XCEL: eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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The U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (DOE-EERE) has identified fast charge — with a goal of 15-min recharge time — as a critical challenge to pursue in ensuring mass adoption of electric vehicles. Present-day high-energy cells with graphite anodes and transition metal cathodes in a liquid electrolyte are unable to achieve this metric without negatively affecting battery performance. 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. This project aims to gain an understanding of the main limitations during fast charge using a combined approach involving cell builds, testing under various conditions, characterization, and continuum-scale mathematical modeling. Expertise from five national laboratories is utilized to make progress on the eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries (XCEL) project.

Cells are built at the Cell Analysis, Modeling, and Prototyping (CAMP) Facility at Argonne National Laboratory (Argonne) using various carbons and different cell designs, in both half-cell and full-cell configurations and with reference electrodes. Cells are tested at both Idaho National Laboratory (INL) and Argonne under various operating conditions (e.g., C-rate, temperature) and under different charging protocols with the aim of identifying the onset of plating, quantifying the extent of the problem, and determining parameters and test data for mathematical models. After testing, cells are opened, and various advanced characterizations are performed at Argonne to determine the extent of plating and to determine whether other failure models, such as particle cracking, also play a role.

A critical part of the project is the use of continuum-scale mathematical models so XCEL participants can understand the limitations at high charge rates and, therefore, suggest possible solutions that can be pursued. Both macro-scale approaches and microstructure-based simulations are pursued and serve to complement each other. Macromodeling at the National Renewable Energy Laboratory (NREL) is used to test cell designs, accompanied by microstructure models to provide deeper insights into the electrochemical phenomena in the battery. This effort is complemented with development of models incorporating new physics, such as phase change and solid-electrolyte interphase growth, at Argonne.

Two exploratory projects aim to study ways to detect Li in situ during operation. NREL is pursuing the use of microcalorimetry to detect heat signatures during plating. INL is working with Princeton University to examine the use of acoustic methods to determine whether plating leads to a signature in the acoustic signal.

Finally, the SLAC National Acceleratory Laboratory is using synchrotron X-ray methods to guide the cell design and charging protocols of extreme fast-charging Li-ion battery cells, and Lawrence Berkeley National Laboratory (LBNL) is investigating the initial onset of Li plating during fast charging and developing a strategy to detect it.
**XCEL R&D: CAMP, Testing, Post-test Characterization, and Modeling (Argonne National Laboratory)**

**Contributors: Alison Dunlop, Andrew Jansen, Dave Kim, Bryant Polzin, and Steve Trask (Argonne)**

**Introduction**

The Cell Analysis, Modeling, and Prototyping (CAMP) Facility continues to support the XCEL Program’s objective of identifying and mitigating causes of lithium plating at fast charge (>4C) in single-layer pouch cells. Efforts in fiscal year (FY) 2018 demonstrated that the choice in graphite did not significantly affect the ability to cycle under fast charge conditions (6C charge, C/2 discharge) — all six of the selected graphites were able to achieve 750 cycles with 80% capacity retention, using a 2-mAh/cm² graphite loading. A decision was made to use SLC1506T graphite from Superior Graphite as the baseline graphite material, and NMC532 as the baseline cathode material. More than 70 single-sided, single-layer pouch cells were fabricated in the Round 1 cell build using a 2-mAh/cm² graphite loading and delivered to lab partners (INL, Argonne, and NREL) for fast-charge testing with a nominal capacity of 19 mAh. Prescreening of anode-cathode pairs with varying electrode capacity loading indicated that loading levels above ~2.5 mAh/cm² were not able to charge at a true 6C rate. Thus, the next pouch cell build was designed with a graphite loading of 3.0 mAh/cm². A total of 48 of these Round 2 pouch cells were delivered to Argonne, INL, and NREL for testing. These two cell builds are now considered the baselines for the XCEL Program.

**Objectives**

The goal of the FY 2019 work is to explore methods of preventing lithium plating via modifications to the electrode architecture. Ideally, the negative and positive electrodes should have low tortuosity to enable fast lithium ion transport to and from the active material closest to the current collector, while maintaining low porosity to maintain high energy density. In addition, the CAMP Facility will support the DOE-EERE-VTO FOA and Lab Call projects and teams that are focused on developing methods of detecting lithium plating.

**Approach**

In FY 2018, the CAMP Facility developed two single-layer pouch cells to benchmark the fast charge capabilities of a typical lithium-ion battery, with the main difference between the cells being electrode loading. These two electrode/cell designs will be used as the baseline designs for this program in FY 2019. The details of the two cell designs are as follows:

Round 1 pouch cells were assembled with 14.1 cm² single-sided cathodes (0.145 grams of NMC532 per pouch cell) and 14.9 cm² single-sided graphite anodes (SLC1506T from Superior Graphite) using Celgard 2320 separator (20 µm, PP/PE/PP) and 0.5 mL of Tomiyama 1.2 M LiPF₆ in EC:EMC (3:7 wt%) “Gen2” electrolyte for an electrolyte-to-pore volume factor of [tbd]. The n:p ratio is between 1.12 to 1.22 for this voltage window (3.0 to 4.1 V). After assembly, the pouch cells underwent formation cycles at ~4 psi in the 3.0- to 4.1-V window as follows: 1.5 V tap charge and hold for 15 minutes, followed by a 12-hour rest, and then three cycles at C/10, followed by three cycles at C/2. The cells were then brought to a safe state of charge by constant voltage charging to 3.5 V for 6 hours, and then degassed, and prepared for shipping/delivery to the battery test labs. A nominal C/3 capacity of 19 mAh was recommended for future tests.

Round 2 pouch cells were assembled with 14.1 cm² single-sided cathodes (0.236 grams of NMC532 per pouch cell) and 14.9 cm² single-sided graphite anodes (SLC1506T from Superior Graphite) using Celgard 2320 separator (20 µm, PP/PE/PP) and 0.615 mL of Tomiyama 1.2 M LiPF₆ in EC:EMC (3:7 wt%) “Gen2”
electrolyte for an electrolyte-to-pore volume factor of 4.20. The n:p ratio is between 1.07 to 1.16 for this voltage window (3.0 to 4.1 V). Figure 1 details the electrode composition and design parameters for the Round 2 electrodes. The formation process was the same as that used in assembling the Round 1 cells. A nominal C/2 capacity of 32 mAh was recommend for future tests.

Anode: LN3107-190-4A
91.83 wt% Superior Graphite SLC1506T
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid
Lot#: 573-624, received 03/11/2016
Single-sided coating, CFF-B36 anode
Cu Foil Thickness: 10 µm
Total Electrode Thickness: 80 µm
Total Coating Thickness: 70 µm
Porosity: 34.5 %
Total SS Coating Loading: 9.94 mg/cm²
Total SS Coating Density: 1.42 g/cm³
Made by CAMP Facility

Cathode: LN3107-189-3
90 wt% Toda NMC532
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF
Lot#: 7273-301
Single-sided coating, CFF-B36 cathode
Al Foil Thickness: 20 µm
Al Foil Loading: 5.39 mg/cm²
Total Electrode Thickness: 91 µm
Coating Thickness: 71 µm
Porosity: 35.4 %
Total Coating Loading: 18.63 mg/cm²
Total Coating Density: 2.62 g/cm³
Made by CAMP Facility

Results

(1) Fabrication of Lithium Iron Phosphate (LFP) and Nickel-Manganese-Cobalt (NMC) Pouch Cells for Cross-Talk Study

A study is underway at Argonne to determine the effect of electrode “cross-talk” (e.g., transition metal cross-over) during fast charge. Ideal cathode electrode choices in this study were determined to be lithium iron phosphate (LFP) and NMC532. Oak Ridge National Laboratory researchers volunteered to coat the LFP electrode based on their prior experience working on this electrode system. The LFP cathode was made with a loading to match the XCEL Round 1 anode baseline. The CAMP Facility fabricated, formed, and then delivered 8 LFP single-layer pouch cells (xx3450 format) and 8 NMC532 single-layer pouch cells to Argonne’s Electrochemical Analysis and Diagnostics Laboratory (EADL) and Post-Test facilities for electrochemical testing and post-test analysis. Figure 2 shows the voltage profiles during formation for a typical pouch cell of LFP and NMC532, and the photo in Figure 3 shows the pouch cells delivered by the CAMP Facility.
Figure 2. Typical voltage profiles during formation of LFP vs. graphite (left) and NMC532 vs. graphite (right) single-layer pouch cells fabricated and formed by the CAMP Facility for cross-talk study during fast charge.

