Université de Picardie Jules Verne
Laboratoire de Réactivité et Chimie des Solides

PhD thesis :	**Fundamental study of interfaces in all solid state batteries by environmental scanning electron microcopy**
Supervisor	**Davoisne Carine ; Morcrette Mathieu**
Laboratory	**Laboratoire de Réactivité et Chimie des Solides**
Adress	33 RUE ST LEU - 80039 AMIENS CEDEX 1
email	**carine.davoisne@u-picardie.fr** **mathieu.morcrette@u-picardie.fr**
website :	**https://www.lrcs.u-picardie.fr/**

Scientific domain : Materials, energy storage

Key words: *in-situ* and operando SEM, all solid state battery, degradation mechanism

Subject :

In the energy storage field, all solid state batteries are of interest due to their security and the possibility to use metallic electrode (lithium, sodium) to reach higher gravimetric energy density. LRCS is heavily involved in the development of specific materials (argyrodites and LISICON / NASICON families for instance) for such applications[1,2].

The batteries behaviour and their **degradation mechanisms** are intensively studied [3,4] but essentially post-mortem and few techniques allow to follow the modifications at the battery scale in real time. The major issues to overcome of such systems are the one link to the interfaces, chemical and electrochemical stability. To reach the target performance, solid-solid interfaces between electrodes and electrolyte as well as between the grains inside the composite electrodes are of high importance. During the all solid state batteries formation by SPS (Spark Plasma Sintering) or cold or hot pressing, parameters such as pressure or temperature will influence the interface quality. During cycling, several factors can change them:

- The formation of new phases or interphases between the electrolyte and the electrodes resulting in more or less detrimental effects,
- The grains volumetric expansion inducing contact loss and crack formation,
- The possible dendrites formation leading to the battery short circuit.

Few techniques allow the study of such changes. Among them, the environmental scanning electron microscopy (ESEM) offers a good compromise in term of size and resolution of observation with the possibility to perform studies on the different type of interface with a good spatial resolution. By combining the imaging with chemical analyses by X-ray energy dispersive spectroscopy (EDX), a complete survey of morphological and chemical modification induced at the interfaces is possible. To follow in real time, the development of in-situ and operando researches in the ESEM in neutral controlled atmosphere is important and LRCS is one of the precursor in this domain[5-6]. The use of specific apparatus in-situ (micromanipulator, low current measurements…) in the ESEM will enable to complete the obtained information (electrochemical impedance spectroscopy EIS, …).

The PhD candidate will have to answer problems related to the interfaces in all solid state batteries. The first studied systems will be composed of oxide or sulfur (argyrodite, LISCON, …) as solid electrolyte, carbon (or metallic anode) and $LiCoO_2$ (or $LiMn_2O_4$,

$LiNi_xCo_yMn_{1-x-y}O_2$) as electrodes. In this aim, the PhD thesis will follow two axes: (i) a fundamental study to understand the influence of parameters (pressure, temperature, particles size, mixture, coating etc …) on the interface quality with a synergistic work with other students, and (ii) the *in-situ* and *operando* study in the ESEM of the degradation mechanisms (interphases formation, cracks apparition, …) through the development and the test of home-made and innovative electrochemical cell adapted to the microscopes at the UPJV electron microscopy platform (PME). The obtained results will be compared to pots-mortem characterizations at different cycling steps to ensure observation reliability.

1. F. Lalère, V. Seznec, M. Courty, R. David, J. N. Chotard, and C. Masquelier, *J. Mater. Chem. A*, vol. 3, pp. 16198–16205, 2015.
2. S. Boulineau, M. Courty, J.-M. Tarascon, and V. Viallet, *Solid State Ionics*, vol. 221, pp. 1–5, 2012.
3. J. Auvergniot, A. Cassel, D. Foix, V. Viallet, V. Seznec, and R. Dedryvère, *Solid State Ionics*, vol. 300, pp. 78–85, Feb. 2017.
4. J. Auvergniot, A. Cassel, J.-B. Ledeuil, V. Viallet, V. Seznec, and R. Dedryvere, *Chem. Mater.*, vol. 29, pp. 3883–3890, 2017.
5. F. Orsini *et al.*, *J. Power Sources*, vol. 76, pp. 19–29, 1998.
6. M. L. Dollé, L. Sannier, B. Beaudoin, M. Trentin, and J.-M. Tarascon, *Electrochemica*, vol. 5, no. 12, pp. A286–A289, 2002.

Candidate necessary Skills / Pré-requis pour le (la) candidat(e) :

The candidate must hold or in the process of obtaining a master degree or equivalent in chemistry, electrochemistry or material science with a high level. Knowledge in the battery field and/or characterization techniques (electron microscopy, electrochemistry, …) will be valued.

Application file :

1. **CV**
2. **transcript of records with ranking**
3. **Master or equivalent diplom**
4. **Recommandation letter**