Electrode Fabrication and Failure Analysis

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LBNL

DOE AMR

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Project ID #

ES081

Timeline

- Start: October 2008
- End: September 2012
- Percent complete: 50%

Barriers

- Barriers addressed
  - Deep discharge cycles (>1000)
  - Low Energy Density (>230 Wh/l)

Budget

- Total project funding: $1.76 M
- Funding received in FY09: $880 k
- Funding for FY10: $880 k

Supports 3 Research Associates and 50% of the PI.

Partners

- BATT PIs and others

LBNL	Daikin
UCB	Wash. Univ.
HQ	Lockheed Martin
UCD	Veeco Instruments

Objective

To make electrodes and cells that are "good enough" to test new materials and assess some sources of cell failure.

- To gain enough fundamental understanding of composite electrode processing to make reasonable modifications for each new material we receive.

- To gain a fundamental understanding of why a cell fails and to be able to distinguish electrode processing failures from material failures.

Providing as good of an evaluation of new materials as possible and determining the reasons for failure of those materials is a sound approach to eventually meeting the life and energy density goals of the DOE/USABC.

Two Main Issues

1. Understanding electrode performance as a function of processing
    1. Characterize relevant material properties.
    2. Investigate variations in processing steps.
    3. Evaluate relevant electrode characteristics and look for correlations to processing or material properties.

2. Understanding failure modes
    - Loading
        - Thicker electrodes appear to fail in fewer cycles than thin electrodes.
        - Cycling electrodes at different rates; working with modelers.
    - Inert Materials
        - Different binders result in different cycleability.
        - Correlate physical properties of slurries and electrodes to cell performance.
    - Dissolution
        - Components from the cathode are found at the anode.
        - Measuring the dissolution of cathodes at different SOCs.
    - Side reactions
        - <u>Some</u> side reactions lead to an imbalance of Li between the electrodes.
        - Differentiating between benign and detrimental side reactions; investigating the effect of additives to mitigate side reactions.

Milestones for 2009 and 2010

2009

- Construct electrodes of nanometer-size active material *via* traditional methods and test their performance, (Sept. '09). **Completed**. (See G. Liu's poster)
- Develop a conductive-polymer binder for nano-Si-based anodes (Sept. '09). **Completed**. (See G. Liu's poster)

2010

- Report the coulombic efficiency of baseline NCM *vs.* graphite and *vs.* a lithium counterelectrode. (Jan. '10) **Completed**
- Report performance characteristics of a SBR-CMC binder-based anode. (Mar. '10) **Completed.**
- Distribute electrodes cycled to different cut-off voltages to other members of the BATT program. (Apr. '10) **Completed**.
- Report the results of the mechanical properties *vs.* cycling capability of Gr./NCM cells. (Sep. '10) **Completed**.

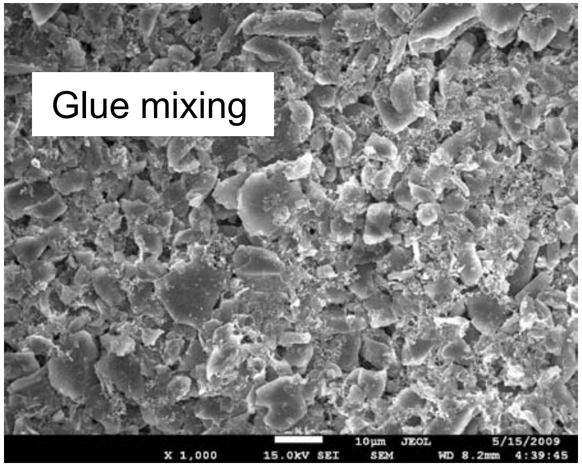
All targeted at better understanding of electrode performance on cell performance!

