SAND2019-14569R

I.E Extreme Fast Charge (XFC)

II.E.9 Research three-dimensional hierarchical graphite architectures for anodes for fast charging

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Project Introduction [Use EERE_Head_03_Shaded]

With current lithium ion batteries optimized for performance under relatively low charge rate conditions, implementation of XFC has been hindered by drawbacks including Li plating, kinetic polarization, and heat dissipation. This project will utilize model-informed design of 3-D hierarchical electrodes to tune key XFC-related variables like 1) bulk porosity/tortuosity 2) vertical pore diameter, spacing, and lattice 3) crystallographic orientation of graphite particles relative to exposed surfaces 4) interfacial chemistry of the graphite surfaces through "artificial SEI" formation using ALD 5) current collector surface roughness (aspect ratio, roughness factor, etc.).

A key aspect of implementing novel electrodes is characterizing them in relevant settings. For this project, ultimately led out of University of Michigan by Neil Dasgupta, that includes both coin cell and 2+ Ah pouch cell testing, as well as comparison testing against baselines. Sandia National Labs will be conducting detailed cell characterization on iterative versions/improvements of the model-based hierarchical electrodes, as well as COTS cells for baseline comparisons. Key metrics include performance under fast charge conditions, as well as the absence or degree of lithium plating. Sandia will use their unique high precision cycling and rapid EIS capabilities to accurately characterize performance and any lithium plating during 6C charging and beyond, coupling electrochemical observations with cell teardown. Sandia will also design custom fixturing to cool cells during rapid charge, to decouple any kinetic effects brought about by cell heating and allow comparisons between different cells and charge rates. Using these techniques, Sandia will assess HOH electrodes from the University of Michigan, as well as aiding in iterative model and electrode design.

Objectives [Use EERE_Head_03_Shaded]

- Work with University of Michigan to establish cadence for receiving improved-electrode cells for characterization via in-person kickoff and weekly update meetings.
- Develop and validate a custom rapid cooling plate fixture to allow the best possible temperature control of cells during fast charging, regardless of cell design, charge current, and environmental conditions.
- Begin baseline COTS cell fast charge characterization.

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- Demonstrate high fidelity dQdV measurements during 6C charging using high precision coulometry.

Accomplishments

- Completed Baseline testing of NMC/Graphite and NCA/Hard Carbon cells made at University of Michigan.
- Took possession of HOH Anode cells from UM, and completed design of experiments to test at 4C and 6C charge rates.
- Obtained dQdV measurements demonstrating lithium plating for NMC/Graphite baseline cell.
- Presented findings at Electrochemical Society meeting, Annual Merit Review, and Advanced Automotive Battery Conference (AABC).

Approach [Use EERE_Head_03_Shaded]

To establish baseline performance for UM-Made cells, a combined rate capability and cycle life approach was used. Cells were cycled with increasing charge rates, followed by a charge taper to C/20, followed by a 1C discharge. After the rate capability portion, the cell was cycled at 1C charge / 1C discharge to a total of 100 cycles to monitor capacity retention after the high rate charge cycles (See Table 1).

Table 1: Cycling profile for baseline COTS and UM cells.

Cycles	CC Charge	Ch Taper	CC Discharge	Rest	Temp	Purpose
1 - 24	0.5 – 6 C	yes	1C	yes	22C, 30C	Rate capability
25-70	1C	yes	1C	yes	22C, 30C	Cycling

Baseline Cells included COTS NMC/Graphite, UM-made NMC/Grahpite, and UM-made NCA/Hard Carbon, with characteristics described in Table 2. Cycling was performed with the Arbin high precision cycler developed through an ARPA-E AMPED program with SNL, Ford, Arbin, and Montana Tech. A rapid response cooling system was used to maintain isothermal operation and avoid complications arising from temperature rise during testing.

Table 2: Cells used to esablish baseline lithium plating performance.

