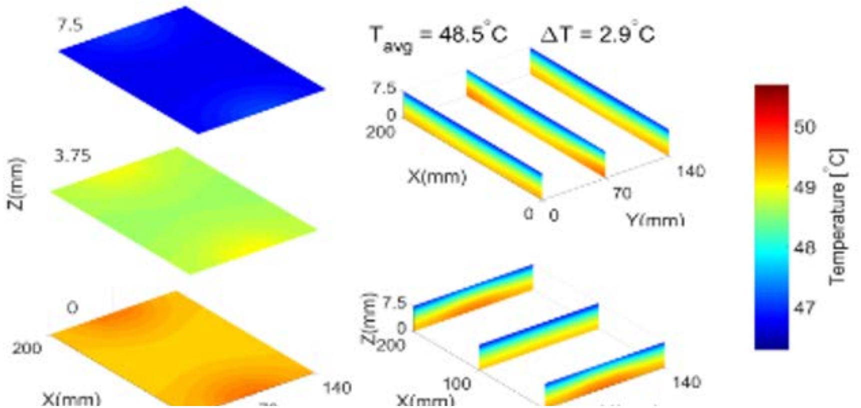
BAT459
U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW

XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

HEAT GENERATION CONCERNS ASSOCIATED WITH EXTREME FAST CHARGING



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June 1-4, 2020
Web Conference

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 75%

Budget

- Funding for FY20 – $5.6M

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells
- Low energy efficiency associated with high specific energy density cells – advanced chemistries

Partners

- Argonne National Laboratory (ANL)
- Idaho National Laboratory (INL)
- Lawrence Berkeley National Lab (LBNL)
- National Renewable Energy Laboratory (NREL)
- SLAC National Accelerator Lab
- Oak Ridge National Lab (ORNL)

RELEVANCE – BATTERY THERMAL IMPLICATIONS

Life, cost, performance, and safety of energy storage systems are strongly impacted by **temperature.**

Objectives of Heat Generation Thrust:

- Provide feedback to DOE on the battery thermal challenges associated with XFC
- Understand temperature nonuniformity within cell during XFC
- Develop techniques for operando interior temperature measurements
- Identify limitations of using high specific energy density cells
- Identify thermal areas of concern with existing battery systems
- Identify how changes to the battery chemistry and cell design affect the cells' **efficiency** and **performance**
- Identify state-of-the-art thermal management strategies and how these can be applied to future battery electric vehicles

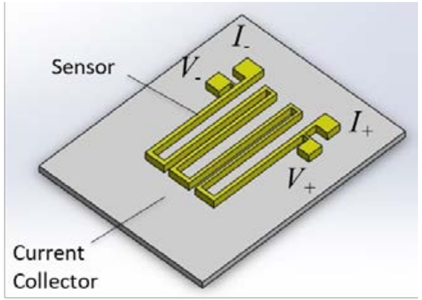
FY 2020 MILESTONES

Milestone	Due Date	Status
Define the critical parameters that affect heat generation within a cell.	12/31/19	Completed
Quantify heat generation of graphite/Nickel-Manganese-Cobalt (NMC) 532 through calorimeter experiments.	3/31/20	Completed
Develop and evaluate techniques capable of measuring the localized heat generation.	9/30/20	On-track
Develop 3D model capable of assessing heterogeneities, heat transport, and strategies to mitigate temperature rise under XFC conditions.	9/30/20	On-track

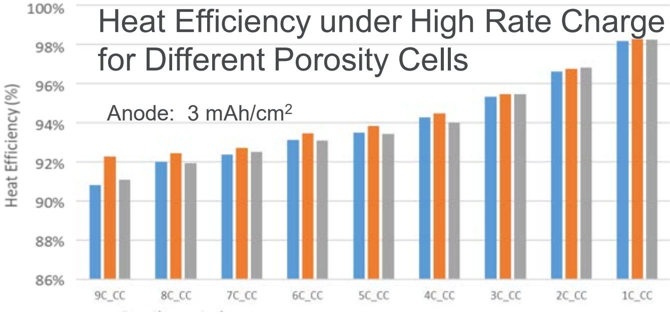
APPROACH – MEASURING HEAT GENERATION AND THERMAL TRANSPORT PROPERTIES FOR MODEL DEVELOPMENT

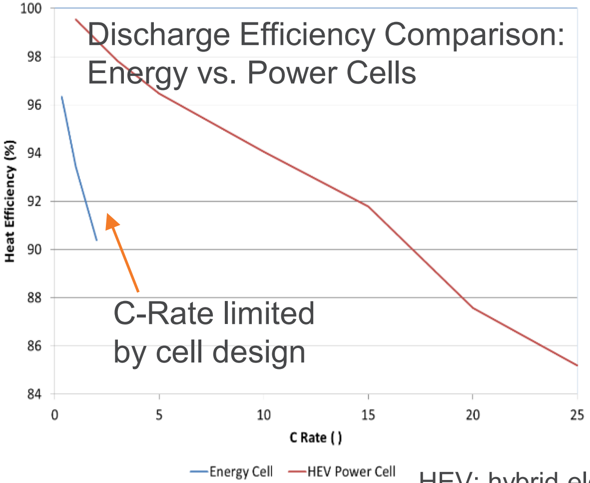
Identify Critical Parameters that affect heat generation in an electric vehicle (EV) cell.

Microcalorimeter: Heat Generation



Sensor for spatially resolved heat transport properties.

