stability. The optimized formulations resulted in free-standing films with ionic conductivities on the order of 10^{-3} S/cm at room temperature and good film-forming properties. These materials were also assessed for thermal stability, lithium-ion transference number, and electrochemical stability window.

This final phase focuses on validating the electrolyte's performance in realistic cell configurations and processing conditions, specifically its compatibility with different cathodes and application methods.

Test Scope and Configuration:

To evaluate the impact of electrode type and electrolyte integration strategy, two test configurations were implemented:

1. **Free-standing electrolyte with cathode:** The electrolyte was used as a self-supported membrane and sandwiched between a lithium metal anode and a cathode electrode.
2. **Electrolyte cured directly on cathode** The photocurable formulation was applied directly onto the cathode surface and cured under UV light to form an integrated electrode–electrolyte interface.

These configurations allow comparative analysis of the electrolyte's performance depending on both the **electrode chemistry** and **processing approach**.

Cell Assembly and Curing:

All cells were assembled in an argon-filled glovebox to prevent moisture or oxygen contamination. For coated configurations, electrolyte formulations were deposited using controlled film-casting techniques (e.g., doctor blade), followed by **UV-curing** under optimized light intensity and exposure time. Free-standing films were pre-cured and cut to size before assembly. Coin cells were used for electrochemical testing.

Electrochemical Evaluation:

The electrochemical performance of each cell configuration was assessed using standard testing methods to evaluate both short-term and long-term behavior. These tests aimed to determine the ionic transport characteristics of the electrolyte, its interface compatibility with electrodes, and its overall stability during operation.

The primary techniques included: Cycling performance tests, to observe capacity retention, and general stability of the cells over multiple charge–discharge cycles. Impedance spectroscopy, to analyze internal resistance contributions, particularly at the electrolyte–electrode interface, and to track changes before and after cycling.

All measurements were conducted under controlled conditions, primarily at room temperature, with selected tests also performed at elevated temperatures to evaluate thermal effects.

5. Results

5.1. Overview of Sample Preparation Method (Summary from Previous Deliverables)

To provide context for the electrochemical results presented in this deliverable, it is necessary to briefly revisit the material development methodology established in previous stages of the project (Deliverables D3.1–D3.3). The SE was designed to balance high ionic conductivity, electrochemical stability, and practical processability for integration into solid-state batteries.

The electrolyte formulation consisted of a mixture of acrylonitrile-based monomers, lithium salt (typically LiTFSI), and plasticizers or reticulation agents. After mixing in an inert atmosphere, UV-curing was employed to initiate polymerization and solidify the electrolyte [by LEITAT]. This method allowed fast transformation of the liquid resin into a flexible and transparent solid film with good mechanical integrity.

The cured films could be used either as free-standing membranes or as coatings applied directly onto electrode surfaces. This versatility in processing supports various cell integration strategies and is a key enabler for the prototyping phases in WP6 and WP7.

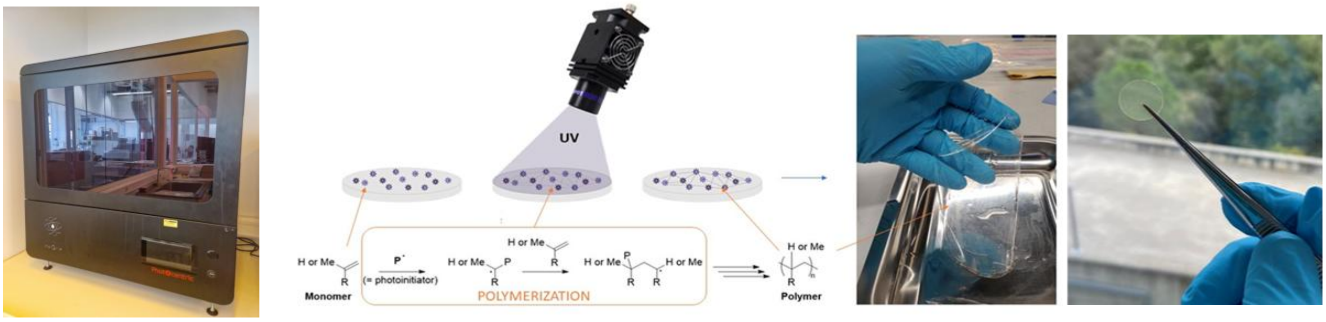

Figure 1. UV-curing process and fabricated electrolyte film. The schematic illustrates the curing mechanism, where UV light activates photo-initiators that generate radicals to initiate rapid polymerization of acrylate monomers, forming a solid polymer matrix. The photographs show the fabricated films after curing: flexible, transparent, and self-supporting, suitable for use as free-standing membranes or as coatings directly cured onto electrodes. The films were cast or pressed onto Teflon or metal substrates and cured using a 405 nm UV system for 5–10 minutes at room temperature, yielding ~100 µm thick membranes.

As part of the SE development in the AM4BAT project, Al-doped LLZO ($Li_7La_3Zr_2O_{12}$) was synthesized and optimized [by TOR] to serve as the inorganic component in hybrid formulations. Two synthesis methods, electrospinning and solid-state reaction, were evaluated. Due to its superior process simplicity, scalability, and life cycle performance, the solid-state route was ultimately selected.

To ensure the phase purity and crystallinity of LLZO suitable for electrochemical applications, extensive X-ray diffraction (XRD) analysis was conducted. These studies aimed to identify optimal calcination conditions (temperature and duration) and assess the impact of various dopant combinations. The primary goal was to promote the formation of the high-conductivity garnet-type cubic phase of LLZO.

The data confirm that higher calcination temperatures (950–1050 °C) and prolonged thermal treatment enhance phase purity. Among the synthesized samples, Al-doped and dual Ta/Nb-doped LLZO exhibited XRD patterns most consistent with the reference cubic garnet structure. These materials were thus selected for integration into HSE formulations.