	COTS NMC/Graphite	UM NMC/Graphite	UM NCA/Hard Carbon
Capacity	5Ah	2.85Ah	2.75 Ah
Anode			
Loading	2.6 mg/cm^2	8.4 mg/cm^2	8.3 mg/cm^2
Capacity Loading	0.9 mAh/cm^2	3.04 mAh/cm^2	3.0 mAh/cm^2
Cathode			
Loading	4.0 mg/cm^2	18.2 mg/cm^2	14.9 mg/cm^2
Capacity Loading	0.65 mAh/cm^2	3.0 mAh/cm^2	3.0 mAh/cm^2
N:P Ratio	1.4	1.01	1.0
Energy Density	112 Wh/kg	200 Wh/kg	165 Wh/kg

Results [Use EERE_Head_03_Shaded]

Figure 1 shows the results of rate capability testing on the NMC/Graphite cell. Voltage indicates normal cycling behavior with some capacity loss to polarization, up to 3C. During the 4C cycles, a longer Constant Voltage portion is noted, and the current trace (blue) indicates an increasing current, which is indicative of short circuit behavior. The plot also shows that the cell fails during the 5C charge section. Figure 2 shows the dQdV calculations for the charge steps. Normal lithiation peaks are seen for the 0.5C and 1C charge steps, but at 2C a small hump is seen forming at around 4.1V. The hump groups at higher charge rates, and is clearly distinct from the earlier lithiation humps. This is an indication of lithium plating, and represents the first time lithium plating has been demonstrated in this project. It is interesting to note that the dQdV reveals the start of plating as early as 2C, whereas the simple voltage/current profile (Figure 1) does not indicate problems until the 4C steps. dQdV shows a clear utility in detecting plating which may otherwise go unnoticed.

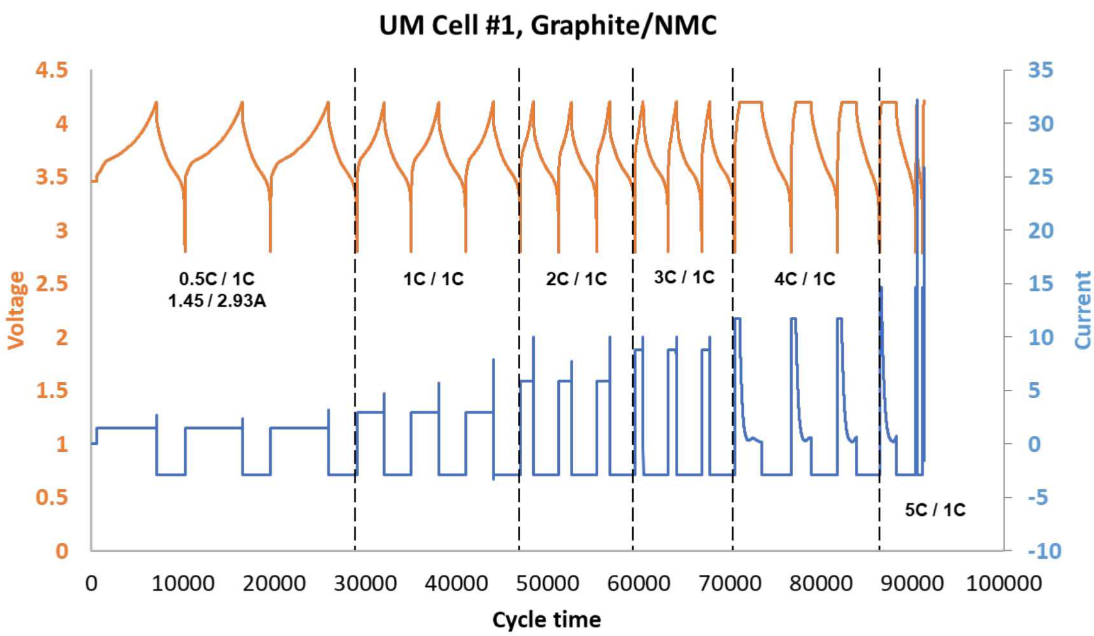

Figure 1: Voltage and Current during rate capability testing of NMC/Graphite UMich cell.

