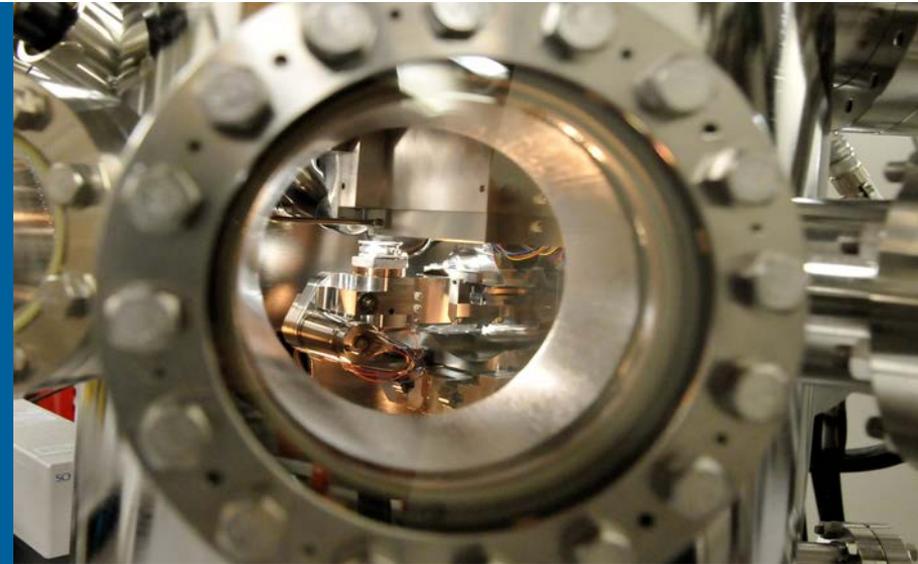


PROJECT ID: ES166



POST-TEST ANALYSIS OF LITHIUM-ION BATTERY MATERIALS



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POST-TEST ANALYSIS OF LITHIUM-ION BATTERY MATERIALS

Overview

TIMELINE

- Project start: October 1, 2015
- Project end: September 30, 2018

BUDGET

- FY16: \$ 1.1 M / y (total)

OBJECTIVES

- Elucidate physical and chemical response of constituent battery materials under battery abuse conditions
- Develop analysis procedures

CONSORTIUM PARTNERS

- Oak Ridge National Laboratory
- Sandia National Laboratory

A CONSORTIUM WAS FORMED

- This is a new start in response to VTO Lab Call 2015
- Argonne, Sandia and Oak Ridge teamed to leverage strengths and abilities at each site to study effects of processing and abuse response of two lithium-ion battery chemistries, high-Ni NMC and LiFePO_4
- What each site contributes
 - Argonne: Post-test Facility – ability to characterize battery materials under inert atmosphere
 - Sandia: Battery Abuse Testing Lab (BATLab) – ability to thermally and electrically abuse cells under controlled conditions
 - Oak Ridge: Battery Manufacturing R&D Facility – ability to make cells with well-defined chemistries, as the project needs



POST-TEST ANALYSIS OF LITHIUM-ION BATTERY MATERIALS

Relevance

Science Issues

- What are the underlying changes in cell components during an abuse event, such as overcharge and thermal abuse? For example, what is the fate of safety-related additives? How do they work?
- What is the impact of processing methods on the performance of the cells? That is, what is the effect of type of binder and drying procedure on the SEI layer, cell impedance, binder degradation, gases, and current collector corrosion?

