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Federal Department of the Environment,
Transport, Energy and Communications DETEC

**Swiss Federal Office of Energy**
Energy Research and Cleantech

**Final report from 13 December 2024**

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# AfreeSSB

## Anode-free all-solid-state batteries: From thin film to bulk

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**Publisher:**
Swiss Federal Office of Energy SFOE
Energy Research and Cleantech
CH-3003 Berne
www.energy-research.ch

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**SFOE contract number:** SI/502460-01

# Summary

The AfreeSSB project aimed to develop anode-free solid-state batteries (SSBs) with high power and energy densities by combining thin-film and bulk technologies. The project was part of the European M-ERA.NET collaboration consisting of three national sub-projects: Swiss (Empa, Fluxim), German (FZ Jülich, Aixtron) and Spanish (IREC, AEInnova). Significant progress was achieved over the two-year project, and specifically:

- Thin-film batteries: Developed anode-free thin-film SSBs using NMC811 cathodes with areal capacities exceeding 50 µAh/cm² and peak currents up to 60 mA, meeting power requirements for applications like industrial Internet of Things (IoT) devices.
- Bulk composite cathodes: Optimized LCO composite cathodes with surface roughness below 5 µm for stable integration with thin-film separators, resulting in cathodes with a stable open-circuit voltage.
- Operando characterization: Established new methods for real-time monitoring of material behaviour during battery operation. SE analyzed optical absorption changes related to the state of charge, while TERS revealed grain boundary dynamics during lithiation.
- Device testing: Developed a battery testing setup with temperature control (5–90 °C) and charge/discharge capabilities. Power electronics with Maximum Power Point Tracking (MPPT) were created to manage energy storage for industrial IoT applications.

The AfreeSSB project demonstrated the potential of anode-free SSBs for high-energy-density applications. Thin-film batteries showed promise for IoT and mobile applications, although further capacity improvements are needed. The concept of the bulk cathode combined with a thin solid electrolyte separator requires additional work to address scalability and cycling stability. The advanced operando characterization methods offer valuable tools for future battery research. Overall, the project laid the groundwork for future development and potential industrial applications of SSB technology. The innovations are expected to drive further research and commercial applications in the energy storage field.

# Zusammenfassung

Das Projekt AfreeSSB hatte zum Ziel, anodenfreie Festkörperbatterien (SSBs) mit hoher Leistungs- und Energiedichte durch die Kombination von Dünnschicht- und Volumentechnologien zu entwickeln. Das Projekt war Teil der europäischen M-ERA.NET-Kooperation, die aus drei nationalen Teilprojekten bestand: Schweiz (Empa, Fluxim), Deutschland (FZ Jülich, Aixtron) und Spanien (IREC, AEInnova). In den zwei Jahren des Projekts wurden bedeutende Fortschritte erzielt, insbesondere:

- Dünnschichtbatterien: Entwicklung anodenfreier Dünnschicht-SSBs mit NMC811-Kathoden mit Flächenkapazitäten von über 50 µAh/cm² und Spitzenströmen von bis zu 60 mA, die die Leistungsanforderungen für Anwendungen wie industrielle IoT-Geräte (Internet der Dinge) erfüllen.
- Bulk-Verbundkathoden: Optimierung von LCO-Verbundkathoden mit einer Oberflächenrauheit von unter 5 µm für eine stabile Integration mit Dünnschichtseparatoren, was zu Kathoden mit einer stabilen Leerlaufspannung führt.
- Operando-Charakterisierung: Etablierung neuer Methoden zur Echtzeitüberwachung des Materialverhaltens während des Batteriebetriebs. SE analysierte optische Absorptionsänderungen in Abhängigkeit vom Ladezustand, während Tip-Enhanced Raman Spectroscopy (TERS) die Korngrenzdynamik während der Lithiierung aufzeigte.
- Gerätetests: Entwicklung eines Batterietestaufbaus mit Temperaturregelung (5–90 °C) und Lade-/Entladefunktion. Zur Steuerung der Energiespeicherung für industrielle IoT-Anwendungen wurde eine Leistungselektronik mit Maximum Power Point Tracking (MPPT) entwickelt.

Das AfreeSSB-Projekt hat das Potenzial von anodenfreien SSBs für Anwendungen mit hoher Energiedichte aufgezeigt. Dünnschichtbatterien sind vielversprechend für IoT- und mobile Anwendungen, allerdings sind weitere Kapazitätsverbesserungen erforderlich. Das Konzept der Volumenkathode in Kombination mit einem dünnen Festelektrolytseparator erfordert weitere Arbeiten, um die Skalierbarkeit und Zyklenstabilität zu verbessern. Die fortschrittlichen Operando-Charakterisierungsmethoden bieten wertvolle Werkzeuge für die zukünftige Batterieforschung. Insgesamt hat das Projekt die Grundlagen für die zukünftige Entwicklung und potenzielle industrielle Anwendungen der SSB-Technologie gelegt. Die Innovationen werden voraussichtlich weitere Forschungen und kommerzielle Anwendungen im Bereich der Energiespeicherung vorantreiben.

# Résumé

Le projet AfreeSSB visait à développer des batteries à l'état solide (SSB) sans anode, à haute puissance et haute densité énergétique, en combinant des technologies à couche mince et à volume. Le projet s'inscrivait dans le cadre de la collaboration européenne M-ERA.NET, qui comprenait trois sous-projets nationaux : suisse (Empa, Fluxim), allemand (FZ Jülich, Aixtron) et espagnol (IREC, AEInnova). Des progrès significatifs ont été réalisés au cours des deux années du projet, notamment :

- Batteries à couche mince : développement de SSB à couche mince sans anode utilisant des cathodes NMC811 avec des capacités surfaciques supérieures à 50 µAh/cm² et des courants de pointe pouvant atteindre 60 mA, répondant ainsi aux exigences de puissance pour des applications telles que les appareils industriels connectés à l'Internet des objets (IoT).
- Cathodes composites en vrac : optimisation des cathodes composites LCO avec une rugosité de surface inférieure à 5 µm pour une intégration stable avec des séparateurs à couche mince, ce qui permet d'obtenir des cathodes avec une tension en circuit ouvert stable.
- Caractérisation operando : mise en place de nouvelles méthodes de surveillance en temps réel du comportement des matériaux pendant le fonctionnement des batteries. La SE a analysé les changements d'absorption optique liés à l'état de charge, tandis que Tip-Enhanced Raman Spectroscopy (TERS) a révélé la dynamique des joints de grains pendant la lithiation.
- Test des dispositifs : mise au point d'un dispositif de test de batteries avec contrôle de la température (5 à 90 °C) et capacités de charge/décharge. Des composants électroniques de puissance avec suivi du point de puissance maximale (MPPT) ont été créés pour gérer le stockage d'énergie pour les applications IoT industrielles.