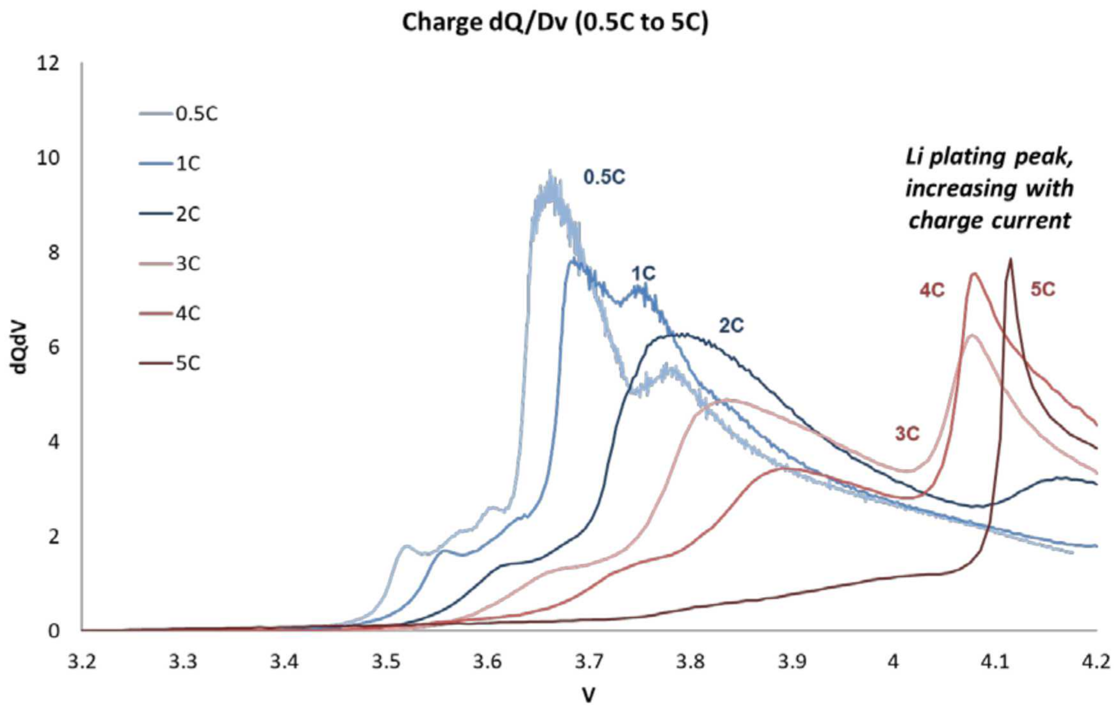

Figure 2 - dQdV of charge steps during rate capability testing of NMC/Graphite cell.

Testing on the NCA/Hard Carbon Cell

Similarly to the NMC/Graphite cell, the same profile was applied to an NCA/Hard Carbon Cell. Figure 3 shows the results, and here a 6C/1C (Charge/Discharge) profile with no CV taper steps was applied after rate capability to stress-test the cell. While large polarization is seen during the high rate charge steps, the total capacity (after charge taper) indicates a smaller loss of capacity indicative of SEI growth common to hard carbon. The sustained 6C cycling shows a stead polarized 1.75Ah, and a recoverable 2.6Ah during 1C/1C capacity check steps. There is no indication of cell failure as seen in the NMC/Graphite cell. Figure 4 shows the dQdV results for the NCA/Hard Carbon cell. While the shape looks quite different than the NMC/Graphite cell due to the unique lithiation behavior of hard carbon, the overall trend does not show the growth of a lithiation peak. This is consistent with Figure 3 and the lack of evidence of cell failure. It can be surmised that the hard carbon cell is much more resilient to lithium plating than the graphite anode. Figure 5 shows the efficiency during cycling of both the NMC/Graphite cell and the NCA/Hard Carbon cell. The graphite cell hits maximum efficiency right away, which is consistent with the expected behavior for graphite. Efficiency begins to slip at 3C, and has fallen precipitously at 4C, which is consistent with the observation of lithium plating in the dQdV. The hard carbon cell takes several cycles to reach maximum efficiency, consistent with hard carbon's longer SEI Formation period, but the efficiency does not drop afterwards, which agrees with the observed lack of lithium plating in the dQdV and voltage/current plots.