Figure 3. Photo of the LFP and NMC532 single-layer pouch cells for transition metal cross-talk study that were fabricated and formed by the CAMP Facility and delivered to Argonne’s EADL for cycling and post-test analysis.

(2) Development of Structured Graphite Electrodes – Freeze Casting by LBNL

Freeze casting of the negative electrode is a unique method to create an electrode structure with very low, almost ideal, tortuosity. LBNL has this capability and has agreed to create electrode samples using the SLC1506T graphite material, which has been sent to them by Argonne. Earlier in FY 2019, LBNL was able to make a trial coating with the SLC1506T graphite and affix it onto copper foil, which they then sent to Argonne for testing. While this electrode had near-perfect tortuosity with straight electrolyte paths to the copper current collector, its high porosity and low mechanical robustness needed to be improved. Argonne provided LBNL with suggestions to improve the binder composition and slurry mixing process. LBNL successfully created a second trial batch, which was provided to Argonne’s CAMP Facility for testing in coin cells. As Figure 4 shows, the porosity and mechanical strength were significantly improved.
A comparison of the electrode properties is made in Table 1. Coin cells were assembled with 13-mm-diameter LBNL freeze-cast graphite electrodes versus lithium metal (with a 15.6-mm diameter) using the Celgard 2320 separator (20 µm, PP/PE/PP) and Tomiyama 1.2 M LiPF₆ in EC:EMC (3:7 wt%) “Gen2” electrolyte. Two duplicate coin-cells were made and were then cycled in the 3.0- to 4.1-V window with three formation cycles at C/10, followed by a rate performance test at C/10, C/5, C/2, 1C, and 2C delithiation and C/10 or C/5 lithiation cycles. The initial capacity of this second batch of freeze-cast electrodes was very similar to the capacity of the first batch and the baseline XCEL anodes. Unfortunately, despite the improved mechanical properties, this second batch suffered a rapid capacity fade — the reason for which is being explored further.

Table 1: Comparison of Anode Formulations.

<table>
<thead>
<tr>
<th>Superior Graphite 1506T Electrodes</th>
<th>Total Electrode Thickness (µm)</th>
<th>Bare Cu Thickness (µm)</th>
<th>Coating Thickness (µm)</th>
<th>Total Coating Loading (mg/cm²)</th>
<th>Total Coating Density (g/cm³)</th>
<th>Porosities (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBNL Freeze Cast I</td>
<td>300</td>
<td>15</td>
<td>285</td>
<td>12.8</td>
<td>0.34</td>
<td>~80.0</td>
</tr>
<tr>
<td>LBNL Freeze Cast II</td>
<td>127</td>
<td>10</td>
<td>117</td>
<td>11.7</td>
<td>0.998</td>
<td>~58.3</td>
</tr>
<tr>
<td>A-A015 (XCEL-R1)</td>
<td>57</td>
<td>10</td>
<td>47</td>
<td>6.38</td>
<td>1.36</td>
<td>~37.4</td>
</tr>
<tr>
<td>LN3107-190-4A (XCEL-R2)</td>
<td>80</td>
<td>10</td>
<td>70</td>
<td>9.94</td>
<td>1.42</td>
<td>~34.5</td>
</tr>
</tbody>
</table>

(3) Pressure Study

The effect of pressure on the formation of lithium dendrites during fast charge was investigated in a scoping experiment using single-layer pouch cells with Round 2 electrodes. Initial concerns centered on the label applied to the cells causing a pressure high spot on the center of the cell during cycling that could favor the formation of dendrites. In this study, the label was removed and four randomly selected plastic letters were located across the face of the pouch cells, which were then mounted in a pressure fixture. It is estimated that the pressure under the letters would be near 60 psi (typical testing pressures used in the XCEL Program are near 4 psi). Three cells were cycled at a 6C charge rate (after formation): the first was cycled for 250 cycles, the second for 5 cycles, and the third for 1 cycle. The cells were disassembled and the anodes were visually inspected for signs of atypical lithium plating. These results are best summarized in the photos depicted in Figure 5.
It is clear that lithium plating can occur during the first cycle. While it does appear that the letters do leave an image on the plated lithium surface, this result occurs because the letters are pressing the mossy lithium surface into a flat shiny surface. To prove this point, the letters were physically pressed onto blank sections of the plated lithium surface to leave identical images. This result can be seen in the photo for the anode cycled for 5 fast charges in Figure 5 (third from left). The cathodes were later supplied to Argonne’s Post-Test Facility for further analysis.

Conclusions

The CAMP Facility successfully fabricated single-layer pouch cells using LFP and NMC532 cathodes for the cross-talk study. These cells were formed and delivered to Argonne’s EADL and Post-Test Facilities for testing and analysis. The second batch of freeze-cast anodes from LBNL were tested. A scoping study on the effects of applied cell pressure indicates that pressure has a minor influence on lithium plating. As in the previous quarter, the CAMP Facility continued to support several fast charge teams this quarter by supplying requested powders, electrode sheets, and pouch cells. Many of the cell builds were fabricated “just-in-time” for beamtime experiments at Argonne’s Advanced Photon Source and LBNL. Technical data and electrochemical results were provided to all team members as needed to aid in their experiments and modeling efforts.

Key Publications


Acknowledgments

Key contributors to this work include: Alison Dunlop, Andrew Jansen, Dave Kim, Bryant Polzin, and Steve Trask (all from Argonne National Laboratory).
XCEL R&D: Extreme Fast Charging (National Renewable Energy Laboratory)

Contributors: Matthew Keyser, Kandler Smith, Shriram Santhanagopalan, Francois Usseglio-Viretta, Weijie Mai, and Andrew Colclasure (NREL)

Background

This report summarizes NREL’s third quarter work in FY 2019 in five areas:

1. Macro-homogeneous modeling updates
2. Simulation of microstructure heterogeneities
3. Electrolyte characterization and modeling of interfacial behavior
4. Electrode architecture optimization with secondary pore network (SPN)
5. Measurement of graphite electrode and NMC polycrystalline heterogeneities

Through electrochemical transport/reaction modeling at several different length scales, NREL is exploring how to best design electrodes for fast electrolyte transport and to minimize degradation and lithium plating. Macro-scale models rank the relative benefits of how much charge batteries employing different design/thermal control strategies can accept at the 6C constant current rate. One of the compelling strategies is to introduce secondary pores into the electrode to provide fast channels for through-plane electrolyte transport. A two-dimensional (2D) mesoscale model explores this design space. Microstructure models explore the role of different microstructures in suppressing the Li plating side reactions. Experiments and modeling are underway to improve understanding of electrolyte interfacial behavior at extremely high salt concentration levels (5 M versus the typical 1.2 M LiPF6 in solvent). Data analysis is being performed on previous diagnostic experiments that measured graphite electrode state-of-charge heterogeneity in operando at the 6C rate, as well as microscopy that resolved the polycrystalline architecture of NMC particles responsible for fracture under high C-rates.