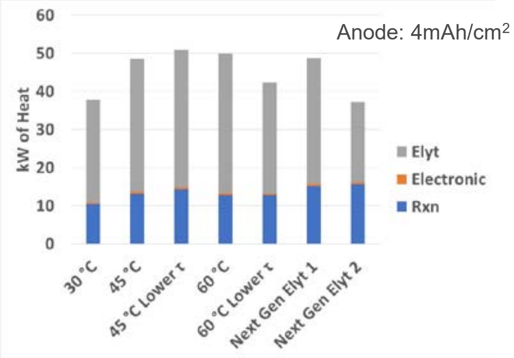


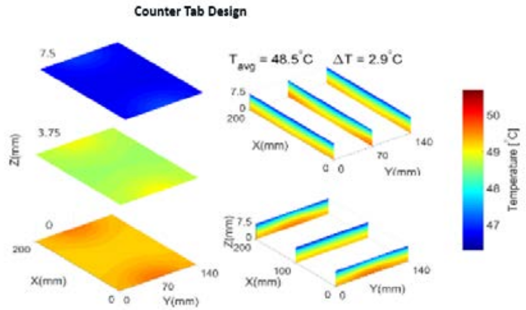


HEV: hybrid electric vehicle

1D/3D Model Development

100 kWh Pack Under 6C Constant Current Constant Voltage (CCCV) Charge





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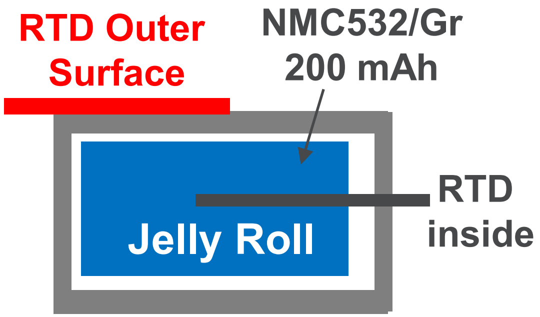
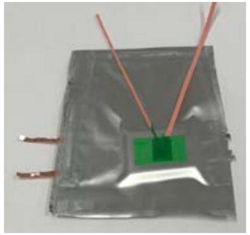
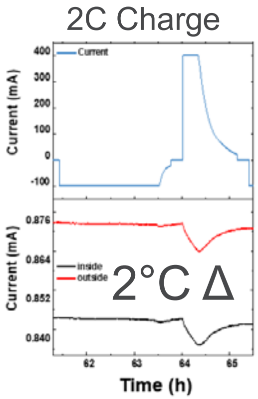
APPROACH: MEASURE AND UNDERSTAND TEMPERATURE VARIATION WITHIN EV CELL

Benefit: Temperature inhomogeneity is often hypothesized to be a culprit in observed inhomogeneous degradation (such as local Li plating, local SOC variation, local solid electrolyte interphase (SEI) thickness variation). Measuring internal temperature will allow for correlation between hot spots to evidence of degradation.

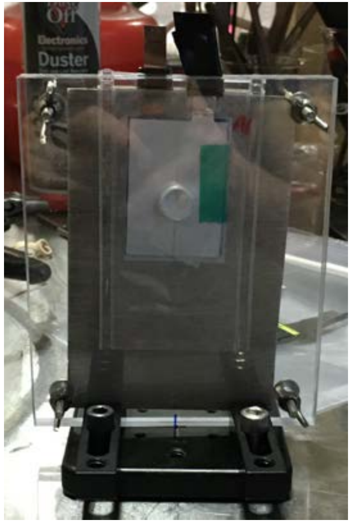
Resistance temperature detector (RTD) **stable** in electrolyte and under cycling



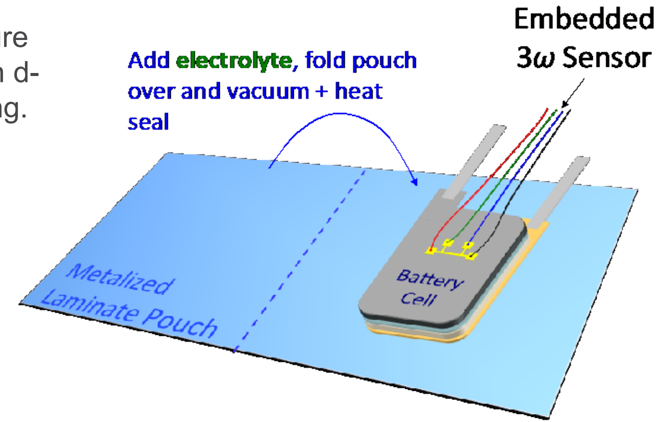




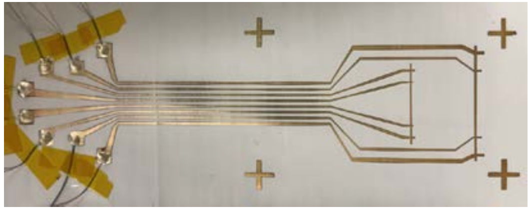
Use X-ray diffraction (XRD)/synchrotron to measure operando temperature gradients via the change in d-spacing of materials in the battery while it is cycling.



Above: Battery assembly with plastic block holder compressing clear pouch cell and AZ31 Mg alloy sheet, whose shift in d-spacing was used for pouch surface temperature measurement



Sweep heating frequency to measure thermal transport properties at different distances from sensor. Used to assess internal temperatures.



Prototype of exterior 3ω sensor.

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OUTLINE

- Understanding heat generation and identifying key parameters that affect heat generation with high energy density cells.
- Operando temperature measurements using an internal RTD.
- Understanding temperature uniformity/nonuniformity through XRD/synchrotron experiments.
- Developing internal/external 3ω sensor to measure thermal transport properties within cell during cycling.

MEASURE HEAT GENERATION WITH A HIGH LOADING EV CELL

Measure graphite/NMC532 efficiency (Heat Generation) for medium porosity (36.4%) cell at three temperatures. Data used in 1-D model to identify critical heat generation parameters.

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#: 573-824, received 03 /11/2016
Single-sided coating, CFF -B36 anode

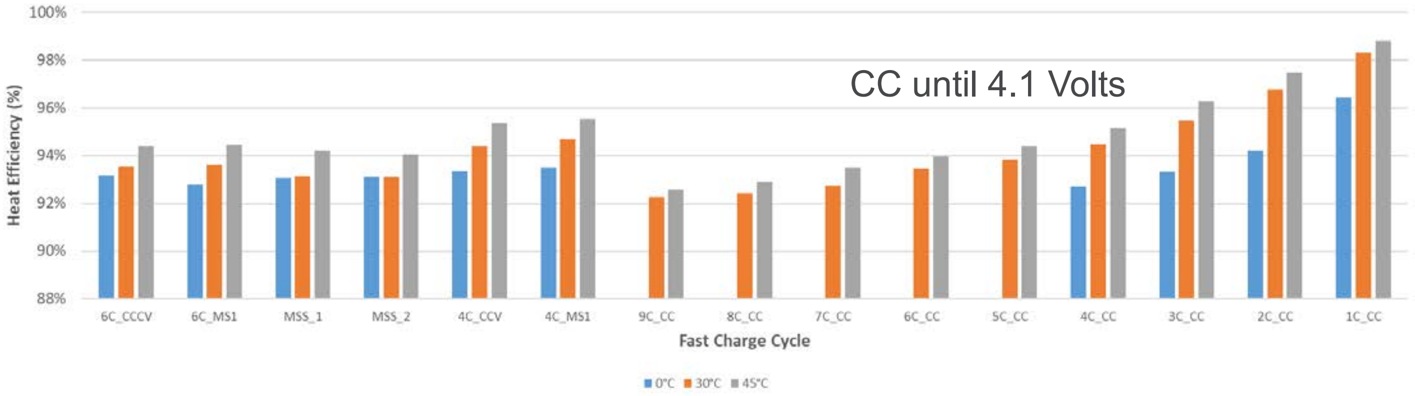
Cu Foil Thickness: 10 µm
Total Electrode Thickness: 80 µm
Total Coating Thickness: 70 µm
Porosity: 34.5 %
Total SS Coating Loading: 9.94 mg/cm^2
Total SS Coating Density: 1.42 g/cm^3
Made by CAMP Facility