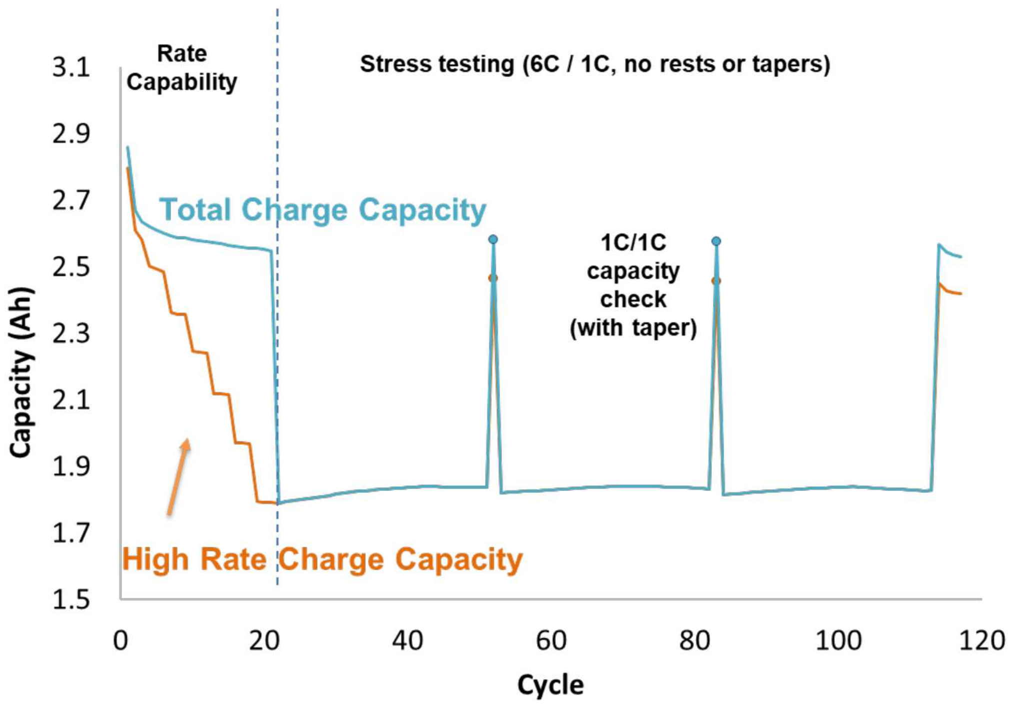

Figure 3: Rate capability and long 6C/1C cycling for NCA/Hard Carbon cell .

