Institut de science des matériaux
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Exploration of MEChaniCAl Properties in All Solid-state Batteries

(E-MAPS)

A. Scientific context of the project (max. 2,5 pages)

- ### Context

Solid-state batteries (SSBs) hold substantial promise over traditional Li-ion batteries, especially for applications in electric vehicles. They offer several advantages, including **higher energy density**, thanks to the use of a **lithium-metal** anode. Additionally, the solid electrolyte can contribute to a longer lifespan, a wider operational temperature range, and improved safety due to the absence of flammable organic solvents.

At present, a **critical limitation** to widespread use of SSBs is their poor mechanical response to the significant **dimensional changes caused by Li^+ ion transport** during battery cycling (Kalnaus *et al.* - see *Figure 1*). On the cathode side, Li^+ **swells** the cathode grains by **ca 10% vol**. On the anode side, the reduction and deposition of the lithium as metal ('plating') introduces **heterogeneous compressive hydrostatic stresses** not just at the interface but also within the solid electrolyte itself, either in pores or along the grain boundaries. In contrast to the traditional liquids, in SSBs, the electrolyte is a **packed assembly of stiff grains** (ca 10 microns radius) and this complex cyclic, heterogeneous, mechanical loading during operation results in **loss of grain-grain contacts** and **fracture** (Lou *et al.*) with a dramatic drop of performances during battery cycling.
To mitigate these phenomena and ensure the integrity of all solid-solid interfaces during cycling, the cells operate under pressures around 100 MPa (Janek *et al.*). However, such a high pressure poses a challenge for lithium metal, a soft material with an elastic limit around 1 MPa. As a result, the design of reliable cells is basically a trial-and-error approach. A deeper understanding of the interplay between the electrochemical response of the materials, the microstructures the global architecture and the cycling conditions is needed.

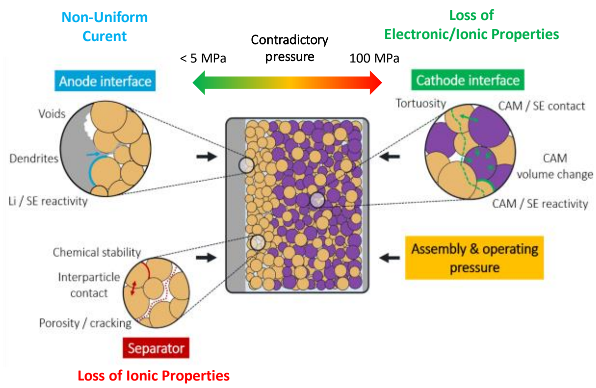

Figure 1. Summary of the different Challenges in All Solid State Battery [refs]

However, although the mechanical factors are the primary drivers of failure in SSBs, research has mostly concentrated on improving ion transport and the electrochemical stability of the electrolytes. The E-MAPS project aims to address this gap by designing a **novel experimental approach** focusing on the **interplay between electrochemical and mechanical processes**. If we hope to aid cell engineering, this project will also advance fundamental knowledge in two very different areas: 1) the micromechanics of important but to date quite ill-known materials such as lithium sulphides and 2) the mechanical response of reactive granular materials, a subject of strong interest in the soft matter community.

- **Preliminary results:**

Since 2022, the LCMCP has been actively investigating the design and performance of all-solid-state batteries (SSBs) produced through a straightforward cold pressing technique of the constituent particles. The electrolyte under study is argyrodite, with NMC (811) as the cathode material and a Li-In alloy as the anode. Recent findings from Laberty's group have underscored the critical role of **incorporating additional polymer grains** into the cathode in enhancing the system's overall performance. Etienne Barthel has developed **micromechanics experiments** to investigate the mechanical response of materials at small scales eg the viscoplastic response of amorphous silicates. Last year, the two groups conducted preliminary experiments which evidenced strong viscoplastic effects in argyrodite grains (publication in preparation). Moreover, **ex-situ tomography** experiments by Laberty's group have revealed intriguing **structural evolutions** at the electrode/electrolyte interfaces and within the electrolyte itself after cycling. It is tempting to assume that the two phenomena are connected: this is why the E-MPAs project aims at providing a more comprehensive understanding of the **relation between material, structure, electromechanical processes and failure** at 3 lengthscales: 1) the grain (non linear, time dependent response) 2) the granular material and its architecture 3) the global cell size. In particular, it is expected that a designed architecture of the materials such as obtained by inclusion of polymer particles can help mitigate the impact of the pressure cycles.