Cathode: LN3107 -189-3

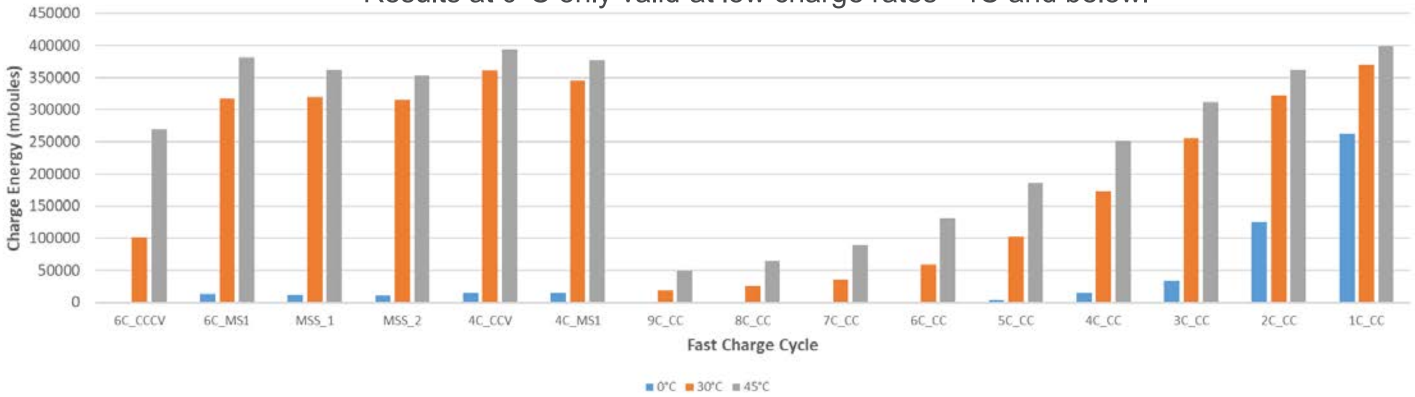
90 wt% Toda NMC532
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF

Matched for 4. 1V full cell cycling
Prod:NCM -04ST, Lot#:7720301
Single-sided coating, CFF-B36 cathode

Al Foil Thickness 20 µm
Al Foil Loading: 5.39 mg/cm^2
Total Electrode Thickness: 91 µm
Coating Thickness: 71 µm
Porosity: 35.4%
Total Coating Loading: 18.63 mg/cm^2
Total Coating Density: 2.62 g/cm^3
Made by CAMP Facility

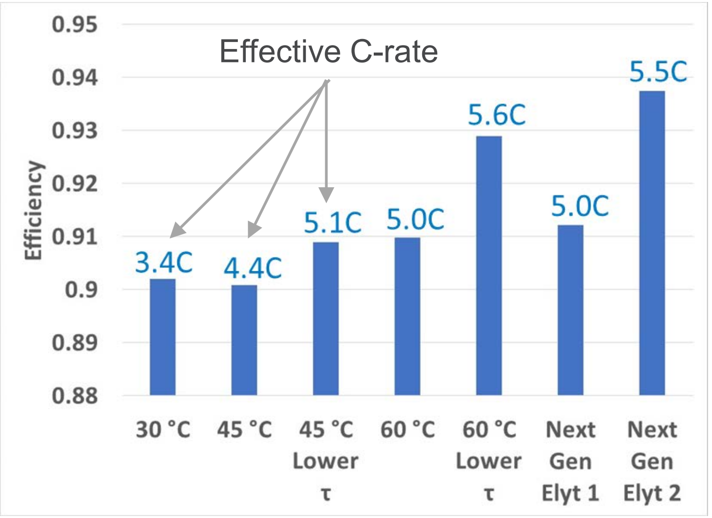


Results at 0°C only valid at low charge rates - 4C and below.



EFFICIENCY FOR HIGH SINGLE SIDED EV CELLS WITH LOADING OF 4 mAh/cm^2

1-D model results to identify critical parameters associated with heat generation.



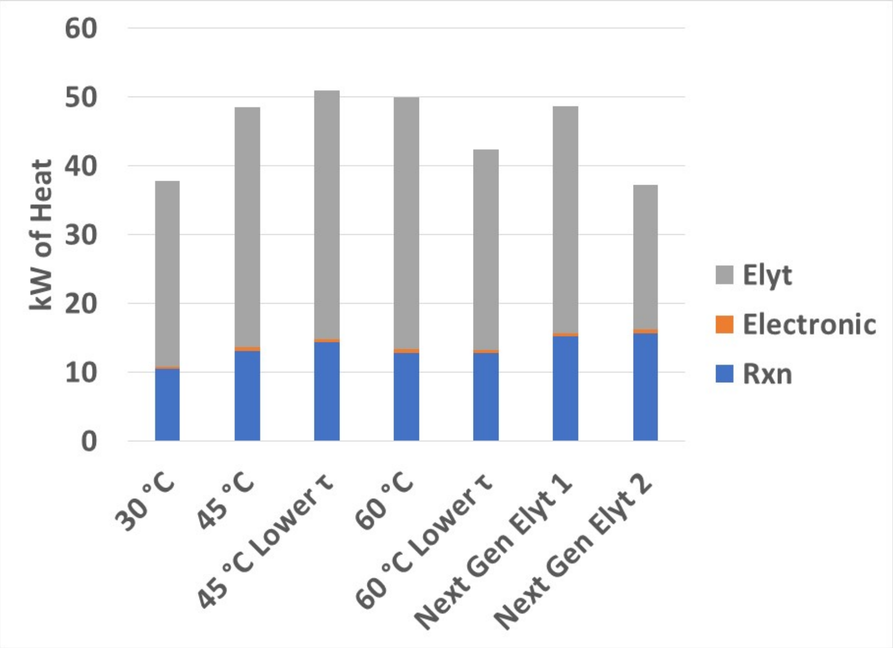
- Efficiency during 10-minute charge of 6 CCCV up to 4.2 V
- Efficiency calculated = Average Heat/Average Power
- Initial temperatures given and cell has <= 8°C rise
- Lower cell overpotential results in significant gains in capacity/effective charge rate

Case Study	State-of- Charge (SOC) Returned
30°C	57.1 %
45°C	73.1 %
45°C – Lower tortuosity (τ)	84.8 %
60°C	84.1 %
60°C – Lower τ	92.5 %
Next Generation Electrolyte 1	83.5 %
Next Generation Electrolyte 2	91.9 %