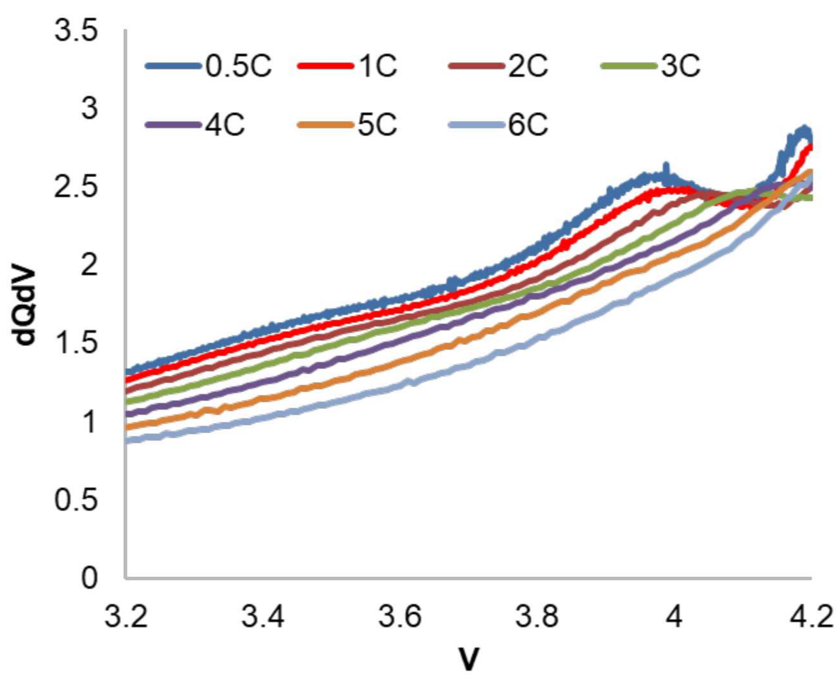

Figure 4: Charge dQdV for NCA/Hard Carbon cells.

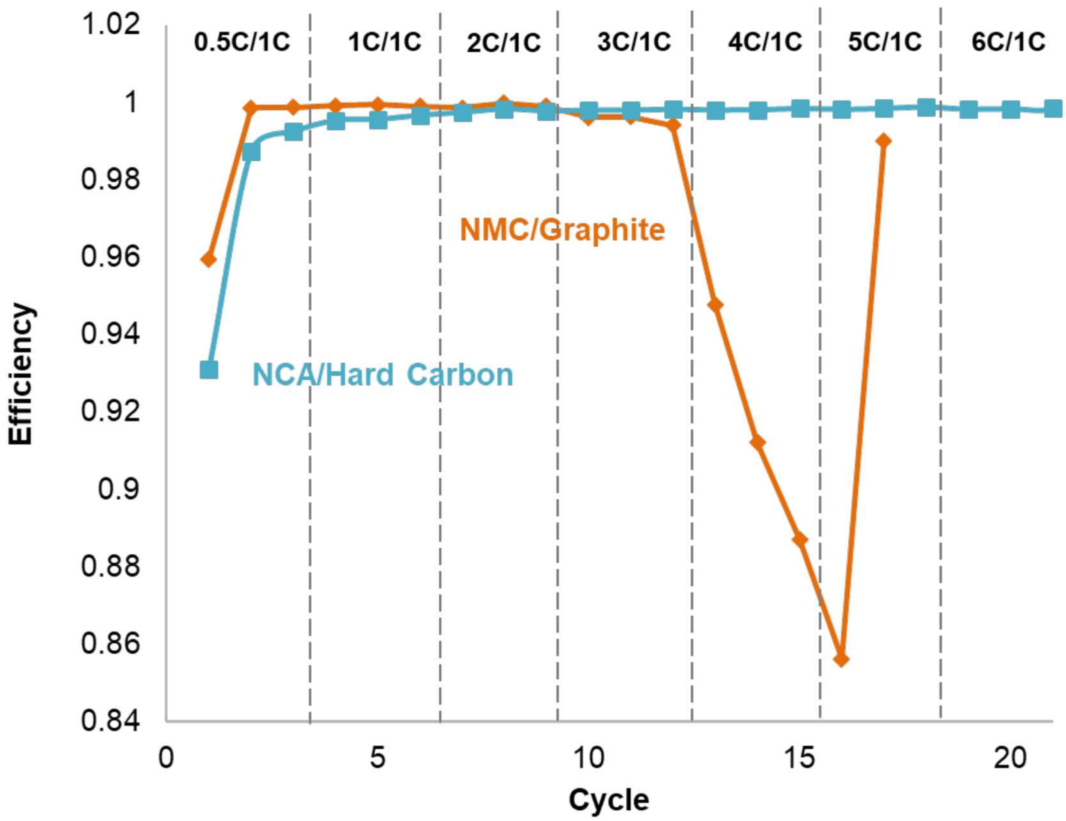

Figure 5: Efficiency for NMC/Graphite and NCA/Hard Carbon cells.

