X-CEL:
eXtreme fast charge
Cell
Evaluation of
Lithium-ion batteries

May 2018

Quarterly Report Period: October-December 2017
Table of Contents

Project Overview .................................................................................................................................................. 4
ANL: CAMP Facility Electrode and Cell Development for Fast Charge ......................................................... 5
Extreme Fast Charging (National Renewable Energy Laboratory) ............................................................... 10
ANL Modeling: Electrochemical and Techno-Economic (BatPaC) ............................................................... 15
XFC: Performance Characterization and Post-Test Analysis ...................................................................... 20
Extreme Fast Charging R&D: Battery Testing Activities (Idaho National Laboratory) .............................. 27
Project Overview

Venkat Srinivasan PI (Argonne National Laboratory) and Samuel Gillard (Department of Energy)

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. Present day high energy cells with graphite anodes and transition metal cathodes in a liquid electrolyte are unable to achieve this without negatively effecting 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 three National Labs are utilized to make progress in the project.

Cells are built at the Cell Analysis, Modeling, and Prototyping (CAMP) facility at Argonne National Lab (ANL) using various carbons, different cell designs, in both half-cell and full cell configuration and with reference electrodes. Cells are tested at both Idaho National Lab (INL) and ANL under various operating conditions (c-rate, temperature) and under different charging protocols with the aim of identifying the onset of plating, to quantify the extent of the problem, and to determine parameters and test data for mathematical models. Tested cells are opened and various advanced characterizing performed at ANL to determine the extent of plating and to determine if 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 to 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 National Renewable Energy Lab (NREL) is used to test cell designs, accompanied by microstructure models to provide deeper insights into the phenomenon in the battery. This is complemented with development of models incorporating of new physics, such as phase change and SEI growth, at ANL.

Finally, two exploratory projects aim to study ways to detect Li in situ during operation. NREL will pursue the use of microcalorimetry to detect heat signatures during plating. INL will work with Princeton University to examine the use of acoustic methods to determine if plating leads to a signature in the acoustic signal.

In this quarter, all aspects of the project have ramped up. CAMP cells on thin, low loading electrodes, wherein the effect of the porous electrode is eliminated, have been used to understand the role of the type of carbon on capacity fade. Results show that all carbons are capable of 6C charging, when the loading is low, suggesting that Li plating is mainly caused by reaction distributions in the porous electrodes in thicker electrodes. Modeling results are consistent with this observation, with the model suggesting that 6 C charging is only possible in electrode with thickness around 40 µm.
ANL: CAMP Facility Electrode and Cell Development for Fast Charge

Alison Dunlop, Andrew Jansen (PI), Bryant Polzin, and Steve Trask (Argonne National Laboratory)

Background

In this first year’s effort, the Cell Analysis, Modeling, and Prototyping (CAMP) Facility’s objective is to develop experimental electrodes that will be used to identify causes of lithium plating at fast charges in single-layer pouch cells. Earlier work at Argonne by Gallagher et al. [1] had studied the influence of capacity loading on material utilization at various discharge rates. This work also touched on the effect of charge rate on capacity retention and lithium plating, which is summarized in Figure 1. These single-layer pouch cells were originally charged for 285 cycles at a C/3 rate, after which the charge rate was increased to C/1 (followed by trickle charging to 4.2 V) up to 549 cycles, and for the surviving cells, the charge rate was further increased to 1.5C. The discharge rate was held at C/3 rate in all cases to remove that rate as a variable. As can be seen in Figure 1, it is clear that the electrodes with loadings higher than ~3 mAh/cm² could not sustain a charge rate higher than C/1.

Figure 1. Discharge capacity as a function of electrode loading (mAh/cm²) and charge rate (left) and photos of lithium deposits on representative graphite electrodes (right). These results were obtained with capacity-matched cells using graphite negative electrodes and LiNi₀.₆Mn₀.₂Co₀.₂O₂ (NMC622) positive electrodes.

Evidence of lithium plating was sought for these cells by disassembling representative cells in a dry room after a 24-h voltage hold at 3.75 V and then washing with dimethyl carbonate. As expected, cells with the largest capacity fade exhibited the most lithium deposits as can be seen in Figure 1. Surprisingly, fully discharging one of the 4.4 mAh/cm² cells at a low rate before disassembly did not remove the lithium deposits from the negative electrode surface, which suggests that the lithium deposits becomes electrically isolated from the graphite electrode.

The goal of the work now is to determine the influence of graphite selection on fast charge capability, at an even faster rate of 6C. Initial expectations are that the physical properties of the graphite particles in the negative electrode will affect the onset of lithium dendrites. These properties include the surface area, particle size, size distribution, surface coatings/modifications, and source of graphite, i.e., natural graphite versus artificial graphite. The CAMP Facility has a range of graphite powders suitable for this study that can provide a basis of comparison for these properties. At least four different graphite powders will be made into negative electrodes and evaluated for fast charge performance against a standard NMC532 positive electrode. This screening test will be performed in coin cells. The best performing graphite material will then be used in
single-sided single-layer pouch cell builds and delivered to battery testing labs in this program for complete
electrochemical characterization under fast charge conditions.

A second single-sided single-layer pouch cell build will be performed based on the preliminary results of the
coin-cell graphite screening results and the first pouch cell build. This second cell build will either use a
different graphite or a higher electrode mass loading (thicker). These pouch cells will also be delivered to the
battery test labs for evaluation and analysis.

Results

Prescreening of Available Graphite Powders
Table 1 lists the available properties for the graphite powders selected in the prescreening tests initiated at the
start of this fiscal year. Since several of these powders were already incorporated into the CAMP Facility’s
Electrode Library, it was decided to evaluate these materials using the Library’s anode capacity loading of 2
mAh/cm² against capacity-matched NMC532 positive electrodes also in the Library. The n:p ratios were ~1.1
to 1.2. Graphite materials not in the Electrode Library were designed and developed at the same capacity
loading (and added to the Library).

Table 1: Graphite powders selected to elucidate causes of lithium plating during fast charges.