- Minimal gains in efficiency with elevated temperature because effective C-rate increases
- NG1: 1.8X, 3X and increase of 0.05 to ionic conductivity, diffusivity, and transference number
- NG2: 2.3X, 4X, and an increase of 0.15 to ionic conductivity, diffusivity, and transference number

1-D HEAT ANALYSIS FOR 4 mAh/cm^2 CELLS IN PACK

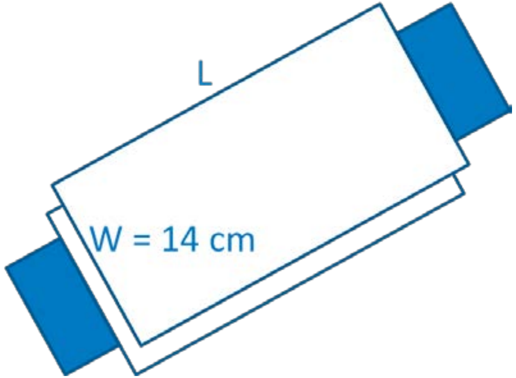
- 4 mAh/cm^2 anode and scaled to 100 kWh battery for EV (neglecting scaling loses)
- Dominant losses are from electrolyte transport and then charge transfer reactions.
- The 5% carbon black results in negligible losses from electron conduction/contact resistance in cathode (verified by 4-point probe measurements by Dean Wheeler)



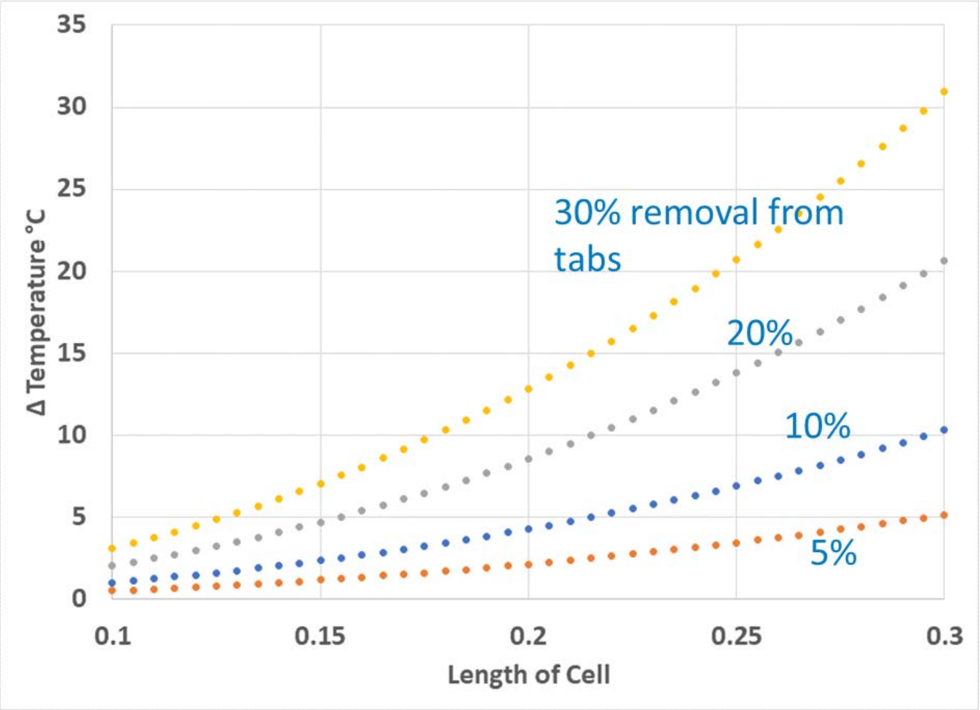
- Each kW of adiabatic heat during 10-minute charge would result in slightly over 1.3°C temperature rise
- For Next Gen 2 electrolyte, 30 kW heat removal during charging would result in 10°C temperature rise
- Requires heat removal much higher than typical heat exchangers in EVs

LATERAL TEMPERATURE DIFFERENCE ACROSS CELL

- Preliminary analysis for temperature difference across cell
- Each line represents different amount of heat removal from tabs
- 91% efficiency for cell operating with Next Gen 1 electrolyte
- Significant amount of heat is laterally conducted through cathode, anode, and closed cycle (CC) foils

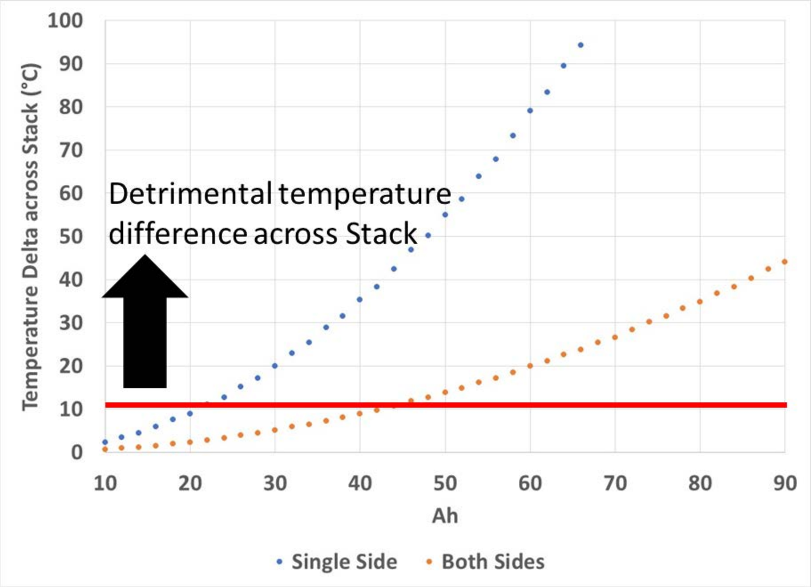


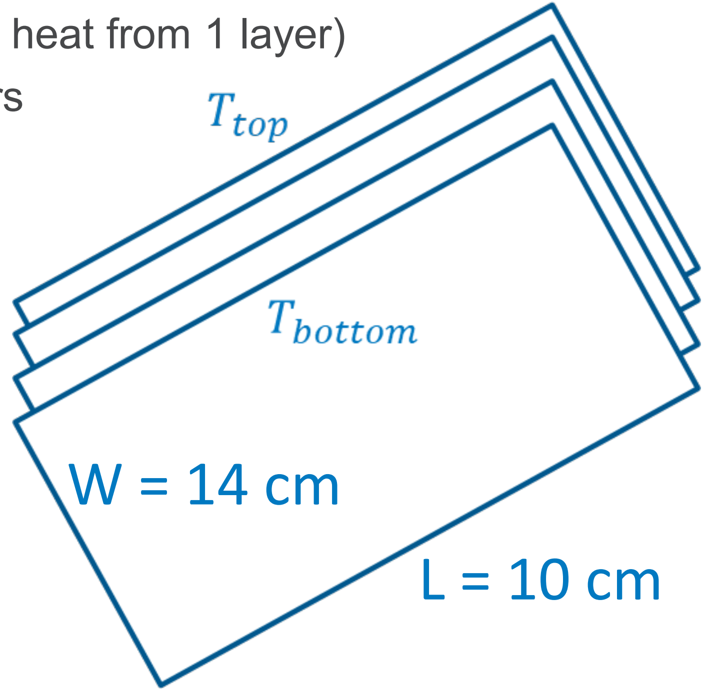
Temperature gain is proportional to length squared