APPROACH

- Effect of processing on cell performance/life

Electrode chemistry

NMC OR
LiFePO₄



Secondary drying

OR

RH equilibration



Electrode making

NMP-based OR
Aqueous



Same kind electrodes

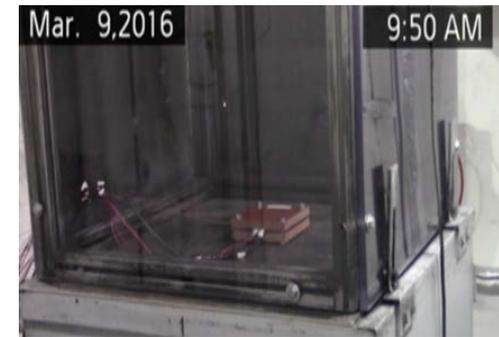
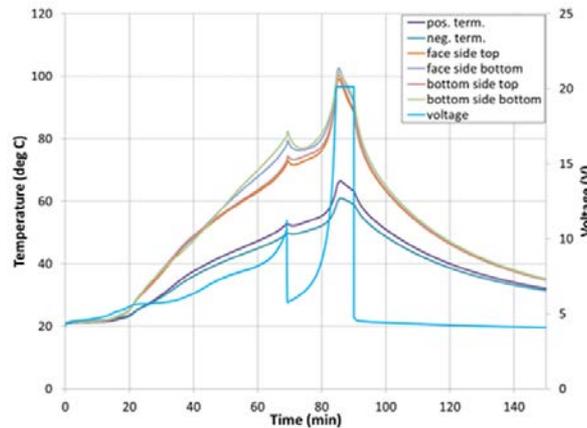
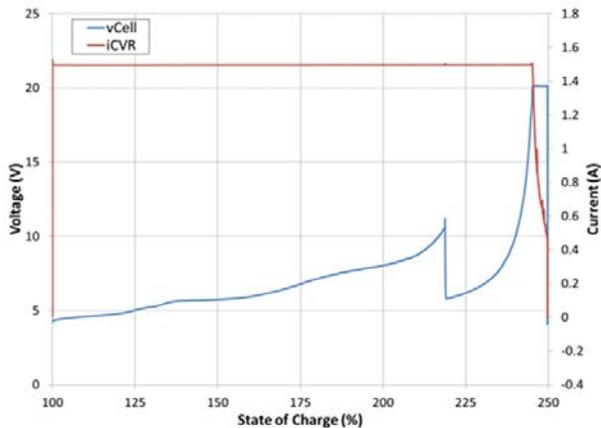
OR

Mixed NMP-Aqueous



APPROACH

- Effect of processing and formation on cell performance/life
- Changes in cell components from abuse events
 - Compare surface and bulk chemistry of electrodes before and after abuse events: Thermal & Overcharge



Cell runaway observed just below 250% SOC
No visual abuse response observed, only audible indication
Ensure safety for handling at SOC < 200% (Planned evaluations)

APPROACH

- Effect of processing and formation on cell performance/life
- Changes in cell components from abuse events
 - Compare surface and bulk chemistry of electrodes before and after abuse events: Thermal & Overcharge
 - Expected outcome
 - Understanding of the physical and chemical changes in the cell during abuse events
 - Design rules to manage/eliminate abuse consequences

APPROACH

- Effect of processing and formation on cell performance/life
- Changes in cell components from abuse events
- Impact of Manufacturing Processes on Cell Abuse Response
 - Combine lessons learned from above tasks
 - Elucidate *combined* effect of *processing* and *selected additives* on materials-level response to abuse events

