

Towards State-of-Health diagnosis and prognosis of Li- and Na-ion cells: Incremental capacity and differential voltage analyses

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In recent years, the number of studies dealing with the degradation of commercial cells has drastically increased. In many of these studies, the experimental design is extremely well planned but the presentation of the results often lacks the desired in-depth of understanding of the degradation modes behind the observed capacity fade and impedance changes.

This lack of in-depth understanding lies mainly in the difficulty of undertaking a complete post mortem analysis (PMA), the most widely accepted diagnosis technique. PMA requires to open the cells at several stage of their life (if possible) and to subject the electrodes to a wide array of techniques: electrochemical; spectroscopical (e.g. XPS, XRD, Raman, FTIR); and/or imaging in order to fully characterize the degradation. In short, PMA requires to test a lot of cells, to have access to a large array of expensive equipment, and to possess a lot of diverse scientific know-how for the interpretation of the results. Consequently, papers that offer an exhaustive analysis of degradation data have been rather scarce.

In order to circumvent these issues, the community have always tried to develop in-situ electrochemical techniques to be able to probe similar information without opening the cells. Beside electrochemical impedance spectroscopy, two other techniques have emerged (or re-emerged) in recent years: the incremental capacity analysis (ICA) and the differential voltage analysis (DVA). They are both based on the derivative of the voltage response of the cell during constant current charge and/or discharge regimes and provide electrode level information relevant to the degradation diagnosis. Both techniques were proven to be extremely powerful in helping to determine the degradation modes and were validated numerous times against PMA. Subsequently, they are gaining a lot of traction in the battery community and are now recognized as viable diagnosis techniques with or without associated PMA.

A key benefit of applying ICA and DVA lies in the fact that these in-situ techniques enable researchers and engineers to obtain a time-resolved understanding of the degradation; the SOH can be assessed on numerous occasions throughout the calendar and/or cycle life of a given cell. This is not possible with PMA unless several cells are tested in parallel since each cell is irreversibly altered in the process. On some occasions, time-resolved tracking of different degradation modes can help understanding the intricate relationships between various degradation modes or mechanisms. Another key advantage of ICA/DVA over PMA is the ability to enable prognosis thank to the time-resolved evolution of the different degradation modes.

As of today, despite being used by a number of well-established research groups around the world, those techniques are not documented as well as they should yet. For instance, there are still no books nor other resources available to train newcomers how to interpret the results in a sound fashion. Although those techniques are fairly easy to implement, the learning curve could be steep and the amount of data to interpret might appear overwhelming initially. Moreover, depending on the cell chemistry (e.g. graphite vs. hard carbon, LiCoO_2 vs. LiFePO_4), the signature of similar degradation mechanisms could be extremely different because of different electrodes' responses or cell designs. The aim of this short course would be

to provide attendees with all the theoretical background as well as the convenient tools to take advantage of these techniques in their own research.

The proposed short class will offer attendees a brief historical background on both techniques, a detailed overview of the principles and limitations of the both methods, the presentation of the impact of the major degradation modes, and the review of several case studies of a selection of conventional chemistries (e.g. graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiCoO_2 , LiMn_2O_4 , or LiFePO_4).

The last part of the class will be interactive and feature live analysis using a Matlab®-based toolbox specifically designed to simplify the use of these techniques, help diagnose the state of health of Li-ion or Na-ion cells and identify and quantify the underlying degradation modes. Attendees will be able to download and retain a copy of this MatLab® toolbox for academic purposes. As a result, attendees will be able to adopt a pro-active attitude during a hands-on toolbox demonstration, as part of this short course.



Dr. Matthieu Dubarry is an Assistant Researcher at the Hawaii Natural Energy Institute within the University of Hawaii at Mānoa (USA). Trained as a ceramic engineer and material scientist at the French National School for Advanced Ceramics (MSc, 2001), Dr. Dubarry learned about lithium batteries during his PhD at the Nantes Institute for Materials under the supervision of Dominique Guyomard and Joel Gaubicher (PhD 2004). He joined HNEI in 2005 focusing, among other things, on the development of methodologies to facilitate the understanding of the degradation mechanisms of Lithium and Sodium ion batteries. In the late 2000s, Dr. Dubarry devoted most of his effort to develop the incremental capacity analysis on full cells. His work led to the development of the ‘alawa approach, a simple modeling approach oriented towards the understanding of single cell degradation. Dr. Dubarry is a well-recognized expert on the subject of electrochemical voltage spectroscopies and is regularly invited as a keynote lecturer to present his approach. He has published over 40 communications including several papers for the Electrochemical Society.



Dr. Arnaud Devie received his electrical engineering degree from INSA Lyon, France, with a major in semiconductor technology. He then worked toward a M.Sc. degree in electrical engineering while modeling and developing silicon carbide integrated circuits at Ampere Lab. Dr. Devie later joined the University of Lyon for a Ph.D. in electrical engineering in collaboration with the French Institute of Science and Technology for Transport, Development and Networks (IFSTTAR), where he undertook the characterization of lithium-ion batteries usage in EV and HEV applications. Dr. Devie joined the Hawaii Natural Energy Institute at the University of Hawaii at Mānoa in 2013 to work on lithium-ion battery degradation diagnosis with Dr. Dubarry and Dr. Liaw. His current work focuses on cell design, diagnosis of abuse and consistency of degradation inside a batch of batteries.