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Company</th>
<th>Type</th>
<th>Particle shape or morphology</th>
<th>Tap Density, [g/mL]</th>
<th>Surface Area, [m²/g]</th>
<th>Particle Size D10, [µm]</th>
<th>Particle Size D50, [µm]</th>
<th>Particle Size D90, [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLC1506T*</td>
<td>Superior Graphite</td>
<td>coated, natural graphite</td>
<td>spherical graphite powder</td>
<td>1.03</td>
<td>1.936</td>
<td>5.37</td>
<td>8.06</td>
<td>13.15</td>
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<tr>
<td>SLC1520P</td>
<td>Superior Graphite</td>
<td>coated, natural graphite</td>
<td>spherical graphite powder</td>
<td>1.19</td>
<td>0.89</td>
<td>11.03</td>
<td>16.94</td>
<td>26.76</td>
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<tr>
<td>MagE3</td>
<td>Hitachi</td>
<td>artificial graphite, combines hard graphite additive</td>
<td></td>
<td>0.90</td>
<td>3.9</td>
<td>-</td>
<td>22.4</td>
<td>-</td>
</tr>
<tr>
<td>MCMB</td>
<td>Gelon</td>
<td>Artificial, Mesocarbon Microbeads standard type-G15</td>
<td>MesoCarbon MicroBeads</td>
<td>1.324</td>
<td>2.022</td>
<td>-</td>
<td>17.649</td>
<td>-</td>
</tr>
<tr>
<td>CPG-A12</td>
<td>Phillips 66</td>
<td>natural graphite core coated with surface treatment</td>
<td>potato</td>
<td>-</td>
<td>2 to 4</td>
<td>-</td>
<td>9 to 12</td>
<td>-</td>
</tr>
</tbody>
</table>
Coin cells were assembled with 14 mm diameter cathodes and 15 mm diameter anodes using Celgard 2320 separator (20 µm, PP/PE/PP) and Tomiyama 1.2 M LiPF₆ in EC:EMC (3:7 wt%) “Gen2” electrolyte. Four duplicate coin-cells were made for each graphite. The coin cells were then cycled in the 3.0 to 4.1V window with 3 formation cycles at C/10 (w/ C/20 trickle charge), followed by 250 cycles of fast charging at 6C with trickle charge down to C/5 until a total charge time of 10 minutes was reached, with C/2 discharges. 2 minute open circuit rests were used between charge and discharge steps. This profile was repeated until <80% of the capacity measured at the 10th cycle remained.

At this relatively low loading, all of the graphite materials in Table 1 are able to cycle under a 6C charge rate for hundreds of cycles – all of which are still on test at the time of this report. A summary of their current performance status is best illustrated in Figure 2, which is a plot of capacity retention versus cycle for two representative cells of each graphite. Cycle 10 was used as the common cycle in normalizing this data, which is a point where the majority of cells were considered to be stabilized. A complete analysis with averages of each graphite cell build and their standard deviations will be performed once all cells have reached either 80% capacity retention or 750 cycles. Nevertheless, a few predictions can be postulated here based on the data collected to date. This includes that: 1) the choice between natural graphite and synthetic graphite is not significant; and 2) SLC1506T graphite and MCMB graphite appear to have slower capacity fade rates compared to the other graphite materials. It remains to be seen if these observations hold true at higher capacity loadings. A decision was made in January (2018) to use the SLC1506T graphite from Superior Graphite for the first pouch cell build deliverable in order to meet the deadline for delivery of these pouch cells to the battery testing labs.

Figure 2. Discharge capacity retention for the graphite materials selected in the coin-cell prescreening study under 6C charge and C/2 discharge between 3 - 4.1 V at 30 °C (anode capacity of 2 mAh/cm²). * cycler issue
Earlier work [1] that addressed the effects of capacity loading on rate performance had indicated that cathode capacity loadings above 2 mAh/cm² experienced lithium plating at charge rates as low as 1.5C. This appeared to be in conflict with the observations from the early prescreening results obtained at the beginning of this quarter. One difference noted was that the electrodes in reference [1] were made by an outside vendor using an aqueous CMC-SBR binder, while the CAMP Facility electrodes use a NMP-based PVDF binder. To test the binder effect, the CAMP Facility remade the MAG-E3 graphite electrode using a CMC-SBR binder. This electrode was then tested at the 6C charge rate in the same manner as the prescreening graphite materials presented in Figure 1 above. The results of this binder comparison are presented in Figure 3, where one can conclude that there is no significant difference in the capacity fade rate for either binder system.

![Figure 3. Discharge capacity for the MAG-E3 graphite using CMC-SBR binder versus NMP-based PVDF binder in the coin-cell prescreening study under 6C charge and C/2 discharge between 3 – 4.1 V at 30°C (2 mAh/cm²).](image)

Coin-cell GITT Study
Lithium-ion diffusion coefficients through these different graphite materials is needed to accurately model the electrochemical processes taking place during fast charges. One of the best methods to obtain these coefficients is obtained via the Galvanic Interruption Titration Technique (GITT). The CAMP Facility is providing 15 duplicate coin-cells for each of the graphite materials listed in Table 1 to Argonne’s EADL (Ira Bloom). The results of this on-going study are presented in the EADL report. The coin cells were assembled with 15 mm diameter graphite electrodes and 15.6 mm diameter lithium metal counter electrodes using Celgard 2325 separator (20 µm, PP/PE/PP) and Tomiyama 1.2 M LiPF₆ in EC:EMC (3:7 wt%) “Gen2” electrolyte. No formation cycles or other cycles were applied to these coin cells so that the EADL could capture the first lithiation electrochemical response. The cells were delivered to EADL and put on test within a few hours of assembly to minimize corrosion of the copper current collector. The list of graphite coin cells produced for this GITT study so far are: MCMB (A-A010), delivered 10/25/17; SLC1506T (A-A015), delivered 12/18/17; SLC1520P (A-A005A), delivered 12/19/17; and MAG-E3 (A-A016), delivered 2/22/18. The BTR-BFC-10 and A12 graphite cells will be produced as EADL testing channels become available.