- Cell fabrication



- Abuse tests



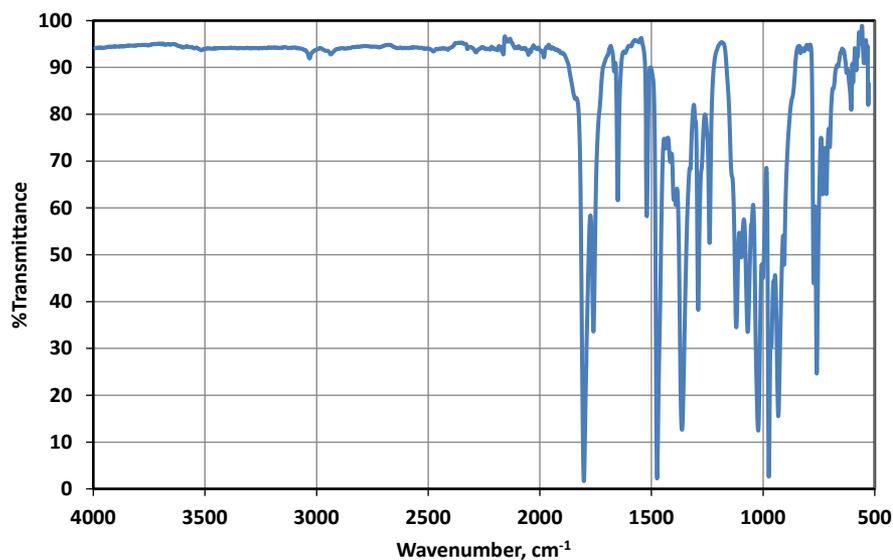
- Post-test characterization



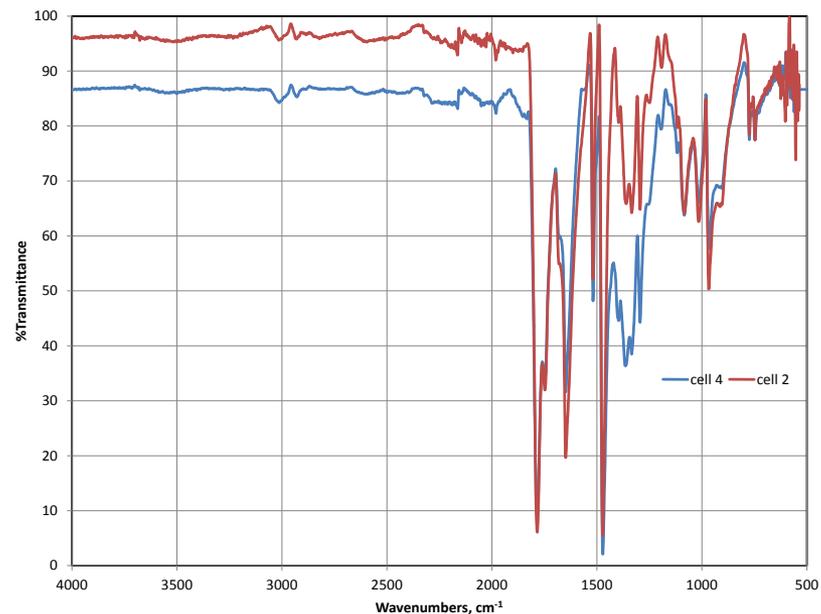
METHOD DEVELOPMENT IS FIRST STEP

Example: FT-IR shows changes in thermally-abused cell

- Scoping experiments to determine what types of changes to expect and how to detect them
- Examine fate of $(C_6F_5)B(\text{oxalate})\text{-LiF}$ (ABA) containing cells. This additive has show promise to reduce thermal-abuse response and overall energetic output of a cell undergoing runaway



Salt before



cell anodes after thermal abuse

BASELINE CELLS WERE MADE FOR OUR STUDIES

NMP-BASED PROCESS

- **Anode:** A12 : carbon black : pVdF 92:2:6 wt%
- **Cathode:** NMC532 : carbon black : pVdF 90:5:5 wt%
- **Electrolyte:** 1.2M LiPF₆ in EC:DEC 3:7 wt%

AQUEOUS PROCESS

- **Anode:** A12 : carbon black : SBR : CMC 92:2:1.2:4.8 wt%
- **Cathode:** NMC532 : carbon black : Latex : CMC 90:5:4:1 wt%
- **Electrolyte:** 1.2M LiPF₆ in EC:DEC 3:7 wt%

FORMATION PROTOCOL

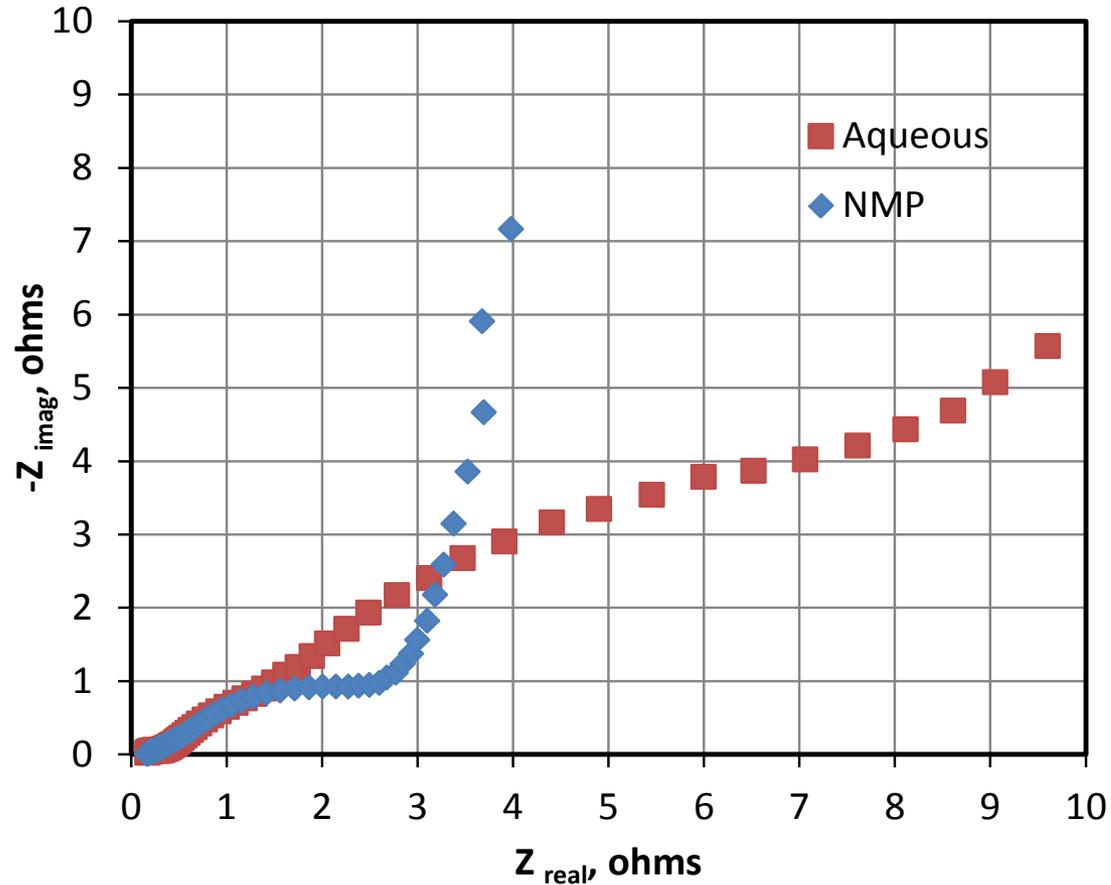
- Tap charge to 2.5V for 5 min.
- 4 full range cycles (2.5V – 4.2V) at C/20 and room temperature

