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| Title | **Study of the knee-point (sudden death) of Li-ion cells by optical sensors** |
| Laboratories | Collège de France (Paris) / EDF Lab Renadières (Moret-sur-Loing) |
| Thesis Director | Jean-Marie Tarascon, Julien Bonefacino |
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**Context**

Li-ion batteries have become essential thanks to their high energy density, their lifespan and their low self-discharge which enable them to develop numerous applications. Understanding and controlling their ageing, *i.e.* the irreversible deterioration of their performance, is a key point in the implementation of these applications.
Some Li-ion cells exhibit a slow, linear and predictable capacity degradation but then reach a turning point sometimes called the "*knee-point",* after which the degradation accelerates rapidly until the cell's End-of-Life. The knee point is the transition point which marks a sudden change of the slope in the ageing curve which is mainly due to a change of the dominant ageing mechanism. The cause and timing of this phenomenon is not well understood and has important implications to the way we estimate battery lifetime and ensure the safety of installations.

The use of optical sensors directly inside the cells opens the door to previously inaccessible chemical and mechanical characterisations. Optical fibre Bragg grating sensors (FBGs) can produce a temperature map inside of the battery by optical interrogation (wavelength shift of the emitted signal) all along the fibre, in addition to the evolution of the pressure/strain/compression during cycling, with high sensitivity and space resolution. By using pairs of FBGs, it is then possible to monitor stress and temperature over various operational and safety-critical scenarios. In-situ IR spectroscopy using fibre optic evanescent wave sensors can provide chemical information on the transformation and degradation of electrodes and electrolyte materials as well as on the cell Li inventory. For example, the use of chalcogenides glass fibres, capable of transmitting light in the IR range, can reveal the appearance and disappearance of chemical species during battery cycling using infrared spectroscopy. This type of "medical follow-up" of the battery should provide very valuable information which can help us elucidate the mechanisms leading to the knee-point and enable new protocols to be drawn up to postpone or prevent this rapid loss of capacity.

**Description of the thesis topic**

The objective of the thesis is to use optical sensors to study and understand the mechanisms leading to the appearance of a knee-point in the lifetime of large format batteries for stationary storage applications (storage of wind and solar production, frequency regulation, peak shaving …). Monitoring the physical and chemical parameters at the heart of the cell will help us understand the degradation mechanisms leading to the knee point and how to mitigate them. The study will take place in several stages:
- Preparation, instrumentation and monitoring of cells made from electrode materials and electrolyte used in commercial cells.
- Preparation, instrumentation and monitoring of laboratory cells (made from new electrode materials) reproducing the characteristics of the cells and the solicitation used in real stationary applications.
- Instrumentation and monitoring of medium and large format commercial cells.
For each step, key parameters will be tracked and analysed to understand the evolution of the physical and chemical state of heath of the cell. Machine learning techniques could be used to optimize data tracking

and analysis. In parallel, the electrode materials can be analysed separately by physico-chemical characterization techniques (SEM, DRX, XPS, ICP, etc.) or electrochemical characterisation. Pre-aged and cells subjected to accelerated ageing under strong constraints will also be used. Several cell chemistries (LFP/Gr, NMC/Gr, etc.) and battery solicitation will be compared. A large part of the manipulations will be done in a glove box.

The PhD student will be employed by EDF R&D under a 3 year contract co-financed by the ANRT under a CIFRE grant, and will work both at the College de France in Paris and EDF Lab Renardières in Moret-sur Loing.

**Recent publications related to the topic:**


- Huang, J., Boles, S. T., & Tarascon, J. M. (2022). Sensing as the key to battery lifetime and sustainability. *Nature Sustainability*, 1-11.
- Huang, J., Albero Blanquer, L., Bonefacino, J. *et al.* Operando decoding of chemical and thermal events in commercial Na(Li)-ion cells via optical sensors. *Nat Energy* **5,** 674–683 (2020). https://doi.org/10.1038/s41560-020-0665-y
- Ma, X., Harlow, J. E., Li, J., Ma, L., Hall, D. S., Buteau, S., ... & Dahn, J. R. (2019). Hindering rollover failure of Li [Ni0. 5Mn0. 3Co0. 2] O2/graphite pouch cells during long-term cycling. *Journal of The Electrochemical Society*, *166*(4), A711
- Zhang, C., Wang, Y., Gao, Y., Wang, F., Mu, B., & Zhang, W. (2019). Accelerated fading recognition for lithium-ion batteries with Nickel-Cobalt-Manganese cathode using quantile regression method. *Applied Energy*, *256*, 113841
- Attia, P. M., Bills, A. A., Planella, F. B., Dechent, P., dos Reis, G., Dubarry, M., ... & Sulzer, V. (2022). " Knees" in lithium-ion battery aging trajectories. *Journal of The Electrochemical Society*.
- Nascimento, M., Novais, S., Ding, M. S., Ferreira, M. S., Koch, S., Passerini, S., & Pinto, J. L. (2019). Internal strain and temperature discrimination with optical fiber hybrid sensors in Li-ion batteries. *Journal of Power Sources*, *410*, 1-9.


**Sought profile**

Master 2 or equivalent in material sciences/physical chemistry of materials, with a strong motivation for scientific research and laboratory work. A plus: professional skills/experience in electrochemistry or batteries.

Curiosity, team spirit, hardworking, experimental creativity will be also essential qualities.

Application file: CV, cover letter, Academic Transcripts, Master's degree or equivalent, any letters of recommendation.