Le projet AfreeSSB a démontré le potentiel des SSB sans anode pour les applications à haute densité énergétique. Les batteries à couche mince se sont révélées prometteuses pour les applications IoT et mobiles, même si des améliorations de capacité sont encore nécessaires. Le concept de cathode massive combinée à un séparateur électrolytique solide mince nécessite des travaux supplémentaires pour résoudre les problèmes de scalabilité et de stabilité cyclique. Les méthodes avancées de caractérisation operando offrent des outils précieux pour la recherche future sur les batteries. Dans l'ensemble, le projet a jeté les bases du développement futur et des applications industrielles potentielles de la technologie SSB. Ces innovations devraient stimuler la recherche et les applications commerciales dans le domaine du stockage d'énergie.

# Main findings («Take-Home Messages»)

- The project advanced anode-free solid-state battery technology through material optimisation, device integration and testing and initial industrial validation.
- For the first time (to the best of our knowledge) tested thin-film separators on bulk, energy dense cathodes. Empa achieved stable OCV with 2-3 µm thick LiPON without successful cycling. Our results demonstrate the potential of this combination for future energy storage solutions but further work is necessary.
- The collaboration of academic and industrial partners was effective and efficient and will be continued further: follow-up projects between Fluxim and Empa were submitted. Collaborations of Empa and IREC as well as Fluxim and IREC are continuing and will be expanded in future projects.
- The Swiss industrial partner – Based on the successfully developed prototype Fluxim is exploring the competitive area of battery testing equipment and data analysis software with support from Empa with the unique selling point of a compact, wide-range temperature chamber de-coupled from the multi-channel testing setup.

# Contents

# List of abbreviations

| | |
|---|---|
| SFOE | Swiss Federal Office of Energy |
| WP | work package |
| SSB | solid state battery |
| AF-SSB | anode-free solid state battery |
| LIB | lithium-ion battery |
| TF-SSB | thin film solid state battery |
| CVD | chemical vapour deposition |
| LMO | lithium manganese oxide |
| NMC | lithium nickel-manganese-cobalt oxide |
| LCO | lithium cobalt oxide |
| LLZO | lithium lanthanum zirconium oxide |
| RTP | rapid thermal processing |
| EIS | electrochemical impedance spectroscopy |
| IoT | internet of things |
| SE | solid electrolyte |

# 1 Introduction

## 1.1 Context and motivation

Generation 4 solid-state batteries (SSBs) offer significant advantages over conventional lithium-ion batteries (LIBs) by using metallic lithium as an anode, which could dramatically improve energy density. However, the tendency of lithium to form dendrites during cycling poses a safety risk, especially when paired with flammable liquid organic electrolytes, as these can lead to short circuits and potential fires. SSBs address many of the safety concerns associated with liquid electrolytes, but dendrite growth remains a challenge even with solid electrolytes.

So called **anode-free batteries** (also called Li-reservoir free) pair a lithiated cathode (most of state-of-the-art cathode materials are manufactured in the lithiated state) with a bare anode current collector onto which the Li is plated with every charging.[1] Anode-free batteries have the advantage of increased energy density (by not including additional Li that is not necessary assuming highly reversible Li plating and stripping. In typical Li-metal batteries, the Li foils used are 20-200 µm in thickness, incurring a significant weight and volume penalty. Additionally, the manufacturing of lithium-metal foils for SSBs requires complex handling in an inert atmosphere, complicating commercialization.[2,3] Lastly, to compete with conventional Li-ion batteries in terms of energy density, the solid separator in bulk solid state batteries must be as thin as a few tens of micrometers,[4] even when metallic Li is employed as an anode. Most solid separators used today, however, are in the order of hundreds of micrometers.[5]

**Thin-film solid-state batteries** are made using thin-film deposition methods such as evaporation or sputtering allowing for manufacturing of dense layers with good solid-solid interfacial contact, in a conformal way and high control over the thickness of the layers.[6] As the functional layers are up to a few µm in thickness, it is possible to miniaturise the batteries for microdevices, on-chip batteries and IoT applications.[6,7] Moreover, the thin layers allow for short diffusion paths of Li ions resulting in faster possible charge/discharge rates. A key component here is the thin-film electrolyte (often LiPON), with sufficiently low electronic conductivity to effectively act as the solid-state separator. In thin-film microbatteries it is often on the order of single µm in thickness. Here, the limiting factor for their performance is usually the cathode energy and power density with Co-containing LCO as the typical cathode material.[7–9]

Several **battery test equipment** solutions are available and with the strong growth in world-wide battery research activities, Fluxim identified the opportunity to develop and commercialize a dedicated multichannel battery testing instrument with a temperature controlled test chamber. The available instruments often are limited to high-throughput multichannel cycling with limited range of characterization routines, whereas high-end and high-cost-per-channel characterization instruments often offer only a limited number channels. It was the motivation of Fluxim to develop a demonstrator (prototype) instrument which serves as a stepping stone for further development beyond project end.