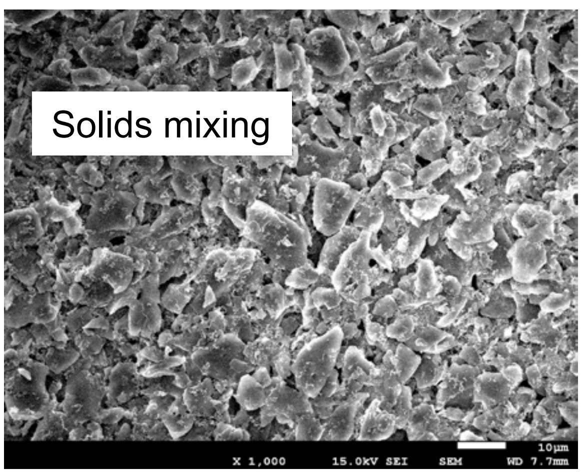
Mixing Order

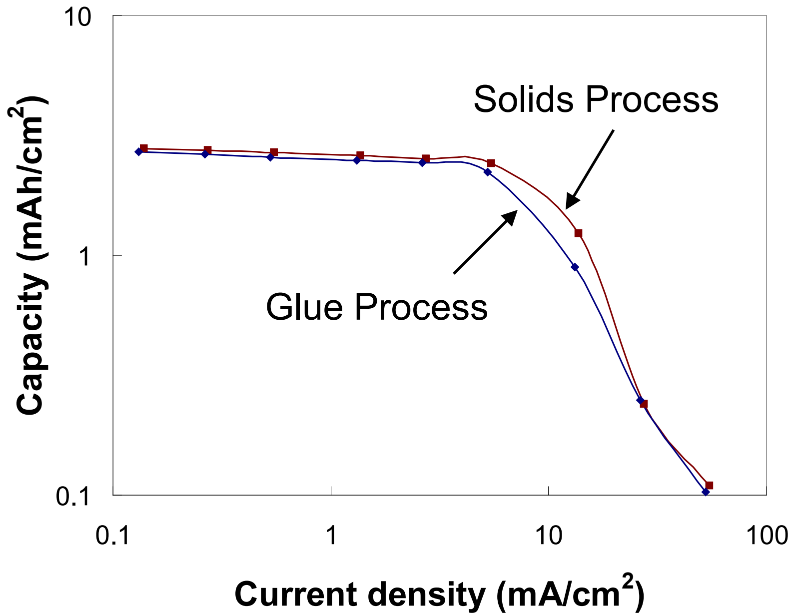
- We investigated the order in which materials are added together to form a slurry.
  - Glue process (G)
    - Binder is dissolved in NMP.
    - Conductive additive is mixed into the binder slurry (glue).
    - Active material is then added to the slurry.
  - Solids process (S)
    - Conductive carbon and Active material are mixed in NMP.
    - Binder is added to this mixture.

Mixing Order

Anode



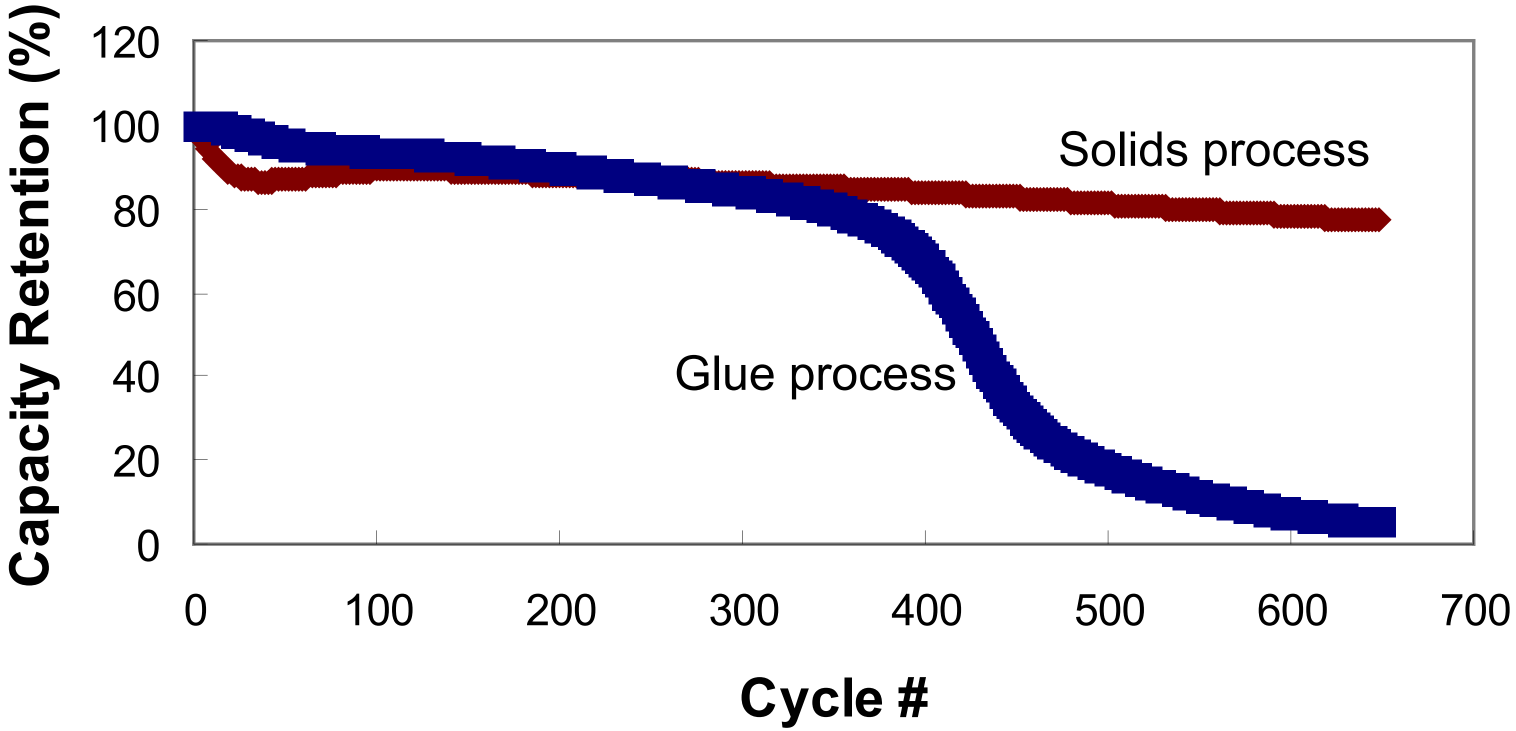




Mixing order

- Both processes lead to electrodes that are well mixed on a 40 μm scale.
- Solids process leads to conductive additive on active material.
- Both lead to electrodes of similar rate performance.

