Summary of Characterization Approaches to Detect Li Plating During Fast Charge

Results of the workshop held at ANL on Dec 6th, 2017

Background: DOE-EERE has identified fast charge as a critical challenge in ensuring mass adoption of electric vehicles with a goal of 15-min recharge time in present day cells utilizing graphite anodes and transition metal cathodes in a liquid electrolyte. There are numerous challenges that limit such extreme fast charging at the cell level, including Li plating, rapid temperature rise, and possible particle cracking. Of these, Li plating is thought to be the primary culprit. While various methods can be explored to reduce the propensity for Li plating during fast charge, the viability of these methods are typically judged by time-consuming methods whereby the cells are repeatedly cycled to detect capacity fade, followed by post-testing characterization to detect the presence of Li. A critical need is to develop methods that can detect Li plating *in situ* under *operando* conditions preferably at nucleation, especially in cell designs that are representative of typical cell designs used today. In addition, techniques that don't necessarily allow standard cell configurations, but promise information that can prove invaluable in gaining an in-depth understanding of the mechanisms are also needed. Development of such methods would ensure that new materials (graphite's, electrolytes), new electrode designs (*e.g.,* low tortuosity electrodes), and new charging protocols are evaluated on a common basis to evaluate their effectiveness. Moreover, such methods can help develop more accurate mathematical models that could, in theory, allow real-time monitoring of the cell to minimize plating.

Experts from across the scientific community met at Argonne National Lab on Dec 6th, 2017, to discuss various techniques that could be used to detect Li, the promise and challenges with each technique and the path forward if a research effort were to be established in each area. The overall consensus was that there is a rich array of techniques that show promise in detecting Li in real cells, and methods that allow an in-depth understanding of the phenomenon that control Li plating at the nm scale. However, no one method is sufficient to thoroughly characterize plating and a combination of techniques are needed (multimodal). Further, a major opportunity lies in combining electrochemistry with other direct techniques to correlate Li plating with electrochemical signatures of the reaction. This document summarizes the methods discussed, their limitations, and recommendations on paths forward.

Techniques to detect Li plating and their limitations: Some of the techniques discussed here allow Li detection in standard cell configurations (*e.g.,* pouch cells), either as-is, or with minimal modifications, while other techniques require the use of specialized cells and/or model samples. We split the discussion with these divisions in mind.

Electrochemical and related techniques in standard cell configurations: Techniques that are known to work well in standard cell configurations are electrochemical techniques, such as coulombic inefficiency and non-linear impedance spectroscopy. While these are effective, it is not clear how early the specific technique can detect Li. In addition, the techniques suffer from not being amenable to detecting the type of deposit (*e.g.,* dendritic *versus* mossy) or even if the signature is indicative of Li plating, rather than another side reactions. More research is needed to quantify these aspects. Ensuring that an electrochemical signature is truly due to Li plating requires combining the electrochemistry with a complementary technique that enables direct detection of Li. The details of electrochemical and related techniques and their limitations are summarized in Table 1.

Detection techniques in cell configurations consistent with standard cells : The use of various visualization techniques, such as optical methods, x-ray tomography, microcalorimetric methods, acoustic analysis, neutron absorption imaging, *etc.* allows for the detection of Li with potential for *in situ* detection during fast charge. While techniques have already been developed to demonstrate Li detection, the spatial and temporal resolution and the field of view need to be improved to ensure high fidelity during early stages of the deposition process across a cell. A downside of these techniques is the need for specialized equipment (*e.g.*, a synchrotron source) or require added probes to be added (fiber optic cable-enabled cells), thereby limiting the widespread use of the methods. However, when combined with the electrochemical methods detailed above, these complementary approaches could lead to the development of electrochemical signatures of plating verified by directly visualizing. No one technique would provide all the information needed: rather what is needed is an optimal pairing of various techniques with orthogonal Li sensitivity and selectivity to provide the insights sought. The details of visualization techniques and their limitations are summarized in Table 2.

