Master Thesis internship (February 1st – July 31st, 2018)

Title of the research topic	Study of Mechanisms and Dynamics of Percolation process in Redox-flow Battery using *in situ* Liquid/bias TEM
Laboratory or Company	Laboratoire de Réactivité et Chimie des Solides
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Compensation	550 euros/month

Scientific project:

The rise in demand for clean energy source drives research in the development of stationary energy storage devices. Redox flow batteries (RFB) turn out to be an promizing electrochemical energy storage due to their inherent technological and electrochemical flexibility. A new type of RFB called the slurry redox flow battery (SRFB) [1] based on the use of liquid electrodes which consist of suspensions of lithium containing active material and conducting carbon in electrolyte. In this novel system, several fundamental questions have to be adressed that are multiphysics, multiscale and multidisciplinary in nature.This project deals with optimization of electrochemical performance of SRFBs, in terms of obtaining maximum possible capacity from the battery device. It is critical to explore the parameters governing the ability of electron conducting carbon particles to form percolation networks to connect the lithium containing active material to the current collector.

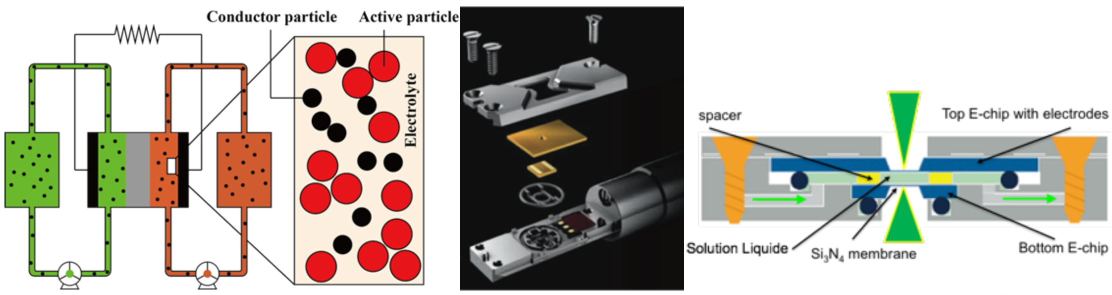

Figure: Schematic of a redox-flow battery with active and conductive particles into liquid electrolyte. Image of our liquid/bias TEM holder, which is both a micro-fluidic system and a micro-electrochemical device (Poseidon 510 from Protochips). Schematic of a cross-section of this micro-fluidic TEM holder in which Si_3N_4 windows designed in each echips allow the electron beam transmission.

We recently published a comprehensive modeling-based study of electroactive suspensions in slurry redox flow batteries using A 3D kinetic Monte Carlo model, which describes the electrochemical discharge of a silicon/carbon slurry electrode in static mode (i.e., no fluid flow conditions). The model accounts for Brownian motion of particles, volume expansion of silicon upon lithium insertion, and formation and destruction of conducting carbon networks. This work lays a theoretical foundation for studying a highly complex system that encompasses electrochemistry, suspension dynamics, particle dynamics, and eventually fluid dynamics [2].

On the other hand, the recent development of *in situ* liquid/bias TEM holders [2,3] allows us to follow electrochemical reaction as well as the motion and the agglomeration of nanoparticles in solution. It opens a new way in our understanding of phenomena that occur during Li-ion battery cycle at nanoscale [4,5] such as the dynamic of percolation, agglomeration process, and electrolyte flow impact. In complex battery architectures, a large variety of phenomena involved in efficiency decay is related to induced effects of exchange dynamics at interfaces. For SRFBs, a better insight into the dynamic of formation of percolation network connecting carbon and active material nanoparticle as well as the dynamic of contact between carbon network and current collector is crucial to improve the performance of this new energy storage device.

This project will focus on the methodological development using our in situ TEM device so as to observe and analyze in real time the mechanisms associated to electrochemical reactions, which are involved in the operation of Li-ion batteries. For each analytical technique associated with TEM, such as electron diffraction, EDX and EELS spectroscopies, EFTEM (filtered imaging), a specific methodology will be definied and optimized.

The sample preparation and the assembly of the echips, the choice of the electrolyte, the electrochemical cycling conditions will be key parameters to get high-quality characterizations. Moreover, the recent acquisition of a new speed camera (Oneview Gatan, 300 frames/s) will improve our ability to observe the kinetics of processes and thus study their impact on changes in percolation path, agglomeration and structure/morphology.

The last part of this project will focus on the image/video processing to quantify particle motion, percolation path and dynamics associated with agglomeration process. These results will be used as input data in our computational models to build a theoretical description of this complex redox-flow system.

This master thesis project will focus on a very exciting new field of *in situ/operando* characterization using transmission electron microscopy and associated techniques. The purpose is to observe and analyze (in a sealed liquid/bias cell) the early stage of the formation of percolation network, which consists of active materials (Si, $LiMn_2O_4$) and carbon particles, in static and flow mode as well as during the electrochemical measurements.

Techniques used: The applicant will carry out the *in situ* experiments using liquid/bias TEM holder (Poseidon 510 from Protochips) [6], which is associated with an ultra-low current potentiostat (1mA-1pA) and a syringe pump for micro fluidic (10-0.1µL/min). TEM Tecnai F20 G2 (equipped of oneview camera) and plasma cleaner will be open access for this project. Both conventional and scanning modes allow visualization of particles in the liquid cell and characterizations could be done with HAADF-STEM, EELS and EDX detectors [4]. Protochips echips with different designs for working electrode will be used. Different type of active materials, carbon and electrolyte will be prepared in LRCS. The student will collaborate with an on-going postdoctoral researcher who works essentially on in-situ electrochemical TEM experiments for cathode Li-ion materials and with a doctoral student working on the computational modeling tool. The applicant should have **a strong motivation** and like work as a teammate in daily interactions with LRCS scientists working on fabrication and characterization of battery materials.

Recent publications related to the topic:

[1] [Duduta, M. *et al.* Semi-Solid Lithium Rechargeable Flow Battery. *Adv. Energy Mater.* **1,** 511–516 (**2011**)

[2] *G. Shukla et al., ACS Appl. Mater. Interfaces*, **2017**, *9* (21), pp 17882–17889

[2] H. Zheng *et al.* Nano Lett. **2014**, 14, 1745−1750.

[3] R.R. Unocic *et al. Nano letters* **2015**, *15*, 2011–2018.

[4] A. Demortiere *et al. Microscopy and Microanalysis* 20(S3), **2016**: 1518-1519.

[5] W. Dachraoui *et al. Microscopy and Microanalysis*, *22*(S5), **2016** 24-25.

[6] http://www.protochips.com/products/poseidon-500.html.