Results

(1) Macro-homogeneous Model Updates

NREL continues to refine its macro-homogeneous electrochemical model as new data become available from the XCEL team. The addition of multiphase graphite transport is underway. Initial comparisons have been made to beamline X-ray diffraction (XRD) data that resolve Li concentrations across a 100-μm electrode thickness in operando during 6C charging. Initial comparisons are reasonable; however, secondary effects are present, and the team is working to further understand them and decouple resultant signals in the data. For instance, lithium plated during the first 6C charge event appears to block (de)intercalation on subsequent discharge and charge events of the electrode. Separately, NREL has added Li plating reaction to its model and is working with the University of California at Berkeley to compare predictions of plated Li to their Round 1 coin cell experiments. In those experiments, UC-Berkeley followed electrochemical cycling with destructive tests in which graphite electrodes are injected with water in an air-free environment and the amount of hydrogen gas evolved is measured via mass spectroscopy and correlated with dead lithium. Figure 6 shows example modeling results. At the 4C rate, the model predicts 4,000 nMoles plated Li versus 2,500 nMoles measured during experiment after the third cycle. Li stripping will be added to the model to further refine predictions and improve agreement.
(2) Simulation of Microstructure Heterogeneities

Electrochemical performance under fast charge is strongly correlated with microstructure architecture and particle morphology. In order to quickly investigate the geometries of various electrode microstructures and reduce expensive experimental imaging, NREL developed a 3D microstructure generation algorithm in MATLAB. The resulting geometries are then simulated with NREL’s 3D microstructure-scale electrochemical model to investigate strategies to suppress Li plating. The model indicates that particle alignment and dual-coated bi-layer electrode architectures are two strategies that can significantly delay lithium plating (Figure 7). Particle-size heterogeneity should be limited as it induces an earlier lithium plating compared with unimodal particle-size distribution. A first journal article, focused on the numerical side of the electrochemical model, is soon to be published. In addition, NREL is continuing to develop an open-source microstructure analysis toolbox (Figure 8), which covers a wide range of microstructure-related numerical analysis relevant for different heterogeneous materials (lithium ion batteries [LIBs] and fuel cell electrodes, for instance). The code, embedded in a user-friendly, graphical user interface, is planned to be published in 2019. In addition, the tool has been used to investigate LIB electrode particle morphology and pore topology and their impact on the tortuosity factor (and thus on ionic transport limitation under fast charging). A second journal article is under preparation.
Figure 7. Impact of graded architecture (dual-coating) on lithium plating onset under fast charge condition.

Figure 8. NREL microstructure analysis toolbox.
(3) Electrolyte Characterization and Modeling of Interfacial Behavior

With screening of new electrolyte candidates for fast charge, the local concentration of charge carriers within the electrolyte and its implication on impedance buildup are important factors to consider. For instance, using a 5M solution of LiPF6 in the Gen-2 solvents to boost transport properties under a 6C charge rate results in steep gradients in the salt concentration across the interface, which, in turn, results in surface energies that differ from the typical Gen-2 electrolyte recipe. In the last quarter, we used wetting speed measurements to quantify these differences in different solvents and salt concentrations. In electrolytes with a higher dielectric constant, these changes are more pronounced (implying additional surface impedance at higher concentrations). These results were incorporated into the macro-homogeneous electrochemical model as a surface energy correction term to the exchange current density in the rate expression. Next steps involve (1) performing case studies using the model to obtain upper and lower bounds on electrolyte wetting (and hence viscosity) to maintain adequate transport while minimizing interfacial resistance buildup and (2) down-selecting electrolyte compositions with the best likelihood of reaching target properties.

(4) Electrode Architecture Optimization with Secondary Pore Network (SPN)

Extreme fast charging of high-energy thick electrodes is significantly limited by poor electrolyte transportation, which can be alleviated by (1) using an electrolyte with improved transport properties, (2) increasing the charging temperature, or (3) using electrodes with advanced architectures. NREL has developed a diffusion-only analytical model as well as a multiphysics numerical model to investigate the effect of secondary pore networks (SPNs) to provide a fast transport “highway” across the electrode thickness direction. The analytical model serves as a prescreening tool of the key design parameters of SPNs. The numerical model further refines the design space of SPNs by incorporating nonlinear material properties of a graphite/NMC532 cell. Adopting the cell energy density after 6C constant-current charging as the optimization objective, the numerical model predicts that SPNs are most effective when both the secondary channel and the porous matrix are narrow, such that a high-volume fraction of SPNs can be used to boost through-plane diffusion without adversely affecting the in-plane diffusion. Combining elevated charging temperature (45 °C) with optimal SPN design, the model shows that the volumetric discharge energy density of a 3-mAh/cm² cell can reach 270 Wh/L after a 6C constant-current charging (Figure 9). A series of papers on NREL’s findings of the effect of SPNs are under preparation.

Figure 9. (left) Schematic of secondary pore network (SPN) and (right) maximum achievable volumetric energy density of a graphite/NMC532 cell with various cell loadings and electrode porosities at 45 °C.
(5) Measurement of Graphite Electrode and NMC Polycrystalline Heterogeneities

High-speed and high-resolution XRD was carried out along the depth of a graphite electrode during fast charge (6C) and discharge (2C). We have quantified the evolving gradient of state of charge (SOC) as a function of depth and time, and have identified the formation of Li plating. We have found that Li plating develops as a function of depth, with the highest quantity being observed near the separator and reaching up to 15 µm below the surface of the electrode. We observed severe underutilization of the electrode with regions close to the current collection not receiving any lithium at all, as shown in Figure 10 at depths >80 µm. Our ongoing work involves relating the formation of Li metal with the rate of formation of the fully lithiated LiC6 phase to determine whether there is a correlation. We are also investigating the reversibility of the Li plating by quantifying the change in Li signal over many cycles at different rates.

We have started a project that aims at developing an experimental and analysis toolbox that can quickly map out the distribution and orientations of subparticle crystal grains in cathode materials such as NMC. Electron backscatter diffraction (EBSD) can map out the orientation of grains from cross sections of NMC particles as shown in Figure 10. We have created a software that reads the EBSD data, identifies grains, segments the grains and their grain boundaries, quantifies the shape and size of the grains, and quantifies the distribution of grain orientations. We have observed that the NMC532 particles have grain structures that are suboptimal for lithium transport. The distribution and orientation of grains leads to a subparticle tortuosity and lithiation heterogeneity. We are currently refining our analysis method and are attempting to extend this analysis to 3D with 3D EBSD datasets. In FY 2020, this geometry will be applied in a fully resolved NMC primary/secondary particle model describing Li transport, mechanical stress, fracture, and cracking under fast charge.

![Quantifying of SOC heterogeneity during fast charge](image1)

![Mapping of grain orientations and orientation heterogeneity](image2)

![Segmentation with borders](image3)

![Grains only](image4)

Figure 10. (left) In operando measurement of local graphite SOC using XRD, and (right) mapping of NMC anisotropic polycrystalline architecture using EBSD.

Conclusions

The macro-homogeneous model was updated with multiphase graphite transport behavior and a Li-plating side reaction. Initial comparisons were made to data, and a Li-stripping reaction will be added in the next quarter. A series of two journal articles are being prepared on SPNs. Combining elevated charging temperature (45 ºC)
with optimal SPN design, the model shows that the volumetric discharge energy density of a 3-mAh/cm² cell can reach 270 Wh/L after a 6C constant-current charging.

A 3D microstructure model explored how graphite electrode particle size, morphology, and graded and dual-coated electrodes either suppress or accelerate the onset of the undesired Li plating side reaction. Compelling designs for suppressing Li plating include (1) single-coated electrodes with uniform particle size and particles aligned in the in-plane direction, and (2) dual-coated electrodes with higher porosity and smaller particles near the separator. NREL is working with Argonne to determine how to fabricate such electrodes.

Surface energy data were collected and a framework was proposed to incorporate this information into electrochemical reaction models accounting for surface energy variation with salt concentration. Analysis continues of in operando XRD data resolving graphite and Li phases versus electrode thickness during 6C charge of a 100-μm-thick electrode. The polycrystalline architecture of NMC cathode particles is being mapped in support of detailed modeling studies of cathode fracture under high C-rate charge to be carried out in FY 2020.

Milestones and Deliverables


Publications

Background

Electrochemical modeling uses continuum-based transport equations combined with kinetic and thermodynamic expressions to allow the potential, concentration, and current distributions to be determined throughout the cell. The recent focus of the electrochemical modeling effort is to improve and better quantify diffusion and phase change in graphite-active materials based on previous modeling efforts [1]. The previous model treats graphite-active materials as multiple phases, also referred to as stages for graphite, where the well-known Avrami equation was introduced to describe the phase changes as a function of lithium concentration. Further, the model effectively correlated lithium diffusion and phase change during galvanostatic intermittent titration technique (GITT) studies. However, based on limited half-cell (i.e., graphite/lithium metal cell) data with a mesocarbon microbeads (MCMB) graphite electrode, the model tended to underestimate the performance of the graphite at high current rates. Work in this program has identified that the diffusion coefficient increases significantly with applied current rate for all phases.

