SUBLIME

Solid state sUlfide Based LI-MEtal batteries for EV applications

Deliverable No. 7.4 Report on the interaction with the battery modelling community

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Publishable summary

Work Package 7 of the SUBLIME project focuses on driving the iterative development of SUBLIME material and cell sulphide solid-state battery technology through physics-based multiscale modeling.

In the rapidly evolving battery technology landscape, solid-state batteries emerge as a beacon of innovation, offering the promise of higher energy densities, enhanced safety, and longer lifespans compared to their liquid electrolyte counterparts. This advancement is crucial in powering the next generation of electric vehicles, portable electronics, and renewable energy storage systems, aligning with global efforts to transition to cleaner energy sources. In the SUBLIME project, we developed numerous multiscale multi-physics models ranging from atomistic to cell levels. To ensure that the developed models align with the guidelines of the Review of Modelling of Materials (RoMM), we organized a webinar with European Material Modelling Council (EMMC).

Under the EMMC's umbrella is SUBLIME, a collaborative effort that exemplifies the synergy between academic research, industry needs, and modeling excellence. SUBLIME's partners, including POL, CIC, FEV, and ABEE, are integrating these advanced models and tools into the fabric of Europe's battery materials research. Their role is twofold: to push the boundaries of what's technologically feasible in solid-state battery materials and cells and to ensure that these innovations are communicated and accessible to a broad community of stakeholders, from researchers and developers to industry practitioners.

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Abbreviations

SYMBOL	SHORTNAME
MEP	Minimum Energy Path
DFT	Density Functional Theory
NEB	Nudge Elastic Band
CI-NEB	Climbed Image-NEB
TAPED	Topological Analysis of Procrystal Electron Density
AIMD	Ab initio molecular dynamics
KMC	Kinetic Monte Carlo
EMMC	European Materials Modelling Council

1 Introduction

For the modeling approaches used in the development of solid-state sulfide-based lithium-metal batteries for electric vehicle (EV) applications within the SUBLIME project, three distinct methodologies have been detailed across the reports. Each approach tackles specific aspects of solid-state battery development, from the mechanisms of lithium-ion transport and dendrite formation to the prediction of electrochemical performance and degradation behaviour. Below is a detailed introduction to each of the modeling approaches that was developed in WP7:

Investigation of Li Transport in Solid-Electrolyte Interface and Dendrite Formation focuses on lithium transport and dendrite formation, which are critical issues in solid-state batteries. This study:

- Utilizes the NEB approach to compute Minimum Energy Paths (MEP) for lithium diffusion in argyrodite electrolytes and interfaces, providing insights into lithium transport mechanisms.
- Employs Kinetic Monte Carlo simulations to deduce lithium-ion diffusivity based on calculated barrier energies, which is critical for understanding lithium transport rates.
- Applies a phase-field modeling approach to simulate dendrite formation under various operating conditions, offering a mesoscale perspective on how dendrites evolve during battery operation and how they can be mitigated.

Predictive Modeling of Electrochemical Performance and Degradation introduces a multiscale physics-based modeling approach to estimate the full performance of sulfide solid-state battery cells and understand and predict degradation. This method involves:

- Developing a continuum model to simulate the electrochemical dynamics within the cell, including potential and concentration distributions within electrodes and electrolyte, based on mass and charge transport theories coupled with electrochemical reaction kinetics.
- Upscaling the validated continuum model to a pseudo-four-dimensional (P4D) model that allows investigation into the effects of non-uniformities during cell operation and aging, especially in cells of larger dimensions.
- Implementing an aging model within the P4D framework to account for degradation mechanisms, mainly focusing on contact loss between active materials and solid electrolytes, significantly impacting battery performance.