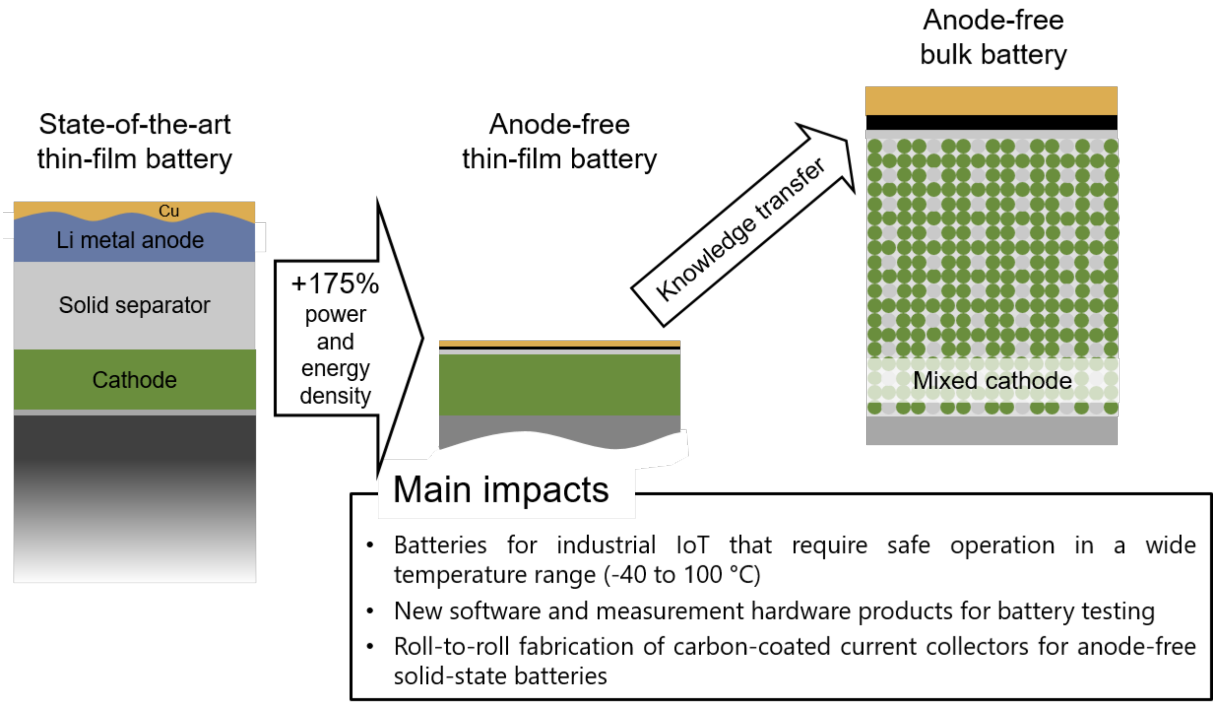


**Figure 1 Schematic representation of the AFreeSSB project motivation and goals.**

The proposed **AfreeSSB project** aimed to (also see Figure 1):

1. Develop better thin-film batteries with high power densities by introduction of better cathode materials and seed layers for Li plating.
2. Leverage the expertise of Empa in thin-film solid state batteries to coat bulk solid-state cathodes with thin-film separators. If successful, this concept will maximise the energy and power densities of such hybrid batteries.
3. Develop anode-free SSBs (thin-film and bulk) without excess lithium, thereby harnessing the advantages of lithium-metal anodes while simplifying manufacturing, and enhancing the energy density.
4. Develop new software and measurement hardware for battery testing, considering the needs of battery scientists such as present in this project consortium.

**Table 1:** Comparison of existing state-of-the-art before the start of the project and the planned improvements over the duration. The achieved goals are highlighted in green.

| High power density thin-film system | | |
|---|---|---|
| State of the art[10,11] | Beyond state of the art | Expected improvement |
| Anode: Li metal (500 nm) | Anode: Anode-free design enabled by amorphous carbon interlayers (50 nm) | ≥0.2% in volumetric energy and power density |
| Solid electrolyte: Amorphous LiPON (1.5 µm) | Solid electrolyte: Ultrathin thin solid electrolyte (100 nm) (300 nm achieved) | ≥0.5% in volumetric energy and power density |
| Current collector: Pt coated Si wafer (276 µm) | Current collector: Thin and flexible Al foil (100 µm)<br><br>Achieved with 11 µm Ti foil | ≥169.8% in volumetric energy and power density |
| Cathode: LCO, LMNO, or LMO thin-films (1 µm) | Cathode: High stable cobalt-free (LMO) thin films, nickel-rich (NMC811) thin films (1 µm) | Further possible improvement of 20.8% in volumetric energy density by using NMC811 instead of LMO |
| Operating condition: Room temperature | Operating condition: Wide temperature range from -40 to 100 °C enabled by carbon interlayers<br><br>**Achieved: built a low-temperature setup for testing thin-film batteries.** | |

| High energy density bulk system in a bipolar stack | | |
|---|---|---|
| State of the art[12] | Beyond state of the art | Expected improvement |
| Anode: Li metal foil (100 µm) | Anode: Anode-free design enabled by 3D structured CNT carpets (5-20 µm) or amorphous carbon interlayers (100 nm) | ≥15.0% in volumetric energy and power density |
| Solid separator: Thick solid separator (200 µm) | Solid separator: Thin solid separators (2 µm)<br><br>**OCV achieved but not stable cycing, stable cycling with cathodes from another project** | ≥47.5% in volumetric energy and power density |
| Cathode: Bulk mixed cathodes (LCO and LLZO) fabricated by high-temperature sintering (>1050 °C, dwell time few hours) | Cathode: Bulk mixed cathodes (LCO and LLZO) fabricated by advanced sintering techniques such as pressure assisted field assisted sintering (<750 °C, dwell time <10 minutes) | Further possible improvement of 13.9% in volumetric energy density by using NMC811 instead of LCO |
| Operating condition: Elevated temperatures (>50 °C) | Operating condition: Wide temperature range from 0 to 100 °C | |

# 2 Approach, method, results and discussion

The AfreeSSB project was divided into four work packages (WPs).

**WP1 - Thin-film System**: Empa lead the development of anode-free solid-state thin-film batteries, focusing on creating stable lithiophilic interlayers through magnetron sputtering and by using vertically aligned carbon nanotube structures with controlled void ratios using CVD (Aixtron). Benchmarking of different thin-film solid separators was also done in TFSSBs. Empa, in collaboration with IREC worked towards high energy density thin-film cells based on thin separators and high energy cathodes such as LMO and NMC.

**WP2 - Bulk System**: Led by FZJ, this WP focused on optimizing bulk cathodes made via tape casting and solid electrolyte separators. Shortly, the composite cathode (cathode active material + conductive additives + catholyte) was optimised to achieve gradient LCO-LLZO cathodes with low surface roughness, low defect density and high energy density. These bulk cathodes were then combined with thin-film separators developed at Empa and IREC to target high energy density anode-free cells.

**WP3 - Advanced Characterization**: IREC lead efforts in operando characterisation of cells made in the project. Operando spectroscopic ellipsometry and Raman spectroscopy were used to measure the behaviour the cells and its evolution over time. Further analyses include nuclear reaction analysis and ion beam scanning to map lithium content and ion profiles (FJZ), providing a multi-layer perspective on the state of charge and degradation mechanisms. Lastly, Fluxim and Empa worked on simulating the behaviour of ions during transient current measurements to develop a new method for quantifying the concentration and mobility of charge carriers.

**WP4 - Industrial Implementation and Dissemination**: Fluxim developed a stress-testing setup with temperature control for parallel testing of batteries, incorporating electrochemical impedance spectroscopy. AEInnova supported device integration of thin-film cells from WP1 as replacements for supercapacitors used currently. Aixtron developed CNT-coated copper foils made by CVD methods and optimised their approach.

Main results

The AfreeSSB project largely fulfilled the objectives outlined in the original work plan, with most milestones and deliverables achieved on time. The project's collaborative nature allowed for effective problem-solving, particularly when deviations from the plan occurred. Several partners reported slight delays or modifications due to unforeseen challenges, but these did not significantly impact the overall timeline or the final outcomes. Results and tasks within the Swiss sub-project are given in normal text, whereas tasks led by German and Spanish partners are provided in light-grey.