In order to examine an increasing diffusion coefficient with charging rate, Li-C phases and Li diffusion in graphite are modeled at the atomic scale to characterize the structure of the starting material and its changes during fast charging. Further, bulk defects, surface, and edge effects on Li diffusion will be investigated for select conditions.

The Battery Performance and Cost model (BatPaC) was developed for lithium-ion battery packs used in automotive transportation. The model designs the battery for a specified power, energy, and type of vehicle battery. The cost of the designed battery is then calculated by accounting for every step in the lithium-ion battery manufacturing process.

Results

(1) Electrochemical Modeling

The previous quarter was focused on developing a phase-change model parameter set for the Superior Graphite (SG) graphite materials (i.e., 1506T and 1520P). Among other activities this quarter, the SG parameter set was exercised to examine the behavior of the graphite negative electrode in the Round 2 cells (i.e., NMC532//SG 1506T). The lithium concentration and phase distributions throughout the graphite negative electrode at the end of a 4C charge are given by the contour plots in Figure 11. The contours are evenly distributed between the maximum and minimum values in their respective plots. In the graphite phase-change model, three phases are tracked: LiC\(_{32}\) (phase 1), LiC\(_{12}\) (phase 2), and LiC\(_{6}\) (phase 3). As Figure 11 shows, the 4C charge creates gradients in lithium concentration and phase within the particles and throughout the electrode. Also, the lithium concentration is the greatest in each phase at the particle surface next to the separator. Because the LiC\(_{6}\) phase is generally growing and the other phases are generally shrinking at the end of charge, their distributions are opposite each other.

The specific ranges of maximum and minimum quantities at the end of a 4C charge and after the cell has completely relaxed following the charge (i.e., long time open circuit) are given in Table 2. In Table 2, \(x_S\) (\(c_S/c_T\)) is the fraction of the maximum concentration (i.e., \(c_T\) for LiC\(_{6}\)), and \(v_S\) is the volume fraction of the specific phase. The corresponding total concentration (\(c_S = c_{S1}v_{S1} + c_{S2}v_{S2} + c_{S3}v_{S3}\)) distribution through the
The total lithium concentration at the end-of-charge (EOC) is similar to what would be obtained with a traditional intercalation model. However, as can be seen in Figure 12(a), there remains a total lithium concentration gradient in the electrode when the cell is completely relaxed. The lithium concentration gradients in an intercalation model would relax to zero. It may also be initially counterintuitive that the total lithium concentration gradients do not go to zero when relaxed. This behavior is easily explained with a phase-change model and is also observed in experiment. Table 2 shows that the lithium concentration gradients within each phase go to zero upon relaxation. However, the gradients in the volume fraction of the two most highly lithiated phases do not approach zero. The specific distributions are shown in Figure 12(b). The net result is that the total lithium content of the electrode is not distributed evenly after the cell is completely relaxed.

From the graphite open circuit voltage curve, LiC$_{32}$ forms a flat two-phase region with LiC$_{12}$, and LiC$_{12}$ forms a flat two-phase region with LiC$_6$. In the two-phase regions, the ratio of the volume fractions of the two stable phases vary but are in equilibrium. Further, there are no potentials where all three phases are stable at equilibrium. All three phases can only coexist during a high rate charge or discharge. Therefore, during relaxation after charge, the LiC$_{32}$ phase converts to the LiC$_{12}$ phase. Some LiC$_6$ is also generated from the LiC$_{12}$ phase until the concentration gradients relax. While it may be possible for the LiC$_{32}$ phase to convert directly the LiC$_6$ phase at high charging rates, this path is not included in the model (i.e., the model allows only LiC$_{32}$ $\leftrightarrow$ LiC$_{12}$ $\leftrightarrow$ LiC$_6$). The model also assumes that the lithium in all three phases at any point is in equilibrium (i.e., at the same potential). This assumption is not a requirement; however, assuming otherwise greatly increases the complexity of the problem.

**Table 2: Maximum and Minimum Fractional Lithium Concentration and Phase Volume after 4C Charge in Graphite Electrode of Round 2 Cells.**

<table>
<thead>
<tr>
<th></th>
<th>LiC$_6$</th>
<th>LiC$_{12}$</th>
<th>LiC$_{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>End-of-Charge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_S$</td>
<td>Maximum</td>
<td>0.95</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>0.90</td>
<td>0.53</td>
</tr>
<tr>
<td>$\varepsilon_S$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>0.82</td>
<td>0.83</td>
<td>0.18</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.01</td>
<td>0.18</td>
<td>0.00</td>
</tr>
<tr>
<td>Relaxed after Charge</td>
<td></td>
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<tr>
<td>$x_S$</td>
<td>Maximum</td>
<td>0.87</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>0.87</td>
<td>0.52</td>
</tr>
<tr>
<td>$\varepsilon_S$</td>
<td></td>
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<tr>
<td>Maximum</td>
<td>0.85</td>
<td>0.98</td>
<td>0.00</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.02</td>
<td>0.15</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Figure 11. Simulation of negative electrode Round 2 cells showing contour plots of phase volume fraction and lithium concentration distributions. Greatest (red) to least (magenta) at end of 4C charge.

Figure 12. Simulation of negative electrode Round 2 cells showing contour plots. Greatest (red) to least (magenta). (a) Left: Total lithium concentration distributions at end of 4C charge and completely relaxed after charge. (b) Right: Phase volume fraction distributions completely relaxed after 4C charge.

Slow electrode and separator wetting during the electrolyte filling and cell formation processes is generally associated with early improvements in cell performance during cycling [2]. It is believed that electrode wetting
of the electrolyte can also be attributed to the non-uniform distribution of lithium plating during extreme fast charging. Similar to a liquid wetting a capillary, a liquid is drawn into a porous material through capillary pressure \(p_c\). Instead of the liquid rising to a single height as in a capillary, in a porous material the pores go from fully saturated (i.e., \(s = 1\)) to partially saturated (i.e., \(s < 1\)) to empty (i.e., \(s = 0\)) over a significant length scale (e.g., tens of centimeters). The distance depends on a number of factors (e.g., porosity, pore size distribution, liquid surface tension); however, generally the fractional level of saturation \(s\) versus height has a characteristic S-shaped curve [3]. Leverett developed an expression relating capillary pressure to the S-shaped curve referred to as the Leverett- or J-function:

\[
p_c = \gamma \left(\frac{\varepsilon \kappa}{\mathcal{J}(s)}\right)^{1/2}
\]

Where \(\gamma\) is the liquid surface tension, \(\varepsilon\) is the porosity, and \(\kappa\) is the permeability. The J-function is generally determined experimentally, but its general shape has implications for our electrodes. The characteristic shape suggests that it is easy to at least partially fill all the pores, but it is relatively difficult to fully fill the pores.

To date, most if not all simulations have been conducted assuming that the pores are completely filled with electrolyte. Also, NREL and others have consistently and justifiably calculated electrode tortuosities \(\tau\) much higher than would be predicted by the Bruggeman equation [4]. Utilizing the Bruggeman equation and relaxing the assumption of completely filled pores, Figure 13 shows how the ratio of effective transport property to its bulk value \((\varepsilon/\tau)\) or inverse of MacMullin number \((1/\text{NM})\) will change with the saturation level of the electrolyte for a given porosity of 38%. The figure shows that when the pores are fully saturated (i.e., \(s = 1\)), the Bruggeman equation value is much higher than obtained by NREL for a negative electrode through fitting. However, the steepness of the Bruggeman curve causes the \(\varepsilon/\tau\) value to approach the NREL value as the pore saturation level decreases from one.

Also plotted in Figure 13 is a J-function for water wetting of a ceramic fiberboard that shows the typical shape of the function [5]. As the figure shows, the capillary pressure drops dramatically once the pores are about half filled. The electrolyte wetting characteristics of our specific electrodes and separator would have to be examined before any definitive conclusions could be made concerning the saturation of the pores in our electrodes; however, the fact that a partial vacuum is used for the electrolyte filling of the cell suggests that the pores are highly saturated. However, the challenge of getting the pores fully saturated and the steepness of the Bruggeman curve also suggests that a 5% or 10% variation in the saturation could have a significant impact on the negative electrode current distribution at high charge rates.