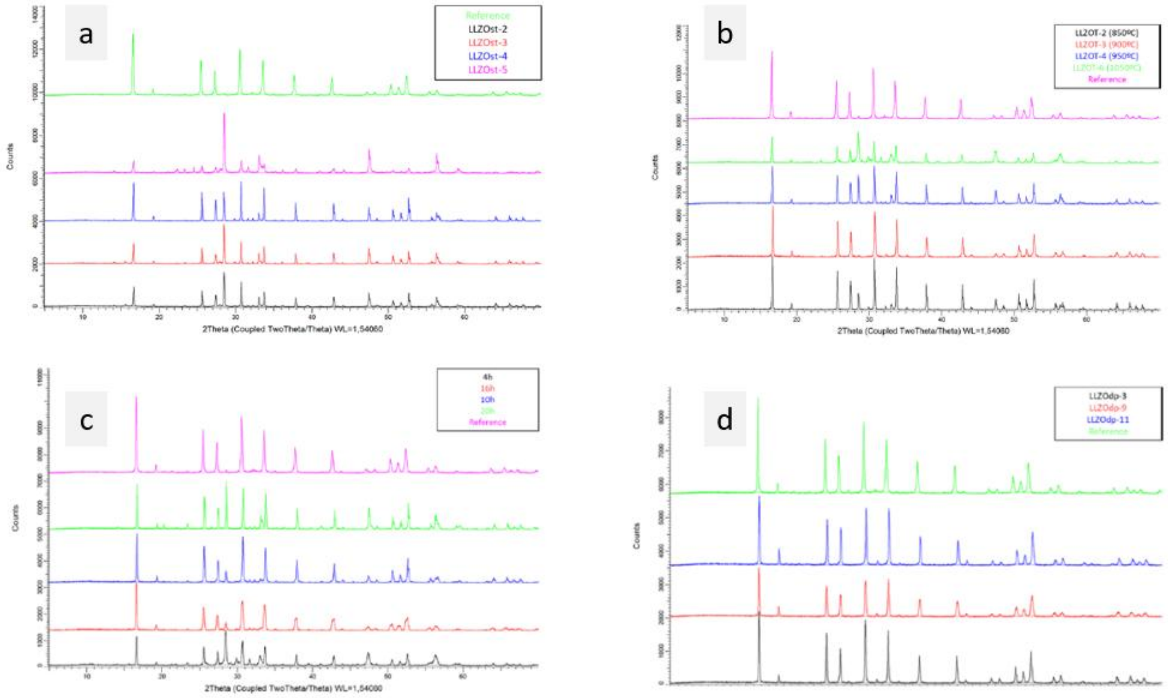

Figure 2 XRD analysis of LLZO synthesized via solid-state reaction: a: Figure 7: Representative XRD patterns from initial one-step thermal trials, exploring basic feasibility and phase presence. b: Effect of calcination temperature (850 °C to 1050 °C). Higher temperatures promote crystallization of the cubic garnet phase. c: Evolution of phase purity over time (4 h to 20 h) at constant temperature. Longer treatments improve crystallinity. d: Comparison of the best-performing doped LLZO samples. LLZOdp-3 (Al-doped) and LLZOdp-11 (Ta/Nb co-doped) exhibit high structural match to the cubic reference.

To improve the integration of LLZO in hybrid electrolyte formulations, the particle size and morphology were optimized [by TOR]. As shown in Figure 3, process refinements led to a marked reduction in particle agglomeration and a more uniform size distribution. This optimization is essential to improve the interfacial contact between the ceramic filler and polymer matrix, which in turn facilitates better ionic conduction and mechanical compatibility within the solid electrolyte composite.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

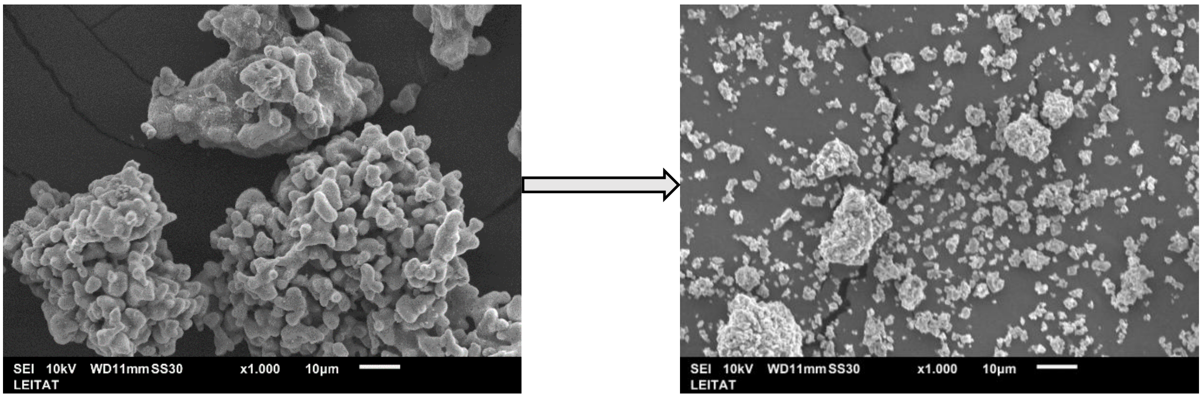

Figure 3 SEM images of LLZO powder synthesized by TOR, illustrating the effect of process parameter optimization on particle morphology and size distribution. The left image shows large, agglomerated particles, while the right image demonstrates a more homogeneous dispersion with significantly reduced particle size and improved surface area. These modifications were achieved through tuning of thermal treatment and milling conditions to enhance dispersion within the polymer matrix of the hybrid electrolyte.

5.2. Thermal Stability of the Photocurable Electrolyte

Thermal stability is a key parameter for evaluating the processability and safety of polymer-based solid electrolytes. In this project, thermogravimetric analysis (TGA) was conducted on various electrolyte formulations and individual components to determine their degradation profiles and suitability for integration into solid-state battery cells [at LEITAT].

All measurements were performed using a TA Instruments TGA Q500 (Build 36) under a nitrogen atmosphere, with a heating rate of 10 °C/min, and covering a temperature range from 25 °C to 900–1000 °C, depending on the material. The selected conditions simulate thermal loads during UV curing, cell assembly, and potential thermal stress during battery operation.

The thermal behavior of individual monomers was first evaluated. The GN monomer (Figure 4) showed a rapid and nearly complete weight loss (~99.98%) at ~239 °C, confirming its volatility and limited standalone thermal resistance. In contrast, TMPTA displayed a broader degradation curve, with main events at ~200.9 °C and 479.9 °C, and a residual mass of ~11%, indicative of partial stability due to its crosslinking functionality. A formulation composed of AN and TMPTA revealed improved thermal behavior. Two major weight loss steps were observed at ~364.6 °C and ~461.2 °C, with a final residue of ~32.7%, confirming a more robust polymer network compared to the individual monomers. This blend reflects the synergistic effect of acrylonitrile and acrylate-based crosslinkers in forming a partially stabilized polymer matrix.

The LiTFSI salt demonstrated a sharp decomposition at ~428.7 °C, with a 92.14% mass loss. This confirms that while LiTFSI remains stable under standard battery operating conditions, its thermal degradation begins above 400 °C, which sets an upper limit for processing.

In a more representative system, the formulation AN_GN_TMPTA + 20 wt% LiTFSI showed multiple degradation events, beginning around 168.9 °C and extending up to ~600 °C. The staged decomposition reflects the complex interactions between polymeric and ionic components. Residual weight (~13%) suggests partial stabilization of the polymer-salt matrix.

The final electrolyte system, containing AN, SN, TMPTA, 20% LiTFSI, and 20% LLZO, represents the complete hybrid formulation used in electrochemical testing. This sample exhibited several degradation events starting at ~174.2 °C and continuing through multiple peaks (~312.8 °C, ~401.8 °C, ~611.6 °C). A substantial residue of ~24% confirms the presence of thermally stable inorganic LLZO particles. These results validate both the structural and thermal integrity of the final material, particularly for applications involving moderate heat exposure during processing or cell cycling.