- **Scientific approach**

We will first focus on ex-situ conditions to establish links between **electrolyte** composition, local mechanical response and the evolution of the structure of the granular material during cycling (WP1). The starting material will be argyrodite particles with varying amounts of polymer (PVDF-HFP, a classical binder). Other related compositions will be considered depending on the first results. Notably, we will investigate the relationship between the **elastoplasticity of both electrolyte and polymer grains** and the **macroscopic mechanical response**. Because a non reactive environment is required, nanoindentation at the small and macroindentation at the larger scale will be used primarily. Other configurations can be developed such as microcompression: they can provide complementary information. **Collective effects** such as eg strong effects of pressure on the mechanical response of granular materials will be investigated through the **architecture of the material**, in particular polymer particle size, shapes, density and distribution. Finally, at the **cell scale**, the mechanics can be investigated by the observation of the deformation – "operando" synchrotron **tomography** will support the project to follow structure evolutions. Given the 100 MPa stress level, **birefringence methods** will be used to evaluate stress distributions using millimetric sized intruders of transparent polymers (PMMA) or silicate glasses (Athanasiou *et al.*).

In WP2, the E-MAPS project will consider the **positive electrode**, which consists of electroactive particles mixed with electrolyte particles and pressed together at 400 MPa (WP2). This aspect of the study will focus on the effects of chemical transformations as the material undergoes **swelling**, with an emphasis on the volumetric changes that depend on its electrochemical state. To explore this, **similar strategies** will be applied with local mechanical property measurements, exploration of various architectures and macroscale deformations and stress measurements to assess how chemical transformations influence the structure and the mechanical properties of the composite electrode.

Finally (WP3), the project will focus more explicitly on the **time-dependent effects**, with particular focus on stress relaxation under indentation and the more complex recovery processes observed after unloading. Microcompression can also be used for **in situ monitoring** of material rearrangements over time, with in situ digital image correlation to follow the details of the particle rearrangements eg with applied current.

- **Risks and mitigation**

The major difficulty is that the electrolyte, a brittle material, is air-sensitive. Last year, Barthel's group has developed a methodology to perform fast, air-free indentation measurements at the surface of argyrodite pellets directly inside the cell. Similar strategies will be developed for the other types of measurements proposed here. Another challenge is the tomography experiments on this object. Laberty's group has privileged collaboration with S. Lyonnard at ESRF that coordinates experimentals studies on battery on various ESRF lines and more specifically the tomography line.

- **Adequacy to the call**

One of the primary objectives of the E-MAPS project is to elaborate design rules towards an all solid-state battery that works at low pressure to implement Li as anode materials. To do so, we will contribute to understanding the relationship between material composition, structure, electrochemical and mechanical properties of advanced materials. The project aligns with both the more finalized and the more fundamental objectives of the call.

- **Bibliography**

Athanasiou *et al.*, Matter 7 (2024) 95 https://doi.org/10.1016/j.matt.2023.10.014
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- **Skills and coherence of team**

Etienne Barthel (SIMM-ESPCI) is an expert in surface mechanics, including: i) adhesion, instability, and rupture of functionalized surfaces—especially glass, ii) adhesive contact of elastic, viscoelastic, and coated materials—both through experiments and modeling, and iii) surface mechanics and plastic deformation mechanisms of amorphous silicates. His team brings expertise in the determination and understanding of the mechanical properties of different types of materials using nanoindentation or macroscopic testing coupled with full field methods such as DIC and birefringence. Recently, they have developed specific cells for working with air-sensitive materials.

Christel Laberty (LCMCP-RMES) is an expert in designing solid-state batteries and studying their electrochemical properties. Specifically, her group specializes in assembling all-solid-state batteries containing argyrodite materials via cold pressing. They have developed electrochemical cells to cycle solid-state batteries under various pressures and easily recover the batteries for ex-situ measurements. The group is also part of the RS2E network, granting them access to advanced characterization tools for battery analysis at the ESRF HUB.

B. Research plan with provisional calendar (max. 0,5 pages)

Primary knowledge on both material and system fabrication on the one hand, and first mechanical measurement tools on the other hand is already present, which guarantees a smooth start for the project. In particular, cell fabrication and nanoindentation methodology are in place and can be used directly. The more advanced in situ measurements require some experimental developments especially for the birefringence measurements. They will be carried out during the first two years. Depending on the results, other electrode/polymer materials and material structures, selected to extend the range of mechanical properties under study, will also be tested.

An approximate temporal distribution of the different tasks involved in the project are specifies in the following Gantt chart:

	t0	t0+6 mois	t0+12 mois	t0+18 mois	t0+24 mois	t0 +30 mois	t0+36 mois
WP1							
WP2							
WP3							