Model electrode/specialized cell-based techniques: While standard cell configurations are advantageous in ensuring that the current distribution and material choice remain the same as real cells used in vehicles, they suffer from resolution challenges that can limit the insights that can be gained from their use. Using model materials and specialized cell designs allows for an in-depth understanding of the spatial and temporal effects of fast charge; however, they induce new concerns regarding their applicability to real cells. Despite this limitation, techniques, such as electrochemical TEM, can provide detailed information at the nucleation stage of Li plating and provide insights on the effect of graphite and electrolyte choice and thereby provide pathways to solve the Li plating challenge. Such model studies complement the real-world techniques described above and provide additional approaches to detect, understand, and ultimately develop materials and methods to enable fast charge. The details of the model materials-based techniques and their limitations are summarized in Table 3.

Recommendations and path forward: Detecting Li plating under *in situ operando* conditions is a critical need to enable extreme fast charging of batteries. Presently-available techniques, including electrochemistry, spectroscopy, microscopy, and others have the clear potential to detect Li plating. Each technique has varying degrees of sensitivity, and differing temporal and spatial resolution. Therefore, complementary techniques need to be brought together in order to ensure early detection of plating, along with detection of the location and correlating it with operating conditions (*e.g.*, current density) and material choice (*e.g.*, type of graphite and electrolyte). However, many of the techniques require specialized equipment or special cells not easily translatable to real-world conditions. Therefore, methods that can link the electrochemical signatures of plating with a more direct Li detection technique could be a path forward to ensure both an understanding of the underlying cause while simultaneously allowing early detection of plating in real cells. In addition, techniques that detect conditions that presage plating (*e.g.*, detecting LiC_6 formation at the surface of graphite particles) could be powerful. While *in situ* methods in standard cells would be ideal, much can be gained by the use of model materials and cells because of the ability to perform careful experiments that can provide deep insights into the underlying case of Li plating at the atomic level. Such an understanding may be crucial in discovering new materials, electrode structures, and cell designs that can enable 15-min recharge of Li-ion batteries.

Table 1: Details of electrochemical techniques that are applicable in standard cell configurations (*e.g.*, coin and pouch cells)

Name of technique	**Relevant technical characteristics**	**Possible future technical improvements**	**Challenges to solve to achieve improvement**	**Types of deposit that can be detected**
3-electrode pouch cells	Operando monitoring anode voltage and impedance in real pouch cells (10s cm X 10s cm)	Reference electrode dimension and location for high accuracy	Need to try various configuration for optimal results	No distinction
Electrochemical: Capacity Fade/Differential capacity/Coulombic inefficiency	About 5% capacity loss means Li plating Sharp increase in CIE means Li plating	Increased sensitivity (low PPT or possibly sub PPT detection)	Existence of other capacity loss mechanisms.	No distinction
Fast EIS macroscale	10 s temporal resolution, mass resolution TBD, no spatial resolution, detection of precursor signatures prior to plating	Higher precision FRA to complement SOA i/V control and measurement precision (25 – 50 ppm)	Commercial development of higher precision, fast FRA modules is underway	Any morphology
Nonlinear Electrochemical Impedance Spectroscopy (NLEIS)	Sensitivity to asymmetric processes like Li deposition	Evaluation of detection limits for Li plating signature and analysis using physics-based models	Experimental signal-to-noise improvements and physics-based model prediction	Should be sensitive to deposit structure
Electrochemical Modeling	Concentration, current, and potential distributions within full cell. Technique is applicable till the breakdown of the continuum assumption. (~ 5 nm).	Improve SEI transport and kinetics of lithium deposition side reaction.	Model improvements limited by experimental data to support models.	Focus will be on initiation of plating, rather than morphology
Phase field modeling	Coupled with electrochemical model gives local concentration, current and potential distributions with formation and propagation of new phases.	Possibility for assessment of strategies to depress electrodeposition/dendritic growth.	Model improvements limited by experimental data to support models.	Can simulate morphology.