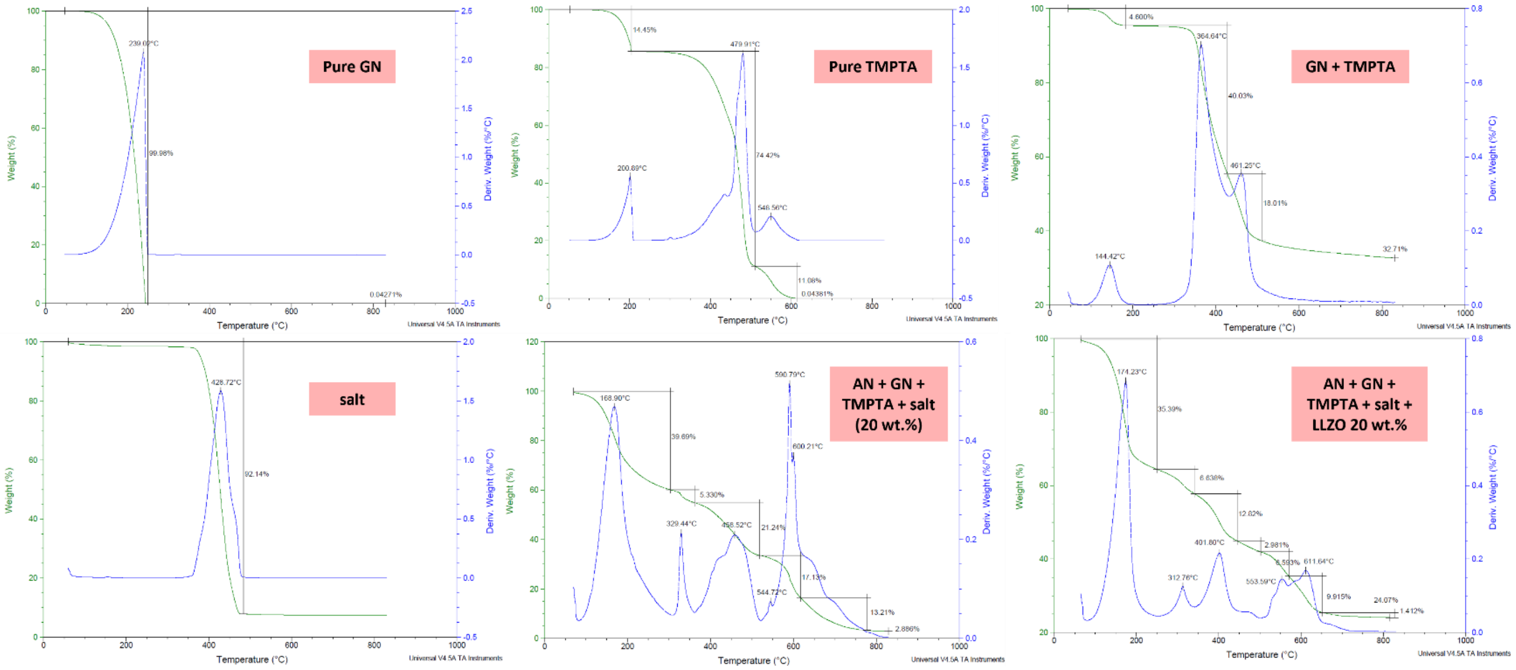

Figure 4 Thermogravimetric analysis (TGA) profiles of individual components and composite formulations used in the photocurable solid electrolyte. The top row shows TGA curves for pure GN, pure TMPTA, and the GN+TMPTA blend. The bottom row presents data for the lithium salt (LiTFSI), the AN+GN+TMPTA formulation with 20 wt.% salt, and the full hybrid formulation including 20 wt.% LLZO. The results highlight the influence of each component on the thermal stability and decomposition behavior of the final electrolyte system.

From a polymer science perspective, the presence of TMPTA promotes formation of a crosslinked polymer network, which resists thermal breakdown up to 400–500 °C. The inclusion of acrylonitrile enhances rigidity and improves the onset of degradation. While GN alone lacks thermal robustness, in mixed formulations it contributes to processability and film uniformity. LiTFSI, though stable within the operational range, introduces additional decomposition steps when interacting with the matrix. Most importantly, LLZO provides

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

thermal reinforcement, increasing residual weight and improving thermal stability without compromising flexibility or conductivity.

In summary, all tested samples demonstrated thermal stability exceeding 300 °C, with no major decomposition observed below 150–170 °C. These findings confirm the suitability of the photocurable electrolyte for battery integration, supporting both free-standing membrane use and direct electrode coating.

5.3. FTIR Analysis: Degradation and Aging Effects

To investigate the long-term chemical stability of the photocurable hybrid electrolyte, Fourier Transform Infrared Spectroscopy (FTIR) was performed [at LEITAT] on samples stored under ambient conditions for different durations, from immediately after curing (0 h) up to three months. The objective was to monitor possible structural or chemical changes in the polymer matrix and its components over time, which could indicate degradation, hydrolysis, or oxidation processes.

Figure 5 presents the collected FTIR spectra of the electrolyte at various aging intervals: 0 h, 24 h, 48 h, 120 h, 14 days, 36 days, and 3 months. The main characteristic peaks of the formulation remained consistently visible throughout the aging period. A broad band around 3400 cm^{-1}, associated with water absorption, was observed and remained relatively stable, suggesting minimal moisture uptake. The C≡N stretching signal from the acrylonitrile-based monomer appeared near 2250 cm^{-1} and showed no measurable variation in intensity or position. The carbonyl (C=O) stretching band from TMPTA, located near 1720 cm^{-1}, remained distinct and unchanged across all time points. Additionally, the CH_2 vibrations from GN around 2950 cm^{-1} and the strong S=O peaks between 1180 and 1040 cm^{-1}, attributed to the sulfonyl groups of the LiTFSI salt, were clearly retained and stable.

No new peaks were detected during the aging period, and no disappearance or significant shift of any functional group was observed. These results confirm that the electrolyte maintained its chemical structure over time. The polymer network did not undergo any detectable degradation or crosslink breakdown, and the lithium salt remained chemically intact within the matrix.

In conclusion, the FTIR study demonstrates that the photocurable hybrid electrolyte exhibits strong resistance to environmental degradation over a period of at least three months under ambient conditions. This stability is a critical requirement for practical manufacturing, storage, and pre-assembly handling in the context of solid-state battery applications.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

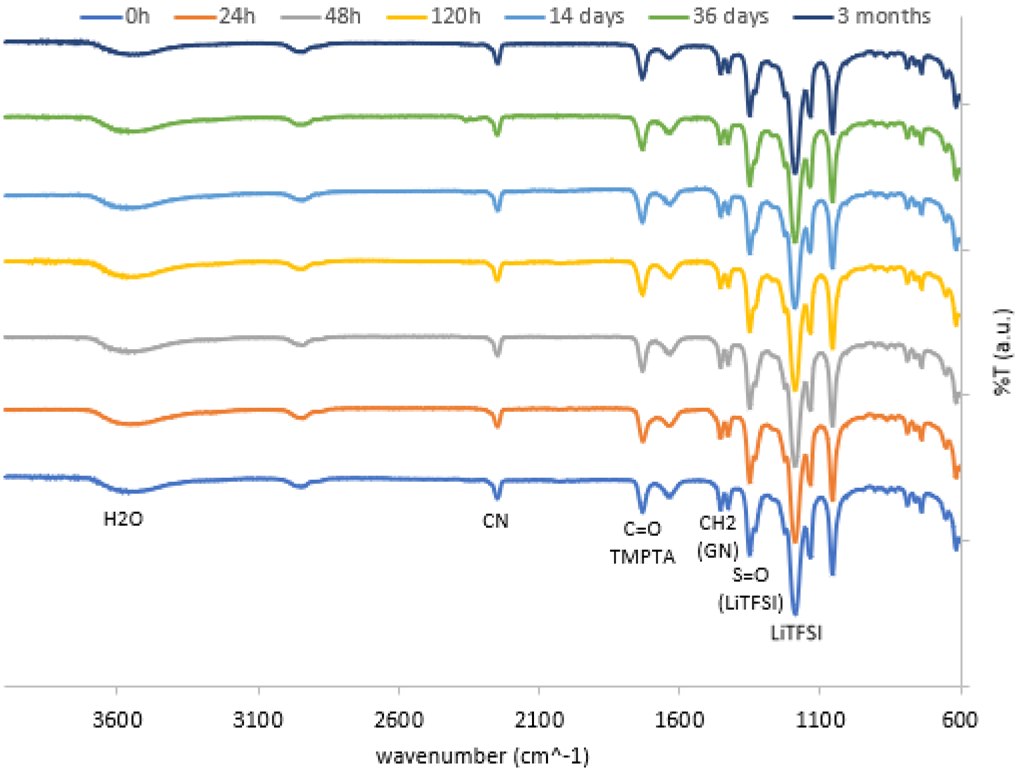

Figure 5 FTIR spectra of the photocurable electrolyte at different aging intervals, from 0 h to 3 months. Peaks associated with key functional groups of GN, TMPTA, AN, and LiTFSI remain unchanged, confirming long-term chemical stability of the formulation.

5.4. Ionic Conductivity Analysis of Hybrid Solid Electrolytes

Ionic conductivity is a critical performance metric for solid-state electrolytes, determining the material's capacity to support efficient lithium-ion transport within a battery cell. The AM4BAT project aimed for conductivity values on the order of 10^{-3} S/cm at room temperature. To approach this target, extensive testing was conducted on different electrolyte formulations [by LEITAT and CEA], as summarized in Figure 7, which organizes results into five main categories using color-coded boxes.

