

Project assistant position 2015-2016

Understanding and modelling of ionic limitations in Li-batteries electrodes

Project summary: we have the ambition to develop a fully-consistent EIS expertise that permits the systematic discrimination of potential mechanisms occurring in lithium batteries via experimental data. This will allow either the isolation or the construction of the most adequate mechanism to describe and predict the phenomena that occur on the electrodes, towards the establishment of an optimization procedure of the performance of the rechargeable batteries.

This work is part of an ANR project, that will begin in December 2015.

Technique and method:

To confirm or infirm the hypothesis of a given mechanism, the output of the model derived from this mechanism at the macroscopic scale must be faced to experimental data.

Active material bulk properties: several series of electrochemical tests (EIS, GITT) will be performed on pristine (and a few on cycled) electrodes in order to probe the ionic conductivity of the active material and to follow the mobility of lithium ions within the host crystallographic structure. Evaluation of lithium chemical diffusion coefficients in these materials will give important values for ionic motion limitations inside the active material. ⁱ Similarly, precise analysis of the impedance spectra will highlight ionic limitations induced by specific morphology of the active material (large grain size, bad inner porosity ...) through the frequency dispersion of the various electrochemical processes over the entire frequency range scanned. ⁱⁱ On this point, a correlation can thus be made with data from the FIB/SEM imaging.

Electrode/electrolyte interface properties: several electrochemical tests (EIS) will be performed to probe the interface properties between active material (electrode) and different electrolytes (with / without protective additives). Two main phenomena can occur at such interface: (i) adsorption through a combination of interactions of solvent molecules or salt species, ⁱⁱⁱ which may lead to a preliminary electrochemical step with specific kinetics constant that can induce electronic/ionic limitations;^{iv} and (ii) possible passivation of the electrodes (SEI, for example). The evaluation of the charge transfer resistance at the active material and the resistance developed by the SEI film will clearly show whether the electronic/ionic limitation observed mainly comes from the active material (intrinsic redox properties) or the interface which is not enough conductive for the correct (rapid) exchange of lithium ions.

Influence of electrode architecture and composition: inside the solid phase, the active material is considered as a juxtaposition of spherical particles and the concentration profile is solved in spherical coordinates. The liquid and solid concentration profile is also solved in the porous media along the thickness of the electrode, and allows the model to be pseudo-2-dimensions (P2D). This model needs numerous input parameters to run properly, and they must be robust enough to ensure a good accuracy of the simulation. The model also needs the implementation of the open circuit potential of the active materials vs. stoichiometry, which can be assessed by electrochemical measurements on half cells like low-rate CCCV or PITT.

Qualifications

- o Expertise and knowledge on batteries
- o Experimental capabilities (electrochemical techniques , XRD, porosimetry ...)

POSITION

Level : bac +4

Expertise : Materials chemistry/electrochemistry

Salary : 2.000 €/month

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ⁱ (a) S. Franger et al. *J. Power Sources*, vol. 109 (2), pp. 262-275 (2002). (b) S. Franger et al. *Electrochimica Acta*, vol. 48 (7), pp. 891-900 (2003). (c) S. Franger et al. *J. Phys. Chem. Solids*, vol. 67, pp. 1338-1342 (2006)

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