Title of the research topic	Toward the optimization of the fabrication process of Na-based All Solid-State Battery and its characterization by transmission operando X-Ray diffraction
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Scientific Project:

Considered as the next generation of energy storage systems, All-Solid-State Batteries (ASSBs) offer several advantages compared to conventional LIBs or NIBs. ASSBs solve the risk of explosion by substituting the highly flammable liquid organic electrolyte by a solid electrolyte (SE), which is stable in a wide operating temperature range. Additionally, they may grant the possibility of using lithium or sodium metal as the negative electrode and thus will increase the energy density of the system[1]. Despite the benefits that ASSBs may present, several issues must be overcome before this technology can reach the market. Firstly, high ionic conductivity comparable to the liquid electrolytes, must be reached. Secondly, unlike liquid electrolytes, SEs cannot completely impregnate the electrode interfaces, meaning that the ionic percolation is less efficient. This results in high interfacial resistance which diminishes the cycling performance and stability. Thirdly, the mechanical strain due to the continuous volume change upon cycling leads to the loss of contact with the active materials and, finally, to complete detachment[1].

In this context, **Na-based All Solid-State Batteries (Na-ASSBs) using NaSICON-type solid electrolyte** such as $Na_{3+x}Zr_2Si_{2+x}P_{1-x}O_{12}$ are of great interest as: *i*) the use of **sodium metal as anode** and different cathode materials to build a full Na-ASSB battery cell is possible[2], *ii*) the conductivity of NaSICON solid electrolyte is in the range of **3-5.10^{-3} S/cm at room temperature**[3,4]. *iii)* NaSICON based Na-ASSB has started to deliver reasonable performances. [5]

Thanks to these very good properties of NaSICON materials, we intend to achieve **two main objectives:**

- **Fabrication of an efficient Na-ASSB** working @ RT with or without Na metal (anode free-concept)
- Use of **Na-ASSB as a tool** to study **charge - discharge mechanisms as function of temperature**

To achieve these two objectives, the steps to follow will be:

- Synthesis of the solid electrolyte and preparation of layers by tape casting (between a few tens to a few 100 µm thick) of NaSICON electrolyte separator supporting the battery cell
- Synthesis of different Na-based polyanionic active materials, such as NVPF for the cathode side
- Fabrication of anode-free Na-ASSB: using the tape-cast solid electrolyte layer, full cells will be assembled either by tape lamination and co-sintering or by Spark Plasma Sintering.

Once these steps will be reached: *i*) **the electrochemical properties** of the different Na-ASSB will be evaluated as a function of temperature using different anode concepts such as thin sodium metal foil, but also **anode-free concept** (where the plating and stripping of Na can be monitored *in-situ*), *ii*) **operando X-ray diffraction in transmission as function of temperature** (up to the melting point of sodium) will be realized in order to assess changes in crystallographic parameters/phases. The difference in lattice parameters will be compared to constraint-free cathode (i.e. without the presence of a constraining rigid electrolyte phase). This will enable to monitor the development of stresses during cycling, which are critical with regards to mechanical stability.

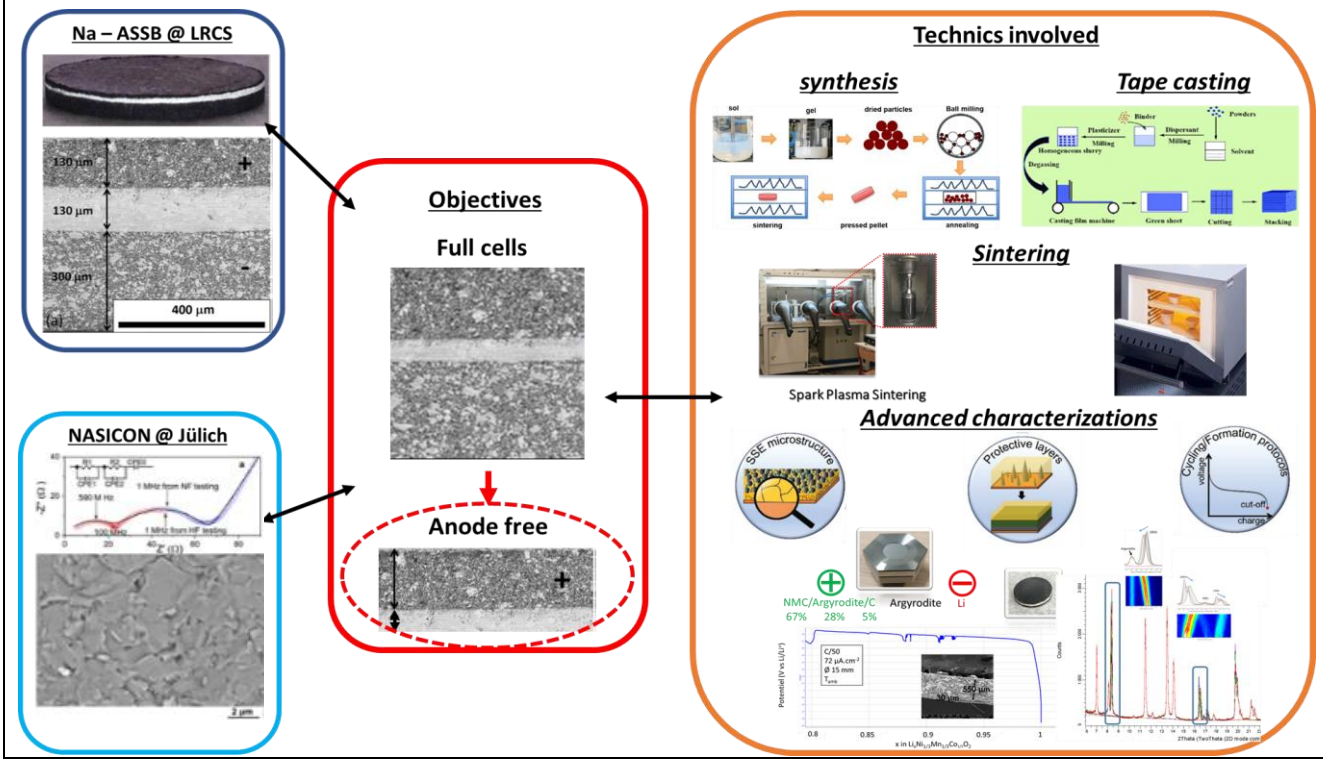
Approach – Work plan (Teams, mobility)

This PhD will be part of a joint project between LRCS and Forschungszentrum Jülich. Some experiments will be done in each lab during the project.

@ Jülich: Synthesis of solid electrolyte, tape casting, characterization of materials and films, battery assembly.

@ LRCS: Polyanionic compound synthesis, battery assembly and advanced characterizations (battery cycling and operando X-ray diffraction)

LRCS & Jülich inputs:



Recent related Publications:

1. Sun, Y. K. *ACS Energy Lett.* **5**, 3221–3223 (2020).
2. Zhang, Z. et al. *ACS Applied Energy Materials*, **3**, 7427-7437 (2020)
3. Ma, Q. et al., *J. Mater. Chem. A*, **7**, 7766–7776 (2019).
4. Liu, Y. et al, *Journal of Power Sources*, **518**, 230765 (2022)
5. Lan, T. et al, . *Nano Energy*, **65**, 104040 (2019).