![Figure 13](image-url)
 Atomistic simulations have been carried out using a combination of spin-polarized density functional theory (DFT) calculations and the Nudged Elastic Band (NEB) method as implemented in the Vienna Ab Initio Simulation Package (VASP) [6, 7]. The exchange-correlation potentials have been treated by the Generalized Gradient Approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE) [8]. The interaction between valence electrons and ion cores was described by the Projected Augmented Wave (PAW) method [9]. All of the ions were allowed to relax until the total energy differences were no more than 0.003eV.

The effect of uncompensated charge during fast charge at very short time and length scales has been updated. As described in previous reports, under fast charging conditions (nonequilibrium), it is assumed that at the beginning of the charge cycle there are more electrons than Li\(^{+}\) ions near the surface layers. It has been shown that the fast charging conditions might lead to Li clustering near the graphite particles. Such Li clusters promote a faster concerted diffusion near the Li-rich/Li-poor interface with high concentration profiles. The NEB method was used to estimate the diffusion barrier for a few representative Li migration configurations [10, 11]. To understand the effect of these mechanisms in the overall diffusivity at the macroscopic level, a different methodology is developed. The Kinetic Monte Carlo (KMC) approach will be used to evolve the system in time and compute a diffusion coefficient. Several new diffusion paths have to be included to complete all of the possible Li hopping energy barriers that are required to be fed into the KMC model. Figure 14 shows several of the possible Li hopping events. All of the events’ energy barriers, including single Li hops or concerted Li hops, have to be simulated at the DFT level.

![Figure 14. Schematic representation of Li hopping events (shown by the arrows) from a high Li concentration cluster near the graphite particle surface. Green spheres represent Li, and brown spheres represent carbon atoms in the graphite lattice (the same color scheme is used in the rest of the figures).](image)

A decreased energy barrier has been found when “the front” of the Li cluster diffuses into the graphite bulk (Li-poor bulk region). Figure 15 shows a representative example of such calculations. In this particular case, the system has to overcome two energy barriers. However, the apparent barrier from the initial to the final state is just \(-0.11\) eV, which is much less than the Li hopping in the dilute case (0.34 eV). In addition, there are two energy wells in the diffusion pathway. Therefore, other diffusion pathways might be possible or the system could get trapped in those states depending on the temperature. The KMC model will help us develop a better understanding of the probabilistic nature of the events pertaining to the fast charging process.
In order to describe the system for the KMC model, a hexagonal lattice has been built. Figure 16 shows a schematic representation of such a lattice. This lattice restricts the movement of the Li ions. They are allowed to hop only through the carbon-carbon bonds. Hence, for each Li ion, there are a maximum of six possible hopping events. As noted above, all of those energy barriers have to have been computed previously at the DFT level. Then, each potential hop rate ($W_i$) will be computed as follows:

$$W_i = \nu \times \exp\left(-\frac{\Delta E_i}{k_B T}\right)$$

where $\nu$ is a pre-exponential factor, $\Delta E_i$ is the DFT-computed energy barrier, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The left boundary represents the particle surface, and the right boundary represents the middle of the bulk particle. The vertical boundaries are set periodic in order to emulate a large region of the surface. The right boundary is closed (diffusion is not allowed beyond that border). Nonetheless, the right boundary could be open (grand canonical ensemble), allowing the simulation of Li interchange with a Li reservoir (electrolyte). That condition could allow the simulation of Li plating conditions. Furthermore, multiple layers of the lattice will be arranged in a tridimensional network to simulate the staging and the effect of d spacing.
Work in progress:

Concerted diffusion of Li atoms for specific configurations will be extended. A KMC simulation based on all of the computed barriers will be used to predict changes in diffusion coefficient under fast charging conditions.

(3) Performance and Cost Modeling

BatPaC is set up to determine the thickest electrode that can enable the desired charge (increase in state of charge) within a specified time. This calculation is based on a constraint defined as the maximum allowable current density during charging that may be considered safe or acceptable with regard to lithium plating and other degradation modes. BatPaC also calculates the temperature increase during the charging period.

Recent results and accompanying discussions from the XCEL project suggest that it may be feasible to design thicker electrodes by considering a stepwise charging protocol that factors in the observations that the risk of lithium plating diminishes with increasing temperature but increases with the cell voltage. Meanwhile, the area-specific impedance (ASI) decreases at higher temperatures but increases at the low and high states of charge.

It is likely that the NREL models are capable of generating the boundary condition combinations of cell voltage and electrode temperature where lithium plating is indicated. The CAMP researchers at Argonne have ASI data as a function of temperature and cell voltage. A spreadsheet-based model is being set up to investigate the effect of a charging current profile on the cell voltage (or state of charge) and electrode temperature. Imposing the lithium plating boundaries to define the charging current profile is expected to provide a combination that can avoid lithium plating and define the cell design and cooling requirements, and ultimately the thickest electrode (microns) and loading (mAh/cm²) capable of the desired charging. These values can then be translated to cell and pack costs using BatPaC.
Figure 17 shows the SOC and electrode temperature profiles for a defined current density protocol, which consists of a series of stepped-down currents. The SOC and temperature response curves reflect the ASI dependence on temperature and cell voltage. The temperature profile assumes adiabatic operations.

![Figure 17. Effect of a charging protocol on the state of charge and the cell temperature, assuming adiabatic operations.](image)

**Conclusions**

The electrochemical phase-change model for graphite-active materials predicts not only gradients in lithium concentration but also phase distributions within particles and throughout the negative electrode during fast charges. During open-circuit relaxation after the fast charge, the concentration gradients relax to zero, but phases that are in equilibrium are stable. This result leads to a stable distribution of lithium throughout the electrode that would not be predicted by a simple intercalation model. Initial examination of the challenge of getting all of the electrode pores fully saturated with electrolyte and the steepness of the Bruggeman curve as a function of saturation suggests that a 5% or 10% variation in the saturation could have a significant impact on the negative electrode current distribution at high charge rates. Atomistic-level studies have shown that a decreased energy barrier for lithium diffusion in graphite exists when a front of the lithium (Li-rich region) diffuses into the graphite bulk (Li-poor bulk region). Incorporating the cell temperature rise during fast charging into the estimation of the maximum allowable current density within BatPaC will allow for thicker electrodes and more reasonably priced packs.

**Milestones and Deliverables**

Determine model parameters: parameter set for SG-based graphite negative electrodes will be developed. – Completed

Examine rate-dependent diffusion: possible mechanisms for apparent increase of lithium diffusion coefficient in graphite at higher rates will be examined. – Ongoing
References

Background

One of the objectives of these projects is to determine how small, pouch cells, which contain selected graphite anodes and oxide cathodes, respond to extreme fast charging. One of the key points here is to detect lithium plating as soon as it occurs using electrochemical methods. Another aspect is to provide materials characterization data, such as X-ray diffraction, Raman spectra, and diffusion coefficient measurements, which can be used to understand the observed performance response and for modeling. Yet another objective is to determine the physical and chemical changes that extreme fast charging has caused. These changes will be characterized by post-test analysis of the fast-charged cells. A suite of materials and surface characterization techniques will be used.

Results

(1) Characterization of Lithium Plating

The object of this work is to quantify the amount of Li plated on the graphite anode as a function of temperature and cycle count during fast charging. We compared the amount of lithium plated at the 6C charging rate that was used for fast charging with that present after 1C charging. The temperatures ranged from 20° to 55°C. Each coin cell consisted of the Li(Ni0.5Mn0.3Co0.2)O2 cathode (NMC532) and 1506T graphite anode. The Gen2 electrolyte (1.2M LiPF6 in EC:EMC [3:7 by weight]) was used. After charging, the cells were discharged at the 0.5C rate. After a total of five fast-charge cycles, cells were disassembled in the glove box and the anodes were washed two times in excess dimethylcarbonate (DMC), swirling for 1 minute each.