VERTICAL TEMPERATURE DIFFERENCE ACROSS STACK

- Preliminary analysis for temperature difference across stack/layers
- Analysis assumes 90% of heat leaves through face
- Efficiency = 91%
- Temperature Difference is proportional to (where q is heat from 1 layer)
  - $dT\alpha \sum_1^N q\,n = \frac{N(N+1)}{2}$ where N is number of layers



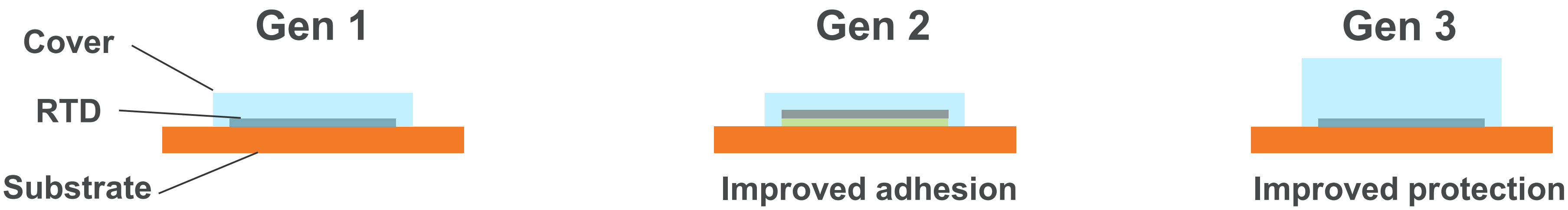


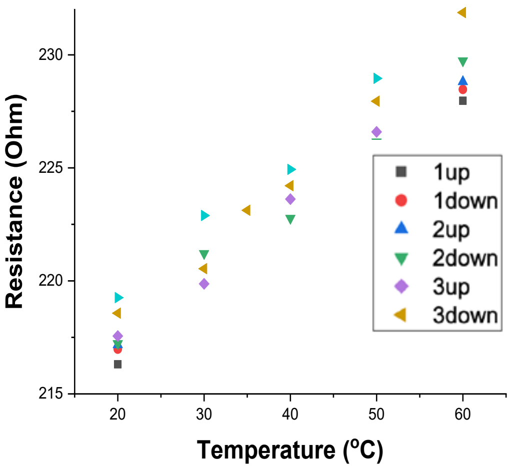
SUMMARY OF HEAT GENERATION FOR EV LOADING (4 mAh/cm^2) WITH 10 MINUTE CHARGE

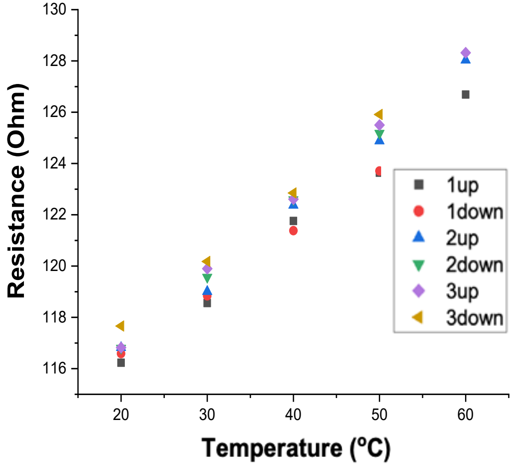
Parameter	Summary/Value
Heat sources	**50%-60% electrolyte** 20%-30% reaction kinetics 5%-10% lateral CC conduction in large cell
Effective C-rate	3.5C-5.5C (depending on temperature/electrolyte/electrode improvements)
Isothermal heat exchange requirements (100 kWh battery)	40kW-55kW
Adiabatic temperature rise	50°C – 70°C
Voltage drop across cell from CC (L is length between tabs)	Proportional to L^2 (need to limit to 10 cm-15 cm to limit voltage drop below 10 mV)
Temperature difference across single cell (center to tab)	Proportional to L^2 (becomes large if 10% or more heat removed from tabs)
Temperature drop across stack	Proportional to N^2 (number of layers) likely limited to 30 Ah or require cooling on both sides.
Increasing CC foil thickness by a factor of 2	Enables cells 20 cm – 30 cm in length. Reduces cell density from 230 Wh/kg to 210 Wh/kg

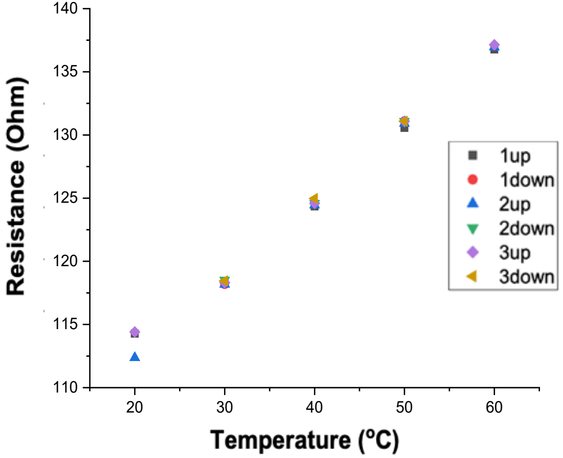
BUILDING WORKING RTD IN ELECTROLYTE

Improving device structure for stability in cell.





