Toward the development of efficient All Solid State Battery using Binder Jetting and Sintering

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The improvement of the energy density of Li-ion batteries requires a significant increase of the surface and volume energy density. For this, two approaches can be considered, *i)* the manufacture of all-solid-state batteries **(ASSB)**, *ii)* the increase of the **thickness of the electrodes** in order to increase the ratio of active material to dead material (i.e. inactive materials).
If we consider the first approach, different technologies of all-solid batteries can be considered, either those using a solid sulphur electrolyte, or those using a solid ceramic electrolyte (Figure 1a). The use of ceramic electrolyte allows to obtain self-supported batteries after sintering by Spark Plasma Sintering (SPS) but requires to operate a quite high temperature because of the average conductivity of this type of solid electrolyte (SE) at room temperature. But decreasing the electrolyte thickness, NASICON type solid electrolyte with a conductivity around 10^{-4} S/cm might allow the use of such device at room temperature as in the case of micro batteries.
Considering the second approach, the progress made both at the level of electrode materials and electrode architectures has led to improvements in terms of battery power in recent decades. However, still today, even the best batteries (eg for laptops) have a small amount of active material (approximately 51% by weight for cells with high energy density), the rest being divided between the current collectors 21%, packaging 13%, electrolyte 6.5%, binders and additives 8.5%. Attempts to increase the thickness of the electrodes and their energy density while keeping the architectures of conventional electrodes have encountered many problems mainly because of limitations in terms of electronic or ionic conduction and of charge transfer at the interfaces, significantly limiting cycling regimes. However, since few years, LRCS has developed thick binder free electrodes which present outstanding electrochemical performances (Figure 1b). Such electrodes can provide up to 40 mAh/cm² for a 3 mm thick porous electrode.

The aim of this PhD topic will be to combine at the same time these two approaches in order to design ASSB with very thin solid electrolyte layer or hybrid ASSB made of porous electrode for liquid or solid electrolyte impregnation.

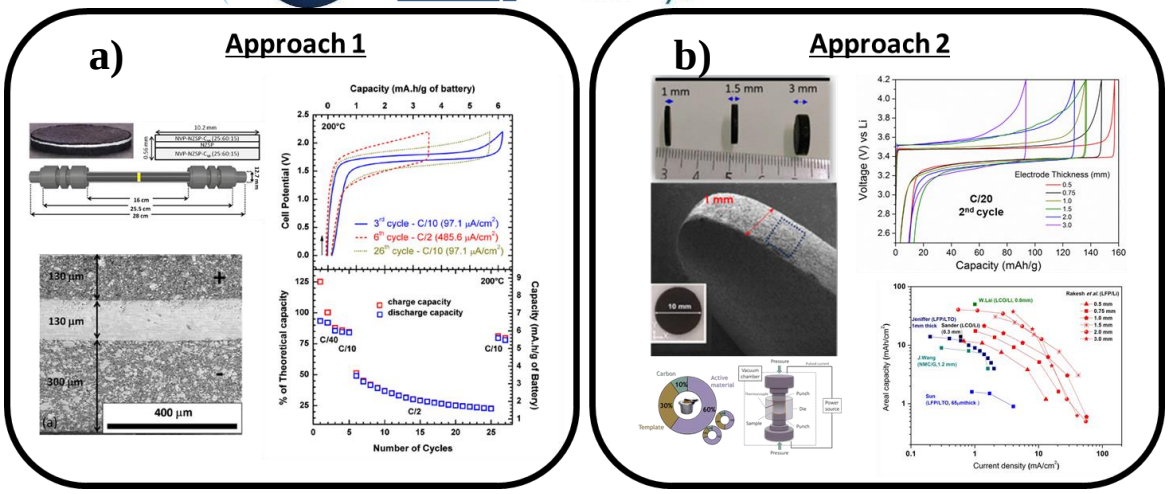

Figure 1: *the 2 approaches, a) Ceramic all solid-state battery (design, electrochemical performances, SEM image), b) Thick porous electrode (SEM image, process, sintering, electrochemical properties, comparison of the performances vs literature).*

The first goal will be devoted to the obtention of thicknesses controlled simple layers by binder jetting followed by a sintering step using SPS or not. These layers will be porous electrodes, composites electrodes for ASSB and finally ceramics solid electrolyte. It will be very important to master this step in order to reach the second goal of the study, i.e. the fabrication of full cells. The desired thicknesses will be between 5 to 50 micro-meters.

Then, the ultimate goal of the PhD (Figure 2) will be to combine these thin layers and especially the solid electrolyte layer to: *i)* two composites electrodes in order to fabricate a full ceramic ASSB with the aim to cycle it at room temperature, *ii)* two porous electrodes to fabricate a hybrid ASSB. This hybrid ASSB will then be impregnate either with a liquid electrolyte, an ionogel or even with a solid electrolyte such as Li_3PS_4, Li_6PS_5Cl or Li_3InCl_6. These three solid electrolytes can be synthetized in solution and will crystallize after the solvent evaporation, leading to materials showing very good conductivity at room temperature. The impregnation with an inorganic SE will allow our hybrid ASSB to work in a wide range of temperature without any gas release or decomposition whereas using a liquid electrolyte limit the temperature range of use.