SAMPLING PROTOCOL

- Disassemble cells under inert atmosphere
- Light rinse in DMC

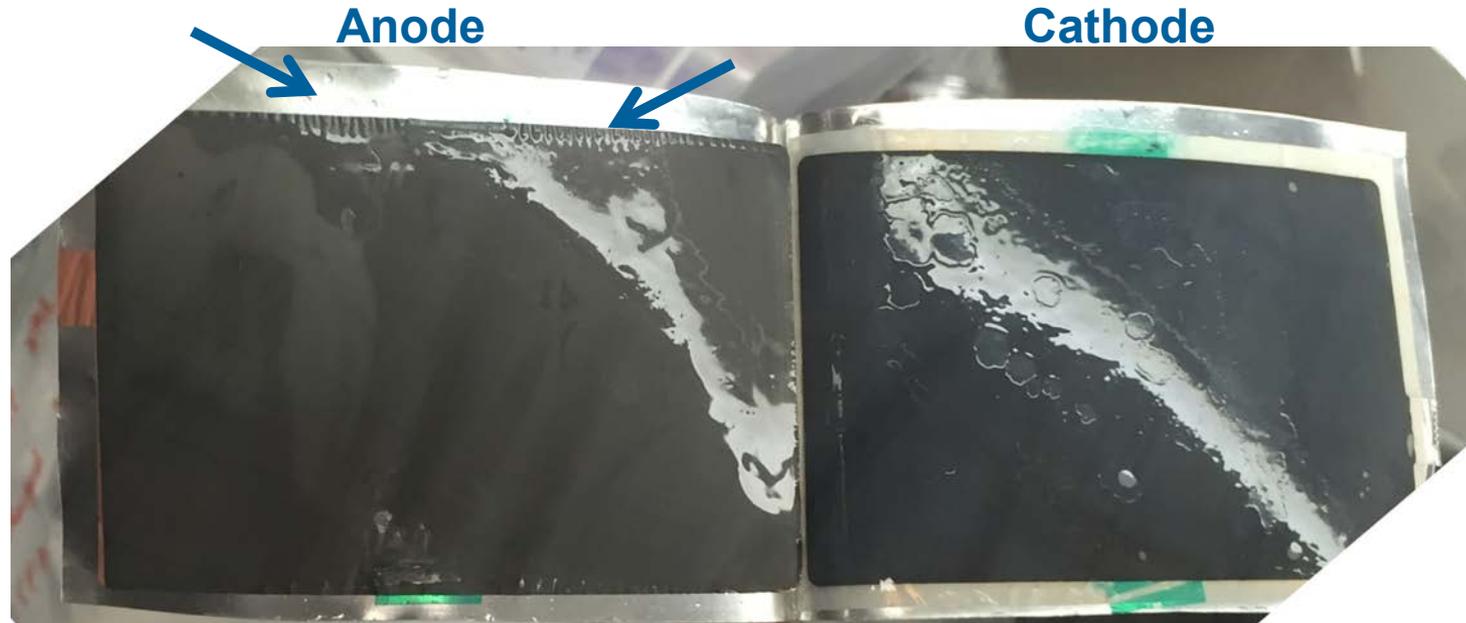
CELL IMPEDANCE (EIS) IS DEPENDENT ON BINDER

Aqueous process results in higher impedance



INITIAL INSPECTION SHOWS MANUFACTURING ISSUES (I)

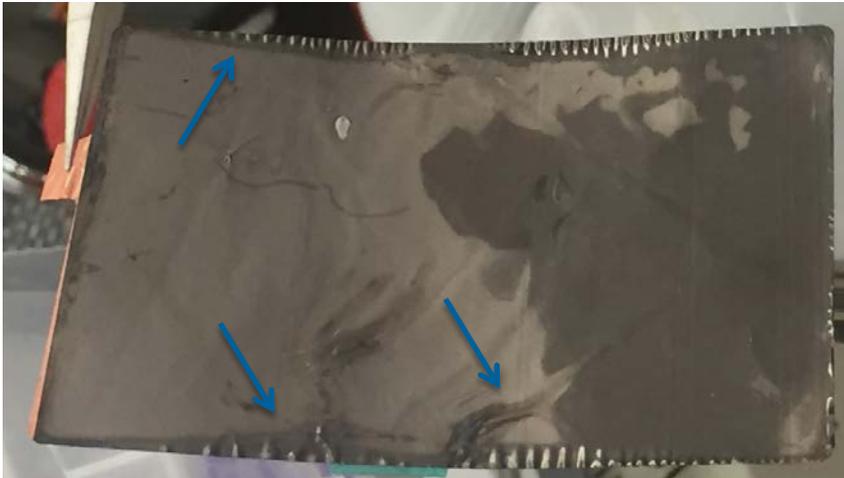
NMP-based



- Electrodes appear fully wet. No signs of electrolyte exhaustion
- Signs of stress-induced delamination (rippling) on edges of anode