Figure 18 shows optical images of graphite anodes after cycling. It was observed that 6C charged anodes have more Li plating on the surface than those from 1C charging at all cycle numbers studied. In addition to optical images, Raman spectral mapping was used to visualize the Li plating in detail as shown in Figure 19. This technique detects the signal from carbide/acetylide species formed when Li nuclei reacts with the solid electrolyte interphase (SEI) on graphite (ACS Appl. Energy Mater. 2019, 2, 873−881). From the Raman analysis, most of the shiny region on the graphite in optical image was plated Li. Raman mapping could also detect additional Li plating on the edges that is hard to see in optical images.
Figure 19. Raman spectral mapping of Li plating on the anodes after 100 cycles. Red areas indicate Li plating.

Inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify the amount of the Li on the graphite anode surface. Anodes were first hydrolyzed with high-performance liquid chromatography (HPLC)-grade water, and amounts of Li and F were measured using ICP-MS and an ion-selective electrode, respectively. It is assumed that F was from LiF, and the amount of Li found in the 1C cells represents the amount that would normally be found in the graphite anode. Figure 20 shows the corrected amount of the Li plating at the 6C charging rate versus cycle count. As ICP-MS was performed on the hydrolyzed solution, initial values were provided in concentration (µmole/ml, left y-axis) and then converted to the capacity (mAh, right y-axis). Figure 20 shows a slight decline after five cycles, then a gradual increase from 20 to 100 cycles. The slight decrease after five cycles could be related to the electrochemical Li stripping during cycling. Further studies on different cycle counts will be performed for further understanding.

Figure 20. Quantification of Li plating at 6C with different cycle numbers. At least three cells were used for each condition, and average values were used.
(2) Cell Testing

Twenty-four cells were tested to determine the effect of electrode porosity on lithium plating. Twelve cells contained the 1506T electrode that had been calendared to 22% porosity and twelve, to 49% porosity. An initial measurement of the C/2 capacity at 30°C showed that the cells were well matched. The average C/1 capacity of the low-porosity cells was 32.062 ± 0.355 mAh (1-σ) and that of the high-porosity cells, 32.421 ± 0.326 mAh. The cells were cycled using a 6C charge (constant voltage [CV] as needed, maintaining 10 minutes total charging time) and a C/2 discharge protocol at temperatures in the range of 20–50°C. RPTs were conducted initially at every five cycles at the testing temperature. The RPT consisted of a C/20 discharge capacity measurement and EIS. After 50 cycles, the RPTs were conducted every 25 cycles.

Last quarter, we took one cell from each temperature off test to examine it for lithium plating, leaving two cells to continue the experiment. All remaining cells have accrued 200 cycles.

Figure 21 shows the effect of cycling on the average, relative C/20 capacity loss of the cells. At first glance, the trend with temperature shown for the low-porosity cells did not seem reasonable. The capacity loss at 40°C was greater than that at 50°C. A closer inspection of the data showed that the capacity of one of the two cells was fading at approximately twice the rate (a “weak” cell) as that of the other. If the data from the weak cell were removed from data set, the plot looks more reasonable, as shown in Figure 22. Now, the relative capacity losses are equivalent within experimental error.

The data from the high-porosity cells in Figure 21 show that the average relative capacity loss from the high-porosity cells tested at 50°C showed excessive capacity loss at cycle counts greater than ~50 cycles. If these data were removed from the plot, Figure 23 would result. Within the error of the experiment, all average, relative capacity losses were the same.

![Figure 21: Average, relative C/20 capacity loss vs. cycle count for the cells in this experiment. The plot on the left is from the low-porosity cells; that on the right, from the high-porosity cells.](image-url)
Figure 22. Average, relative C/20 capacity loss vs. cycle count for the low-porosity cells in this experiment, with the data from the weak cell at 40°C removed. The error bars on the plot represent the standard deviation (1-σ) at the given cycle count. Because the 40°C data were from one cell, a value for the standard deviation was not calculated.

Figure 23. Average, relative C/20 capacity loss vs. cycle count for the high-porosity cells in this experiment, with the data from cells at 50°C removed. The error bars on the plot represent the standard deviation (1-σ) at the given cycle count.
Plots of the standard deviation vs. cycle count are shown in Figures 24 and 25. Both plots show that the standard deviation vs. time for both groups of cells tends to increase with cycle count, especially at the higher temperatures. It appears that the standard deviation tends increase very rapidly after 75 to 100 cycles.

Figure 24. Standard deviation vs. cycle count for the low-porosity cells. The data from the 40°C temperature were omitted due to low cell count.

Figure 25. Standard deviation vs. cycle count for the high-porosity cells. The data from the 50°C cells were omitted for the sake of clarity.

(3) Diffusion Coefficient Measurement

The diffusion coefficient versus state-of-charge for 1506T is being measured in “T”-shaped cells (external lithium reference electrode) at temperatures in the range of 20–50°C. These data will be used as input to the modeling effort.
Two experiments were performed to determine whether the charging rate influenced the measured diffusion, when charging at the C/20 and 4C rates. These experiments were performed in full cells, and the anode voltage limits were 1.5 to 0.1 V, corrected for iR. At the C/20 rate, the current was on for 15 minutes and off for 90 minutes. The current-on time was reduced to 45 seconds at the 4C rate, keeping the amount of capacity removed during each pulse approximately constant.

A typical galvanostatic titration curve at the C/20 rate at 30°C is shown in Figure 26. The diffusion coefficients were estimated using Huggins’s method from the data in the single-phase region shown in Figure 27. The estimated diffusion coefficients were in the range of 0.3 to $6 \times 10^{-12}$ cm$^2$/s and are shown as a function of capacity density in Figure 26.

![Figure 26. Estimated diffusion coefficients vs. capacity at 30°C and the C/20 rate.](image)

![Figure 27. Anode potential vs. Li/Li$^+$ vs. specific capacity at the C/20 rate. The red oval indicates the single-phase region.](image)
Figures 28 and 29 show the analogous results from the measurement at the 4C rate at 30°C. The estimated diffusion coefficients were in the range of 1.0 to $3.0 \times 10^{-8}$ cm$^2$/s, much larger than those shown in Figure 28.

**Figure 28.** Anode potential vs. Li/Li$^+$ vs. specific capacity at the 4C rate. The red oval indicates the single-phase region.

**Figure 29.** Estimated diffusion coefficients vs. capacity at 30°C and the 4C rate.

**Conclusions**

The amount of lithium plating on the 1506T anode is sensitive to cycle count at 30°C. After ~20 cycles, the amount of plated lithium seems to depend linearly on cycle count.
Capacity fade vs. cycle count in the low- and high-porosity cells shows a lot of cell-to-cell variability. The variability tends to increase with cycle count. The diffusion coefficient on 1506T was calculated using Huggins’s method. It seems to show a sensitivity to charge rate.

**Future work**

We will continue the work to characterize the factors that affect lithium deposition, time, and temperature. We will also continue to characterize cathode cracking using the materials from the lithium plating work as part of a more general aging project. The question here is how does fast charging affect cathode capacity? In a separate line of work, we will continue testing the effects of electrode porosity.

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Extreme fast charging (XFC) of Li-ion batteries can create life and safety issues. Among the issues are shortened battery life due to enhanced loss of lithium inventory and electrolyte degradation and enhanced safety concerns due to potential short creation by Li dendrites. The detection and monitoring of the onset of Li plating and evolution over aging are significant challenges. In operando detection schemes to understand the dynamics of Li plating and the role that aging has on Li plating are vital to enable the safe fast charging of specific energy cells.

Discreetly identifying Li plating is difficult without performing a destructive post-test analysis. The objective of the proposed work at INL and Princeton is to overcome these limitations using electrochemical analysis and nondestructive ultrasonic acoustic methods that can be directly applied in operando to understand the onset and growth of Li plating during XFC. The team is closely coordinating with other efforts at NREL and Argonne to understand the key limitations that enhance the probability of Li plating. A key to the efforts is understanding the interplay between materials, electrode structure, and use conditions. The ability to understand the interplay will be distinctly aided in this project using the joint electrochemical and ultrasonic tools, which ultimately will aid in the scientific understanding required to facilitate the safe XFC of batteries for electric vehicles.