Technical Accomplishments: Electrode Processing



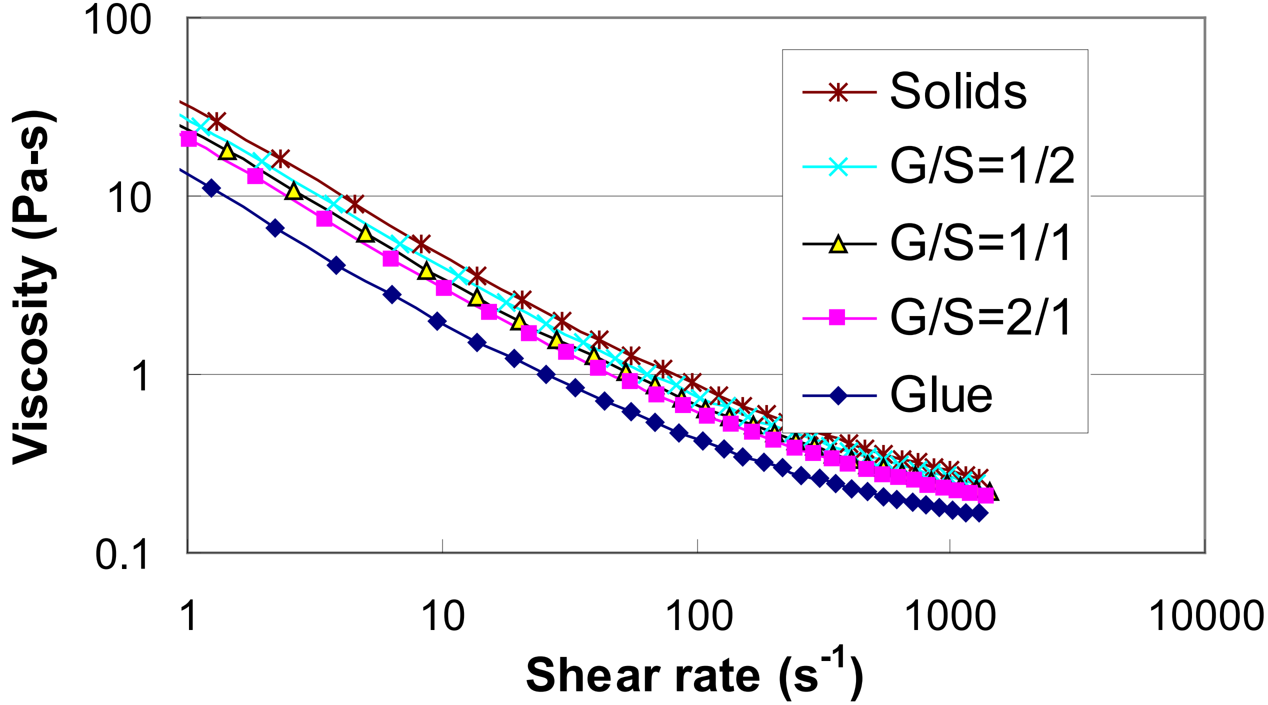
Mixing order has dramatic effect on cycleability!

We believe this is a result of non-uniform mixing where carbon additive is stuck in the binder.

Mixing Order

- The investigation proceeded by looking at combinations of the two mixtures and studying their physical properties.
  - Slurries were made of the following ratios of the two initial slurries, G:S = :
    - 1:0
    - 2:1
    - 1:1
    - 1:2
    - 0:1
  - Both slurries contain the same amount of inactive and active material, thus, this ratio remains constant in the final solutions.
  - All electrodes were cast to the same loading.

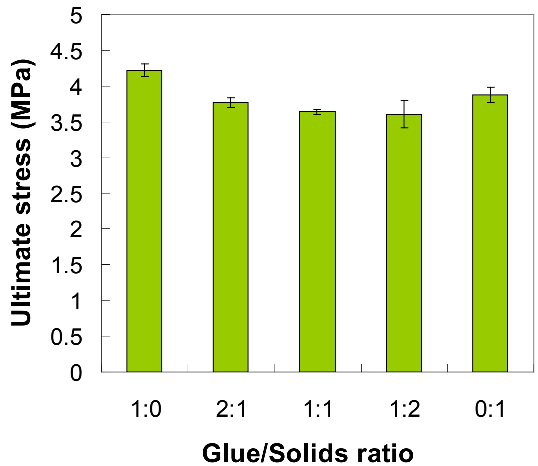
Slurry Viscosity as a Function of Mixing Order



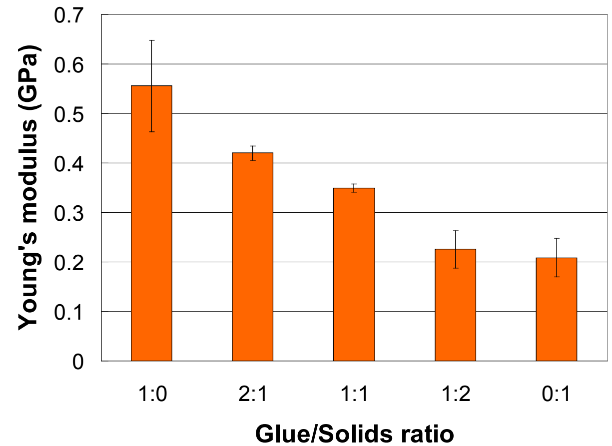
More uniformly mixed slurries are expected to have higher viscosities.