INITIAL INSPECTION SHOWS MANUFACTURING ISSUES (II)

Anodes



NMP-based

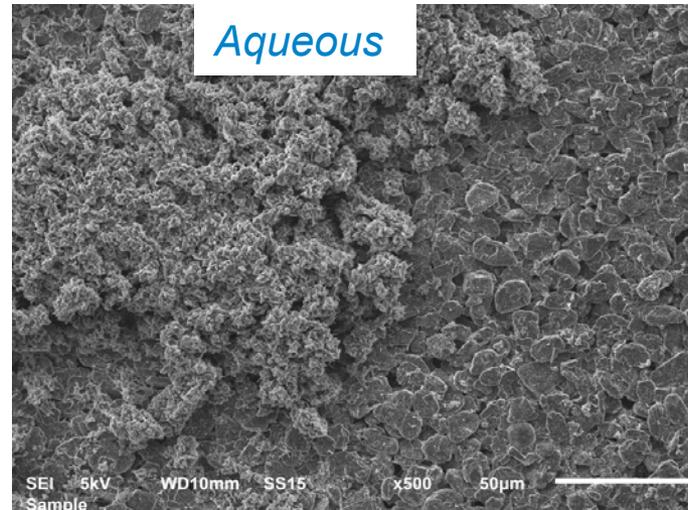
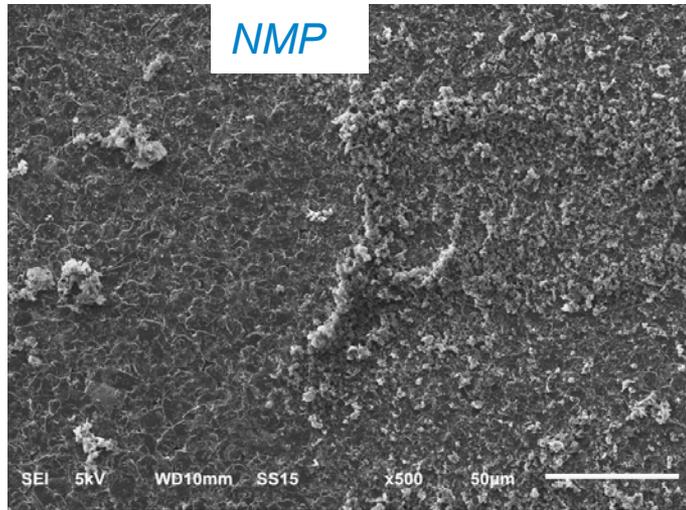
Aqueous process

- Signs of stress-induced delamination (rippling) on edges of anode
- Possible pin hole formation during aqueous process

SURFACE MORPHOLOGY IS SENSITIVE TO BINDER

May affect cell performance and life

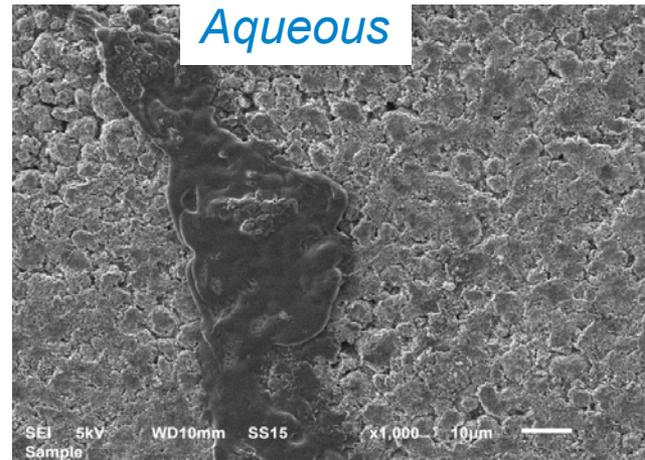
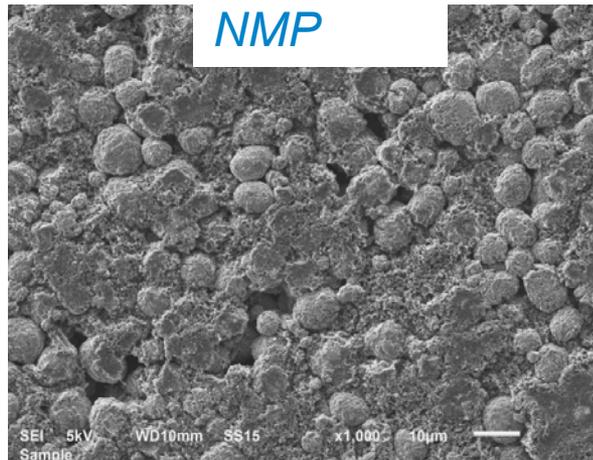
EDS characterization:



Anodes

Precipitates richer in F, and P than exposed particles

Composition differences more prominent in aqueous electrodes



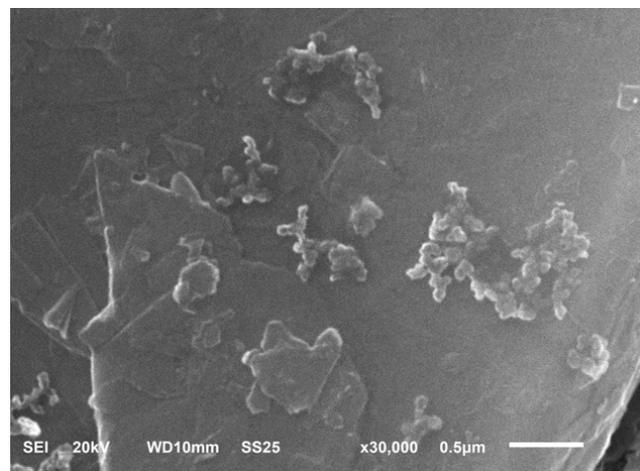
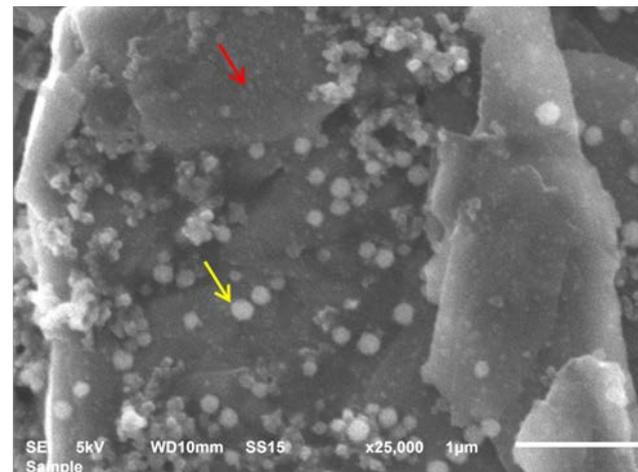
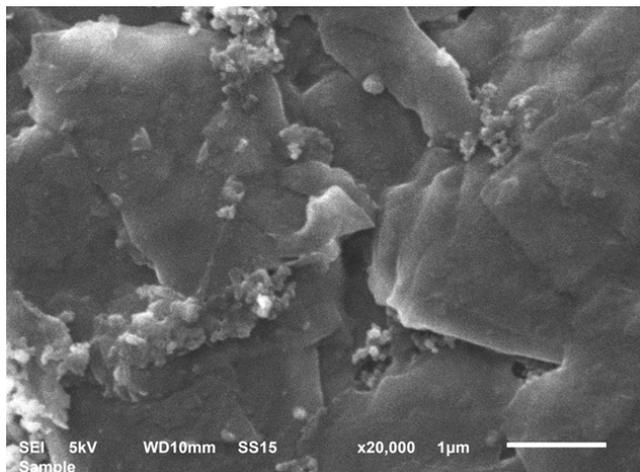
Cathodes

On NMP-based, F only at precipitates

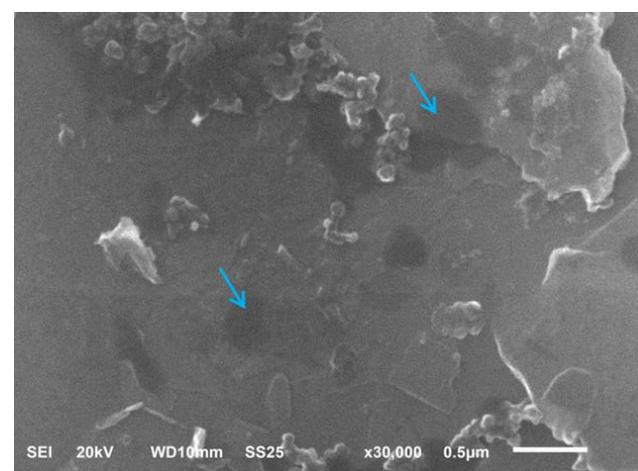
Aqueous has more F. Concentrated at precipitates, but also present on particles