Electrochemical methods that can be used to identify Li plating include the use of differential capacity (dQ/dV) and quantitative analysis of the cells’ charge and discharge profiles. These tools yield pertinent information associated with both the kinetic and thermodynamic processes that occur in batteries, and as such provide direct ability to better understand how variation in materials and electrodes have an impact across the life of a battery. There are limitations on the type of techniques that can be used to complement electrochemistry in operando using standard cell formats. One method that is showing promise is the use of ultrasonic measurements. Ultrasonic measurements rely on acoustic waves propagating through a structure, such as an electrode, which are modulated by its properties and encode structure/property relationship data. These relationships are directly tied to the material and mechanical changes that occur in a cell during cycling and can be used to characterize change in a nondestructive, real-time manner. Coupling ultrasonic and electrochemical measurements will enable a more complete evaluation of the impacts of XFC to be understood. In particular, both methods are expected to produce distinct and complementary signals that alert for the deposition of Li on the negative electrode of a battery during aggressive charging conditions. Tracking changes with the coupled ultrasonic and electrochemical methods over battery life and as batteries age will provide pertinent information related to the distinct conditions that drive Li plating during XFC.

Results
Understanding the limitations of detection is crucial for any analytical technique. During the third quarter of FY 2019, work related to understand the challenges of electrochemically detecting Li plating and stripping were investigated. This work, which was recently accepted for publication, involved the careful overlithiation of graphite samples and then prescriptively analyzing voltage, capacity, and differential voltage signatures to understand how signals are affected by rest time, extent of overlithiation, and other experimental parameters. The work found that during lithiation of a negative electrode, it is possible to have lithium plating prior to full electrochemical lithiation of the graphite. When this occurs, the lithium is then available to chemically lithiate the graphite, causing a significant reduction in the electrochemically detectable signature from lithium metal stripping (Figure 30).
Using the combination of signals and inputs, it was possible to characterize the coulomb count going toward irreversible lithium plating, reversible lithium plating, and graphite capacity, as shown in Figure 30. By distinctly isolating each of the different processes, tracking of both the overall coulombic efficiency (CE) and the stripping efficiency (SE) is possible. During early cycles where overlithiation occurs, both SE and CE experience slight drops, but both increase to the point where CE remains above 99% and SE increases above 80%. XRD analysis of the samples before and after overlithiation and at different stages confirmed that the chemical lithiation was predominantly resulting in additional staging in the LiC₆ stage. The XRD data were mirrored by analysis of samples with 1 h or no rest. When no rest between lithiation and delithiation occurred, there was a distinct change in the capacity associated with lithium stripping (increase) and graphite capacity (decrease), although only slight changes in CE were observed.

The combination of chemical lithiation, increases in efficiency, and decreased detectability and enhanced irreversible losses with variable rest time has highlighted the need to better understand the full constraints of electrochemical detection of lithium plating during fast charge conditions. Extensions of the work are in progress.

In addition to detection work, results highlighting performance failure and issues with the intergranular separation of secondary cathode particles during cycling advanced with the publication of a manuscript in Q3 (item 1 below). Experimental electrolyte characterization and identification of new blends based on results from initial experiments and advanced acoustic methods were also investigated and advanced in Q3 to continue progress from Q2 and in line with Q4 milestones.

**Conclusions**

Key challenges in the electrochemical detection of lithium plating and stripping were identified in Q3. Specific challenges due to chemical lithiation and the length of rest suggest that unless proper and full knowledge of the system is known, detection of lithium plating will be difficult using standard electrochemical methods.
Milestones and Deliverables

Q1 – Quantitate single-layer pouch cell failure modes – Complete, manuscript published [1]
Q2 – Identify enhanced transport electrolytes – Complete, manuscript in preparation
Q3 – Characterize electrochemical Li reversibility – Complete
Q4 – Correlate electrochemical and acoustic signals – In progress

Publications


**XCEL R&D: SLAC National Accelerator Laboratory**

**Contributors:** Hans-Georg Steinrück, Chuntian Cao, and Michael Toney (SLAC)

**Approach**

Our approach has been to exploit the nondestructive nature of synchrotron X-ray-based methods to characterize the formation of parasitic Li plating in lithium ion batteries (LIBs) across multiple length scales to guide cell design and charging protocols of extreme fast-charging LIBs. These synchrotron techniques use diffraction-based techniques and tomography to furnish information about the salient microstructural and morphological features most likely responsible for the battery degradation by correlating them to the battery performance. The aim is to understand the mechanism of battery failure through these experiments in order to design the next generation of XFC-enabled LIBs.

XRD experiments at the synchrotron with an area detector allow for fast data acquisition, thus enabling the characterizations of Li plating over the entire cell at a sub-mm resolution. This characterization is of importance to understanding the spatial heterogeneities in plating (and eventual failure) over the entire cell. The high energy and flux of the X-rays at synchrotron facilities also allow for studying cells under fully assembled conditions without the explicit need for destructive characterization. For this purpose, single-layer pouch cells, consisting of a single sheet of cathode (NMC), anode (graphite) and polymer separator with electrolyte, are used (Figure 31). These are Round 2 cells from CAMP at Argonne.

The total amount of plated Li can thus be found over the entire cell, along with the characteristics of the Li crystallites (such as orientations, size, etc.). These full-cell characterizations are carried out over different charging rates (4C, 6C, and 9C), under different charging protocols (constant current [CC]-CV, 2-step, and 5-step), and with different cycling histories (number of cycles). In addition, the effect of SOC in the anode is also studied, where a cell is characterized at 100% SOC after extreme fast charging and then characterized after slow discharging to 0% SOC.

After the full cell experiments, the cells are disassembled for analysis of morphological changes in X-ray microcomputed tomography. The aim of these experiments is to study the local spatial correlations between Li plating and loss of anode porosity. In addition, tomography can also furnish corresponding information on the cathode, to allow investigation of cracking in the cathode, particularly in regions that show a high amount of plated Li. These combined results from XRD and uCT will be crucial in understanding the factors that most influence the failure of the battery.

**Results**

XRD scans were first conducted on fully assembled cells cycled 450 times at the INL test facility under three charging rates (4C, 6C, and 9C). Earlier characterization of spatial heterogeneities across similar full cells
consisted of optical images that showed distinct regions of Li plating. The XRD scans taken on the full cells showed a good correlation to the optical images, while also quantifying the exact variation in Li intensities across the cell, as shown in Figure 32 on two cells cycled times at a 9C charging and a C/2 discharging rate.

![Image](image.png)

Figure 32. Direct (anti) correlation between the optical image of a delithiated anode after 450 XFC cycles at a 9C charging rate and C/2 discharging rate and lithium (graphite) intensity, as obtained by XRD.

In terms of capacity fade of the battery, these cells showed varying drops, from ~6% in the 4C cycled cell to ~28% in the 9C cycled cell. In addition, there was a large variation in the cell capacity after 450 cycles, even for cells cycled under the same conditions. However, the capacity fade was qualitatively well correlated to the total amount of Li detected over the cell using XRD, as shown in Figure 32, in the central panel for both cells. The top row shows a cell that lost 28% of its capacity over 450 cycles and shows a significant amount of plated Li, whereas the bottom row shows a cell that lost ~10% of its capacity under the same conditions and shows significantly lower Li intensity. Thus, dead Li from parasitic plating is seen to play an important part in determining degradation of cell capacity.

To study the effect of state of charge, the same cell was analyzed under ‘pseudo-operando’ conditions at fully charged condition (V = 4.1V) and 0% state of charge (V = 3.0V), after 25 XFC cycles at the 6C rate. These experiments are one step closer to doing “operando” studies, where the scans are completed within a few hours of cycling the cells. Figure 33 shows the relationship between the peak position of NMC (cathode) and plated Li intensity at 0% SOC (bottom row). The peak position of the NMC is reflective of the lattice parameters, which are a function of the local SOC in the NMC. Thus, the bottom row shows that in regions that have plated Li at full discharge, the NMC peak shows a higher value, which indicates the absence of Li in the corresponding regions of the NMC. Thus, the local SOC at the NMC is a function of Li plating and is very heterogeneous as compared to the overall SOC of the cell. The top row in Figure 33 shows the same cell at 100% SOC. Here, the NMC lattice parameter is uniform throughout, indicating that during charging, all the Li has left the cathode. Comparison of the Li intensity maps at 0% and 100% SOC also shows that Li plating at 0% SOC primarily occurs in the regions of maximum Li intensity at full charge.