- The seed layers tested (Au, Pt, amorphous C) were benchmarked against a bare Cu current collector in Cu/Li/LiPON/Li/seed layer/Cu cells. Briefly, all seed layers reduced the overpotentials for Li plating across all current densities. Notably, Pt and C exhibited best performance with <0.1 V overpotentials even at high 8 mA/cm$^2$ plating rates. The critical current density was not reached then, which is excellent as, for comparison, the typical critical current densities reported in the literature are on the order of 1-3 mA/cm$^2$ with only rare reports of >8 mA/cm$^2$.[13–15] The results are summarised in **Figure 2** and were published in *ACS Appl. Mater. Interfaces.*[16]

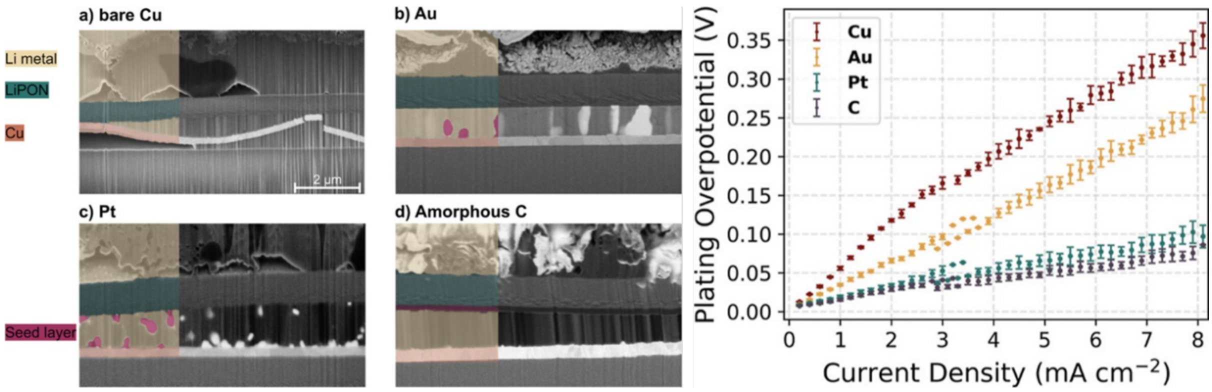


**Figure 2:** Left: cross-sectional micrographs of the 3 seed layers and bare Cu current collector and their microstructure after Li plating. Clear re-structuring of the Au and Pt seed layers is seen. Right: Li plating overpotential versus current density for the four sample types highlighting the best performance (lowest overpotentials) and excellent current densities for Pt and C.

- CNT-forest coated Cu foils were also tested as host layers for Li plating. However, they exhibited extremely irreversible Li uptake and were also not suitable for RF-sputtering coating with LiPON separator and therefore, that line of research was discontinued shortly into the project.
- Empa made substantial progress in thin-film solid-state batteries through development of NMC811 cathodes with high energy and power densities. Figure 3 shows RF-sputtered NMC811 batteries with conventional furnace-annealed NMC811 that achieved >50 µAh/cm$^2$ at 1C rate with stable cycling at capacity fade of 3.5%/cycle.

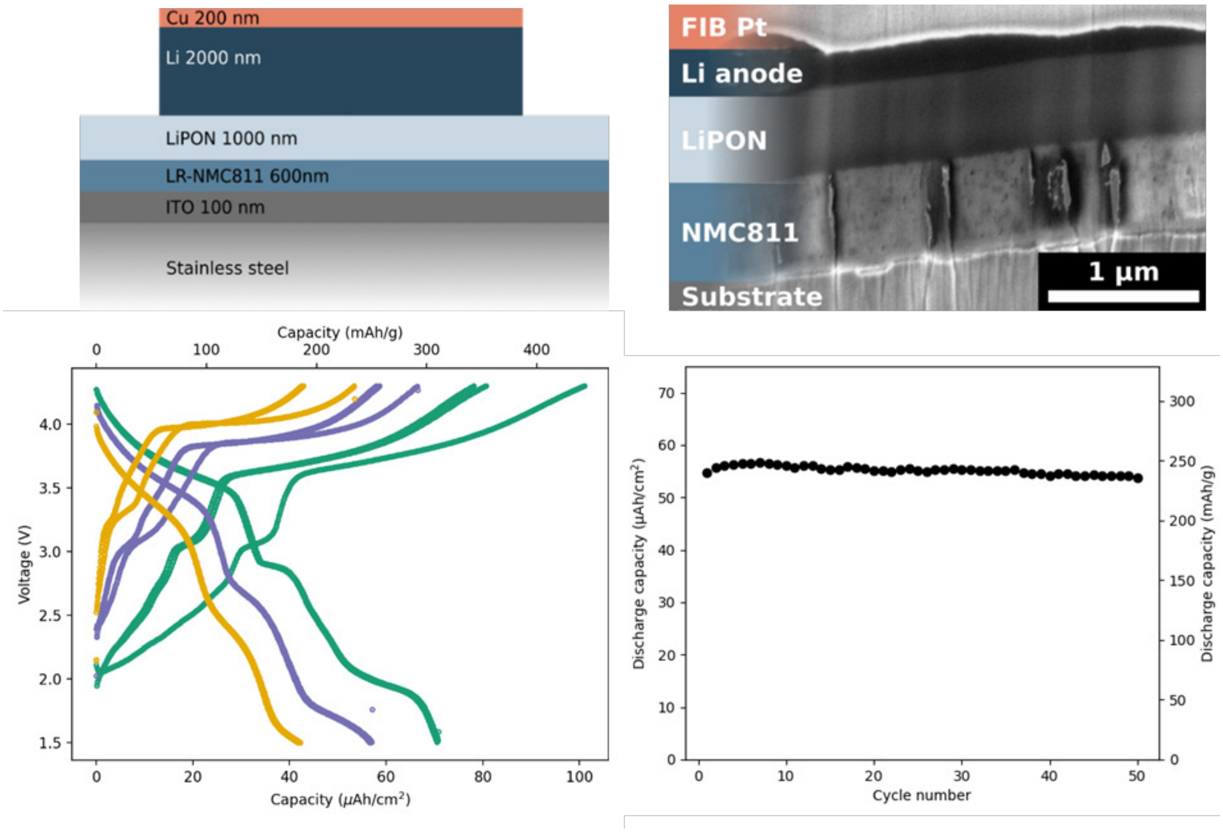


**Figure 3:** High energy density thin-film NMC811 cells. Top: schematic and FIB-SEM views of the samples. Bottom left: voltage profiles for rates of C/5 (green), 1C (purple), 2C (yellow). Bottom right: electrochemical performance showing stable >50 µAh/cm2 discharge capacities at 1C rate.

- Empa also developed anode-free NMC811 cells on foil substrates using rapid photonic crystallisation achieving excellent power and energy densities, almost reaching the ambitious goals of the project, as highlighted in Figure 4.