Pouch Cell Deliverables (Single-sided Single-layer)
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. 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 3 cycles at C/10, followed by 3 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 recommend for future tests.
A plot of the discharge capacities during the formation cycles applied to the 30 pouch cells delivered to INL is shown in Figure 4.

INL requested 30 of these pouch cells for testing. These 30 cells were received at INL the week of 2/13/18. Argonne’s EADL requested 16 of these pouch cells for testing now. These 16 cells were delivered to Argonne on 2/15/18 in 4 test fixtures at ~4 psi. An additional 16 pouch cells were assembled and kept dry (no electrolyte) for Argonne’s EADL for future rounds of testing, upon which they will be filled with electrolyte and electrochemically formed by the CAMP Facility and delivered to EADL.

In addition, NREL requested 4 of these pouch cells fully formed similar to INL and Argonne’s EADL pouch cells for micro-calorimetry studies. They also requested 2 dry pouch cells and several punched pristine anodes and cathodes that are used in the pouch cells. All of these cells and electrodes were shipped to NREL at the end of February. NREL also requested 4 graphite (SLC1506T) half-cell pouch-cells and 4 NMC532 half-cell pouch-cells. These half cells will be assembled and shipped in April.

**Conclusions**

Six different graphite negatives were chosen from the CAMP Facility’s Electrode Library for fast-charge prescreening and GITT study in coin-cells. Surprisingly similar fade rates were observed at the 6C charge for many of these graphite materials. A decision was made early in the prescreening study to use SLC1506T graphite from Superior Graphite for the first single-sided single-layer pouch cell build using a 2 mAh/cm² graphite loading.

CMC-SBR vs. PVDF binder showed little difference at the 2 mAh/cm² graphite loading.

Over 70 single-sided single-layer pouch cells were fabricated and delivered to lab partners (INL, ANL, and NREL) for fast charge testing with a recommended 19 mAh capacity at the C/3 rate.
Future work will include completing the fast charge life cycle testing of the six prescreening graphite materials, and completing the remaining coin cell builds for Argonne’s GITT study. The dry pouch cells for Argonne’s EADL will be formed and delivered to Argonne as needed. The half-cell pouch-cells for NREL will be designed, fabricated, and delivered to NREL in April. Efforts are now underway to perform a quick prescreening of the effects of graphite loading in preparation of the second single-sided single-layer pouch cell builds, which are due to INL and Argonne by April 27, 2018. It is hoped that the second pouch cell build will perform sufficiently at a graphite loading near 4 mAh/cm².

### Milestones and Deliverables

<table>
<thead>
<tr>
<th>Status of tasks this quarter and beyond:</th>
<th>9/1/2017 - 11/15/2017</th>
<th>Completed</th>
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<tr>
<td>B1000 Select candidate materials for first cell builds</td>
<td>11/1/2017 - 1/31/2018</td>
<td>Completed</td>
</tr>
<tr>
<td>B1010 Deliver all known characterization information to NREL modeling team for selected graphite candidates</td>
<td>12/6/2017 - 1/28/2018</td>
<td>Completed</td>
</tr>
<tr>
<td>B1020 Workshop on lithium plating detection</td>
<td>3/15/2018 - 4/27/2018</td>
<td>On-schedule</td>
</tr>
<tr>
<td>B1030 Build and deliver first cell builds to ANL/INL test lab</td>
<td>3/15/2018 - 4/27/2018</td>
<td>On-schedule</td>
</tr>
</tbody>
</table>

### References


### Extreme Fast Charging (National Renewable Energy Laboratory)

**Matthew Keyser, Kandler Smith, Shriram Santhanagopalan, Francois Usseglio-Viretta, and Andrew Colclasure (NREL)**

### Background

To understand fundamental Li-ion cell limitations from transport/kinetic losses during extreme fast charging (XFC), NREL performed initial modeling studies representing a baseline graphite/NMC532 cell chemistry fabricated at Argonne National Laboratory’s (ANL’s) Cell Analysis, Modeling and Prototyping (CAMP) facility. These initial studies were performed with macro-homogeneous electrochemical models. Models were tuned starting from parameters collected under an earlier DOE Computer-Aided Engineering of Batteries (CAEBAT) program and updated using new ANL data for thin electrodes at charge rates up to 7C. The model predicts the baseline design can only sustain 6C charging to 60% SOC when electrodes are less than ~50 μm thick, which corresponds to an energy density of <115 Wh/kg during constant current (CC) charging. A small amount of lithium plating is predicted for this condition. To enable XFC, the initial study indicates the need to:

- Reduce electrode tortuosity
- Improve electrolyte transport properties
- Use electrodes with high surface area and intercalation kinetics
- Optimize electrode porosity for rate capability and energy density
Results

Figure 1 illustrates 3 main transport limitations that can occur during XFC and their consequences. During charging lithium ions de-intercalate from the NMC positive electrode active particles and transfer into the electrolyte phase. These lithium ions migrate and diffuse from the positive through the separator and into the negative electrode where they intercalate into the active graphite particles. At the high current densities required to support XFC of $>10\text{mA/cm}^2$, large concentration and electrolyte potential gradients develop to drive the necessary flux of lithium ions within the electrolyte. Sustained fast charge can result in electrolyte Li ion depletion within the negative and/or saturation within the positive electrode. These electrolyte transport limits can also occur at lower charge rates for cell designs when electrolyte conductivity is low, electrolyte diffusivity is low, electrode tortuosity is high, porosity is low, and/or electrode thickness is high. Due to limited solid-state diffusivity for graphite and NMC, lithium ions can become saturated at the graphite surfaces and depleted at the NMC surfaces. Saturation of Li ions at the graphite particle surface along with sluggish kinetics can result in lithium plating, causing cell degradation and safety concerns.