BINDER AFFECTS PRECIPITATES

Round precipitates and “stains” on aqueous processed anode



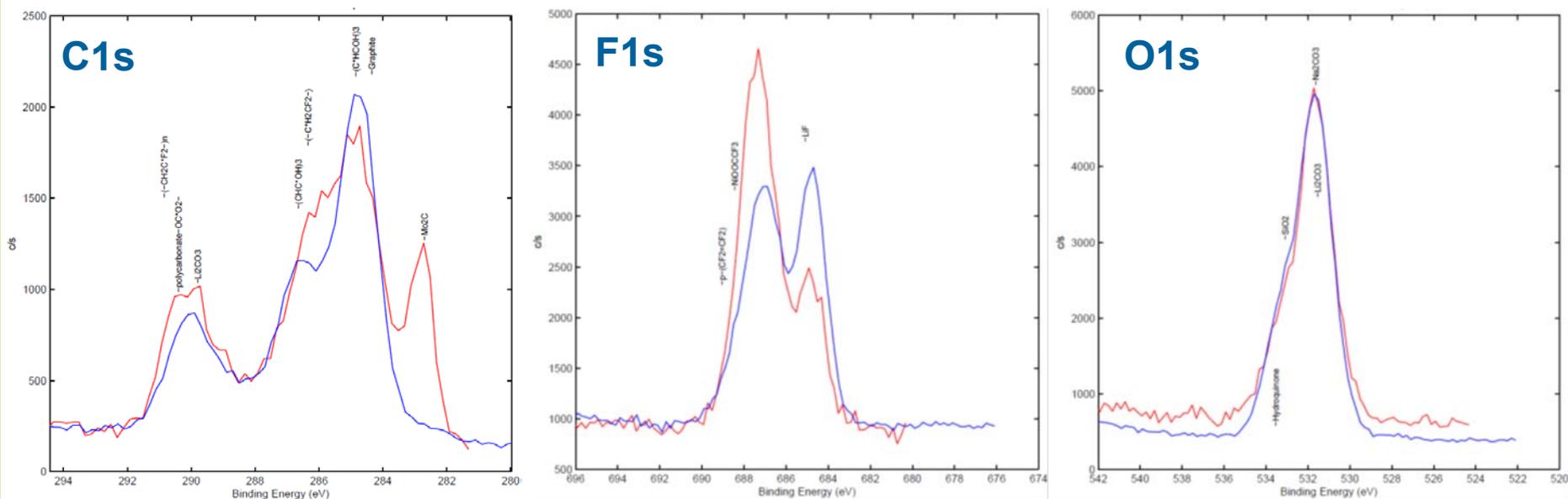
NMP



Aqueous

BINDER AFFECTS NATURE OF SEI

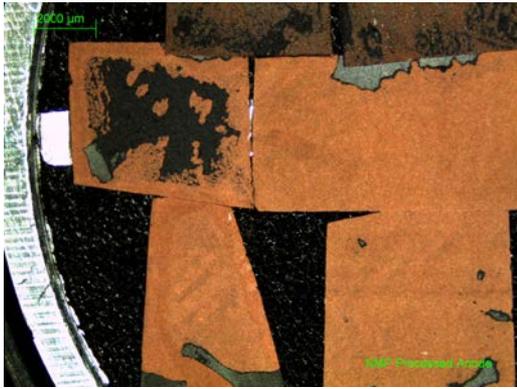
Differences in C and F structure between aqueous and NMP anodes