Physical Properties of Slurry and Electrodes

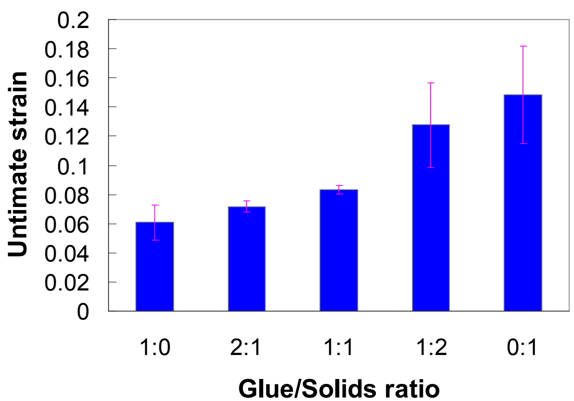
Ultimate Stress



Young's Modulus (stiffness)

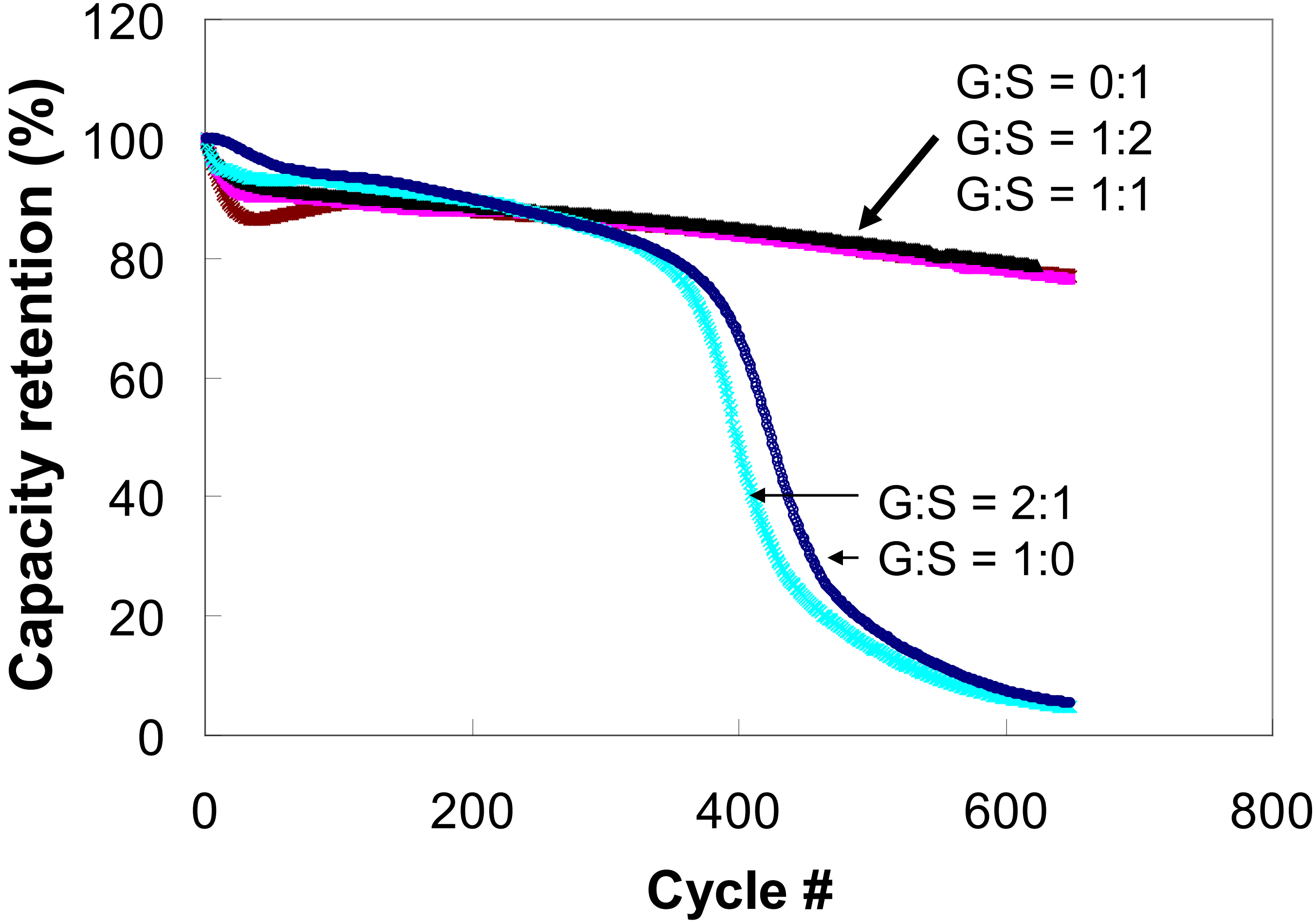


Ultimate Strain



- All electrodes require around the same amount of stress to break.
- Electrodes made with more of the Glue mix are stiffer.
- Electrodes made more with the Solids mix, therefore, have a higher ultimate strain.