On the left-hand side of the graph (light blue box), the "Polymer" section includes measurements from base formulations containing only the polymer matrix and lithium salt, without ceramic filler. Among these, formulations based on AN, GN, and TMPTA exhibited the best conductivity, reaching values in the 10^{-4} S/cm range, and also demonstrated good mechanical and film-forming properties. This performance confirms that a well-designed polymer matrix alone can achieve relatively high ionic mobility.

Moving to the "Hybrid Solid Electrolyte" section, the first subset of bars is enclosed in the green box, highlighting early trials using 25 wt.% LLZO in combination with the AN:GN:TMPTA matrix

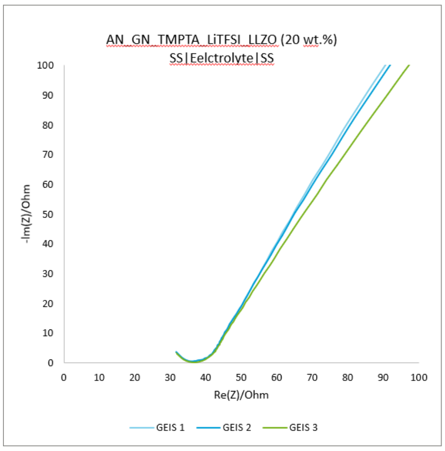

Figure 6 Nyquist plot of the basic electrolyte formulation in an ion-blocking (Stainless steel|sample|stainless steel) system to measure the ionic conductivity.

and LiTFSI salt. These tests confirmed compatibility between the in-house developed LLZO and the polymer blend. While the conductivity values were acceptable, these formulations were often mechanically brittle, complicating film processing and handling.

This led to a second phase of optimization, shown in the yellow box, where the LLZO content was systematically varied. These experiments revealed that reducing LLZO to 20 wt.% resulted in an ideal compromise: conductivity values remained close to or above 10^{-4} S/cm, while the mechanical flexibility and homogeneity of the films improved significantly. Compositions with higher ceramic loading showed diminishing returns in conductivity and suffered from poor flexibility, while lower loading slightly reduced conductivity without providing significant processing benefits.

The purple box contains a variety of alternative polymer formulations tested with different acrylate systems or plasticizers. Despite some moderate successes, these alternatives generally underperformed compared to the AN:GN:TMPTA system. In many cases, lower conductivity values and weaker film integrity were observed, reaffirming the AN-based system as the most promising for this application.

Finally, the orange box represents a benchmark comparison using the reference commercial LLZO instead of the AM4BAT-developed material. The results clearly show that the hybrid electrolytes made with the project's LLZO consistently outperformed those using the reference powder. This confirms the high quality of the in-house LLZO and its suitability for integration into functional electrolyte systems. It was also noted that no significant performance differences were detected between LLZO doped with Al and that doped with Ta/Nb, consistent with earlier structural characterizations.

Overall, these studies demonstrate that the optimized HSE formulation—composed of AN:GN:TMPTA with 20 wt.% LLZO and 20 wt.% LiTFSI offers the best balance of ionic conductivity (~10^{-4} S/cm), film-forming ability, and mechanical stability. While the nominal target of 10^{-3} S/cm was not fully reached, the achieved conductivity is comparable to many state-of-the-art hybrid systems and is suitable for further cell integration. Moreover, it was observed that even without LLZO, conductivity values remained within a reasonable range,

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

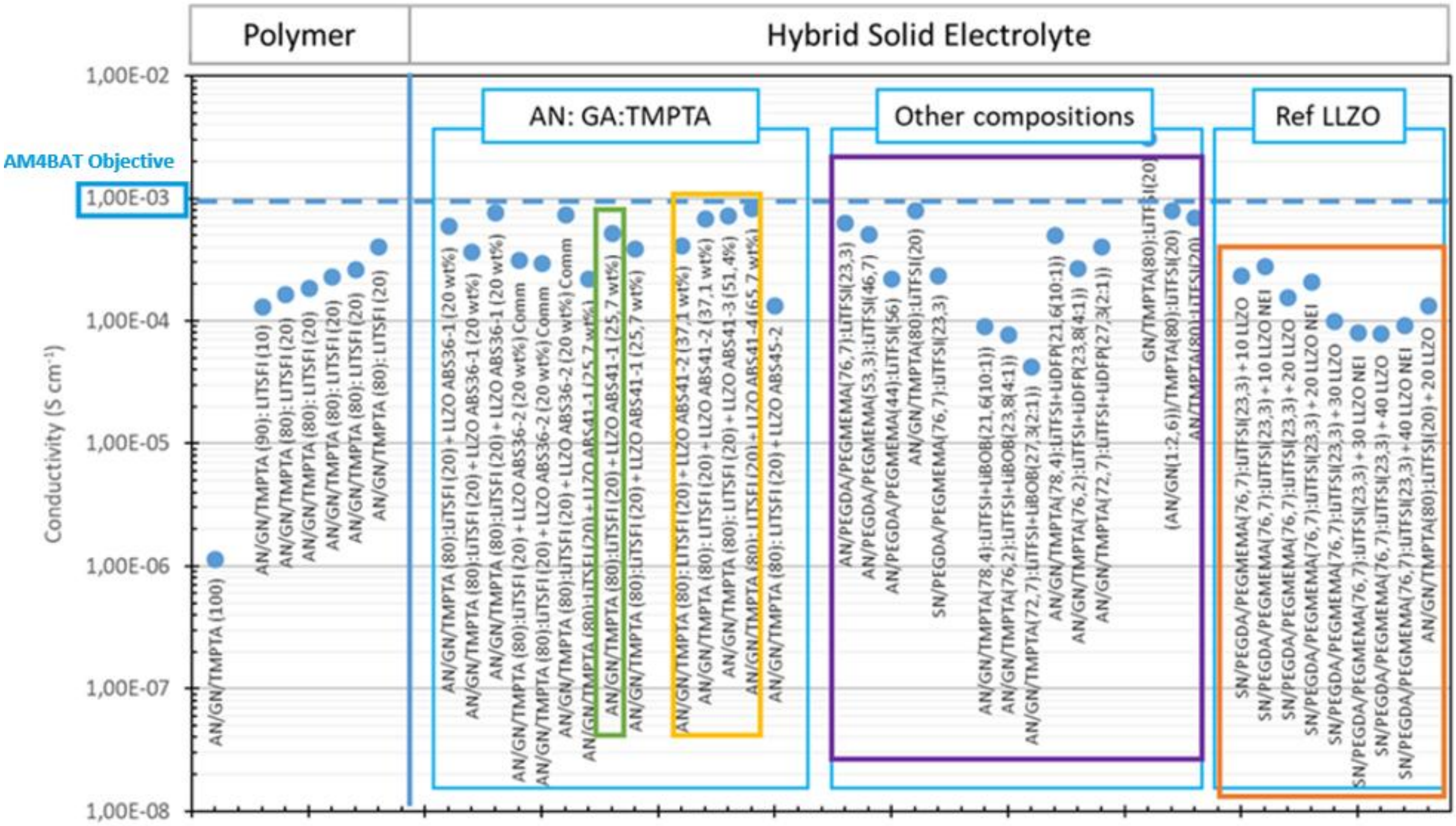

Figure 7 Ionic conductivity results of polymer-only systems (left) and hybrid solid electrolyte (HSE) formulations (right), evaluated at room temperature. The graph is divided into five color-coded categories: blue box: polymer matrices with lithium salts but without ceramic filler; green box: early HSE trials using 25 wt.% LLZO; yellow box: HSE formulations with varying LLZO content to study its effect on conductivity and film properties; purple box: alternative polymer formulations tested with LiTFSI and LLZO; and orange box: benchmark comparison using reference commercial LLZO. The best performance was obtained using the AN:GN:TMPTA polymer with 20 wt.% LiTFSI and 20 wt.% project-developed LLZO, reaching conductivity values near 10⁻³ S/cm.

offering flexibility for applications where ceramic inclusion might be undesirable due to mechanical constraints.