Aqueous anode

NMP-based anode

BINDERS DISPLAY DIFFERENT LEVELS OF ADHESION



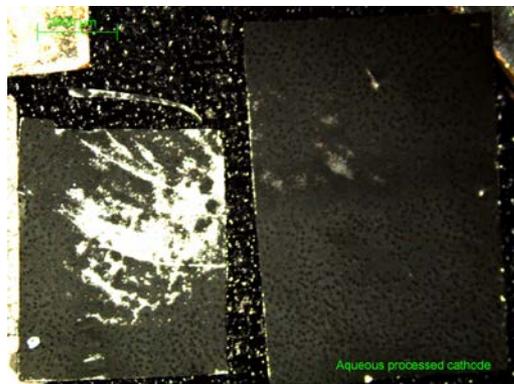
NMP-based anode



Aqueous process anode



NMP-based cathode

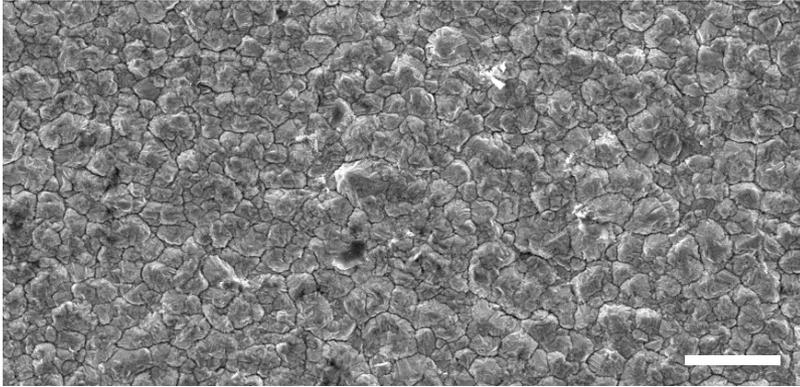


Aqueous process cathode

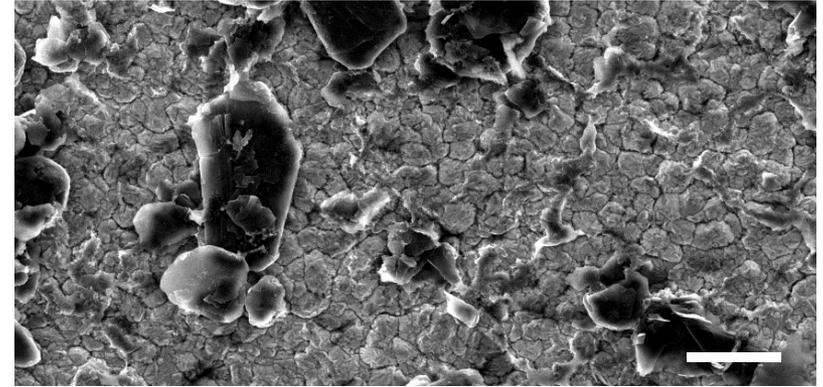
- ‘Scotch’ tape used to test adhesion
- Aqueous processed coatings have better adherence to the collector than the NMP processed cell
- In the NMP processed anode, the coating was completely lifted with minimal effort
- In the aqueous processed anode, residual coating stuck to the collector after multiple strippings

OTHER EFFECTS OF BINDERS

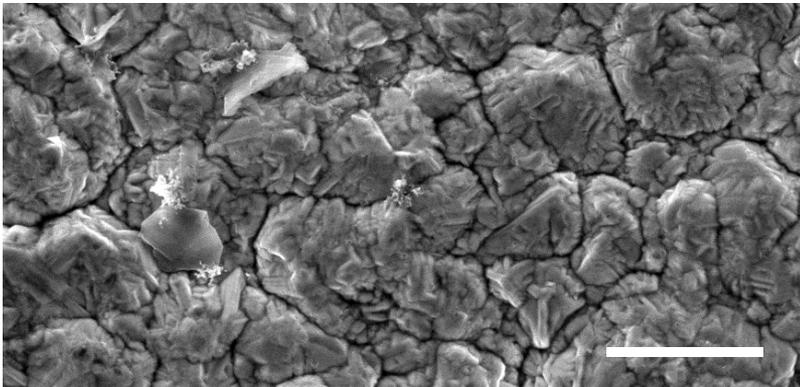
Extensive grain boundary corrosion in both electrodes (!)



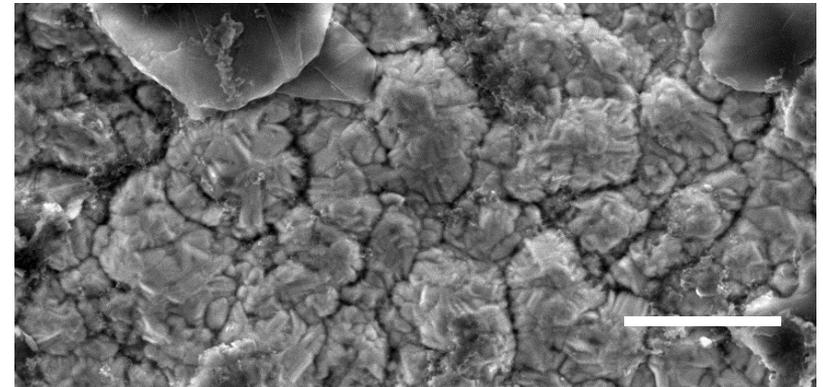
NMP-based 10 μm scale bar



Aqueous process 10 μm scale bar



NMP-based 5 μm scale bar



Aqueous process 5 μm scale bar

EXPERIMENT TO PROBE SOURCE OF GRAIN BOUNDARY CORROSION

A science question

- Grain boundary corrosion does not appear to be sensitive to binder type
- What caused corrosion in minimally-aged cells?
- Is some part of the fabrication process, common to both, the cause of the observation?
- Are the electrolyte/electrode interacting to cause the corrosion?
- To understand the underlying phenomenology, perform systematic experiments
- Fabricate and characterize Cu foil from --
 - Pristine anode (just fabricated)
 - Anode that has seen cell chemistry, but has not been cycled/formed

FUTURE WORK

- **Cu current collector corrosion**
 - Characterize pristine and formed electrodes to determine origin and extent of corrosion
- **Effect of abuse**
 - Determine effect of *additive* on cell response to overvoltage and overheating, and determine mechanism

ACKNOWLEDGMENTS

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