Table 2: Details of techniques that are applicable in standard cell configurations (*e.g.*, coin and pouch cells)

Name of technique	**Relevant technical characteristics**	**Possible future technical improvements**	**Challenges to solve to achieve improvement**	**Types of deposit that can be detected**
***Operando* optical video microscopy**	1 micron resolution. Field of view of several mm, can be stitched together to get cm field of view. 50 ms per image.	Use of confocal/laser microscopes to obtain sub-micron resolution. Integrate with confocal Raman to couple interfacial/SEI chemistry with location of plating.	Design of customized *in situ* cells, thinner windows for higher magnification lenses	All types
X-ray microCT	Images density contrast. Resolution of 1-2 microns. Field of view of 5 – 50 mm	50 nm resolution	Need good calibration and modifications to existing instruments	All features within resolution
X-ray diffraction imaging	Resolution of roughly 10 microns; Field of view of sub-mm to 10s mm.	Demonstrate that this can work & improved speed	Careful tests need to be run	Any crystalline deposit
Neutron absorption imaging	Images Li concentration through 6Li absorption. Present resolution ~100 microns with field of view of 1-2 cm. Minutes to 10s minutes required for data acquisition.	Decrease resolution to ~10-50 microns through new optics.	Improved optics and collection speed. Easier access.	Anything containing Li.
NMR	μg scale detection with temporal resolution of seconds to a few minutes. Cell must operate in confined space (in a coil of about a centimeter in diameter and 2 centimeters in length) and without any ferromagnetic components (inside a superconducting magnet > 7T)	Cell performance	With cell fabrication facility collaborations near operando conditions can be achieved	Can distinguish mossy from dendritic or from smoothly deposited Li
Electrochemical Acoustic Signal Interrogation (EASI)	Examines full stack and potentially layer by layer modulus and density changes to find signatures for lithium plating. Signature determination in μs.	Currently a correlation method: for a given battery plated lithium presents a unique signal. In the future we should be able to *predict* what a deposited signal would be	Apply methods like forward modeling and potentially Full Waveform Inversion (FWI) to indicate what lithium should look like	Plate and Mossy (via attenuation)
Micro-calorimetry	Full cells, temporal resolution. Simultaneous with electrochemistry (voltage, current, EIS)	Couple with other techniques for calibrating heat signatures	Improve signal to noise. Ensure ability to measure at high rate.	Does not distinguish type at present.

Fiber-optic (FO) sensors attached to cells	Monitors directly the electrode strain caused by Li intercalation. If the Li incorporation is limited by Li diffusion excess strain occurs. This constitutes a precursor to plating.	Should be combined with other technique (e.g., imaging) to directly correlate FO signal with the onset of dendrite growth	Define exact cor-relation between dendrite form-ation and growth for standard cells and normal operation conditions	No distinction. Detects Li getting accumulate near surface of electrode
Fiber-optic (FO) sensors (attached to cells and/or embedded)	Monitors directly the electrode strain caused by Li intercalation. If the Li incorporation is limited by Li diffusion excess strain occurs. This constitutes a precursor to plating.	Should be combined with other technique (e.g., imaging) to directly correlate FO signal with the onset of dendrite growth	Define exact cor-relation between dendrite form-ation and growth for standard cells and normal operation conditions	No distinction. Detects Li getting accumulate near surface of electrode
Cell Dilatometry	Monitors cell thickness change due to plating. Resolution of ~ 1 um. Technique can be directly applied to large automotive cells without any modifications.	Exact location of the onset of Li plating cannot be determined. Large cells are required to produce measurable displacements. Additional LVDTs needed to filter out expansion due to gas.	Can serve as a straightforward diagnostics of unmodified automotive cells. In addition can provide data for model validation.	Cannot distinguish between different types.

Table 3: Details of techniques that require the use of model electrodes and unique cell designs.

