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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

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

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

Accomplishments

- Attended project kick-off in Ann Arbor, MI where SNL PI Mohan Karulkar presented initial data on SNL's cooling fixture design.
- Attended weekly teleconferences with the University of MI team to discuss progress and propose next steps.
- Demonstrated effective temperature control of cell using custom cooling plate hardware.
- Performed baseline rate capability and capacity retention cycling on 5Ah COTS cells, combining high precision coulometry with the rapid cooling fixture, calculating high fidelity dQdV data

Approach

To perform baseline cell testing and establish testing protocols for the study moving forward, 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). The first baseline cell chosen was a commercial Kokam 5Ah NMC/Graphite cell, with measured energy density values of 112 Wh/kg and 211 Wh/L. Cycling was performed with the Arbin high precision cycler developed through an ARPA-E AMPED program with SNL, Ford, Arbin, and Montana Tech.

Table 1: Baseline cell cycling profile

Cycle	CC Charge Rate	CV Charge Taper	CC Discharge
1-3	0.5 C	C/20	1C
4-6	1 C	C/20	1C
7-9	1.5 C	C/20	1C
10-12	2 C	C/20	1C
13-16	3 C	C/20	1C
16-18	4 C	C/20	1C
19-21	5 C	C/20	1C
22-24	6 C	C/20	1C
25-100	1C	C/20	1C

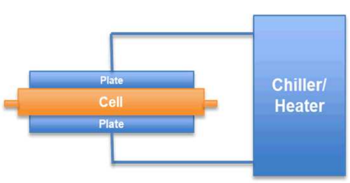

Figure 1 - Cooling plate fixture.

To minimize effects of cell heating, a rapid-response cooling plate fixture was designed specifically with University of Michigan prototype cells in mind, but flexible to acocmodate the baseline cells as well. A 50/50 WEG solution was used with a chiller and circulated through channeled brass blocks, with temperature monitoring on the cell surface, sides, and tabs. (Figure 1)

Results

Figure 2 shows temperatures during 6C/2C (charge/discharge) cycling of a Kokam baseline cell in the cooling fixture, for purposes of fixture validation. The cell edge showed the largest temperature swing of about 3ºC during the 6C charge, compared to 7-8ºC swings with environmental chamber alone. Then negative tab showed about 1.5C temperature swing and the cell-plate interfaced showed almost no swing at all. The stable cooling bath temperature and intimate cell contact allow for much more precise control / steadying of cell temperature than is possible in an environmental chamber. The cooling fixture is a key part of continuing cell assessment, since cell heating can otherwise affect kinetics during charging and complicate the effort of comparing cell performance between different charge rates, as well as cell performance between improvement iterations.

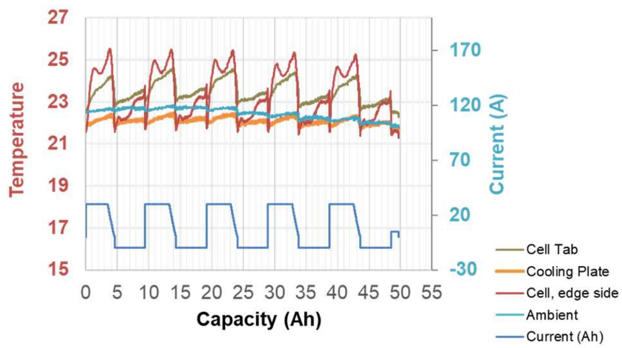

Figure 2: Cell temperature (Kokam 5Ah pouch) during 6C charge, 2C discharge cycling, inside the cooling fixture.

Figure 3 shows the result of cycling a Kokam 5Ah baseline cell according to the cycling profile in Table 1. The orange line shows the capacity from just the high rate portion of the charge, while the blue line shows the charge capacity with the high rate and taper step together. The gray line (overlapped with blue) shows the 1C discharge capacity. The data shows that the baseline cell was able to accommodate charge rates up to 6 C, though polarization lowered the charge passed during that step. The overall cell capacity and efficiency remained mostly unchanged, with an efficiency of > 99.9%.