5.5. Voltage stability and Ion transference number

AIT performed electrochemical characterization of the photocurable film composed of TMPTA/AN/GN/LiTFSI (8:36:36:20 wt.%). Lithium-ion transference number (t^+) was determined using DC polarization and EIS methods. As shown in Table 1, the calculated t^+ value was 0.84, which is notably high for a polymer electrolyte and significantly exceeds typical liquid electrolyte values (ca. 0.5).

Table 1 Parameters from lithium-ion transference tests and the calculated transference number.

I_0 (mA)	I_{ss} (mA)	R_0 (Ω)	R_{ss} (Ω)	t_+
0.02809181	0.02646	195.5	187.7	0.84

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

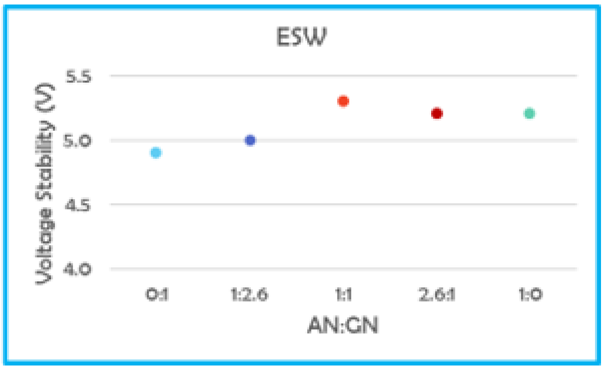

Figure 8 Electrochemical stability window (ESW) measurements of polymer electrolytes with different AN:GN monomer ratios. All formulations demonstrate voltage stability above 5.0 V, suitable for high-voltage solid-state battery applications.

To assess the electrochemical stability of the polymer electrolyte, voltage stability window (ESW) measurements were conducted for various AN:GN ratios [by PHO]. As shown in Figure 8, all tested formulations demonstrated voltage stability above 5.0 V vs. Li/Li$^+$, with maximum values approaching 5.5 V, depending on the specific monomer ratio. The highest stability was observed in compositions with balanced or GN-rich content, particularly at AN:GN ratios of 1:1. These results confirm the excellent electrochemical robustness of the polymer matrix, making it compatible with high-voltage cathode materials.

5.6. EIS Evolution During and After Formation

To assess the electrochemical interface stability of the developed SE, EIS measurements were conducted before and after the formation cycling. As previously shown, cells were monitored during stabilization (1 h to 48 h after assembly), revealing a progressive decrease in

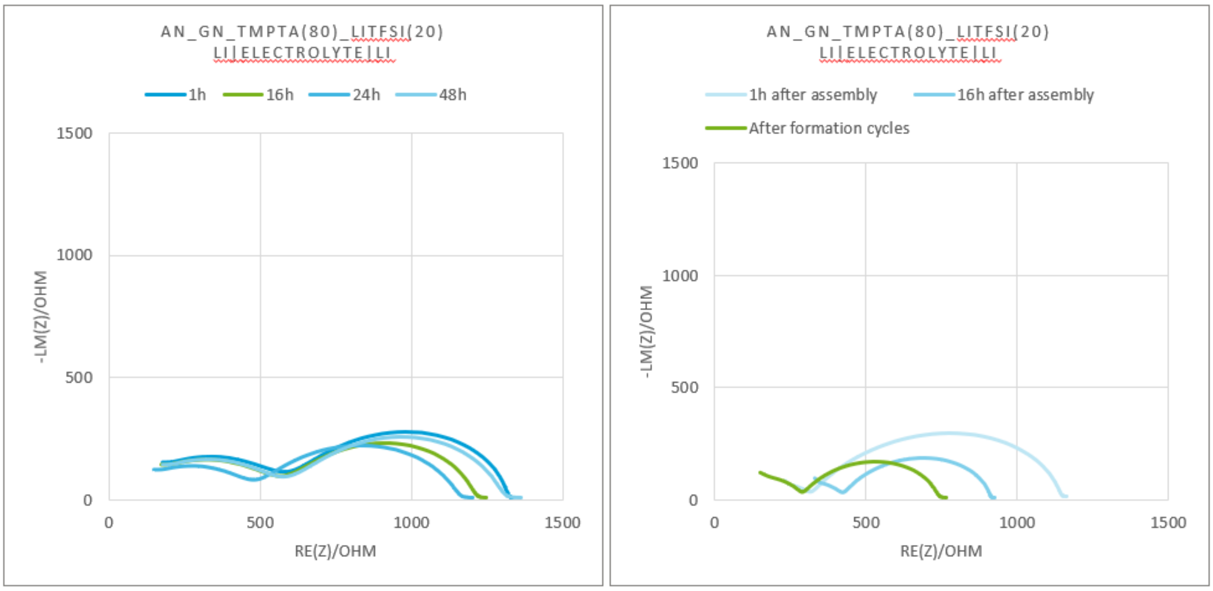

Figure 9 EIS spectra of Li | HSE | Li cells during stabilization (from 1 h to 48 h after assembly). Right: Evolution of impedance after formation cycling, showing substantial resistance drop compared to the initial spectra, reflecting improved interfacial behavior.

impedance, indicative of improved contact between lithium electrodes and the SE (left panel of Figure 9). After this stabilization phase, additional EIS spectra were recorded following a set of formation cycles (right panel of Figure 9). A marked reduction in total cell resistance was observed post-formation, demonstrating enhanced ionic transport and interface conditioning. The comparison confirms that both time and cycling contribute significantly to interfacial stabilization, making the formulation based on AN:GN:TMPTA (80) with 20 wt.% LiTFSI a promising candidate for long-term operation in lithium-metal batteries.

5.7. Cycling Performance

To assess the electrochemical stability and interfacial behavior of the developed Solid electrolyte, symmetric Li|SE|Li coin cells were subjected to galvanostatic stripping and plating experiments at a constant current density of 0.1 $mA \cdot cm^{-2}$ [at PHO and LEITAT]. Two types of polymer-based films were evaluated: one consisting solely of the polymer-salt matrix (AN:GN:TMPTA + LiTFSI), and another incorporating 20 wt.% of LLZO particles synthesized via the solid-state route by TOR.

The results are shown in Figure10, where voltage profiles over time reveal the cycling behavior and onset of interfacial degradation. The polymer-only film demonstrated relatively stable voltage response during the initial stages, characterized by narrow and symmetric voltage