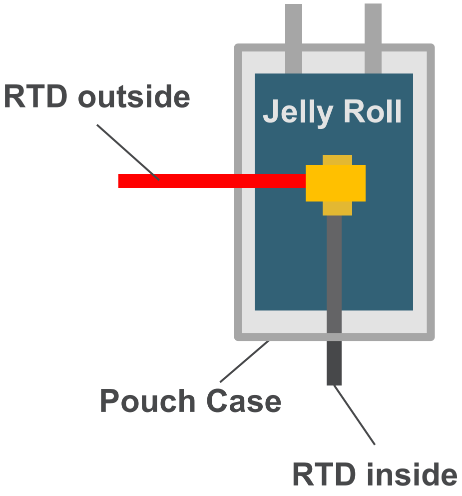




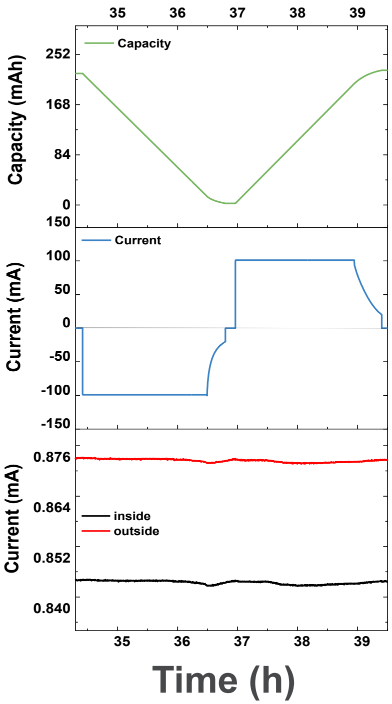
Stable and reliable temperature responses are demonstrated with Gen 3 RTD

RTD - OPERANDO TEMPERATURE MONITORING

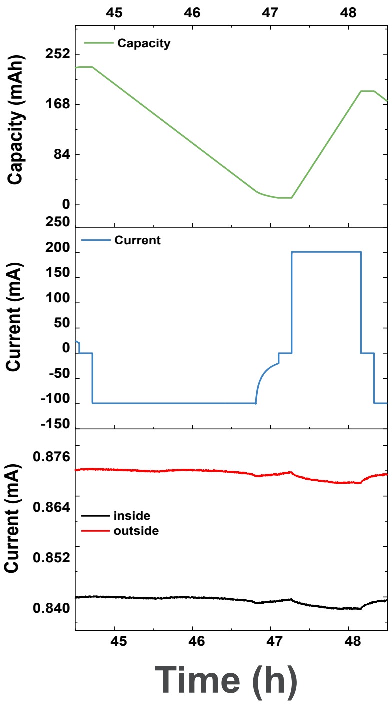
Resistance change observed at different C-rates



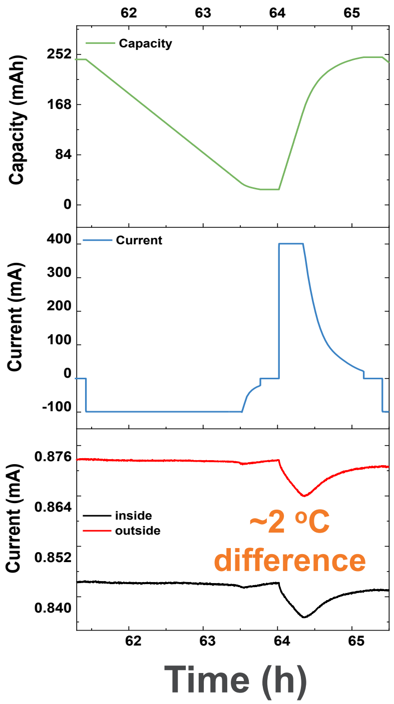
NMC 532/Graphite
200 mAh



Observable change at 0.5C



Moderate change, 1C

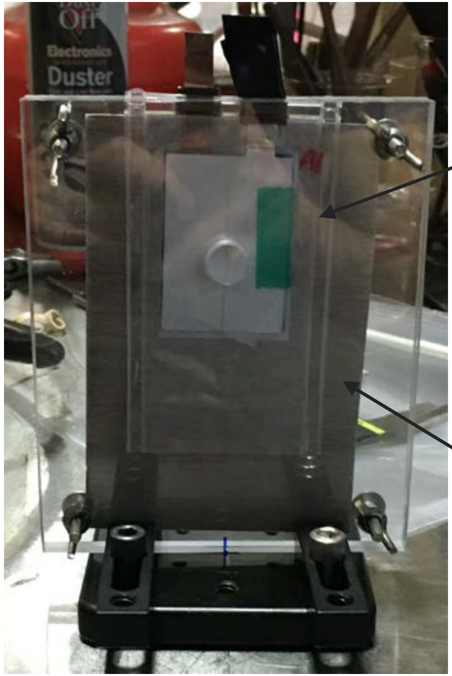


Significant change, 2C

Temperature change should be more significant with larger capacity cells

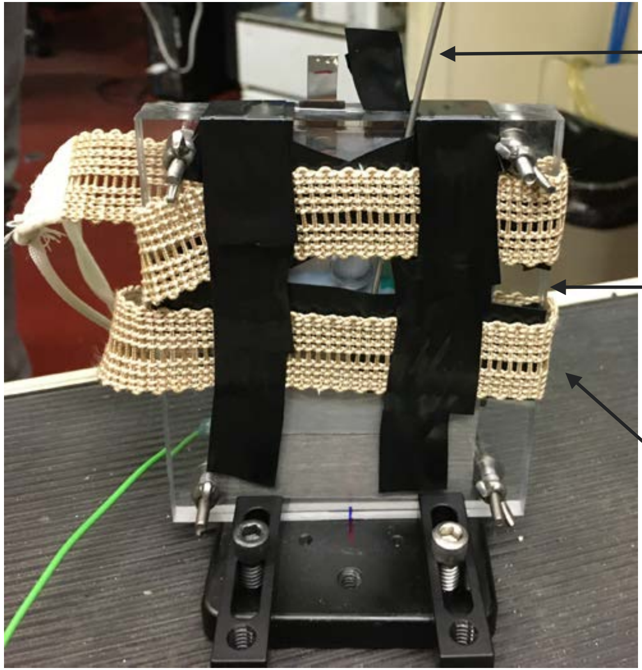
OPERANDO TEMPERATURE MEASUREMENTS IN POUCH CELLS

XRD/synchrotron experimental setup for single layer pouch cell.



Clear pouch cell (standard pouch material aluminized, obscuring aluminum CC peak)

Mg alloy sheet to assess pouch temperature.



Thermocouple (plastic block surf.)

Thermocouple inserted between plastic blocks (not shown)

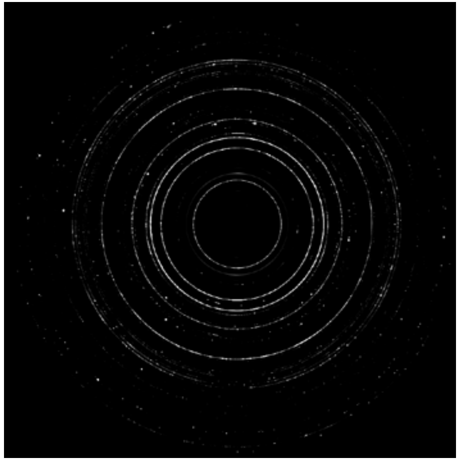
Heat tape for calibration experiments

OPERANDO TEMPERATURE MEASUREMENTS IN POUCH CELLS

Beamtime experiments completed on February 26th and 27th at Advanced Light Source.