Figure 1. Schematic of the various transport limitations during XFC that can result in poor charge acceptance, heat generation, lithium plating and capacity loss.
Tortuosity of the positive and negative electrode is a significant factor impacting electrolyte transport losses and thus cell fast charge acceptance. The effective diffusivity and conductivity of the electrolyte within the composite electrodes are related to the pure phase values as

\[ D_{\text{eff}} = \frac{\varepsilon}{\tau} D_0 = \frac{1}{N_m} D_0 = \varepsilon^p D_0 \]

where \( \varepsilon \) is the electrolyte phase volume fraction and several equivalent metrics found in the literature are electrolyte phase tortuosity \( \tau \), McMullin number \( N_m \), and Bruggeman exponent \( p \). Typically a Bruggeman exponent of 1.5 has been used throughout the literature, which is the theoretical value for an electrode packed with mono-sized spheres and neglecting any effects from carbon-binder phase. Figure 2 illustrates estimates for tortuosity of graphite and NMC electrodes fabricated and electrochemically tested at ANL under the CAEBAT program. The tortuosity was estimated with three methods: macro-homogeneous electrochemical modeling for 80-200 \( \mu \)m thick electrodes (where electrolyte transport becomes important), detailed microstructure reconstruction (including carbon/binder phase numerically generated by Purdue University/Prof. Partha Mukherjee), and direct experimental measurements (performed by Brigham Young University/Prof. Dean Wheeler) using a symmetric cell with blocking electrolyte. For a calendared NMC electrode a tortuosity of ~3 was estimated (Bruggeman of ~2-2.3) and for graphite a tortuosity of ~6-8 was estimated (Bruggeman of 2.9-3.2). The tortuosity of the negative electrode is higher due to the potato-like graphite particle shape.

In addition to tortuosity, estimates for solid-state diffusivity, particle size, electrolyte phase properties, and exchange current density were also taken from previous CAEBAT work [1]. Next, NREL used initial XFC data supplied by ANL to refine the macro-homogeneous model. ANL ran XFC tests for cells with an electrode capacity of 1.5 mAh/cm\(^2\) (~40 \( \mu \)m thick electrodes with ~34% porosity) at charge rates of 3, 5, and 7 C. The only parameters adjusted to this data were the Bruggeman coefficient for these electrodes and lithium lost due to SEI formation. Negative and positive electrode Bruggeman exponents were set to 2.7 and 2.0, respectively, consistent with previous values for similar electrodes shown in Fig. 2. First cycle lithium loss was estimated as 10%, matching values reported in the literature. Figure 3 illustrates initial data collected by ANL together with macro-homogeneous model predictions for a 14.1cm\(^2\) cell at high rate charging (nominal capacity of 21 mAh).
The model reasonably captures the voltage response and capacity achieved during CC charging with increasing rate. Charge capacities achieved at 3, 5, and 7C were 87%, 77%, and 60%. The model predicts a small amount of lithium plating may occur at the end of 7C charging. Model prediction of Li plating onset will be refined as validation data becomes available in the future.

![Figure 3. Comparison of initial ANL results for XFC of graphite/NMC cell with loading of 1.5 mAh/cm² to macro-homogeneous model predictions.](image)

After matching the macro-homogeneous model to the baseline ANL cell, NREL used the model to predict how other cell designs with higher loadings would perform during XFC (see dot-dash lines in Fig. 4). For automotive application, an electrode loading of > 3mAh/cm² is desirable which corresponds to an electrode thickness of >85 µm. The model predicts that CC charge capacity and achieved energy density during XFC quickly drop with an increase in electrode thickness/loading. This is a result of limitations due to relatively poor negative electrode tortuosity, low electrolyte diffusivity, and low electrolyte conductivity leading to electrolyte saturation/depletion, non-uniform electrode utilization, and lithium plating. The model also predicts lithium plating occurs at much lower charge rates with an increase in electrode thickness/loading. For instance, at 42 µm thick (1.5 mAh/cm²) the model predicts only at a rate of 7C does plating start to occur. At 85 µm thick however, lithium plating is predicted to occur at rates as low as 2C. If the anode tortuosity alone could be reduced to that of the cathode by using spherized graphite, then the maximum electrode thickness that could achieve 60% SOC at a given charge rate improves by about 20%.

To enable XFC of energy dense cells with high loadings, it is important to improve electrolyte properties and reduce negative electrode tortuosity. Figure 4 and 5 illustrate how a next generation electrolyte and negative electrode could improve the charge rate capability of thick electrodes. At 30°C and ~1M, the present Generation 2 electrolyte (LiPF6 in 30% wt EC/70 wt% EMC) achieves an electrical conductivity of 10 mS/cm and diffusivity of 1.5e-10 m²/s. The hypothetical next generation electrolyte has a conductivity of 15 mS/cm and diffusivity of 4.5e-10 m²/s at 30°C and ~1M and negative electrode has a Bruggeman exponent of 2. The model predicts these improvements help prevent lithium plating and electrolyte saturation/depletion for electrodes as thick as 100 µm and at charge rates up to 7C. Other researchers have noted the importance of enhancing electrolyte properties to enable XFC within high energy density cells. Recently, Jeff Dahn and coworkers have published results indicating incorporating ethers as a co-solvent improves electrolyte conductivity with values reported up to 13 mS/cm at 30°C enabling slightly higher rate charging without plating [2-3]. The addition of ethers is also shown to reduce viscosity and thus likely improve diffusivity since the two are inversely related. It should be noted, the present estimate for lithium plating considers very fast lithium intercalation kinetics (a_i = 6 A/cm³ at 50% intercalation fraction). Further, the model only considers the potential of the electrode phase relative to the electrolyte phase and simple chemistry. More detailed models incorporating SEI chemistry, SEI potential drop, and multiple lithium-graphite phases will be adopted as needed during the course of the XFC project to more accurately predict the onset of lithium plating.
Conclusions

A macro-homogeneous electrochemical model was performed to predict limitations on XFC charge rate versus electrode thickness and energy density for cells employing graphite negative and NMC532 positive electrodes. Model results indicate that, for current electrodes and electrolyte, 6C charging to 60% capacity can only be achieved for ~40 μm thick electrodes, corresponding to a relatively low loading of 1.5 mAh/cm². Increasing porosity above 35% slightly improves high rate capability >3C, but at the expense of low rate energy density (e.g. at 1C). Initial results provide motivation to reduce electrode tortuosity and improve electrolyte transport properties. Model results indicate a next generation electrolyte with 1.5X conductivity and 3X diffusivity along with reduced negative electrode tortuosity should enable XFC of energy dense cells with high loading. These results are preliminary and may be further refined pending experimental data from the XFC team to account for multiple phases present in graphite and SEI losses. In the next quarter, NREL will also begin to apply a detailed 3D microstructure model to more accurately quantify electrode inhomogeneity and investigate its impact on Li plating onset.
Milestones and Deliverables

References

ANL Modeling: Electrochemical and Techno-Economic (BatPaC)

Dennis Dees and Shabbir Ahmed (Argonne National Laboratory)

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 focus of the electrochemical modeling effort this quarter is to improve an existing phase change model developed for graphite active materials [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 an MCMB graphite electrode, the model tended to underestimate the performance of the graphite at high current rates.