Name of technique	Relevant technical characteristic + sample size range	Possible future technical improvements	Challenges to solve to achieve improvement	Types of deposit that can be detected (mossy, dendritic)
Far-Field (ATR) FTIR	Ex situ and in situ optical technique. Direct detection of Li metal on flat model surfaces. Sample size: a few mm to a few cm	Possible new ATR crystals to improve specificity toward Li. Use of high intensity, broadband synchrotron IR source or IR tunable lasers.	Deconvolution of signals from SEI and Li. Design specialized in situ cells	Early detection of Li (a few monolayers)
Near-Field AFM-FTIR	Ex situ technique with resolution <20 nm. Direct detection of Li on flat model samples as well as micron-roughness specimens. Sample size: from a single particle to a few cm	Develop in situ capabilities. Use of high intensity, broadband synchrotron IR source or IR tunable lasers	Very difficult to achieve adequate electrode/electrolyte selectivity at electrochemical interfaces. IR tunable lasers limited to just a few hundredscxm-1	Early detection of Li (a few monolayers) Can also directly image morphology of Li-deposits.
Ellipsometry	Ex situ and in situ optical technique. Extreme sensitivity to surface phenomena on flat model samples. Surface sensitive <100 nm for optically dense materials) Sample size: a few mm to a few cm	Mature analytical technique for surface analysis.	Relatively easy measurements. Very complex data analysis and interpretation, especially in dynamic multicomponent systems.	Early detection of Li (a few monolayers) Can also differentiate between various types of Li deposits.
XAS	Ex situ and in situ X-ray technique. Indirect Li sensing via electronic structure of C, O, Cu in the electrode. Can detect <1% of Li in the electrode Surface/bulk (TEY vs. TFY) sensitive from <5 nm to >100 nm.	Mature analytical technique can still benefit from the use of better detectors and/or high intensity synchrotron-based x-ray beams	In-situ cell can be made transmission geometry with 25 nm spatial resolution. Special design the vertical cell to achieve the same level of spatial resolution	Early detection of LiC_6 in graphite, Li-metal on Cu and/or in the SEI
Nano- RIXS	Ex situ and in situ X-ray technique. Extremely sensitive to the electron and charge transfer from Li-intercalation to	Mature analytical technique at intermediate energy resolution at current high intensity synchrotron-based	Challenge to achieve 200 nm spatial resolution	Early detection of LiC_6 in graphite, Li-metal on Cu and/or in the SEI of multicomponent environment

	C, O, and Cu in the electrode and electrolyte. Can detect Li-intercalation of complex interface from its chemical sensitivity	x-ray beams, can benefit from the new detector of energy resolution for chemical sensitivity		
Pattern-Enhanced Micro-spectroscopy	Ex situ/in situ X-ray scattering technique, monitoring size changes on ms timescales. Sensitivity depends on energy; for “soft” x-rays (Cu, O, C, etc), <0.5 nm surfaces have been detected. Sample Size: Resolve 1 µm to sub-nm scale features on samples between 100 nm – 20 µm thick	Relatively new approach, still under development. Need alternative in-situ X-ray window materials that mitigate bowing and absorption effects will further improve signal quality. Faster triggering between electrochemical, synchrotron, and X-ray detector controls. Use of extreme UV (Li K-edge) and “tender” x-ray sources.	A grazing incidence scattering configuration may be preferable in certain situations, but the cell design and data interpretation will be more challenging. Modeling real space spatial reconstruction of complex morphologies.	Early indirect detection of Li (a few monolayers) enables insights into growth mechanism through chemical bonding info. Thereafter, growth rate may be monitored with high spatial (sub-nm) and temporal (ms) resolution. Potential to differentiate between mossy and dendritic morphologies.
EC-TEM visualization coupled with differential capacity	2 nm Li deposits in 1 sec, precise location of deposit	Multiple EELS detectors for simultaneous chemical detection in 1 sec – e.g., Li plus SEI constituents	Next generation electron detectors	Any morphology
In situ X-ray diffraction on thin layer graphite electrodes	In-situ X-ray technique can provide insight into the initial stages of Li nucleation and growth and dependence on XFC parameters.	Use micro-diffraction to improve spatial resolution to microns	Design of experiments that are relevant to real cells	Li metal (crystalline)
Microwave Spectroscopy	In situ tens to hundreds of nm in thickness. Precise location of deposited	Increase speed of detection electronics Seconds to resolve 9 x9 micron cross sectional area.	Next generation electronics.	Any morphology in the tomography mode which require wavelength scanning