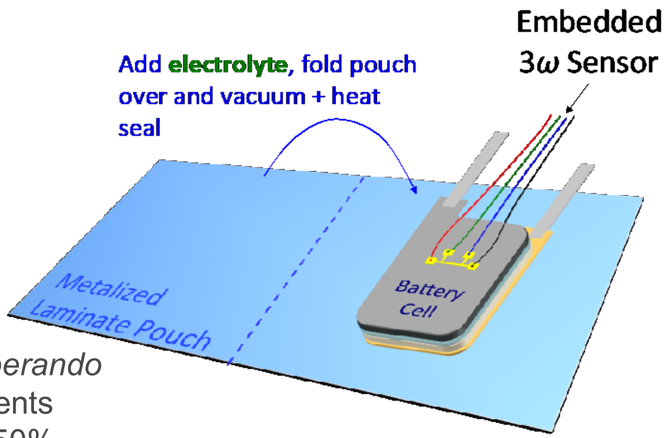
- **Control Experiments**
  - Temperature varied with heat tape (Room Temperature, 25°C, 30°C, 35°C, 40°C) at constant SOC
  - Slow C/2 CC cycling (3.0-4.1 V) while pouch held at 30°C
- **Fast Cycling Experiments**
  - 4C CCCV from 3.0-4.1 V
  - 8C CCCV from 3.0-4.1 V
- Thermal analysis pending from recent beamtime.

Representative XRD spectrum

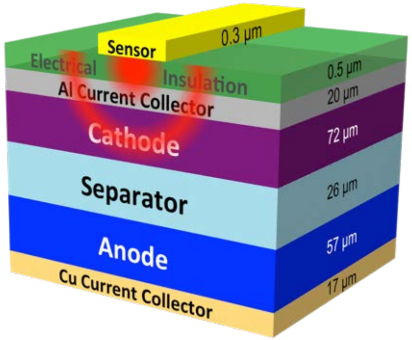


OPERANDO BATTERY THERMAL TRANSPORT MEASUREMENTS

Developing in-situ 3ω sensor to quantify thermal impedance changes in cell to quantify internal temperatures.

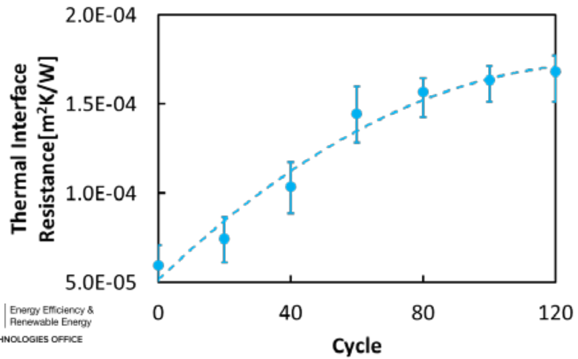


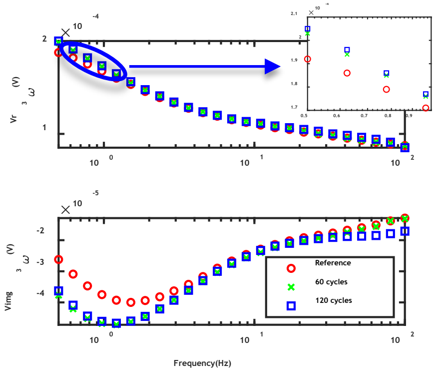
Above: *Operando* measurements revealed ~50% increase of total thermal resistance after over 100 cycles



Left: Sweep heating frequency to measure thermal transport properties at different distances from sensor

Used to calculate temperatures within a cell.



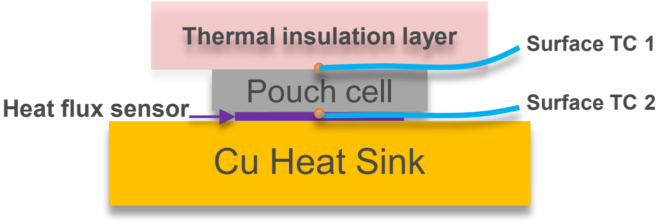


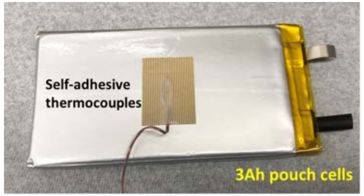
Left: 3ω sensor raw data shows impedance changes after cycling

MEASURE EFFECT ON FULL CELL

Quantifying thermal transport changes as the cell ages.

Measure heat flux leaving cell and *T*-drop across cell at a 2C charge and 1C discharge rate.

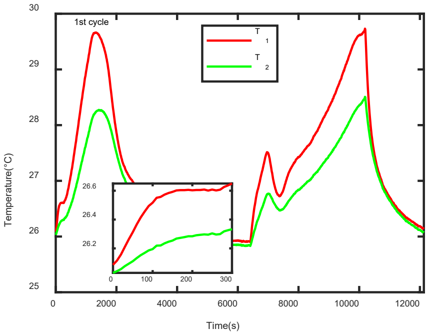




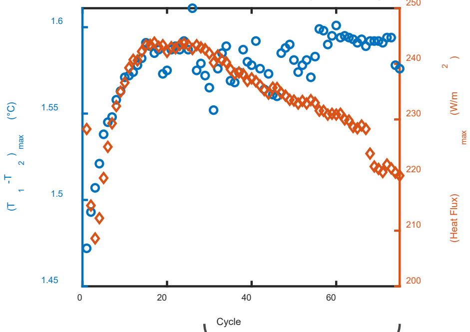
Below: Top view of experiment to understand cell impedance changes

Future experiments: vary C-rates, T_∞, and pressure to understand how these parameters affect impedance changes within cell.