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

Electrochemical Model

Two ways to improve the electrochemical phase change model were identified. First, the previous model development implicitly assumed that the Avrami equation rate constant was time independent, even though the rate constant was also assumed to be lithium concentration dependent. Correcting for the time dependence of the rate constant was explored. Examination of the modified phase change model behavior did not show a significant improvement and further the modification adversely affected the stability of the numerical simulation.

The model assumes that phase changes in the graphite can only occur from one phase to the adjacent phase. Specifically, in the model lithiating the LiC_{32} phase will cause it to go to LiC_{12}. Further, lithiation of the LiC_{12} phase will cause it to go to LiC_6. Note that the model only has three possible phases for the graphite, which covers most of the lithium concentration range of the graphite. The model was modified to allow the LiC_{32}
phase to go directly to LiC₆ at high lithiation rates. While in principle one may expect this modification to improve the model’s ability to accept lithium, the improvement was minimal at best (see below).

Paralleling the phase change model modifications, an existing improved data set was utilized to develop a new parameter set for a graphite. The graphite electrode, fabricated by CAMP, whose composition is shown in Table 1, has exhibited reasonably good fast charge characteristics. Further, it is thin enough that electrochemical model simulations indicate that the electrode is not limited by lithium ion transport through the electrolyte at a 6C rate. The results of a half-cell GITT study (i.e. repeated C/18 current for 16 minutes followed by 45 minutes rest) is shown in Figure 1. Also shown in Figure 1, the thermodynamic functions of the three single phases. While all three phases utilize the same thermodynamic like function, the parameters are modified to fit the data. The data indicates that the LiC₃₂ phase is predominately linear in the single phase region with respect to concentration. Also, the LiC₆ phase is logarithmic, while one can use either linear or logarithmic for the narrow concentration single phase region of the LiC₁₂ phase. The logarithmic behavior was adopted initially because it gives a better fit of the LiC₁₂ single phase data.

Table-1: Graphite electrode description used in range of studies presented.

<table>
<thead>
<tr>
<th>Negative Electrode:</th>
<th>A-A002A(-): made by CAMP</th>
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<tbody>
<tr>
<td>91.8 %wt ConocoPhillips: CGP-A12 graphite</td>
<td></td>
</tr>
<tr>
<td>2 wt% C45 (Timcal) + 0.17 %wt Oxalic Acid</td>
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</tr>
<tr>
<td>6%wt KF-9300 Kureha PVDF binder</td>
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<tr>
<td>5.51 mg/cm² active loading (A12 graphite + C45)</td>
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<td>38.4% electrode porosity</td>
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<td>44-µm-thick composite coating</td>
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<tr>
<td>10-µm-thick Cu current collector</td>
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</table>
Figure 1. Half-cell GITT studies on A12 graphite electrode. Assumed thermodynamic functions for single phase regions shown.

Half-cell data can be problematic because the lithium electrode is generally unstable during cycling. As long as the changes in impedance of the lithium electrode with time are small compared to the graphite electrode impedance, then the lithium electrode instability effects are small. An indication that the lithium electrode effects are small in the present GITT data can be seen in Figure 2, which shows the fit of charge and discharge data in the LiC$_{32}$ single phase after more than a week between acquisitions. Both sets of data were fit with an electrochemical half-cell single phase intercalation active material model using the same parameter set [2]. Also, a typical fit of the two phase regions using the phase change half-cell model is shown in Figure 3. Observations of note include the diffusion coefficient for the single phases varied from 1.2 to $2.0 \times 10^{-13}$ cm$^2$/s, based a graphite active surface area equal to the BET surface area. Also, the rate of phase change on charge was much faster than discharge. Previous work assumed equal rates for charge and discharge.

Figure 2. Charge (left) and discharge (right) A12 graphite half-cell GITT data in the LiC$_{32}$ single phase taken more than a week apart. Simulations use same parameters.
Full reference electrode (i.e. lithiated 25 micron copper wire between two separator layers) cell (NMC532 cathode//graphite anode) data with the present graphite electrode indicates that it can be easily charged at 1C without lithium deposition. A full cell electrochemical model developed by modifying an existing dual intercalation electrode model [3] to have the graphite electrode include phase change of the active material was utilized to examine the graphite electrode’s 1C charge behavior. Exercising the full cell model with the present graphite electrode parameters (see Figure 4) indicates that the full reference electrode cell cannot be charged at 1C without the graphite electrode dropping below lithium potential.

Analysis of the full reference electrode cell electrochemical modeling results indicate that as the LiC$_{32}$ phase becomes more highly lithiated the LiC$_{12}$ phase starts to form initially at the graphite active area surface working its way into the bulk of the particle. The phase change to the higher concentration LiC$_{12}$ phase is able to accept more lithium. However, as the concentration gradient builds up in the LiC$_{12}$ phase the assumed logarithmic behavior of the thermodynamic function causes the electrode potential to drop precipitously, thus effectively shutting down the cell. Changing the LiC$_{12}$ phase thermodynamic function to a linear behavior (see Figure 4) allows the simulation to go much longer before the graphite electrode reaches lithium potential, but far short of the one hour charge. Finally in Figure 4, including a direct path from the LiC$_{32}$ phase to the LiC$_6$
phase does not significantly improve the ability of the graphite electrode to accept lithium. Similarly to the \( \text{LiC}_12 \) phase, the logarithmic behavior of the thermodynamic function for the \( \text{LiC}_6 \) phase causes the electrode potential to drop precipitously as the concentration gradient builds. Varying the graphite model parameters reveals that the only way to fully charge the electrode at 1C is to substantially increase the diffusion coefficient of all three phases.