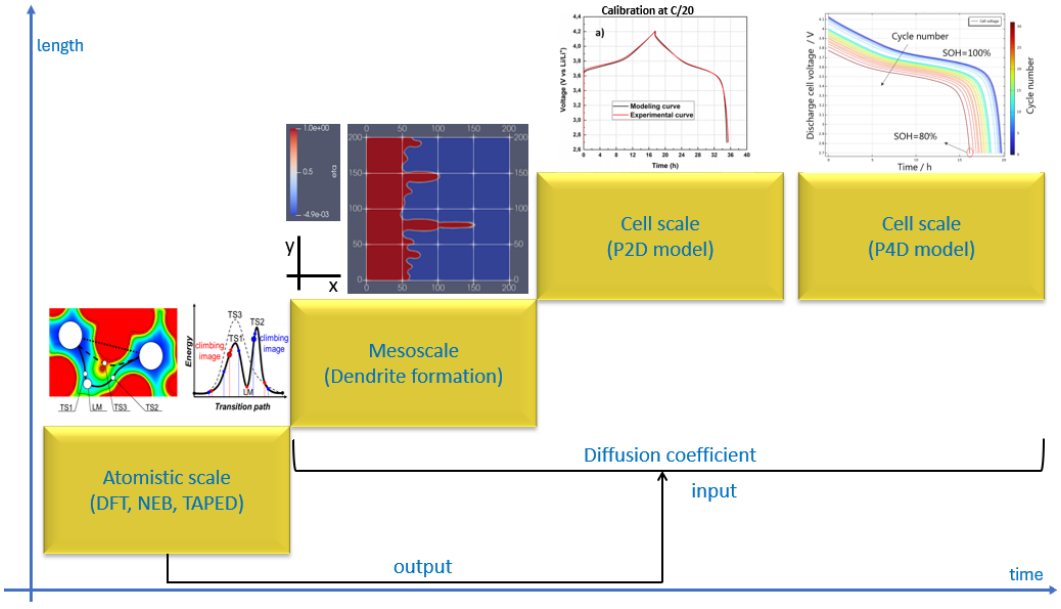

Figure 1 Multiscale modeling approach used in WP 7 framework. The output from the atomistic scale is used as an input for higher scales.

Figure 1 shows the models developed within WP7 at different scales and their connectivity. Together, these modeling approaches provide a solid foundation for advancing the understanding and development of solid-state batteries by addressing key challenges in lithium transport, dendrite formation, and cell performance and longevity prediction.

We have communicated these models to the battery community, which has been achieved through EMMC by organizing a webinar through their platform.

In this report, we address each of the models developed within WP7 in a separate section, followed by the Result section, where we discuss the details of the webinar that was organized within the framework of task 7.6.

2 Model to capture interfacial phenomena

Introduction

The model developed is to understand the Li-ion transport through sulfide electrolytes and their interfaces with electrodes. It emphasizes the significance of predicting the kinetic properties of argyrodite Li_6PS_5Cl sulfide solid electrolyte using advanced computational techniques, such as Density Functional Theory (DFT) and Ab Initio Molecular Dynamics (AIMD) simulations, to guide the design of high-performance solid-state batteries.

Methodological Approach

The computational strategies employed to investigate the sulfide electrolyte's properties were DFT-based calculations and AIMD simulations. These were crucial in evaluating interfacial geometries, reactivity, and Li-ion conductivity across various interface models. Additionally, a novel computational technique, the Topological Analysis of Procrystal Electron Density (TAPED), was introduced to calculate kinetic properties associated with Li-ion mobility efficiently. These methodologies provided insights into the electrolyte's behavior at both bare and coated Li-metal anodes and assessed the effects of humidity on electrolyte stability through thermodynamic calculations.

Key Findings

- **Reactivity at Interfaces**: AIMD simulations revealed the argyrodite electrolyte's degradation in contact with Li metal, characterized by the breaking of P-S bonds in thiophosphate groups, forming lower energy reaction products. This degradation varies across different crystal planes, indicating that electrolyte surface morphology and crystal orientations play significant roles in interface reactivity.
- **Li-ion Conductivity**: Through TAPED and AIMD, distinct Li-ion migration pathways were identified, showcasing the complex diffusion mechanisms within the electrolyte and at its interfaces with Li metal. These findings are critical for understanding Li-ion transport kinetics and designing interfaces that optimize ionic conductivity.
- **Impact of Humidity**: DFT calculations on electrolyte hydrolysis provided a quantitative assessment of the argyrodite electrolyte's instability in humid environments, underscoring the importance of controlling moisture to ensure cell safety and longevity.

Conclusions

From the findings, one can conclude that the argyrodite sulfide solid electrolyte exhibits significant reactivity at Li metal interfaces, with electrolyte degradation and interface impedance posing challenges to battery performance. The results are discussed in detail in D7.1 and are also published in the journals, (Andrey Golov, 2021), (Andrey Golov, 2023). Coating strategies using materials like Li_2Sn_5 and LiF were recommended to stabilize the electrolyte interface, enhance ionic conductivity, and improve overall battery performance. The hydrolysis calculations reaffirmed the need for moisture management in solid-state battery systems.