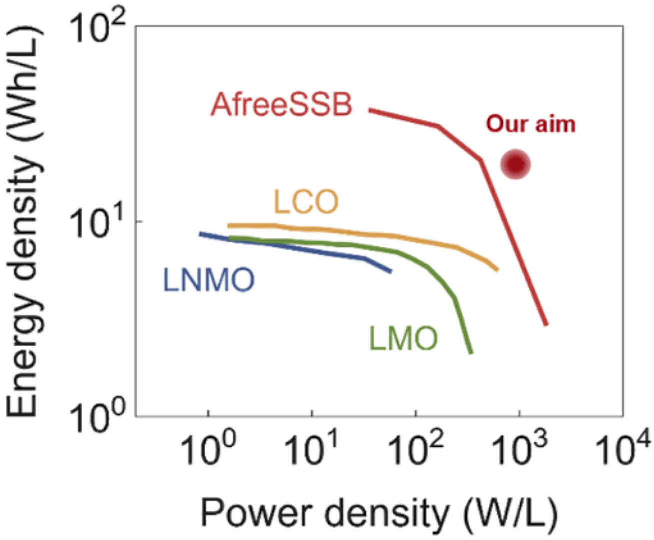


**Figure 4:** Ragone plot of the record anode-free thin-film cell made at Empa with the aims of the project and the SoA results for comparison.

- Another exciting aspect of the AfreeSSB project was the attempt to coat bulk solid state cathodes from FZJ (LCO+LLZO sintered into a thin pellet) with thin-film separators for high energy density cells. Briefly, the samples from FZJ were successfully coated with initial tries ending in short-circuited cells. After optimisation of the surface morphology, a stable OCV was measured but without successful cycling. Our working hypothesis is that while the roughness of the cathode has been improved to levels handled by LiPON coating (see **Figure 5**), the contact between layers is not sufficient for full cell cycling. There may also be issues with local defects as only one pit or defect of the surface can be enough to short the cell. This approach was also being explored further as part of other projects and will be pursued in the future.

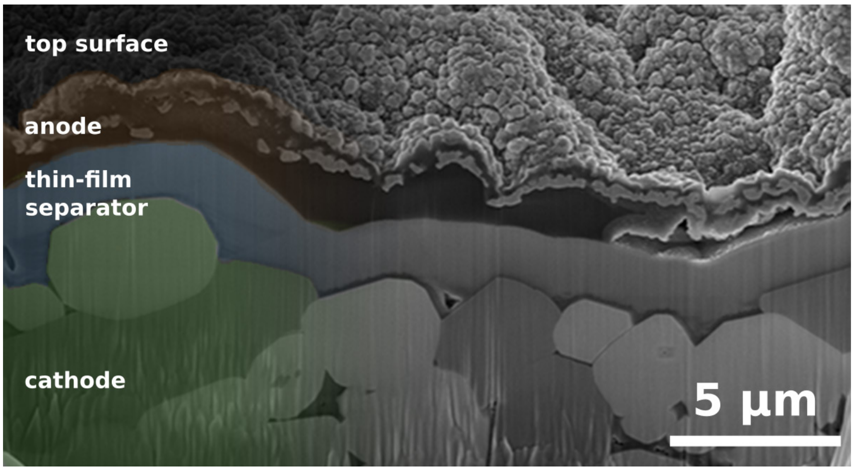


**Figure 5:** Cross-sectional SEM image of a mixed bulk cathode from FZJ coated with LiPON thin-film separator at Empa.

- Fluxim successfully developed a prototype battery testing setup with temperature control and charge/discharge capabilities (see Figure 6). The control of the chamber temperature was successfully validated using several temperature sensors placed in the chamber and read out during temperature ramps. The electrical signals acquired during recurring cycling were validated against a reference measurement of a commercial galvanostat. The main deviation occurred in the testing of only one channel of the setup, while eight were originally planned. Full integration of the EIS instrument is still pending and will require further work beyond the project's duration. Collaborations with Empa and IREC on device simulations with Fluxim's software Setfos contributed to the achievement of additional project objectives. A dedicated solver for simulating Li ion battery cells was developed after project completion and promises to be effective and useful for simulating battery signals.

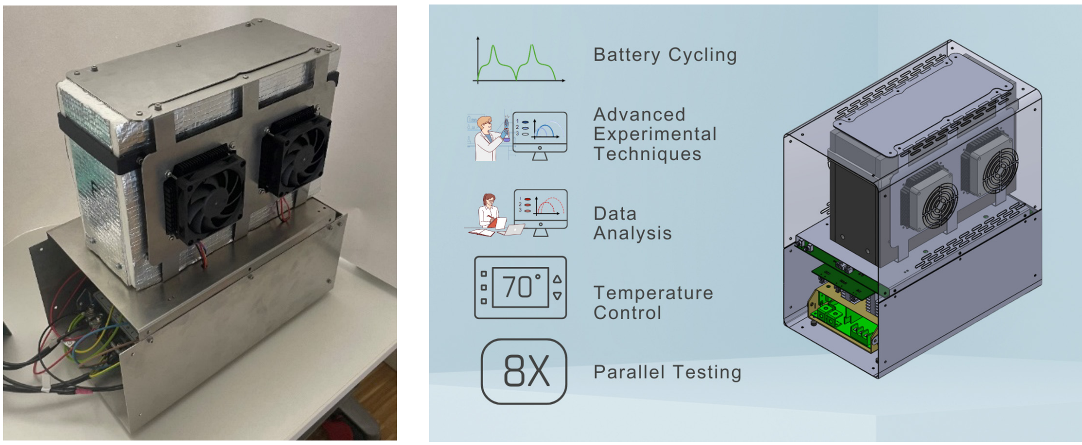


**Figure 6: Picture of the demonstrator developed by Fluxim. The bottom part contains the electronics for charge/discharge, the temperature controller and the power suppliers. The upper part is the temperature chamber. The illustration on the right shows the corresponding CAD drawing and some specifications.**

- FZJ: FZJ achieved substantial progress in optimizing LLZO-LCO cathodes, reducing surface roughness below 5 µm and identifying methods to minimize surface defects. This work enabled the fabrication of larger cathodes for hybrid battery cells, meeting the performance requirements for industrial applications.
- AIXTRON: AIXTRON made important advancements in the growth of CNT carpets, increasing the growth rate by 3.5x and achieving uniform CNT lengths. The development of 3D-structured CNT carpets with a 50%/50% void/bunch-ratio opens opportunities for enhanced electrode integration in energy storage devices.
- IREC: IREC developed thin-film NASICON-based solid electrolytes using Rapid Thermal Processing, reducing the processing time significantly. These electrolytes were successfully integrated with bulk mixed cathodes for the first time. IREC also led the implementation of advanced characterization techniques such as TERS, providing valuable insights into grain boundary behavior
- AEInnova: AEInnova developed new power electronics with Maximum Power Point Tracking (MPPT) to manage the charge and discharge of bulk batteries. In the absence of a physical battery, AEInnova successfully emulated the battery using a 5F supercapacitor and a 470Ω resistor. This configuration allowed their commercial device to operate, demonstrating the viability of energy storage management in industrial IoT applications .