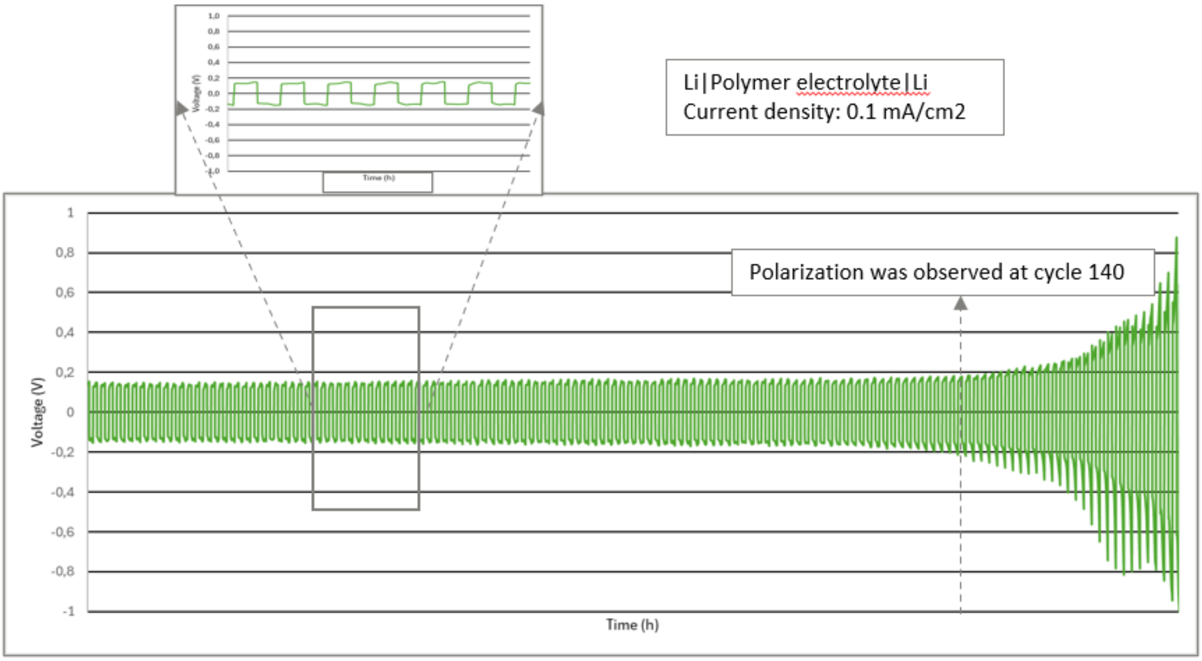

Figure 10 Voltage profile of a symmetric Li|Polymer electrolyte|Li cell cycled at a current density of 0.1 mA/cm^2. Stable voltage behavior is observed during the initial cycles, followed by a gradual increase in overpotential. Significant polarization emerges at cycle 140, indicating potential electrolyte degradation or interfacial instability. The inset highlights the initial stable cycling behavior in greater detail.

oscillations over approximately 140 cycles. This indicates good initial interfacial contact and mechanical stability of the polymer layer against lithium metal. However, a progressive increase in overpotential was observed beyond this point, indicating the onset of interfacial polarization, likely driven by lithium dendrite formation, local delamination, or accumulation of interfacial resistive species. The resulting voltage profile showed a broadening and drift, suggesting the eventual failure of electrochemical reversibility.

In contrast, the hybrid electrolyte containing LLZO exhibited significantly extended cycling performance, with polarization effects becoming prominent after approximately 221 cycles. The incorporation of ceramic fillers such as LLZO is known to enhance mechanical rigidity and suppress dendrite propagation due to their high shear modulus and interfacial ionic transport contribution. The extended lifespan observed in this case supports the hypothesis that the LLZO particles reinforce the polymer matrix, providing better resistance to electrochemical degradation mechanisms. However, the voltage response in these LLZO-containing cells appeared noisier and more irregular compared to the polymer-only system. These fluctuations may arise from non-uniform dispersion or partial agglomeration of the LLZO particles within the polymer host, creating local heterogeneities in ionic conductivity and interfacial impedance.

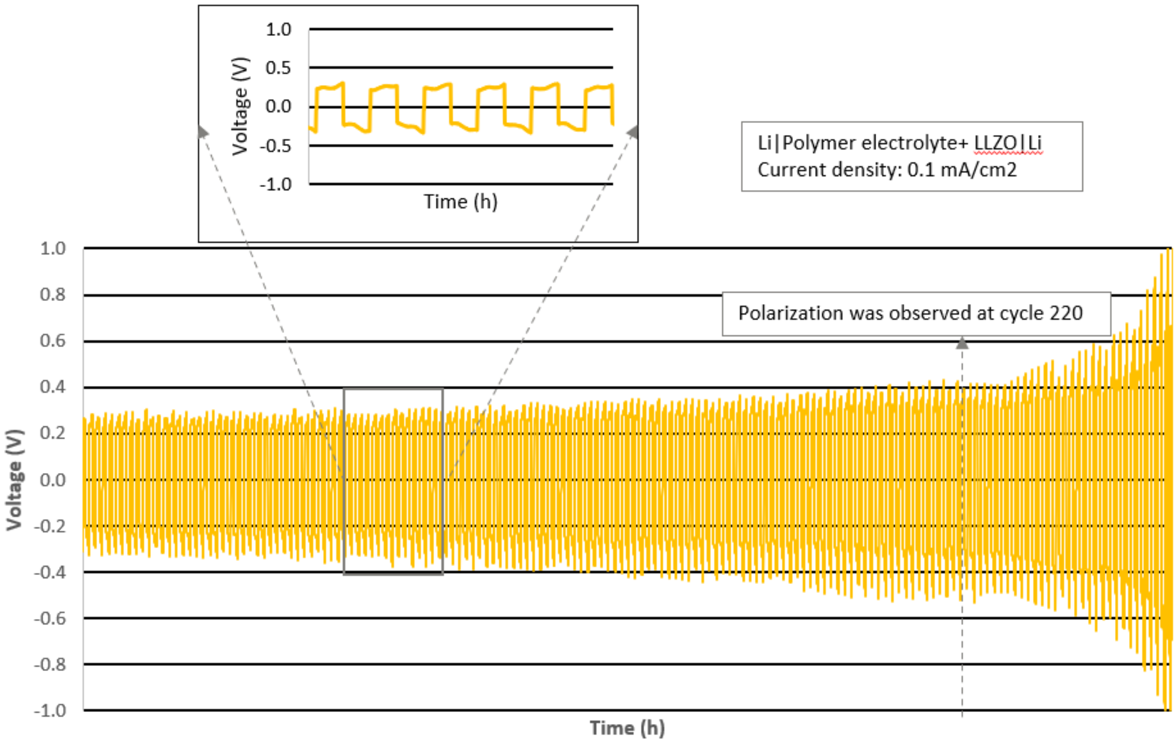

Figure 11 voltage profile of a symmetric Li|Polymer electrolyte + LLZO|Li cell. The cell exhibits stable cycling performance for an extended period, with polarization observed only at cycle 220, indicating improved interfacial stability compared to the cell without LLZO. The inset shows a magnified view of the initial voltage behavior, highlighting the regular and symmetric cycling response.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

This effect can lead to uneven current distribution during lithium deposition and stripping, which explains the higher degree of voltage noise despite the longer cycle life.

Despite the observed voltage irregularities, the LLZO-containing films demonstrated a clear advantage in total cycle count, underscoring the benefit of ceramic-polymer hybridization. However, the results also indicate that further formulation optimization, including filler dispersion, surface functionalization, and interfacial engineering, will be essential to simultaneously achieve mechanical stability, long cycle life, and smooth electrochemical operation.

5.8. NMC-Based Half-Cell Performance: Effect of Electrolyte Curing Method

To investigate the influence of interface engineering on cell performance, half-cells were assembled using NMC622 cathodes and the optimized SE [PHO and LEITAT]. Two distinct electrolyte integration strategies were evaluated: (1) using a free-standing polymer electrolyte film pressed against the cathode, and (2) directly casting the liquid monomer mixture onto the surface of the NMC cathode followed by in situ UV curing.

The EIS results of both methods are presented in Figure 12. The cell employing the free-standing electrolyte exhibited the highest interfacial resistance, as indicated by the larger semicircle in the Nyquist plot. This is attributed to incomplete physical contact and imperfect wetting between the solid electrolyte and the porous cathode surface, which can lead to poor ionic transport and interfacial polarization during operation. In contrast, when the monomer mixture was cured directly on top of the NMC cathode, a significant reduction in interfacial resistance was observed. This approach facilitates intimate interfacial adhesion and mechanical interlocking between the cathode particles and the polymer matrix as it crosslinks in place.

Moreover, the extent of this improvement appears to be time-dependent. The cell cured after 1 hour of contact showed lower resistance compared to the one cured after 5 days, suggesting that prolonged storage of the uncured electrolyte before polymerization may hinder optimal interface formation, possibly due to early diffusion effects, monomer rearrangement, or surface passivation.