The next steps in XRD analysis are extending the results shown in Figure 32 for cells at the 9C charging rate to cells cycled at 6C and 4C rates. Similarly, in the pseudo-operando experiments, characterization has been
performed on cells after 10, 25, 40, and 50 XFC cycles at the 6C charging rate. The effect of increasing the number of cycles can be analyzed through this study to complement the SOC charge presented in Figure 33.

Complementary tomography was conducted on the cells in Figure 32 to obtain morphological information on the plated Li and to support the structural data obtained from XRD. The spatial resolution of the tomography is 1.38 μm with a field of view of ~1.4 mm. Figure 3 shows a projection of the bottom cell in Figure 32, where XRD showed significant intensity of plated Li. The projection shows that the thickness of the plated Li is on the order of 10s of μm for an anode which is ~70-μm thick, which can be used to complement the modeling studies by NREL on penetration depth of plated Li. The image also shows that the Li plating is exclusively on the separator side, that is, without percolation into the collector side of the anode.

The next steps in the tomography analysis include correlating the presence of Li plating to changes in porosity in the anode and cracking in the cathode in similar regions. This step is performed by comparing tomography reconstructions across different cells in regions that show different amounts of Li plating.

Figure 33. The top row indicates the cell at 100% SOC, where all of the Li has left the cathode (left) and is on the anode side. The left panel shows the peak position of the NMC, while the right panel indicates the integrated Li intensity. The bottom row indicates the cell at 0% SOC. The local variation in the NMC lattice parameter shows that the local SOC is very different from the overall cell SOC. The bright regions in the left correspond to the bright regions on the right bottom that show plated Li.

Figure 34. Projection of a tomographic reconstruction from microCT of an anode. The cell was cycled at a 9C charging rate for 450 cycles and disassembled at 0% SOC (bottom row of Figure 32). This region corresponds to a part of the cell that showed significant Li plating in the XRD scan. The purple regions indicate Li while the gold regions indicate the graphitic anode. The Li converts to LiOH, thus enabling detection by X-ray tomography.
XCEL R&D: SLAC National Accelerator Laboratory

Contributors: Yi Cui, William Chueh, and Mike Toney (SLAC)

Approach

XFC Battery Health Detection with Resistive Temperature Detectors (RTDs)

Thermal management is critical to the safe operation of LIBs. At XFC conditions, heat generates and accumulates rapidly in LIBs, possibly causing electrolyte/electrodes’ aging and Li dendrite formation at anodes, etc., which leads to fading or even (hazardous) failures. However, a lack of understanding and probing tools of temperature distribution inside LIBs (in three dimensions) and its relation to battery failure limit the high performance of LIBs, especially at XFC conditions.

In the XFC program, we are developing a set of resistive temperature detectors (RTDs), which potentially enable time/spatial-resolved temperature monitoring in LIBs in operando. During the past quarter, we have developed techniques for good metal/polymer substrate adhesion, as well as polymer surface coating (protection) for RTDs, and have managed to demonstrate accountable calibration of homemade RTDs in flooding electrolyte pouch cells (photo images show a typical pouch cell and RTD array in Figure 35a and 35b, respectively). Relative stable resistances vis-à-vis step times can be achieved with RTD/electrolyte/pouch cell inside a temperature-controlled environmental chamber (Figure 35c). The resistance and temperature show a linear relation (Figure 35d), which is consistent with a linear resistivity temperature coefficient of deposited RTD metal. The RTDs will be inserted in real LIBs for operando temperature monitoring in the next quarter.

![Figure 35. Temperature monitoring in pouch cell with RTDs. (a) A photo image of RTD inside pouch with flooding 1M LiPF₆, EC/DEC (v:v=1:1) liquid electrolyte. (b) An image of a typical RTD array from red square region sealed inside pouch in (a). (c) RTD resistance vs. time plot in operando at controlled temperature of (a). (d) RTD resistance vs. temperature plot.](image-url)
Background

The goal of the LBNL team is to detect the initial nucleation event using data available in typical battery management systems. Identifying the initial onset of Li plating during fast charging is a multifaceted, challenging “needle-in-a-haystack” problem. First, there may be a barely perceptible chemical signature of this event. For example, the presence of lithium may lead to the sudden formation of a small amount of gases due to irreversible reactions between the plated lithium and the electrolyte-soaked SEI. Second, identifying the particular particle where the overlithiation and Li plating occurs can be challenging at the immediate onset of Li plating. Clearly, the particular particle that is overlithiated first will depend on the state-of-charge of the electrode, as it will be governed by the amount of lithium intercalated at that time and the lithium concentration in the surrounding liquid electrolyte. The third and final challenge is identifying electrical signatures of the overlithiation event so that our work can be used in practical battery management systems. We note here that the signatures may be different at different states-of-charge and that the electrical signature may be inherently nonlinear and thus not clearly evident in standard electrochemical measurements. Our objective is to address all three challenges.

In addition, graphite anode architectures with low-tortuosity open pores parallel to the ion transport direction during cycling will be developed by a freeze tape casting method. Various types of commercial graphite, carbon, and binder will be tested for slurry stability. The down-selected combinations will be used to produce graphite anodes with controlled porosity, pore size, and layer thickness. The final product may serve as a drop-in replacement for the conventional graphite anode, but with a goal of improved charge acceptance capability. Modeling efforts of the Kandler group (NREL) will provide guidance to the desired overall porosity and pore structure. Tomography data will be shared with NREL to improve model accuracy. The Jansen group (Argonne) will aid with cycling the produced freeze tape cast graphite anodes to compare with conventional counterparts.

Results

To enable high-resolution X-ray microtomography of lithiated graphite, the Balsara group is collaborating with Finegan (NREL) and Tong (LBNL). Shown in Figure 36 is a microtomography sample holder designed by Finegan. Tong’s group has constructed a current-collector-free anode. In a feasibility study, a piece of the anode was placed in the sample holder and imaged on the X-ray microtomography beamline at LBNL. The results show a clear image of the graphite particles. In future work, we will seek to find the instrument configuration that gives us the clearest images of the anode.
The McCloskey group uses differential electrochemical mass spectrometry (DEMS) to detect gases evolved during cycling of graphite electrodes. A representative gas evolution signature collected for a Li-graphite half-cell is shown in Figure 37. A clear ethylene ($\text{C}_2\text{H}_4$) signature is observed during the first intercalation due to the SEI-forming reduction of ethylene carbonate, but only modest traces of gas evolution are seen thereafter, even after intentional overlithiation of the graphite. Future work will involve coupling in-operando gas detection with ex-situ titrations to quantify the surface species present (both SEI and plated Li) on graphite electrodes that have been fast charged.

To characterize Li plating using operando optical microscopy, the Chen group first performed ex situ studies of graphite electrodes subjected to various cycling under fast charging conditions. Figure 38a shows the half-cell coin-cell configuration with the graphite electrode (SLC 1506T) provided by Argonne. The cells were cycled at C/10 for three cycles and then followed by a 6C charge and C/2 discharge for 20 cycles. Optical microscopy images of the pristine graphite electrode at 1500x and 2500x magnifications are shown in
Figure 38b and 38c. A uniform layer of large graphite particles with an average particle size of \( \sim 10-15 \mu m \) was seen on the Cu current collector. After 20 cycles, the recovered lithiated graphite electrode showed a combination of gold-colored graphite particles along with silver-colored mossy and dendritic Li deposits (Figure 38d), demonstrating the feasibility of using optical microscopy in detecting Li plating. In future work, we will construct in situ cells that allow for operando observation of Li plating, as well as its correlation to real-time signals of the electrochemical reactions.

Figure 39 shows SEM images of a freeze tape cast 1560T graphite anode cast at 23 vol.% graphite at -8°C with porosity of 74%. Vertical pore channels are observed with average channel widths of 15±5 µm. Improvements to the electrode fabrication process have been suggested and will be attempted next quarter. A goal is to reduce the secondary pore network porosity to 20% per recommendation by NREL modelers.
Figure 39. SEM (a), (b) fracture surface, and (c) surface images of freeze tape cast graphite anode. The graphite layer is 150-µm thick, showing vertical pore channels. Graphite columns are composed of 1506T graphite, Timcal C45 conductive additive, and NaCMC binder. Porosity is 74 vol.%. 