Importance of Temperature Controls

SNL's use of cooling plates is designed to minimize temperature fluctuations due to XFC heating and environmental temperature changes. A key tool in detecting lithium plating is analysis of voltage response, both in terms of intra-cycle dQdV, and inter-cycle efficiency. Since cell capacity is highly dependent on temperature, it follows that temperature fluctuations should be kept at a minimum if one is using those metrics to assess Li plating. Figure 6 shows the temperature profile during 6C charge / 1C discharge cycling of the COTS 5Ah cells, with (orange) and without (blue) temperature control. The temperature swings during high rate charging are limited to 2^{o} C with cooling plates; the swing is 6^{o}C – three times as large – without cooling plates. Moreover, the average temperature drift due to environmental changes is significant without cooling plates, with a cyclic pattern corresponding to day-night cycles. Similar cycling is only somewhat visible with cooling plates, and the temperature swings are cut by half. Figure 7 shows cycle-to-cycle efficiency for cycling with and without cooling plates. Temperature-induced efficiency swings are clearly visible in the case without temperature control, making efficiency tracking impossible. For the case with temperature control, no pattern is noticeable, leading one to believe that efficiency fluctuations better correlate to genuine cell events like lithium plating rather than heating.

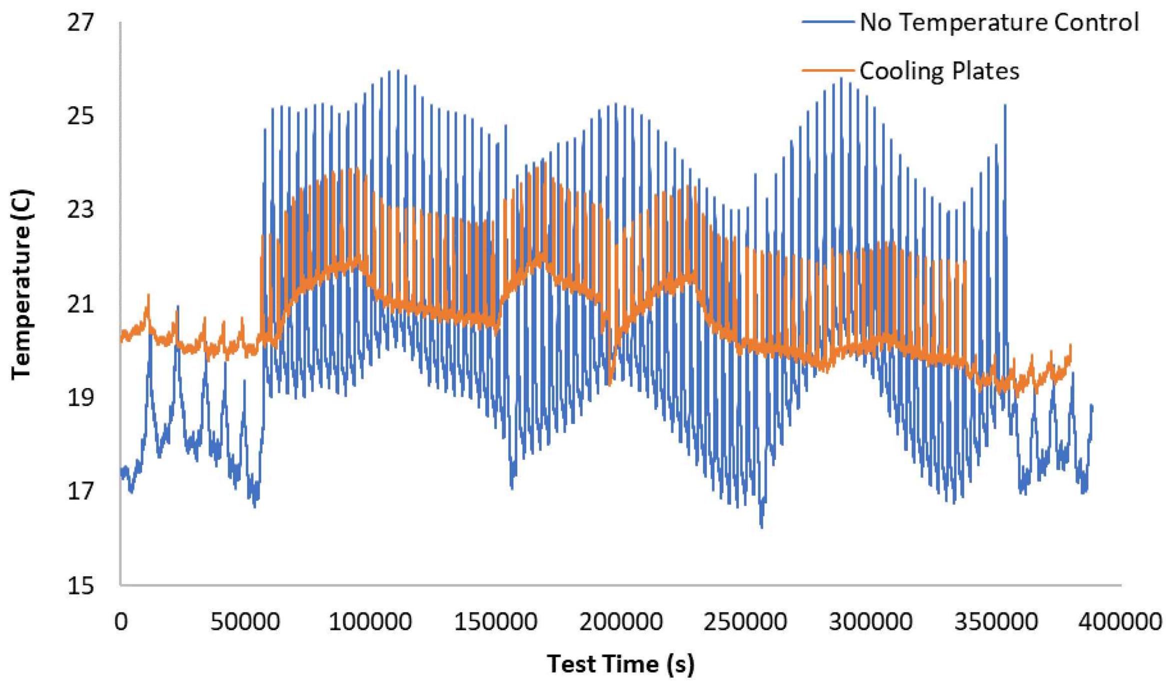

Figure 6: Temperature profile for 6C/1C cycling, with and without temperature control plates.