3 Model to capture Li Transport and Dendrite Formation in All-Solid-State Batteries

Introduction

The model developed focuses on understanding lithium-ion transport and dendrite formation within solid-state batteries, specifically targeting sulfide-based electrolytes. This deliverable aims to shed light on the critical phenomena affecting the reliability and safety of solid-state batteries, including lithium dendrite formation, which poses significant risks to battery performance and longevity.

Methodological Framework

The research employs a comprehensive computational approach combining Density Functional Theory (DFT), Nudge Elastic Band (NEB) method, Kinetic Monte Carlo (KMC) simulations, and phase-field modeling to investigate lithium transport mechanisms and dendrite growth:

- **DFT Calculations**: Used for the initial stabilization of the argyrodite structure and its decomposition products, providing a basis for further analysis of lithium diffusion.
- **NEB Method**: Applied to calculate activation barriers for lithium-ion migration within the solid electrolyte and at the electrode/electrolyte interface, identifying the Minimum Energy Paths (MEP) crucial for understanding lithium transport dynamics.
- **KMC Simulations**: These simulations leverage the energy barriers obtained from NEB calculations to deduce lithium-ion diffusivity, offering insights into the mobility of lithium ions within the electrolyte.
- **Phase-Field Modeling**: This approach simulates lithium dendrite growth under various conditions, providing a mesoscale perspective on the morphological evolution of dendrites during battery operation.

Key Findings

There were several critical insights into lithium-ion transport and dendrite formation:

- The activation energy barriers calculated using the NEB method indicate that lithium diffusion is significantly influenced by the structural characteristics of the electrolyte and its decomposition products.

- KMC simulations reveal variances in lithium-ion diffusivity across different components of the electrolyte, highlighting the complexity of lithium transport within solid-state batteries.
- Phase-field modeling demonstrates the influence of operating conditions, such as temperature and charging rates, on dendrite formation, offering potential strategies for mitigating dendrite growth through the design and operation of solid-state batteries.

Conclusions

A foundational understanding of lithium transport and dendrite formation in solid-state batteries, emphasizing the importance of computational modeling in addressing these challenges. The findings suggest that careful consideration of electrolyte composition, structure, and interface engineering can enhance lithium-ion transport and suppress dendrite formation, pointing to avenues for further research and development in solid-state battery technologies.

4 Prediction of Electrochemical Performance and Degradation Behaviour

Introduction

Through this type of model, we ambitiously seek to enhance the understanding and predictive capabilities concerning the electrochemical performance and degradation mechanisms of solid-state sulfide-based lithium-metal batteries. Emphasizing a multiscale physics-based modeling approach aims to integrate material properties and cell design parameters to forecast battery performance and longevity, addressing one of the critical challenges in solid-state battery technology.

Methodological Approach

A progressive modeling strategy is used that evolves from a continuum model to a more sophisticated Pseudo-four-dimensional (P4D) model. This approach allows for a comprehensive examination of the battery's electrochemical behavior:

- **Continuum Model Development**: The first phase involves developing a continuum model to simulate the dynamic interactions within the battery, focusing on mass and charge transport coupled with electrochemical reactions. This model serves as a foundation for understanding the fundamental processes governing battery performance at the beginning of life (BoL).
- **Upscaled P4D Model Integration**: Subsequently, the validated continuum model is expanded into a P4D framework, incorporating the geometrical and dimensional intricacies of the cell. This enhancement enables the exploration of non-homogeneities and degradation mechanisms that could impact the battery's end of life (EoL) performance.
- **Aging and Degradation Modeling**: Finally, the P4D model integrates an aging mechanism to simulate degradation processes, particularly focusing on the detrimental effects of contact loss between the active material and solid electrolyte which is a significant factor in the aging of solid-state batteries.

Findings and Insights

Through meticulous modeling and simulation, several insights into the performance and degradation patterns of solid-state batteries are listed below:

- The continuum model efficiently predicts coin cell performances, highlighting the importance of material properties and electrochemical parameters.
- The P4D model provides a granular view of the battery's internal processes, revealing the significance of non-uniformities and their impact on the battery's health and capacity over time.
- The aging model incorporated into the P4D framework effectively simulates the capacity loss and degradation phenomena observed in experimental setups, validating the model's predictive accuracy and relevance.

Conclusions

This modeling approach underscores the vital role of multiscale modeling in advancing solid-state battery technology. It offers predictive insights to guide material selection, cell design, and operational strategies to mitigate degradation and enhance performance. The methodologies and findings contribute significantly to the SUBLIME project's overarching goal of developing reliable and efficient solid-state batteries for electric vehicles.