To achieve these goals, we propose to use the additive manufacturing technology called Binder Jetting (BJ) to obtain the different green parts (electrolyte and electrodes) of the battery before sintering. This printing process consists of spraying a liquid onto a bed of powder, solidifying the cross section of the piece, layer by layer. Based on the binder location, this technology is categorized as a binder jetting on powder bed and solvent jetting on powder bed in which binder materials were either selectively deposited in a liquid state by a print head or homogeneously mixed the powder feedstock. The main advantage of this technology is to obtain a green part with a microporosity (40%) due to the process but also macroporosity due to the design of the part. The use of porogent agent can be also added to the powder to better control the porosity. All the concepts for this PhD are presented in figure 2.

The topic of this PhD is to develop a new solution to achieve efficient batteries with thick electrodes and very thin SE layer through innovative processes. The electrodes prepared will be characterized by various techniques to determine the microstructure, porosity and physical properties of the samples and will be tested in Li-ion batteries.

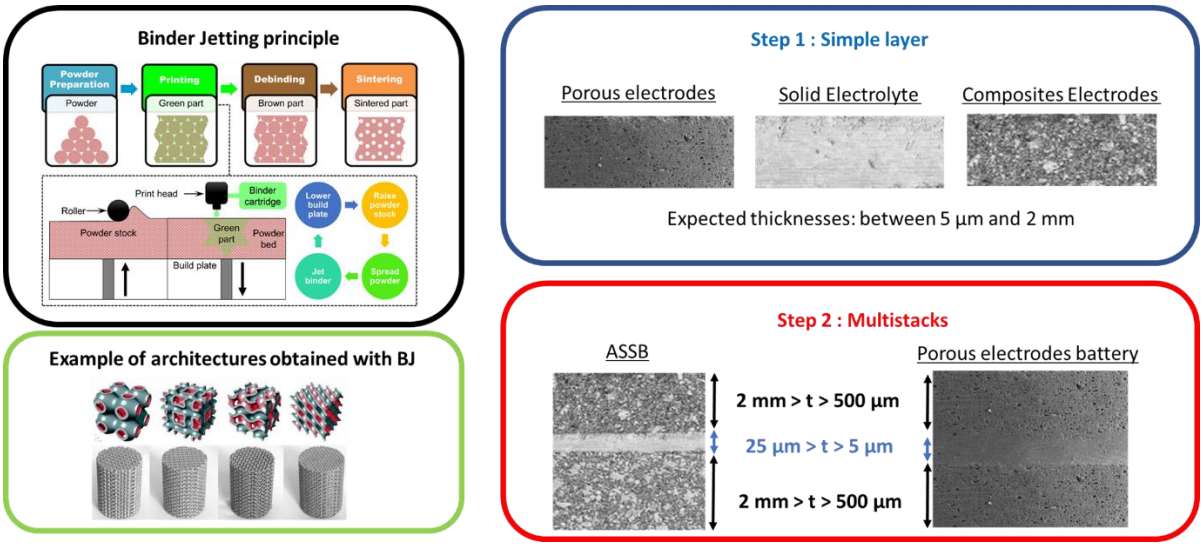

Figure 2: *Objectives of the PhD*

This approach has never been reported in the literature, i.e. combining sintering of a full cell with then impregnation of a solid electrolyte as well as the use of Binder Jetting to design batteries. Thus, it will not be necessary to apply pressure upon cycling like in the case of conventional sulfide based ASSB because our devices are self-supported, and moreover the impregnation of sulfide solid electrolyte in very thick electrodes will improve the ionic conductivity of the ASSB compared to the ceramic SE.
In this project, cells up to 30 mm diameter and 5 mm thick can be targeted.

The selected PhD student for this very ambitious topic will also highly interact with others PhD students involved in others projects such as *i)* ANR Na-Master project which goal is to develop a ceramic All Solid-State Battery operating at room temperature but also *ii)* with a PhD starting in October 2021 in the frame of the Destiny Program which one of the goals is to do *operando* X-ray diffraction in transmission using ASSB.
For these two projects, the necessity to have very thin layer of solid electrolyte in the ASSB is highly needed, so the input of this PhD will be a huge added value to the others projects.

Objectives and plan of work:
This work will imply some the following tasks:

- Choice of the porogen/solvent agent with respect of the selected active material
- Choice of the binder
- Synthesis and optimization of the microstructure of the porogen agent
- Optimization of the composite electrode formulation
- Optimization of the liquid electrolyte with respect to the pore.
- Solid electrolyte impregnation
- ‘Upscaling’ study, i.e thickness, size of the final electrode
- Electrochemical studies (galvano, eis, power)
- Improvement of the mechanical properties
- Printing of the electrodes and electrolyte (optimization of the printing parameters)
- Optimization of the printing parameters and the powder to reach the desired porosity
- Printing of a full battery in one shot

Materials, SPS experiments, electrochemical characterizations, will be performed at LRCS. A specific binder jetting printer allowing the use of small amount of powder will be developed and provided by the LTI. The complementarity of the two laboratories has already been proven thanks to the projects OBI-ONE and IODA.

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