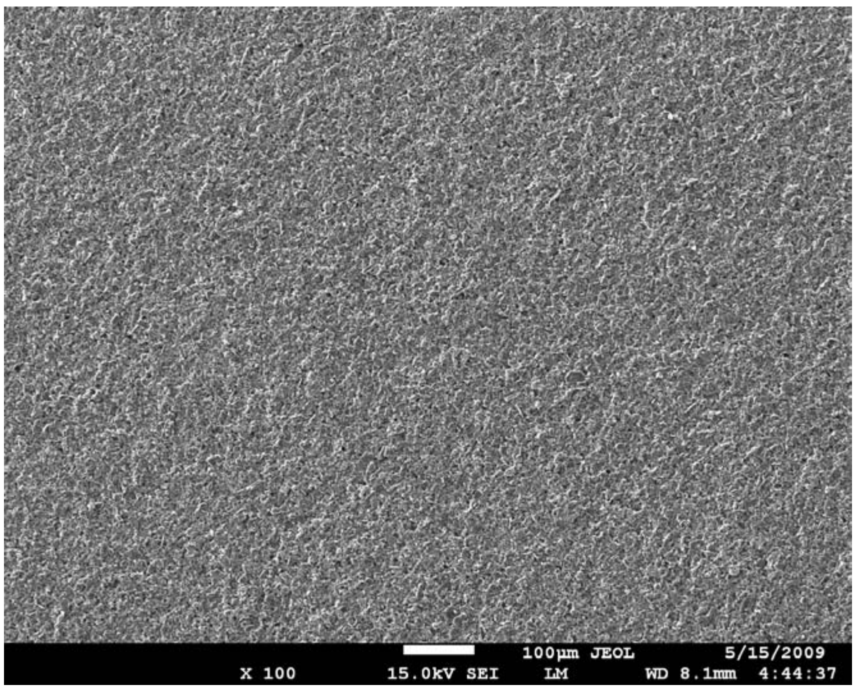
Cycleability follows trends in slurry viscosity and electrode mechanical properties



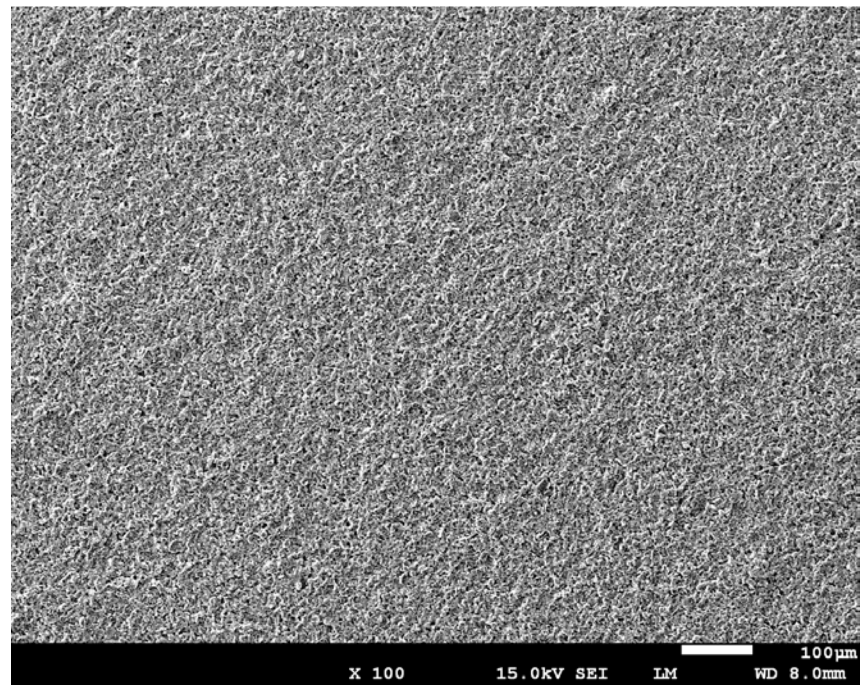
A step change in cycleability; suggests a minimum ultimate strain limit.

Anodes Before Cycling

Glue Process
High Young's Modulus



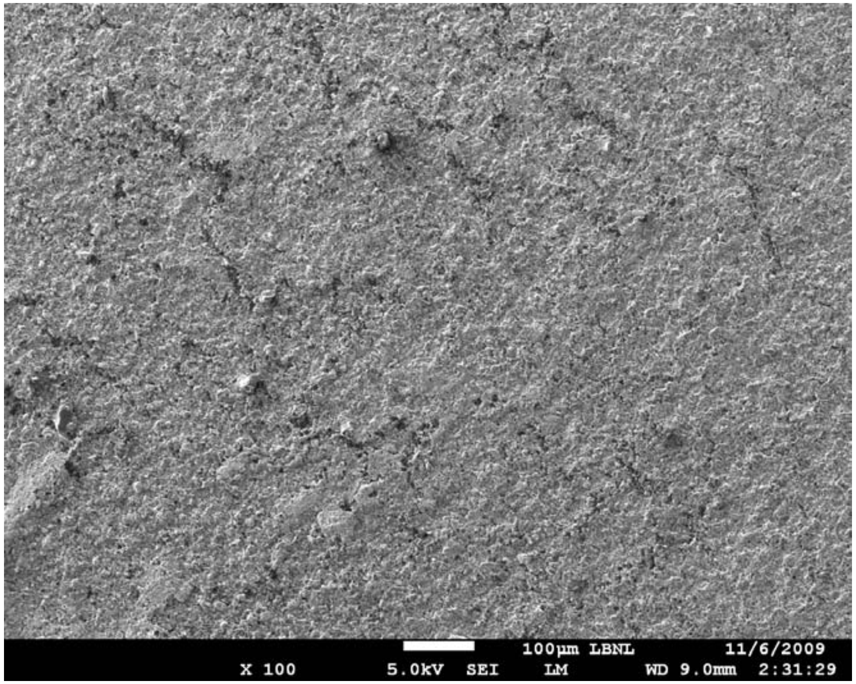
Solids Process
Low Young's Modulus



Appear virtually identical before cycling (close-up slide 7).