**BatPaC**

The issue of lithium plating usually generates the question of whether lithium titanate (LTO) anodes (instead of graphite) can offer the solution for fast charging (see Table 2 below). Analysis has shown that the lower specific capacity of the LTO combined with the lower cell voltage of the NMCxxx-LTO chemistry leads to higher costs at the cell level. A simple example of this is demonstrated by comparing the cell level costs of a 100 kWh, 300 kW pack, 900 V (240 cells in series). The packs were designed to be capable of raising the SOC by 80% in ~15 minutes. Use of the LTO allows the use of thicker electrodes.

Table 2: BatPaC fast charge pack calculations.

<table>
<thead>
<tr>
<th></th>
<th>NMC622-G</th>
<th>NMC622-LTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Specific Capacity, mAh/g</td>
<td>360</td>
<td>170</td>
</tr>
<tr>
<td>Average Cell Voltage, V</td>
<td>3.75</td>
<td>2.31</td>
</tr>
<tr>
<td>Cathode Thickness, µm</td>
<td>58</td>
<td>98</td>
</tr>
<tr>
<td>Cell Cost, $/kWh</td>
<td>107</td>
<td>175</td>
</tr>
</tbody>
</table>

The manual for the new version (3.1) of BatPaC, released in October 2017, is being prepared. Some example calculations for different types of EV (compact, sedan, sport-sedan, and SUV) batteries will illustrate the impact of fast charging on electrode thickness and pack prices.

**Literature Update**

Kim et. al. [4] reports on the use of an “implanted amorphous silicon nanolayer and edge-site activated graphite,” where lithium plating has not been observed in half-cells after 50 cycles at current densities of 10.2 mA/cm². Yang and Miller [5] reports charging a 5 Ah prismatic cell in 3 minutes at a constant 20C rate from 0-85% SOC without any significant losses in 50 cycles.

**Conclusions**

The initial phase change electrochemical model modifications did not yield the needed improved rate capability. The phase change model was successfully applied to GITT studies on an A12 graphite half-cell that yielded relatively high phase change rate constants during charging. However, model simulations with the new data still indicated it was underperforming at high rates, based on experimental results. Further higher rate studies with the reference electrode full cell data are needed.

**Milestones and Deliverables**

None to report this quarter.
References


XFC: Performance Characterization and Post-Test Analysis

Contributors (Argonne National Laboratory): David Robertson, Alison Dunlop, Eungje Lee, K. Pierre Yao, Stephen Trask, Bryant Polzin, Andrew Jansen and Ira Bloom

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. Another objective is to determine the physical and chemical changes that extreme fast charging 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

Recycling Extreme-Charged Cell Materials (David Robertson, Ira Bloom). The impact of high-rate charging on the positive electrode has not been discussed in the open literature. There are, however, reports that some positive electrode materials (lithiated metal oxides) are not dimensionally stable with cycling [1, 2, and references therein]. The diffusion of ions into and out of the host lattice can induce stress because of the associated volume change and concentration gradients [3]. A known cause of accelerated performance fade of lithium-ion batteries is voiding, cracking, and ultimate fragmentation of positive electrode active material particles due to diffusion-induced stress caused by high and repeated lithium intercalation/de-intercalation to and from the positive electrode matrix [4]. The fragmented primary particles disconnect from the positive electrode matrix and expose the active material to the electrolyte.

The question now is, what is the impact of the extreme fast charging process on the oxide? Can the oxide material be recovered simply for reuse or does the oxide have to be totally remade? To answer a part of this question, three small LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2/A12-graphite-based pouch cells were subjected to fast charging using the Chinese protocol (constant current at 25°C) using the 6-C charge rate and 1-C discharge rate. The cells accrued 100 charge/discharge cycles before they were taken off test due to low capacity.

After the test, the cathode materials were harvested and made into coin, half-cells. The coin cells were then subjected to a rate study, with the approximate rates shown in Table 1. The rated capacity of the cathode
laminate was \( \approx 1.5 \text{ mAh/cm}^2 \). The average, observed capacities, in mAh/cm\(^2\), from this study are also given in Table 1. The results indicate that the cathode still performed well.

<table>
<thead>
<tr>
<th>Discharge rate</th>
<th>C/10</th>
<th>C/5</th>
<th>C/1</th>
<th>5-C</th>
<th>10-C</th>
<th>final C/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average capacity</td>
<td>1.82</td>
<td>1.77</td>
<td>1.58</td>
<td>0.22</td>
<td>0.11</td>
<td>1.71</td>
</tr>
</tbody>
</table>

**Table-1: Results from rate study used fast-charged cathode materials.**

**Characterization of candidate materials** (I. Bloom and Eungje Lee). Five graphite materials were selected as part of the modeling effort of the cell performance under extreme fast charging conditions. They were MAG E and E3 (Hitachi), MCMB (Gelon G15), Superior Graphite SLA1506 (coated, natural, spherical graphite) and Superior Graphite SLC1506T. These materials were characterized using Raman spectroscopy and X-ray diffraction (XRD) to determine if there were any physical characteristics that could be related to differences in performance.

Since all are graphitic materials, the Raman spectra were very similar. A typical spectrum is shown in Figure 1. The ratio of the area of the D and G bands varied from sample to sample. These ratios are given in Table 2.

![Raman spectrum of MAG E3](image_url)

**Figure 1.** Raman spectrum of MAG E3. The band marked ‘G’ is from the vibrational mode of ordered (crystalline) graphite. The ‘D’ band is from disordered graphite. All spectrum displayed the same bands but with different intensity ratios, including the band at \( \approx 2700 \text{ cm}^{-1} \) (an overtone/harmonic of D band at \( \approx 1350 \text{ cm}^{-1} \)).
Table 2: Ratio of the areas of the D and G bands of the selected graphite materials.