Challenges:

- Empa: Empa faced challenges with integrating CNT-coated copper foils as lithiophilic layers due to their incompatibility with RF sputtered thin-film separators. Attempts to coat these CNT carpets with LiPON were unsuccessful, and as a result, the integration of CNTs was discontinued. Additionally, in the bulk cathode/LiPON/Li cells, achieving stable cycling proved difficult due to surface roughness and shorting issues. Further optimization of the bulk cathode and thicker LiPON layers is necessary to resolve these problems.
- Fluxim: The initial prototype of Fluxim's battery testing setup was tested with only one channel, whereas the original design included eight channels. Although the single channel performed well, full-scale testing of the multi-channel system is still required. Additionally, while the EIS instrument was incorporated into the system design, further tests are needed to fully validate its integration with the testing setup
- FZJ: While FZJ succeeded in optimizing the surface roughness of the LLZO-LCO cathodes, scaling up the cathode size introduced new challenges, particularly in maintaining uniformity across larger areas. Surface defects, identified as a critical factor in device performance, require further optimization, and more work is needed to refine cathode thickness to improve mechanical stability and discharge rates under industrial load conditions.
- AIXTRON: AIXTRON encountered difficulties in managing the surface roughness of the thin Cu foils used for CNT growth. The roughness of the foils impacted the uniformity of the CNT carpet, which necessitated additional efforts to either refine the Cu foil preparation process or adapt the CVD growth process to compensate for these variations. Though CNT growth on smoother surfaces was successful, further work is needed to mitigate this issue for large-scale applications.
- IREC: IREC experienced delays due to a shortage of neon gas, which affected their ability to use pulsed laser deposition (PLD) for coating bulk mixed cathodes. This resulted in a three-month delay in experiments and limited the amount of testing that could be done within the project's timeframe. Despite these challenges, IREC completed proof-of-concept work on key interfaces and continued optimizing their RTP processes.
- AEInnova: AEInnova developed new power electronics with Maximum Power Point Tracking (MPPT) to manage the charge and discharge of bulk batteries. In the absence of a physical battery, AEInnova successfully emulated the battery using a 5F supercapacitor and a 470Ω resistor. This configuration allowed their commercial device to operate, demonstrating the viability of energy storage management in industrial IoT applications .

# 3 Conclusions and outlook

The AfreeSSB project successfully advanced the development of anode-free solid-state batteries (SSBs). Significant achievements included:

1. Benchmarking of seed layer materials with amorphous carbon being the best choice from the ones tested,
2. Initial proof-of-principle results from the combination of bulk cathodes with thin film separators, with stable OCV.
3. Prototype, industrially relevant battery testing setup with the unique capability of separate heating chambers for 8 samples in a compact form factor.

While some challenges with material integration and device scaling persist, the results validate the potential of anode-free SSBs for high-energy applications such as industrial IoT. Looking ahead, Empa will continue efforts to refine the thin-film + bulk combination and to further push the performance of TFSSBs as essential for future commercialization of both battery types. Fluxim is continuing the development of the battery test instrument and heating chamber and collect test run feedback from relevant battery research groups. Moreover, a standard Li-ion battery model will be implemented to explore further simulation opportunities.

Future collaborative projects are planned with the partners from AFreeSSB: FZJ, IREC, Fluxim. Moreover, during the project, an Empa spin-off was founded, focusing on scale-up and commercialisation of thin-film, anode-free batteries which will also be an attractive partner for future projects. Overall, the insights gained from this project lay a solid foundation for future Swiss research and commercial applications, positioning anode-free SSBs as a promising technology for sustainable energy storage aligned with Swiss energy goals.

# 4 National and international cooperation

Efficiency of the consortium's cooperation

The AfreeSSB consortium worked efficiently throughout the project, with all partners contributing actively to the progress of key tasks. Regular meetings and data exchanges ensured smooth coordination, particularly in areas requiring shared expertise such as materials characterization, device integration, and battery testing. Empa, IREC, and Fluxim collaborated closely on developing methodologies for testing and validating project outcomes. A notable example of the consortium's strong cooperation was the visit of Fernanda Monteiro Freitas, a PhD student from IREC, who spent two months at Empa from May 2 to June 28, 2024. During this visit, she successfully fabricated a thin-film solid-state battery using LFP cathodes, strengthening ties between the two institutions and laying the groundwork for future joint publications and collaborations.

Changes in the consortium composition

There was one significant change in the consortium during the project: AEInnova opted to self-fund its portion of the project rather than receiving funding from its designated funding organization, CDTI. This decision led to AEInnova being unable to attend in-person meetings abroad, though they remained fully engaged in developing the prototypes as outlined in the project proposal. Despite this change, the overall goals and outcomes of the project were unaffected, and all project partners and funding organizations acknowledged and supported this adjustment.

Difficulties encountered by the consortium

The consortium encountered several technical difficulties that required careful management. IREC faced delays due to a neon gas supply shortage, which disrupted their ability to use pulsed laser deposition for coating bulk cathodes. This resulted in a three-month delay in some of their experimental work, but the team was able to adapt by adjusting schedules and continuing with other tasks while waiting for the issue to be resolved. Additionally, Empa experienced challenges related to the integration of CNT-coated copper foils as lithiophilic layers, which ultimately led to the discontinuation of this approach due to incompatibility with the RF sputtering process.

Fluxim encountered difficulties with their prototype battery testing setup, initially testing only one channel instead of the planned eight. While the single channel performed well, further testing of the full multichannel system remains pending. The integration of an EIS instrument into the setup also required additional work beyond the project's timeline.

FZJ faced challenges in scaling up their optimized LLZO-LCO cathodes for prototypes to be sent to AEInnova and Fluxim. While the surface roughness and defect minimization objectives were met, maintaining uniformity across larger cathode areas proved difficult. As a result, the consortium was unable to obtain a stable open-circuit potential with FZJ's cathodes. However, the consortium adapted by using other solid-state bulk cathodes with a polymer electrolyte, which were successfully coated with thin-film layers and cycled for a few cycles, partially addressing this challenge. This result shows promising potential for the hybrid concept of bulk and thin films and will be further worked on by members of the consortium.

New industrial collaborations and opportunities

New business opportunities emerged as a direct result of the project. Empa's work on thin-film solid-state batteries led to the exploration of commercializing thin-film technologies through the startup BTRY AG. During the project, Empa established new connections with AEInnova, creating a potential business opportunity for collaboration between BTRY and AEInnova in the field of industrial IoT. This partnership, which focuses on integrating BTRY's thin-film solid-state battery technology into AEInnova's IoT applications, highlights the economic impact of the project and its potential for future commercialization.