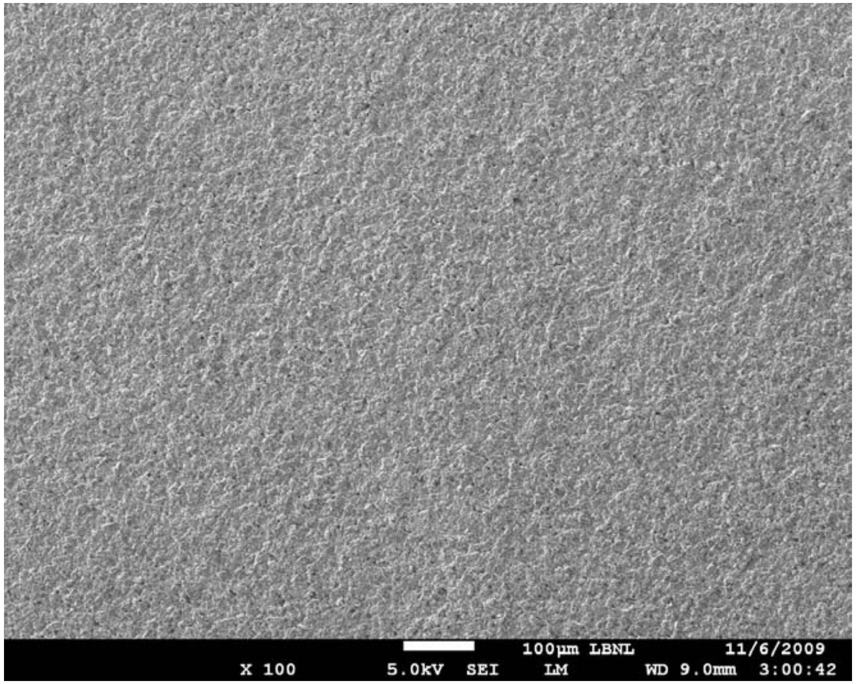
Anodes After Cycling

Glue Process
High Young's Modulus



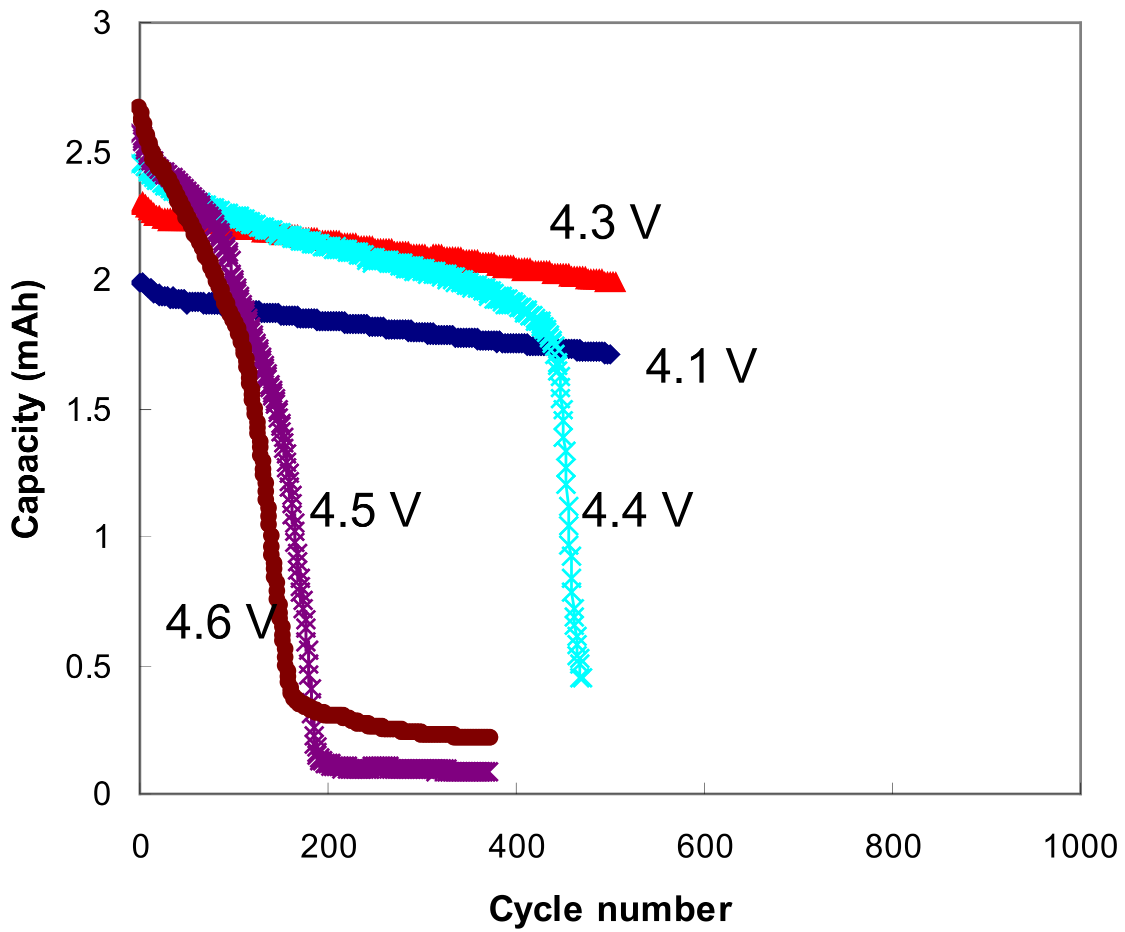
Short Cycling,
Micro cracks throughout!

Solids Process
Low Young's Modulus



Long Cycling!