5 Results

On March 14th, 2024, ABEE, in association with the European Materials Modelling Council (EMMC), hosted an insightful webinar titled "From Atomic Scale to Cell Scale: Advancing Lithium-Ion and Solid-State Battery Modeling." The event, organized to disseminate innovative modeling frameworks within the battery community, saw registration from over 40 participants, with more than half attending the live session. The webinar was structured around four comprehensive sections, covering topics from atomic-scale phenomena to cell-scale applications. Esteemed speakers included Andrey Golov from CIC EnergiGune, Arpit Mishra from ABEE, Pierra Di Prima from Polito, and Mohammadali Mirsalehian from FEV. Each expert presented their cutting-edge research carried out in WP7 and methodologies, highlighting advancements in battery modeling techniques aimed at improving performance, safety, and longevity of lithium-ion and solid-state batteries. The EMMC platform facilitated the sharing of these pioneering ideas, fostering collaboration and discussion within the battery research community.

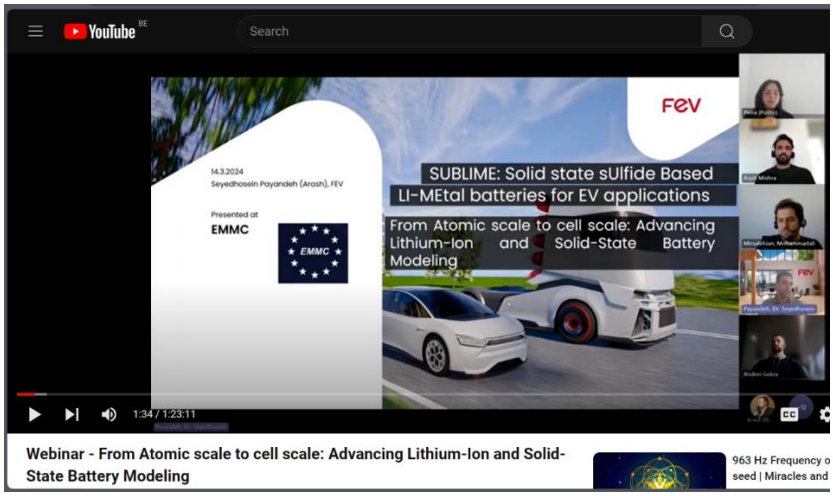

Figure 2 Snapshot of the webinar conducted through EMMC to interact with the battery community.

In the webinar, Andrey Golov from CIC EnergiGune introduces a new approach for calculating ion diffusion characteristics using Topological Analysis of Procrystal Electron Density (TAPED). He discusses advanced modeling methods, including lattice mismatch algorithms, kinetic Monte Carlo simulations, and the climbing image nudged elastic band (CI-NEB) technique. Golov explains the use of Voronoi tessellation to identify potential ion migration paths and compares TAPED with CI-NEB, demonstrating the advantages of TAPED in predicting ion trajectories. He presents case studies on $LiTiS_2$ and Li_3ClO grain boundaries, highlighting the impact of structural flexibility on ion diffusion. The talk emphasizes the integration of atomic-scale insights into cell-scale models to improve battery performance, encouraging further interdisciplinary research and application of these advanced modeling techniques.

In the webinar, Arpit Mishra from ABEE discusses a phase-field model for studying lithium metal electrodeposition. The model, developed using the MOOSE framework, captures the dynamics of lithium deposition, including dendrite growth. Mishra explains how different temperatures and overpotentials impact dendrite formation and electrochemical stability. High temperatures delay dendrite growth, while lower temperatures accelerate it. Lower overpotentials result in slower dendrite growth, whereas higher overpotentials cause rapid and extensive dendritic structures, highlighting the importance of managing operational conditions to mitigate risks in solid-state batteries.

Piera Di Prima from POLITO presents a P2D model of a lithium-ion cell with a solid-state electrolyte. The presentation begins with an overview of solid-state batteries, highlighting their high energy density, safety advantages, and interface challenges. They introduce the P2D electrochemical model, which incorporates physical models essential for understanding solid-state batteries. The P2D model simulates lithium-ion diffusion, intercalation kinetics, and electrochemical reactions using the COMSOL framework. Results from the model show calibration and validation at various charge rates, demonstrating its effectiveness in describing experimental data and its potential for future scaling of solid-state battery technology. The presentation concludes by emphasizing the importance of physical models in advancing battery performance and reliability.