Future collaborations planned

Several partners have expressed interest in continuing collaborations beyond the AfreeSSB project. Empa and Fluxim have already applied for additional funding to extend their work on solid-state batteries. Furthermore, the collaboration between Empa and IREC is expected to result in joint publications, following the successful research visit by IREC’s PhD student Fernanda Monteiro Freitas. Future collaborations with IREC and AEInnova are also being explored. In addition, Moritz Futscher from Empa and Alex Morata from IREC will co-organize a symposium at the 2025 European Materials Research Society (E-MRS) Spring Meeting, providing a platform to share results from this project and foster new collaborations in the solid-state battery field.

# 5 Publications and other communications

Each partner has actively contributed to increasing the visibility and impact of the project, engaging with diverse audiences through various channels such as scientific publications, conferences, workshops, outreach, and more. The project had a very strong representation in international conferences and workshops. All partners contributed to at least several conferences during the project with topics and scope ranging from large multi-disciplinary conferences such as Solid State Ionics (Empa, Fluxim, IREC) to smaller, more specialised ones such as International Operando Battery Days (IREC). The dissemination was done in the form of oral (12 across partners) and poster presentations (6) as well as industrial exhibition stands (AEInnova) and prototype demonstrations (Fluxim).

Over the course of the project, two peer-reviewed publication in respected journals have been published with one more in preparation. One from Empa on the influence of materials for lithiophilic seed layers (T1.1): one from IREC on LiMn2O4 thin film cathodes: (T1.3), and three in preparation: two from FZJ regarding the bulk cathodes (T2.1, 2.3) as well as one between Empa and Fluxim on the transient current measurements for quantification of conductivities (T3.3).

Other dissemination activities include outreach in the form of events, institutional communications and prototype demonstrations for a broad range of audiences, from high school students to experts.

A detailed list of the dissemination activities can be found in **Appendix 1: Dissemination activities**

# 6 Appendix

## Appendix 1: Dissemination activities

### Overview of publications and communications

| Type of publication | Total no. | Doi, website address |
|---|---|---|
| Peer reviewed articles | 2 | https://pubs.acs.org/doi/10.1021/acs.chemmater.4c00888<br>https://pubs.acs.org/doi/full/10.1021/acsami.3c14693<br>+ 3 publications in preparation |
| Books or book chapters | 0 | |
| Articles directed at the general public | 1 | To be published |
| Communication at scientific congresses/in proceedings | 18 | 12 oral + 6 poster presentations |
| Scientific degrees | 0 | |
| Others | 0 | |

### Peer reviewed articles

List the peer review articles that are in preparation (P), under review (R), or accepted (A).

| | | | |
|---|---|---|---|
| André Müller*, Luis Paravicini, Jędrzej Morzy, Maximilian Krause, Joel Casella, Nicolas Osenciat, Moritz H. Futscher, Yaroslav E. Romanyuk*, *Influence of Au, Pt, and C Seed Layers on Lithium Nucleation Dynamics for Anode-Free Solid-State Batteries*, ACS Applied Materials & Interfaces, 2023, 16, 1, 695-703 | **Empa** | **8.3** | **A** |
| Juan Carlos Gonzalez-Rosillo*, Maxim Guc, Maciej Oskar Liedke, Maik Butterling, Ahmed G. Attallah, Eric Hirschmann, Andreas Wagner, Victor Izquierdo-Roca, Federico Baiutti, Alex Morata*, Albert Tarancón*, *Insights into the LiMn2O4 Cathode Stability in Aqueous Electrolytes*, Chemistry of Materials, 2024, 36, 12, 6144-6153 | **IREC** | **7.2** | **A** |
| Sandra Jenatsch, Davide Moia, Markus Wied, Jordi Sastre, Andreas Schiller, Balthsar Blülle, Vanessa Wood , Beat Ruhstaller, Yaroslav Romanyuk, Moritz Futscher, *Quantification of mixed ionic-electronic conductivity using current transient measurements* | **Fluxim, Empa** | **n/a** | **P** |
| M. Rosen, V. Mathivanan, E. Drude, B. Friedrich, O. Guillon, M. Finsterbusch, D. Fattakhova, *Regeneration of oxide-ceramic battery components* | **FZJ** | **n/a** | **P** |
| M.Rosen, T. Lammert, Y. Collette, V.Kiyek, M.Finsterbusch, *Co-sintering of oxide based half-cells for all-solid-state lithium batteries* | **FZJ** | **n/a** | **P** |

### Books or book chapters

No books or book chapters that resulted from the funded project.

**Articles directed at the general public**

| Authors, title, publisher, year, link | Partner(s) involved |
|---|---|
| Benedikt Vogel, im Auftrag des Bundesamts für Energie (BFE)<br>*Batterien, reduziert auf das Wesentliche* | **Empa, Fluxim** |

**Communication at scientific conferences**

| Authors, title, meeting name & place, year | Partner(s) involved | Oral Communication | Poster |
|---|---|---|---|
| Nicolas Osenciat, Erica Clinton, Andre Muller, Joel Casella, Jedrzej Morzy, Moritz Futscher, Kumar Yalamanchili, Yaroslav Romanyuk, *Sputtering of C- and Si-doped LiPON as thin-film electrolyte separator for all-solid-state Li-ion batteries*, Solid State Ionics, London UK , 2024 | **Empa** | **yes** | |
| Casella Joel, Morzy Jedrzej, Evgeniia Gilshtein, Maksym Yarema, Moritz Futscher, Yaroslav Romanyuk, Electrochemical activation of Fe-LiF conversion cathodes in thin-film solid state batteries, Solid State Ionics, London UK, 2024 | **Empa** | | **yes** |
| Casella Joel, Morzy Jedrzej, Evgeniia Gilshtein, Maksym Yarema, Moritz Futscher, Yaroslav Romanyuk, Electrochemical activation of Fe-LiF conversion cathodes in thin-film solid state batteries, Swiss Battery Days, Zurich CH, 2024 | **Empa** | | **yes** |
| Jedrzej Morzy, Abdessalem Aribia, Moritz Futscher, Yaroslav Romanyuk,<br>Assessing transport limitations of battery materials using thin film model systems, Solid State Ionics, London UK, 2024 | **Empa** | | **yes** |
| Jedrzej Morzy, Joel Casella, Moritz Futscher, Yaroslav Romanyuk, Electron microscopy of thin film solid state battery model systems, Swiss Battery Days, Zurich CH, 2024 | **Empa** | | **yes** |
| Moritz Futscher, Jedrzej Morzy, Yaroslav Romanyuk,<br>Anode-free all-solid-state batteries: From thin film to bulk, Workshop Battery 2030+, Online, 2023 | **Empa** | **yes** | |
| B. Ruhstaller, S. Jenatsch, M. H. Futscher, A. Schiller, B. Blülle, Y. E. Romanyuk, Extracting Ion Density and Mobility - Transient Current Method Revisited, ModVal, Baden CH, 2024 | **Fluxim, Empa** | **yes** | |
| D. Moia, S. Jenatsch, M. H. Futscher, A. Schiller, B. Blülle, Y. E. Romanyuk, B. Ruhstaller, Extracting Ion Density and Mobility - Transient Current Method Revisited, Solid State Ionics, London UK, 2024 | **Fluxim, Empa** | | **yes** |