Gr./NCM Cycled to Different Cut-off Voltages in 1M $LiPF_6$ in EC:DEC 1:2

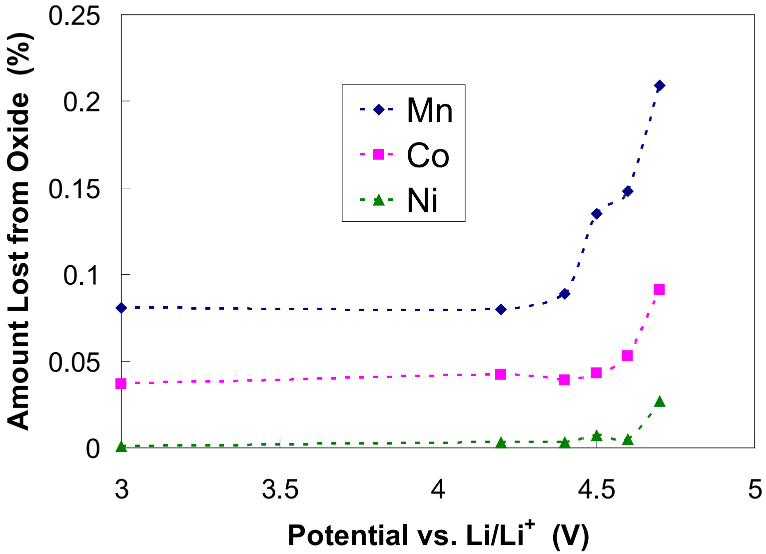


Electrodes at 4.3 and 4.1 V are still cycling.

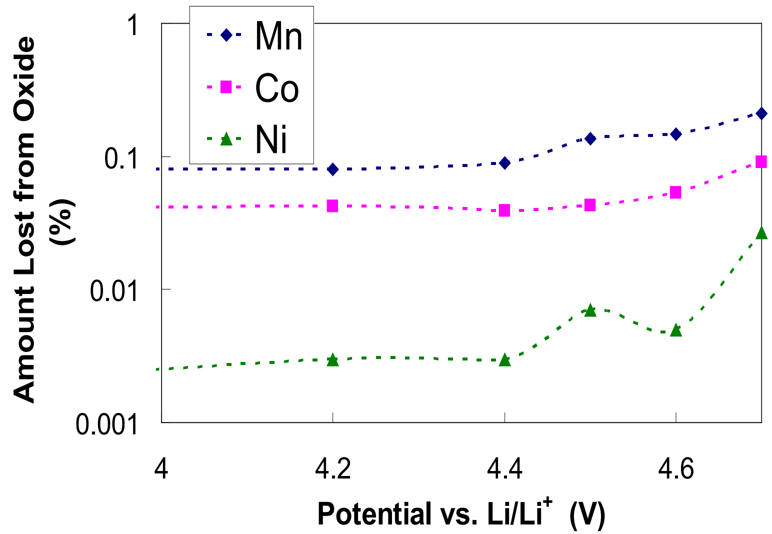
Measurement of Cations from Cathode found on a Li Counter Electrode as a Function of Voltage

Electrolyte: 1 M $LiPF_6$ in EC: DEC 1:2

Mn, Co, and Ni Dissolution *vs*. Potential When Held for 10 days at 30°C.



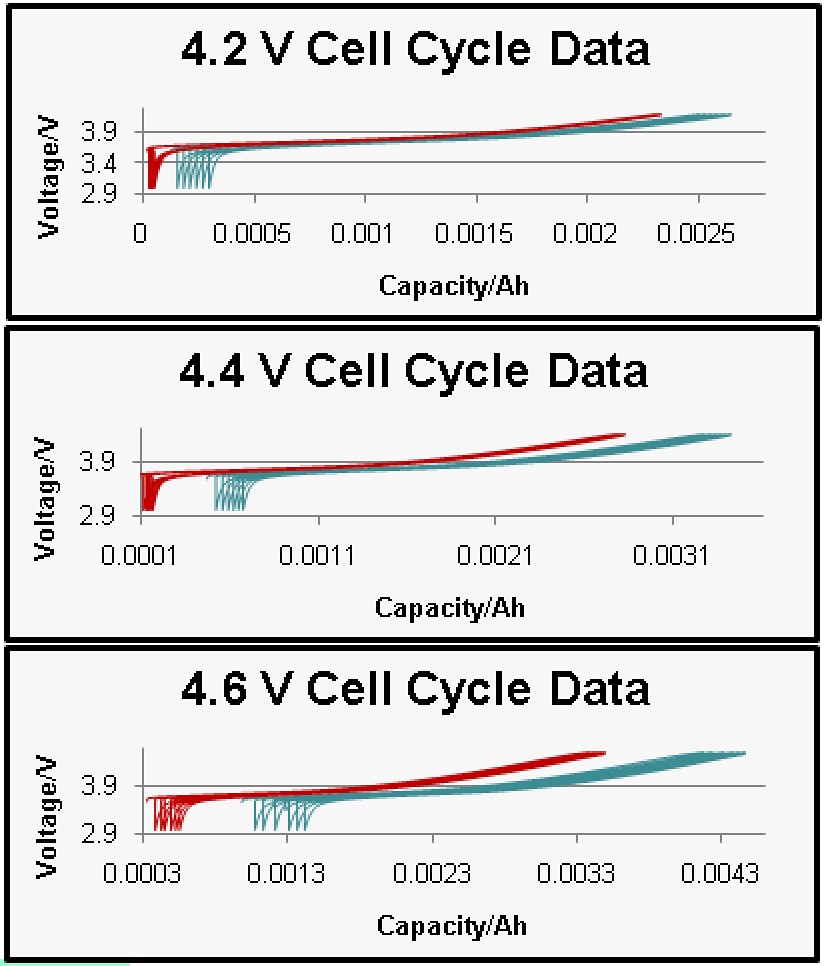
Mn, Co, and Ni Dissolution *vs*. Potential When Held for 10 days at 30°C