These findings highlight the importance of electrolyte processing and curing strategy on the overall electrochemical performance of the hybrid solid-state system. In situ curing of the electrolyte directly onto the cathode surface proves to be a more effective method for minimizing interfacial impedance and promoting efficient lithium-ion transport at the cathode–

electrolyte interface, which is critical for improving the rate capability and cycle life of solid-state lithium-ion batteries.

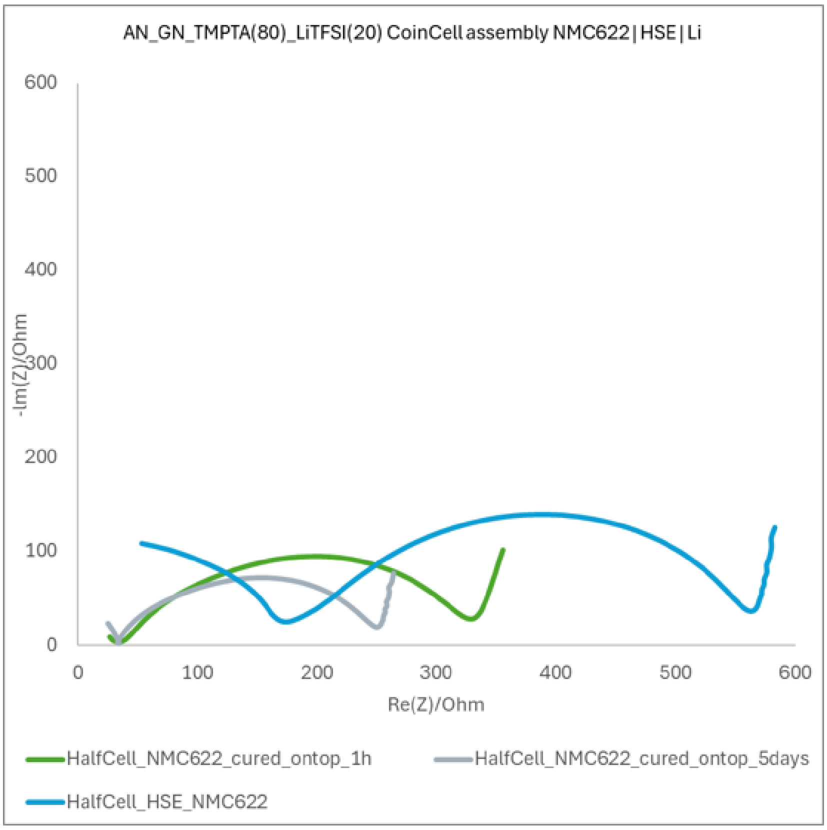

Figure 12 Nyquist plots comparing half-cell impedance with NMC622 cathode using free-standing polymer electrolyte (blue), and polymer electrolyte cured directly on top of cathode after 1 hour (green) and 5 days (light blue) of contact. In situ curing clearly lowers interfacial resistance.

The long-term cycling performance of a half-cell assembled with a free-standing SE and an NMC622 cathode was evaluated under galvanostatic conditions. The results, shown in Figure 13, illustrate the discharge capacity over 43 cycles. The cell exhibits an initial discharge capacity of approximately 105 mAh/g, which progressively decreases with cycling. After the first 5 cycles, the capacity drops below 70 mAh/g, and after 40 cycles it stabilizes around 40 mAh/g. This rapid initial fading followed by gradual stabilization suggests both interfacial limitations and insufficient ionic/electronic conductivity within the electrode-electrolyte system.

The limited capacity retention can be attributed primarily to poor interfacial contact between the NMC cathode and the free-standing polymer electrolyte. The absence of conformal contact restricts effective lithium-ion transfer across the interface, leading to increased impedance and underutilization of the active cathode material. Furthermore, the mechanical rigidity of the solid

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

film may hinder interfacial adaptability during cycling, exacerbating contact loss and contributing to capacity fade.

These findings, when contrasted with EIS measurements of in situ cured electrolytes (as discussed in Section 4.10), emphasize the critical role of electrolyte processing in hybrid solid-state cell architectures. While the polymer matrix exhibits promising electrochemical properties on its own, optimizing the integration with high-voltage cathodes such as NMC requires curing strategies that promote continuous ionic pathways and strong interfacial adhesion.

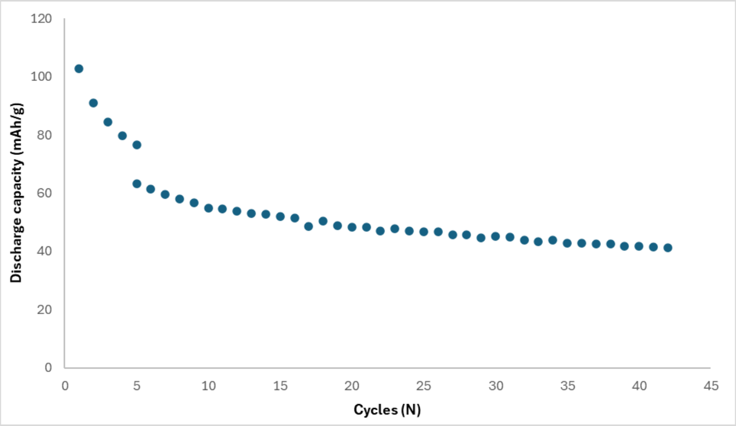

Figure 13 Discharge capacity vs. cycle number for a half-cell using free-standing electrolyte and NMC622 cathode. The cell shows rapid initial capacity loss and stabilizes around 40 mAh/g after 40 cycles, indicating interfacial and transport limitations.

To overcome the interfacial limitations observed with free-standing SE, an alternative processing method was employed whereby the uncured electrolyte formulation was directly cast and photocured onto the surface of the NMC622 cathode. This technique allows the polymer network to form in direct contact with the cathode, improving interface conformity and reducing interfacial resistance.

The cycling results from this approach are shown in Figure 14. The green data series (0.1C_1) corresponds to a cell prepared by curing the electrolyte on top of the cathode, while the blue series (0.1C_2) corresponds to a cell using a pre-formed free-standing film. The cured-on-top configuration demonstrates markedly higher initial capacity (~185 mAh/g), with gradual capacity fading over 40 cycles but still retaining around 75–80 mAh/g. In contrast, the free-standing film shows almost no usable capacity after just a few cycles, highlighting the detrimental effect of poor interfacial contact.

These results underscore the critical importance of processing strategy in solid-state cell design. The improved adhesion, ionic connectivity, and reduced interfacial impedance provided by in situ curing lead to a significant enhancement in electrochemical performance.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

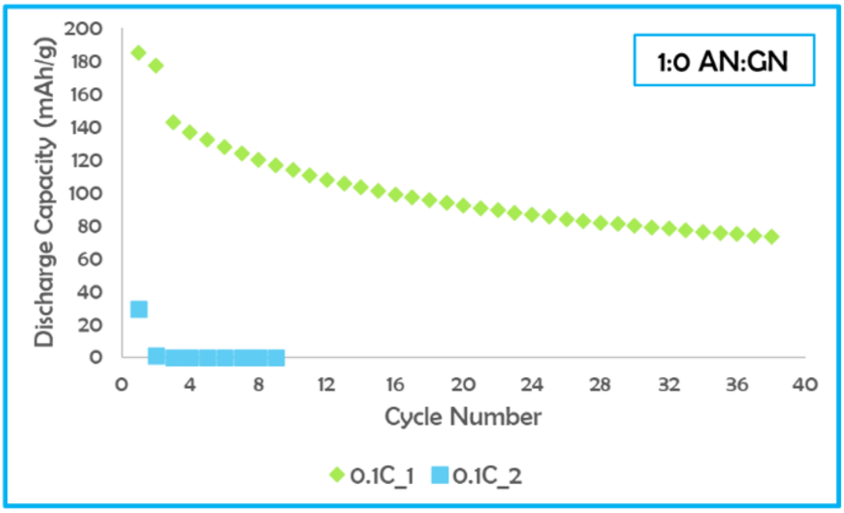

Figure 14 Discharge capacity vs. cycle number of NMC half-cells using AN:GN-based electrolyte with two configurations: electrolyte cured on top of cathode (green, 0.1C_1) and free-standing film pressed onto cathode (blue, 0.1C_2). The cured-on-top method shows superior performance due to improved interfacial contact and ionic transport.