<table>
<thead>
<tr>
<th>Graphite</th>
<th>Ratio of D:G bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAG E</td>
<td>1.00</td>
</tr>
<tr>
<td>MAG E3</td>
<td>1.08</td>
</tr>
<tr>
<td>MCMB</td>
<td>1.35</td>
</tr>
<tr>
<td>SLC1506T</td>
<td>1.89</td>
</tr>
<tr>
<td>SLA1506</td>
<td>2.01</td>
</tr>
</tbody>
</table>

The graphites were also characterized using XRD. In general, the patterns were similar, such as that shown for MAG E in Fig. 2. Most of the lines in the patterns could be indexed in the space group \( P6/mmc \). There were additional reflections in the \( 2\theta \) range of 40 to 60° (see Figure 3) that could not be indexed in that space group. All but MCMB contained extra reflections. The crystallographic parameters and interslab distances were calculated from the XRD data and are given in Table 3. There was not much variation in these parameters among the graphites.

![XRD pattern for MAG E graphite using Cu K\(_\alpha\) radiation. The numbers in parentheses represent the Miller indices (hkl) for the reflection. The indices for the smaller peaks are shown in Figure 3.](image-url)

Figure 2. XRD pattern for MAG E graphite using Cu K\(_\alpha\) radiation. The numbers in parentheses represent the Miller indices (hkl) for the reflection. The indices for the smaller peaks are shown in Figure 3.
Figure 3. A portion of XRD patterns (Cu Kα) of the selected graphites in the 2θ range of 40 to 60°. The numbers in parentheses represent the Miller indices (hkl) for the reflection. The peaks marked with an asterisk (*) could not be indexed in the P6/mmc space group. Only two peaks from the unknown were visible. It takes, at a minimum, three peaks to get a good fit for space group assignment.

Table 3: Crystallographic parameters of selected graphites and interslab distances

<table>
<thead>
<tr>
<th>Graphite</th>
<th>a, Å</th>
<th>c, Å</th>
<th>Interslab distance, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAG E</td>
<td>2.465</td>
<td>6.72</td>
<td>3.36</td>
</tr>
<tr>
<td>MAG E3</td>
<td>2.464</td>
<td>6.72</td>
<td>3.36</td>
</tr>
<tr>
<td>MCMB</td>
<td>2.463</td>
<td>6.73</td>
<td>3.365</td>
</tr>
<tr>
<td>SLC1506T</td>
<td>2.465</td>
<td>6.72</td>
<td>3.36</td>
</tr>
<tr>
<td>SLA1506</td>
<td>2.465</td>
<td>6.72</td>
<td>3.36</td>
</tr>
</tbody>
</table>

**Diffusion coefficient measurements** (David Robertson, Alison Dunlop, K. Pierre Yao, Ira Bloom). Coin, half-cells were constructed from CAMP laminates of the MCMB anode material. After two formation cycles at the C/20 rate, a galvanostatic intermittent titration (GITT) experiment was performed at 25, 35, 45 and 55°C. Here, cells were charged and discharged using C/20 currents. The current was on for 15 min and off for 90 min.
Because the graphites were not a single phase in most of the compositional range, the usual GITT equation, shown below, could not be used to estimate the diffusion coefficient.

\[
D = \frac{4}{\pi} \left( \frac{I V_m}{n F S} \right)^2 \left[ \frac{dE_{OCV}}{d\delta} \right] \left[ \frac{dE_{POL}}{d\sqrt{t}} \right]
\]

Instead, a depolarization analysis [5-7] was performed. The model used is shown below.

\[
\ln(|E(t) - E(t = \infty)|) = \text{constant} - \frac{t}{\tau^6}
\]

\[
\tau^6 = \frac{L^2}{\pi^2 D_{Li^+}}
\]

This model is based on the relaxation of the concentration gradient and should be less susceptible to interference from phase response. Here, \(E(t)\) and \(E(t = \infty)\) are the electrode potentials at time \(t\) and at infinite time, respectively. \(\tau^6\) is the relaxation time constant for the process, \(L\) is the characteristic length, and \(D_{Li^+}\) is the diffusion coefficient for Li\(^+\) (in cm\(^2\)/s). \(L\) was calculated from the BET surface area (\(A_{BET}\)) and the density of carbon, as shown below.

\[
\frac{1}{L} = 10000 \times A_{BET} \times \text{density}
\]

The density of carbon was 2.267 g/cm\(^3\) and the BET surface area of MCMB was 2.022 m\(^2\)/g. This calculation method does not assume a fixed particle geometry. With all the pores in graphite, one cannot assume that each particle is spherical.

Figures 4 and 5 show the relaxation time constant, \(\tau^6\), as a function of state of charge and temperature for both the discharge and charge subcycles, respectively. From the plots, changes in \(\tau^6\) appear at approximately the states of charge where phase changes would be expected. Additionally, \(\tau^6\) during lithiation (discharge) appeared sensitive to temperature at the extrema more so than at intermediate states of charge. There was almost no sensitivity to temperature during delithiation.
Figure 4. $\tau$ vs. state of charge (SOC) for the discharge subcycle. The discharge voltage limits were 1.5 V to 5 mV and represented the lithiation process. Each dot represents the average of three cells. The solid curve represents the potential vs. SOC for MCMB at 25 °C. The numbers in the legend represent temperature in °C.

Figure 5. $\delta$ vs. state of charge (SOC) for the charge subcycle. The discharge voltage limits were 5 mV to 1.5 V and represented the delithiation process. Each dot represents the average of three cells. The solid curve represents the potential vs. SOC for MCMB at 25 °C. The numbers in the legend represent temperature in °C.
Conclusions

It appears that the LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2 oxide still retains its performance characteristics after one hundred, 6-C/1-C charge/discharge cycles at 25°C. This may make recycling the material ‘in place’ easier.

Characterization of the selected graphites showed that there were significant differences in the Raman spectra, which may correlate with the electrochemical performance of the material under extreme fast-charge conditions. There were differences in the peak area ratio of the D and G bands. No such simple indicators were seen in the X-ray diffraction patterns. Instead, the patterns of some graphites contained extra reflections that could not be indexed in the space group P6/mmc.