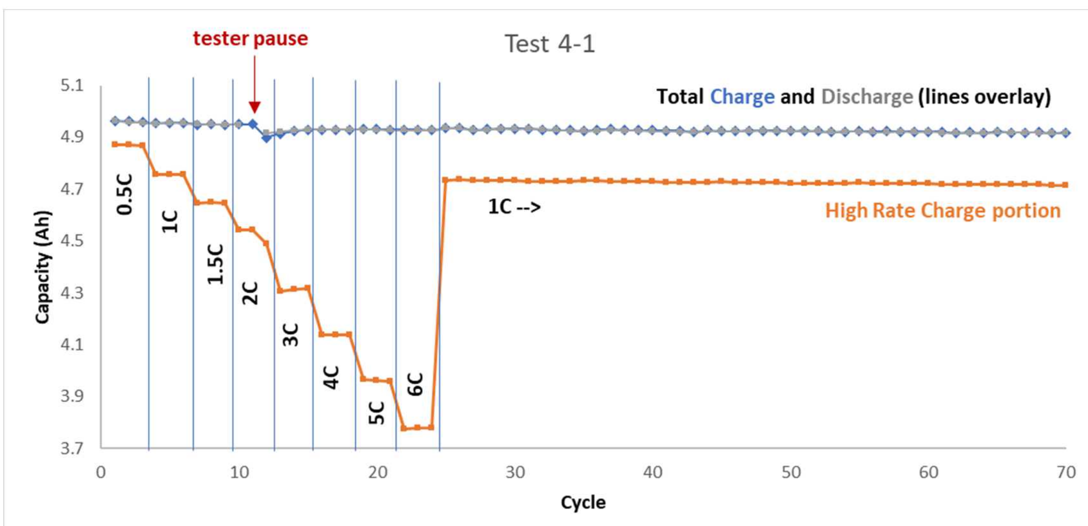

Figure 3: Baseline cell rate capability performance.

Figure 4 shows dQdV vs V for charge rates of 0.5C, 1C, and 6C during the rate capability, as well as the subsequent 1C discharge cycles, and the first 1C/1C cycle *after* the rate capability (cycle 25). Of note is the general line smoothness and clear representation of peaks, a benefit of Sandia's high precision cycling capability. Peaks are seen to shift right with increasing charge rate, a reflection of cell polarization. 1C discharge steps are identical, showing a lack of fundamental electrode changes that would alter discharge steps throughout the cycling profile. Likewise, the 1C charges at cycle 3 and 25 are identical, showing no changes due to the subsequent charge steps. Figure 5 shows the 1C discharge step after every step change in charge rate (line reflected to positive axis for ease of viewing). In every case, the discharge dQdV pattern is identical, suggesting a lack of lithium plating that would otherwise cause distinct lithium stripping peaks.

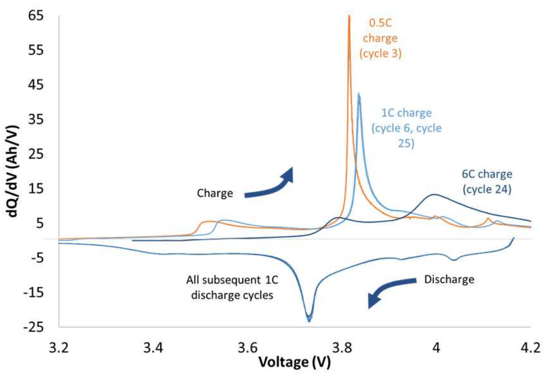

Figure 4: dQdV vs V for various cycles in baseline rate

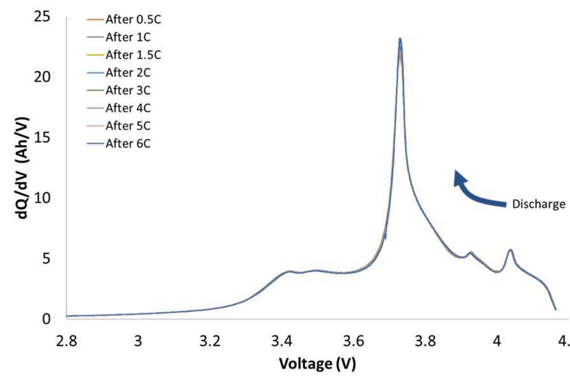

Figure 5: dQdV vs V for 1C discharge steps after each charge rate increase.

Conclusions

The baseline COTS cell was able to accommodate 6C charge with no issue other than expected cell polarization, but it is important to note that the cell sports 112 Wh/kg, well below DOE targets. Experience has shown that cells with more aggressive design perform much worse at high charge rates, often polarizing to an extreme where almost no charge is passed, or degrading rapidly via heating and lithium plating. Our baseline cells also showed no evidence of cell damage or lithium plating in dQdV analysis, however we should note that the taper step during charge may have allowed time for plated lithium to diffuse into the graphite, making it invisible to subsequent charge steps. Further testing is underway without the taper or any rest steps to try and capture lithium plating that could have been missed.

Importantly, the dQdV techniques developed during this short first FY will be used to assess optimized project cells for such negative effects, and quantify the improvements seen through HOH applications. Additionally, the rapid cooling plate fixture showed excellent temperature control, with only 3ºC temperature increase during the highest charge rates. This ensures that, moving forward, cells made in different iterations and cycled at different charge rates will be absent of temperature-driven inconsistencies.

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