5.9. Cycling Performance with LFP Cathode: Effect of Nickel-Free Chemistry

To further evaluate the electrochemical compatibility of the developed SE, cycling tests were conducted using $LiFePO_4$ (LFP) cathodes. This choice was motivated by the need to investigate whether reduced nickel content in the cathode improves cell stability and performance, particularly considering that Ni-rich materials like NMC often present interfacial challenges in solid-state configurations.

The results are presented in Figure 15. Two configurations were tested: free-standing SE films (0.1C_1, green markers) and on-top cured electrolytes (0.1C_2, blue markers). The performance of the free-standing electrolyte was limited, showing a rapid drop in discharge capacity and stabilizing at relatively low values (~70–80 mAh/g), consistent with poor interfacial contact and possibly higher interfacial resistance. However, the electrolyte cured directly onto the LFP electrode exhibited significantly improved results. The initial discharge capacity exceeded 160 mAh/g and remained above 130 mAh/g over 50 cycles with very stable capacity retention

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

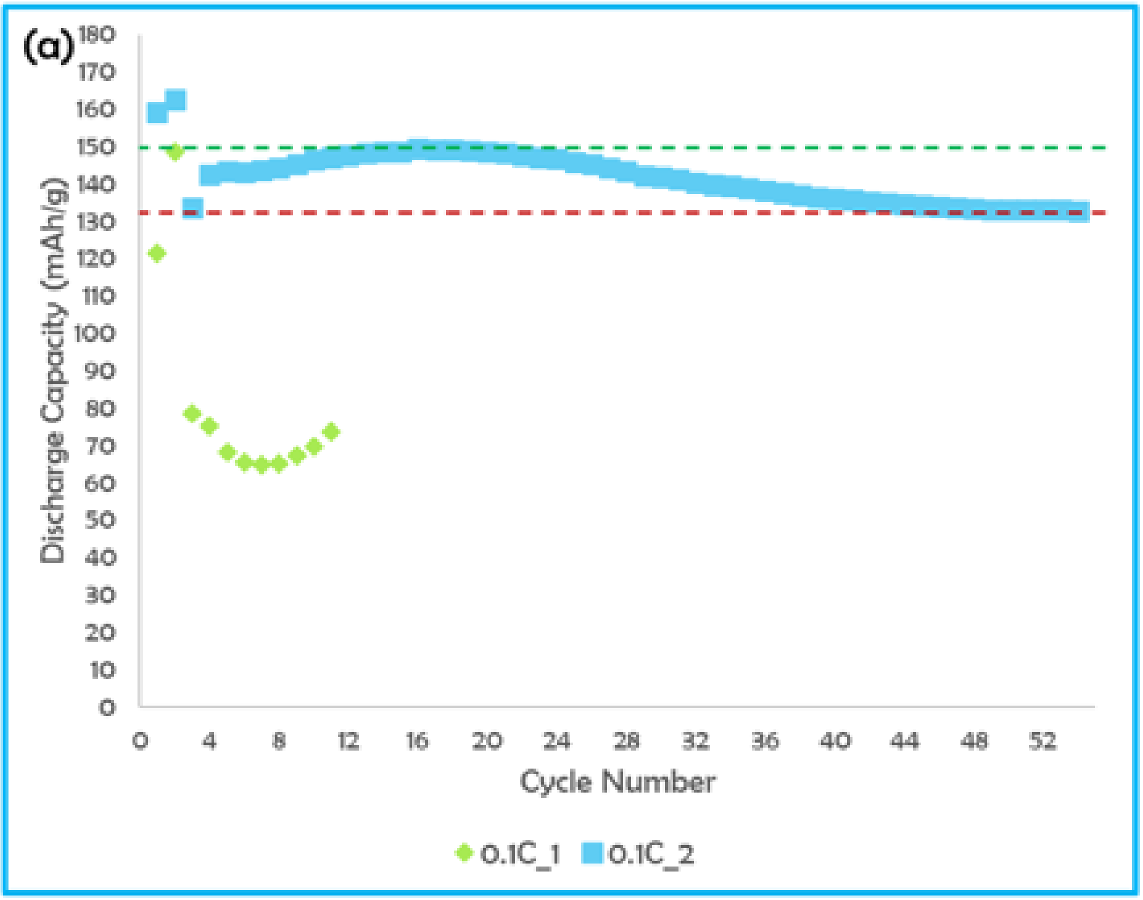

Figure 15 Discharge capacity versus cycle number of LFP-based half-cells using hybrid solid electrolytes with two configurations: 0.1C_1 (free-standing HSE) and 0.1C_2 (electrolyte cured directly on cathode). The latter shows significantly better stability and performance due to improved interfacial contact and reduced chemical reactivity compared to Ni-rich cathodes.

These results demonstrate that the absence of Ni in the LFP cathode contributes positively to interfacial stability, likely due to fewer parasitic side reactions and better chemical compatibility with the SE. Moreover, the in-situ curing strategy once again proves essential for minimizing interfacial resistance and enabling efficient lithium-ion transport. The combination of a chemically stable cathode like LFP with optimized processing of the SE yields a promising configuration for high-performance solid-state lithium batteries.

6. Conclusion

In WP3, a UV-curable solid electrolyte combining a polymer matrix with LLZO ceramic filler was successfully developed and optimized over the first 36 months of the AM4BAT project. The formulation achieved room-temperature ionic conductivity approaching 10^{-3} S/cm, an impressive result considering that conventional polymer electrolytes often require elevated temperatures to reach similar performance levels. This value is particularly relevant for enabling solid-state batteries that can operate efficiently at ambient conditions, contributing to safer and more practical battery systems.

Beyond conductivity, the electrolyte exhibited high thermal stability, a lithium-ion transference number, and a broad electrochemical stability window (>5 V), all of which exceed or meet the project's performance benchmarks. These properties make the formulation suitable for high-voltage cathodes and long-term cycling without significant electrolyte degradation or side reactions.

To support the next phases of the AM4BAT project (WP6 and WP7), which involve cell assembly and prototyping, initial full-cell tests were performed to evaluate integration strategies. These trials revealed that the method of electrolyte deposition is a key parameter. Free-standing membranes, while mechanically stable, resulted in poor interfacial contact with the cathode, leading to increased impedance and reduced cycling stability. In contrast, in-situ photopolymerization of the liquid precursor directly on the cathode surface significantly improved interface formation, reduced interfacial resistance, and delivered higher and more stable discharge capacities over cycling. This outcome highlights the importance of electrode–electrolyte interface engineering in polymer-based solid-state systems.

Preliminary cycling studies also suggested that cathodes with lower nickel content may exhibit better compatibility with the polymer-based electrolyte. While this may be related to the reduced reactivity of low-Ni chemistries (e.g., LFP or low-Ni NMC), further systematic investigation is needed. Notably, the compatibility of the hybrid electrolyte with NMC cathodes coated with protective surface layers (developed in WP4) remains to be tested and is a planned activity for WP7. These coatings may address some of the degradation mechanisms observed in high-Ni systems and further improve the electrochemical interface.

Finally, the formulation's UV-curing capability, ambient-temperature processability, and compatibility with scalable coating techniques position it as a strong candidate for industrial implementation. The findings from WP3 not only provide a validated electrolyte platform but also offer essential processing guidelines for successful integration into next-generation solid-state lithium battery prototypes.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.