Measurement of the diffusion coefficients during the lithiation and delithiation of MCMB graphite showed that the diffusion coefficient, as indicated by its time constant, changed at SOCs where one would expect phase changes during lithiation and delithiation. Further, the time constant was not very sensitive to temperature during delithiation. During the lithiation process, however, the time constants tended to be in two groups. The time constants at 25 and 35°C formed one group, and those at 45 and 55°C formed another.

Future work

The GITT experiment will be repeated using other graphites, such as those listed in Table 2. The GITT experiment at the four temperatures will be performed on the NMC532 oxide to determine the temperature dependency of the time constant/diffusion coefficient.

After cells are delivered from CAMP, they will be charged at 4- or 6-C rates (1-C discharge rate) at temperatures of 25, 35, 45 and 55°C as part of the effort to detect lithium plating as soon as it occurs using electrochemical methods. The cells will be then subjected to post-test analysis to further the understanding of the causes of performance decline.

References


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Extreme Fast Charging R&D: Battery Testing Activities (Idaho National Laboratory)

Eric Dufek (INL), Tanvir Tanim (INL), Daniel Steingart (Princeton), Shrikant Nagpure (INL)

Background

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 Li plating onset and evolution over aging is a significant challenge. In operando detection schemes to understand the dynamics of Li plating and the role that aging has on Li plating are vital to enable fast charging of specific energy cells.

Discretely 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 non-destructive ultrasonic acoustic methods that can be directly applied in operando to understand onset and growth of Li plating during XFC. The team is closely coordinating with other efforts at the National Renewable Energy Lab (NREL) and Argonne National Lab (ANL) 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 XFC of batteries for electric vehicles.

Electrochemical methods which 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 give pertinent information associated with both kinetic and thermodynamic processes which 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 which can be used to compliment electrochemistry in operando using standard cell formats. One method which 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 which occur in a cell during cycling and can be used to characterize change in a non-destructive, 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 complimentary signals which signal 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 life and as batteries age will provide pertinent information related to the distinct conditions which drive Li plating during XFC.

Results

During the first quarter of FY2018 the key aspects of the project were the identification of cells to use for analysis, preliminary identification of electrochemical methods and test plans for the evaluation of cells which undergo XFC and the initiation of analysis of ultrasonic methods to identify plating of Li in a cell. With regard to cells, it was decided that single layer graphite/NMC 532 pouch cells fabricated at ANL. Preliminary test plans were also developed based on the hypothesis that a key issue from plating arises due to transport issues which emerge in thick electrodes. To mitigate and understand the impact of transport in a systematic way a set of experiments using variable rates and distinct relaxation periods was developed that could be applied and directly compared across multiple sets of cells.

Princeton, in parallel with cell and evaluation method identification at INL, initiated activities to understand ultrasonic measurements occurred. These included the simulation of response to understand the ultrasonic
sensitivity of Li plating in a cell. A simple 1-D layer-wise model has been setup to gather bounds of sensitivity to Li plating (irrespective of fast charge condition). In this approach Li is introduced on the graphite surface as a single layer and the specific interactions of lithium metal with graphite or electrolyte are ignored as first order of simplification. Figure 1 shows the result of simulation with Li layer thickness of 1 µm which is nominally the equivalent to a capacity of 0.2 mAh/cm². The resultant acoustic signal has a frequency of 4.5 GHz. Commercially available transducers are capable of detecting such high frequency transmitted signal.

Figure 1: Preliminary simulation results showing propagation of wave through a stack of battery components (upper left) and a low frequency wave propagating through a series of layers with small thickness (lower left). Right: The simulated wave form signal received over time.

On the experimental front for ultrasonic analysis, small multilayer pouch cells (16 layers and 210 mAh) were cycled at a C/2.5 rate at 8°C to reduce the diffusion coefficient of Li and intentionally plate Li on the graphite anode. Using these conditions two distinct shifts in the transmitted wave were observed with the standard operating frequency of 2.25 MHz. A 1µs time of flight shift over a period of 10 minutes was observed in the ultrasonic signal in the cells cycled at 8°C with no signal observed when the same charging protocol was used at 21°C (Figure 2).
Figure 2: Preliminary data showing acoustic signal for Li plating for cells cycled at 0.2C. LCO pouch cell at 8 °C (a, with Li plating) and 21 °C (b, no plating). Circles on the left show nucleation of Li metal, discharge of Li metal and Li ion de-intercalation from graphite.

Moving into the second quarter of FY2018 and beyond a thorough characterization of the transmitted signal in simulation and experimental results will be performed to establish the extreme upper bounds and lower bounds on the Li detection threshold using ultrasound. Also, thorough characterization of the graphite anode will establish the relation between extent of lithium deposit and ultrasound signal. With respect to the analysis of charge scheme, INL will perform analysis of the cells received from ANL after first characterizing rate performance. INL will also initiate ultrasonic measurements capabilities.

Conclusions
During the first quarter of FY2018 activities focused on identification of cells and coordination with ANL. An initial test plan was also developed for discussion with the remainder of the XFC team from ANL and NREL. With regard to ultrasonic measurement a simulation of the deposition of 1 μm of Li on a graphite anode suggests that it is feasible to detect the Li using commercial ultrasonic equipment. Experimental acquisition of ultrasonic signals during charging at low temperature also suggests Li plating can be readily detected.

Milestones and Deliverables
Q1 – Identify and initiate acquisition of cells (COTS or CAMP) and establish baseline procedures for initial evaluation (Go/No-go) – Complete, received 30 Graphite/NMC single layer pouch cells
Q2 – Assess variation in cells and provide initial understanding on variability and electrode balance. Start initial aging_characterization efforts – in process
Q3 – Perform initial proof-of-concept experiments to identify the impacts of fast charging at the cell level using non-destructive, in operando techniques including ultrasonics – in process
Q4 – Report summarizing full cell, electrochemical evaluation methods that should be used for analysis of future XFC activities. This includes the ability to identify variability in cells and means to maintain safe operating conditions (SMART). – in process

References
None