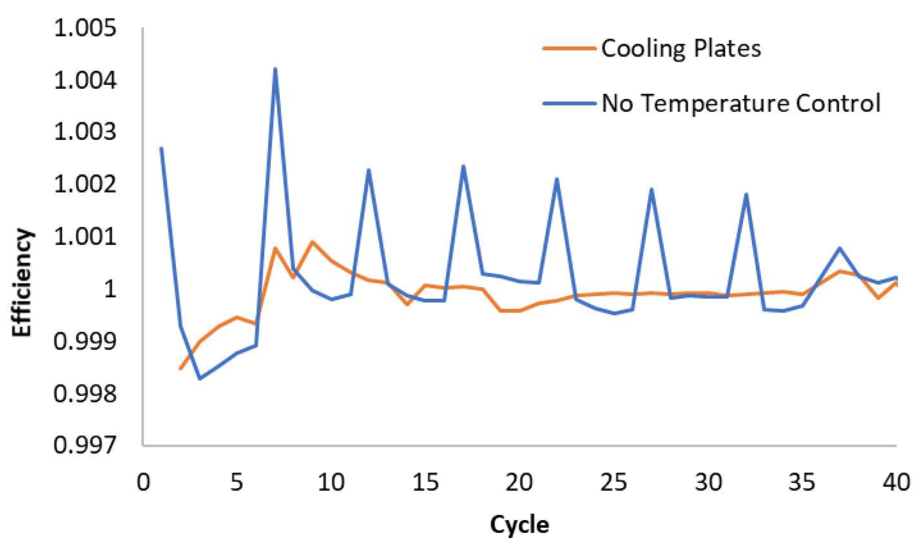

Figure 7: Cycle to cycle efficiency for 6C/1C cycling, with and without temperature control plates.

Conclusions [Use EERE Heading 3]

The work performed in FY19 demonstrated the use of High Precision dQdV analysis to detect lithium plating, at both the earliest stages when lithium appears to re-strip during discharge, and later stages when dead lithium accumulates to reduce battery capacity and ultimately cause failure. NMC/Graphite cells showed a strong relationship between increasing energy density and propensity for lithium plating. COTS cells with 112 Wh/kg showed no evidence of plating, while UM cells with 200 Wh/kg showed clear plating at as low as 3C charging. Conversely, NCA/Graphite cells with 165 Wh/kg showed no evidence of plating, though a high amount of polarization rendered most of the anode capacity inaccessible with 6C charging. FY19 work also demonstrated the importance of isothermal operation in R&D applications. Without temperature control, efficiency tracking becomes nearly impossible because of the cell heating effects brought on by fast charging.

In FY20, cells with anodes using HOH improvements will be compared to baseline cells. The methods established during FY19 will be used to quantify the improvements as they related to lithium plating.

Key Publications [Use EERE Heading 3]

M. Karulkar, L. Castro-Torres, J. Lamb, "High Precision Characterization of Li-Ion Batteries during Extreme Fast Charging," 235th Meeting of the Electrochemical Society, Abstract MA2019-01 47, Dallas TX (2019).

M. Karulkar, "Anode Improvements for Better Fast Charge Tolerance in Cells of High Energy and Powder Density," Advanced Automotive Battery Conference, San Diego CA (2019).

Acknowledgements [Use EERE Heading 3]

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