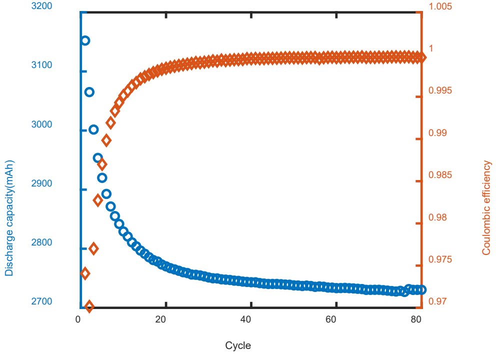
Representative charge + discharge Temperatures



∇T vs. *Q"* with cycling



Cell performance with cycling

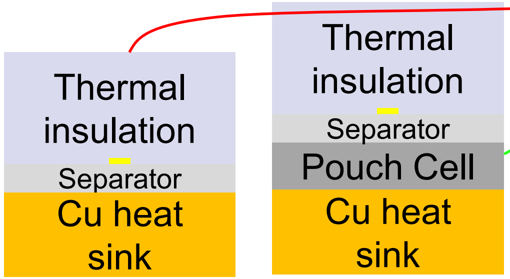


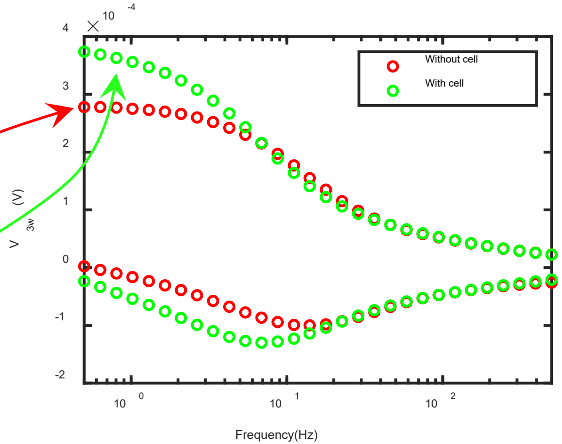
Full cell thermal properties change with cycling

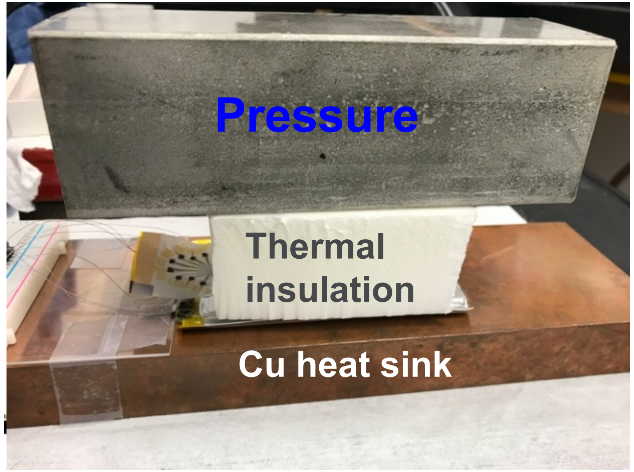
DIRECT THERMAL RESISTANCE MEASUREMENT OF COMMERCIAL CELLS

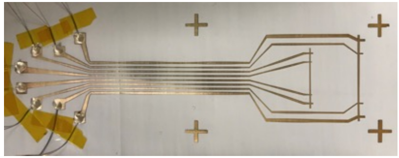
Developing an external 3ω sensor to simplify use with commercial cells.

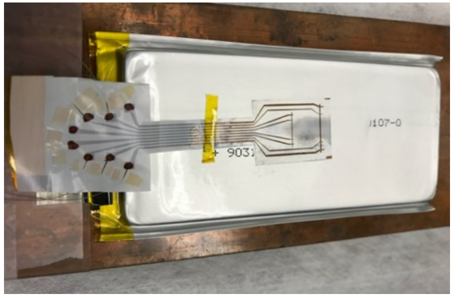
Preliminary results: sensors **outside** pouch to directly measure thermal conductivity











Left: External 3-omega sensor “sticker”

RESPONSES TO PREVIOUS YEAR'S COMMENTS

Not reviewed during the previous AMR.

CONTRIBUTORS AND ACKNOWLEDGEMENTS

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Daniel Abraham
Daniel Steingart
Dave Kim
David Brown
David Robertson
David Wragg
Dean Wheeler
Dennis Dees
Donal Finegan
Eongyu Yi
Eric Dufek
Eric McShane
Eva Allen
Francois Usseglio-Viretta
Guoying Chen
Hakim Iddir
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REMAINING CHALLENGES AND BARRIERS

- **Heat Generation**
  - Determine methods to reduce the heat produced from electrolyte transport and charge transfer reactions.
  - Fast charging at elevated temperatures limits lithium plating and allows for the cell to be charged at higher efficiencies. However, life/degradation, gassing, and delamination concerns will have to be addressed.
- **RTD**
  - Decrease RTD size and improve reliability in electrolyte solvents.
  - Determine reliable method to pass electrical feedthroughs into cells.
- **XRD/Beamtime**
  - Incorporate different current collectors into multi-layer cell to understand temperature difference between interior/exterior of cell.
- **Thermal Transport Experiments**
  - Reduce size of internal/external 3ω sensors.
  - Link model with data from 3ω sensors in multi-layer pouch cells to calculate internal temperatures.

PROPOSED FUTURE WORK

- **Heat Generation**
  - Use heat generation data and incorporate into 3-D thermal model.
  - Understand how tab configuration, length/width of cell, thickness of electrodes affects temperature uniformity within cell.
- **RTD**
  - Continue to optimize RTD size and chemical resistance to electrolyte solvents.
  - Incorporate optimized RTD in multi-layer lithium-ion pouch cell.
- **XRD/Beamtime**
  - Analyze results to determine temperature changes between aluminum, copper, and pouch material via the magnesium sheet adhered to outside of cell.
- **Thermal Transport Experiments**
  - Optimize internal/external 3ω sensors.
  - Carrying-out direct temperature rise observation experiments.
  - Exploring sensor material options to boost sensitivity.

SUMMARY

- **Heat Generation Critical Factors for an EV Pouch Cell**
  - 100 kWh battery would produce 50 kW of heat during a 10-minute charge, with significant amount of heat being from li-ion transport/conduction within the electrolyte phase.
  - 1 kW of heat generation during a 10-minute charge results in a 1.3°C adiabatic temperature rise.
  - If allowable temperature rise is kept to 20°C, then 35 kW of heat must be removed which is substantially more than present-day heat exchangers in electric vehicles.
  - If cooling is only available from one face side of cell, then capacity is likely limited to ~30 Ah.
  - Cooling both sides of pouch would enable cells up to 50 Ah - 60 Ah.
  - Large amounts of heat can be removed via tab cooling. However, the temperature difference between the center and edge of layers becomes large when > 20% of heat is removed through tabs.
  - Significant benefit to improving thermal conductivity of anode, cathode, separator, and electrolyte ➡ not much benefit from enhancing electrical conductivity of current collectors.
- **Measuring Internal Temperatures**
  - Successful fabrication and test of an internal RTD within a cell.
  - Demonstrated XRD imaging of a single layer pouch cell at the Advanced Light Source.
  - Coupled modeling results with data from 3ω sensors to understand the thermal transport properties within a cell.

XCEL

eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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