In the webinar, Mirsalehian from FEV presents the development and comparison of P2D and P4D models for lithium-ion coin cells. The P4D model, an upscale from the P2D model, incorporates detailed geometry with the cathode and electrolyte modeled as cylinders and lithium foil as the electrode boundary condition, excluding components like spacers and cell casing to reduce uncertainties. The presentation outlines the differences between P2D and P4D models, highlighting that P4D predicts higher cell voltages and different reaction kinetics compared to P2D. This discrepancy prompted further investigation into the deviation. The P4D model provides a detailed depiction of electrolyte current streams and current density at the electrolyte/electrode interface. The insights from this advanced modeling approach are crucial for understanding and improving the lifetime degradation of lithium-ion cells, aiding in developing more reliable and efficient battery technologies.

For EMMC registered members, the presentations and webinar recording can be accessed through the link https://emmc.eu/sublime-webinar-2024-03/

For non-members, here is the link: https://www.youtube.com/watch?v=l2NQbSe_xz0.

6 Discussion and Conclusions

The report outlines the descriptions of different models developed at different scales in the SUBLIME project. All the models developed were presented to the battery community through the EMMC platform. In this regard, a webinar was organized on 14th March 2024.
The webinar "From Atomic Scale to Cell Scale: Advancing Lithium-Ion and Solid-State Battery Modeling," hosted by ABEE in association with the European Materials Modelling Council (EMMC), was an insightful session that featured leading experts discussing advanced battery modeling techniques. Andrey Golov emphasized the integration of atomic-scale insights into cell-scale models using TAPED for improved ion diffusion predictions. Arpit Mishra highlighted the importance of managing temperature and overpotential to mitigate dendrite growth in solid-state batteries using a phase-field model. Piera Di Prima validated the P2D model as a cost-effective tool for understanding solid-state batteries, showing its potential for up-scaling. Mirsalehian from FEV compared P2D and P4D models, demonstrating the enhanced predictive capabilities of the P4D model for cell voltages and reaction kinetics. Overall, the webinar provided comprehensive insights into the latest advancements in battery modeling, underscoring the importance of interdisciplinary research and collaboration in advancing battery technology.

Risk register

Risk No.	What is the risk	Probability of risk occurrence[1]	Effect of risk[2]	Solutions to overcome the risk
WP7	No risk	NA	NA	NA

Table 1: Risk Register

[1] Probability risk will occur: 1 = high, 2 = medium, 3 = low

[2] Effect when risk occurs: 1 = high, 2 = medium, 3 = low

7 References

Andrey Golov, J. C. (2021). Molecular-Level Insight into the Interfacial Reactivity and Ionic Conductivity of a Li-Argyrodite Li6PS5Cl Solid Electrolyte at Bare and Coated Li-Metal Anodes. *ACS Applied Materials & Interfaces*, 43734–43745.

Andrey Golov, J. C. (2023). Unveiling Solid Electrolyte Interphase Formation at the Molecular Level: Computational Insights into Bare Li-Metal Anode and Li6PS5- xSexCl Argyrodite Solid Electrolyte. *ACS Energy Lett*, 4129-4135.

https://www.youtube.com/watch?v=I2NQbSe_xz0

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Project partners

#	PARTICIPANT SHORT NAME	PARTNER ORGANISATION NAME	COUNTRY
1	FEV	FEV Europe GmbH	Germany
2	ABEE	AVESTA BATTERY & ENERGY ENGINEERING	Belgium
3	CICE	CENTRO DE INVESTIGACION COOPERATIVA DE ENERGIAS ALTERNATIVAS FUNDACION, CIC ENERGIGUNE FUNDAZIOA	Spain
4	FORD	FORD OTOMOTIV SANAYI ANONIM SIRKETI	Turkey
5	CRF	CENTRO RICERCHE FIAT SCPA	Italy
6	AIT	AIT AUSTRIAN INSTITUTE OF TECHNOLOGY GMBH	Austria
7	MIM	MIMI TECH GMBH	Germany
8	POL	POLITECNICO DI TORINO	Italy
9	SAFT	SAFT	France
10	SOL	RHODIA OPERATIONS	France
11	TNO	NEDERLANDSE ORGANISATIE VOOR TOEGEPAST NATUURWETENSCHAPPELIJK ONDERZOEK TNO	Netherlands
12	Fraunhofer	FRAUNHOFER GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V.	Germany
13	CEA	COMMISSARIAT A L ENERGIE ATOMIQUE ET AUX ENERGIES ALTERNATIVES	France
14	UMC	Umicore	Belgium
15	UNR	Uniresearch BV	Netherlands

Table 2: Project Partners

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