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|---|---|---|---|
| D. Moia, S. Jenatsch, M. H. Futscher, A. Schiller, B. Blülle, Y. E. Romanyuk, B. Ruhstaller, Extracting Ion Density and Mobility - Transient Current Method Revisited, Swiss Battery Days, Zurich CH, 2024 | **Fluxim, Empa** | | **yes** |
| Stefano Sem, Prototype demonstration, SimOEP, Winterthur CH, 2024 | **Fluxim** | **yes** | |
| Alex Morata, Juan Carlos Gonzalez-Rosillo, Beatrice Laurenti, Francesco Chiabrera, Marc Nuñez, Fernanda Monteiro Freitas, Albert Tarancón, Study of diffusion in Li-ion electrodes by operando spectroscopic ellipsometry, Solid State Ionics, London UK, 2024 | **IREC** | **yes** | |
| Alex Morata, Juan Carlos Gonzalez-Rosillo, Fernanda Monteiro, Francesco Chiabrera, Apostolos Panagiotopoulos, David Diercks, Ainara Aguadero, John Kilner, Albert Tarancon, Improving the Interfaces in Ceramic Thin-film Solid State Li Ion Batteries: Materials Exploration and Devices,<br>48th International Conference and Expo on Advanced Ceramics and Composites, Daytona Beach USA, 2024 | **IREC** | **yes** | |
| Alex Morata, Beatrice Laurenti, Juan Carlos Gonzalez-Rosillo, Fernanda Monteiro, Francesco Chiabrera, Marc Nuñez, Valerie Siller, Albert Tarancón, Study of ion transport in Li-ion batteries electrodes by operando spectroscopic ellipsometry, International Operando Battery Days, Grenoble FR, 2024 | **IREC** | **yes** | |
| Juan Carlos Gonzalez-Rosillo, Unlocking Extra Functionalities: Exploring Energy Storage Materials for Iontronic Applications with Li-Based Materials, MATSUS Fall, Torremolinos ES, 2023 | **IREC** | **yes** | |
| Alex Morata, Juan Carlos Rosillo, Beatrice Laurenti, Fernanda Monteiro, Francesco Chiabrera, Marc Nuñez, Albert Tarancón, Study of ion transport in thin-film batteries by operando spectroscopic ellipsometry, EMRS, Strasbourg FR, 2023 | **IREC** | **yes** | |
| Alex Morata, Juan Carlos Rosillo, Beatrice Laurenti, Fernanda Monteiro, Francesco Chiabrera, Marc Nuñez, Albert Tarancón, Solid-state architectures based on ultra-thin NASICON electrolytes and oxide-based anodes, EMRS, Strasbourg FR, 2023 | **IREC** | **yes** | |
| Martin Finsterbusch, Melanie Rosen, Christian Schwab, Dina Fattakhova-Rohlfing, Olivier Guillon, Enabling LLZO based all-solid-state batteries: utilizing the unique advantages of garnets to re-design the cell production, The 4th World Conference on Solid Electrolytes for Advanced Applications: Garnets and Competitors, Tromso NO, 2023 | **FZJ** | **yes** | |
| Martin Finsterbusch, Markus Mann, Melanie Rosen, Vivien Kiyek, Christian Schwab, Dina Fattakhova- | **FZJ** | **yes** | |

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|---|---|---|---|
| Rohlfing, Olivier Guillon, Ceramic all-solid-state batteries based on garnet LLZO, 48th Int'l Conference and Expo on Advanced Ceramics and Composites (ICACC 2024), Daytona Beach USA, 2024 | | | |

**Scientific degrees**

No scientific degrees that resulted from the funded project.

**Other scientific dissemination products**

| Authors, title, year, link (if applicable) | Partner(s) involved |
|---|---|
| Juan Carlos González-Rosillo, Les bateries del futur (pròxim): bateries d'estat solid, 2024, https://www.enciclopedia.cat/divulcat/Les-bateries-del-futur-proxim-bateries-estat-solid | IREC |
| Juan Carlos González-Rosillo, Alex Morata, IREC Scientifc communication officer (Anna Magrasó),<br>https://www.irec.cat/press-society/news/final-results-and-achievements-of-the-afreessb-project/<br>https://www.linkedin.com/feed/update/urn:li:activity:7242859683802214400<br>https://x.com/IREC_Energia/status/1837092552383619385<br>2024 | IREC |
| https://www.irec.cat/press-society/news/on-the-development-of-anode-free-all-solid-state-batteries/<br>https://x.com/IREC_Energia/status/1579841213351735299<br>2022 | IREC |
| Juan Carlos Gonzalez-Rosillo, El rol clave de las baterías en la transición hacia la energía sostenible, European Researcher's Night 2023 | IREC |
| Juan Carlos Gonzalez-Rosillo, El rol clave de las baterías en la transición hacia la energía sostenible, Ad-hoc training for the Department of Education of the Catalan Government, 2023 | IREC |
| IOT Solutions World Congress, Spain (BCN), 2024 | AEInnova |
| Hannover Messe, Germany (Hannover), 2024 | AEInnova |
| Advanced Factories , Spain (BCN), 2024 | AEInnova |
| Smart Manufacturing Summit, Japan (Nagoya), 2024 | AEInnova |
| Tokyo Decarbonization Expo, Japan (Tokyo), 2024 | AEInnova |
| Mobile World Congress, Spain (BCN), 2024 | AEInnova |
| Exposolidos, Spain (BCN), 2024 | AEInnova |
| Gitex, UAE (Dubai), 2023 | AEInnova |
| Gastech , Singapore, 2023 | AEInnova |

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|---|---|
| ENERH2O, Porto (Portugal), 2023 | **AEInnova** |
| European Sustainable Week, Brussels (Belgium), 2023 | **AEInnova** |
| Maintenance - BeDigital, Bilbao (Spain), 2023 | **AEInnova** |
| Tokyo Decarbonization Expo, Japan (Tokyo), 2023 | **AEInnova** |
| Middle East Energy Dubai, Dubai (UAE), 2023 | **AEInnova** |
| Mobile World Congress, Barcelona (Spain), 2023 | **AEInnova** |
| IOT Solutions World Congress, Barcelona (Spain), 2023 | **AEInnova** |
| Ecomondo , Rimini (Italy), 2022 | **AEInnova** |
| ADIPEC, Abu Dhabi (UAE), 2022 | **AEInnova** |