Same data re-plotted

Clear increase in dissolved species starting at 4.5 V

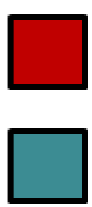
Half-cell Evaluation of High-Voltage Electrolyte from Daikin

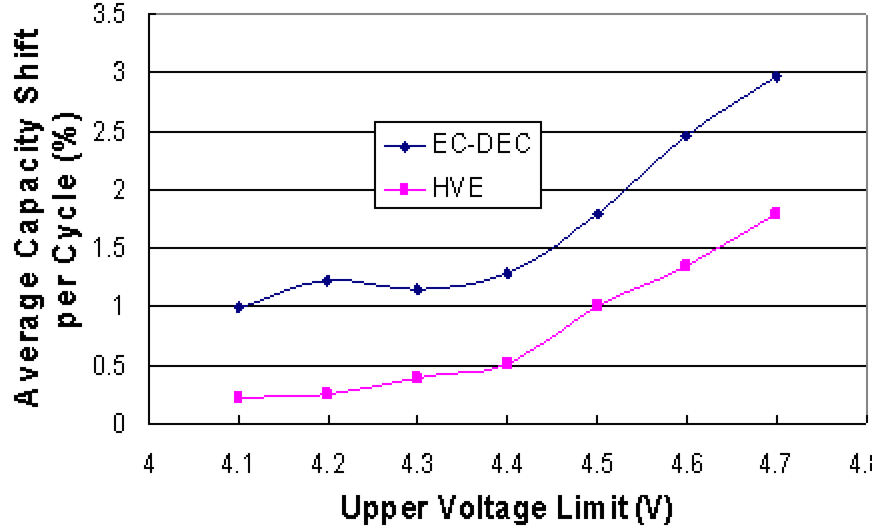


D. Cheung

Speed: C/10

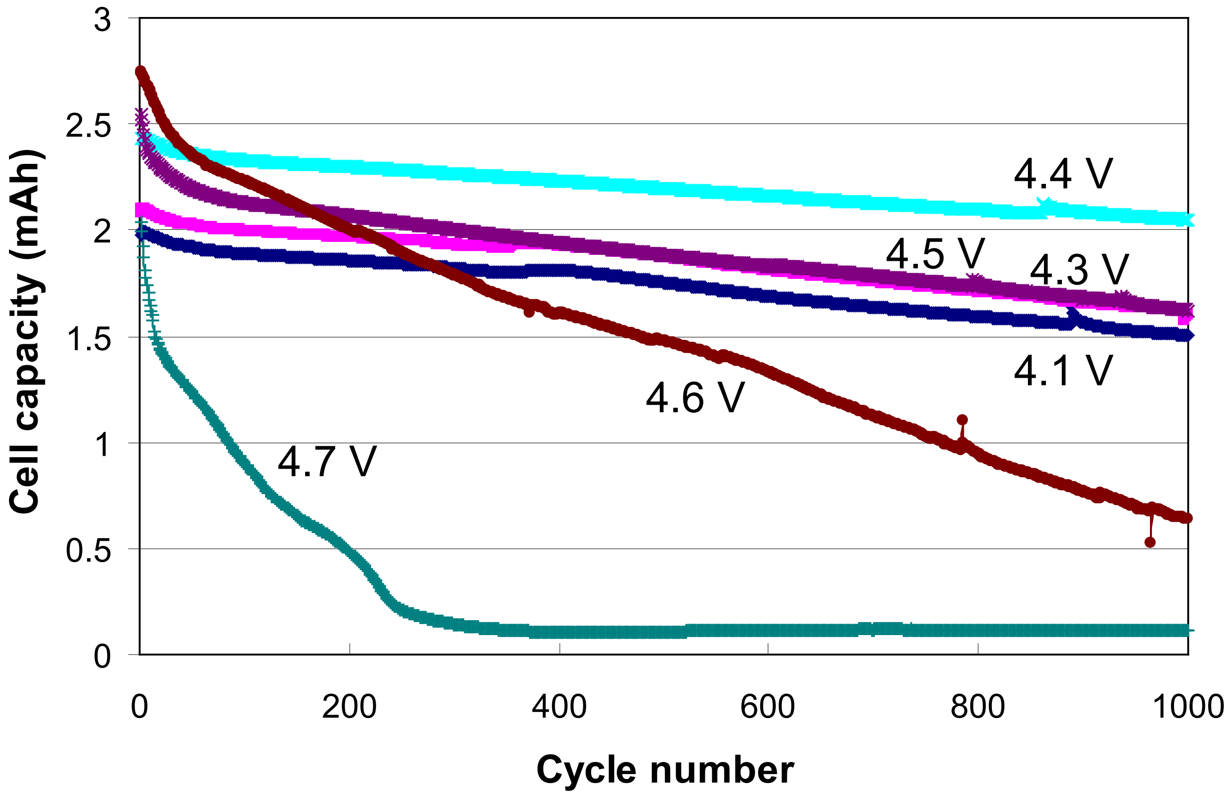
Step up in Voltage





- The side reaction in EC:DEC is greater than in the high voltage electrolyte (HVE) at all voltages.
- The difference is relatively constant at 0.75% shift of capacity every 20 hours.

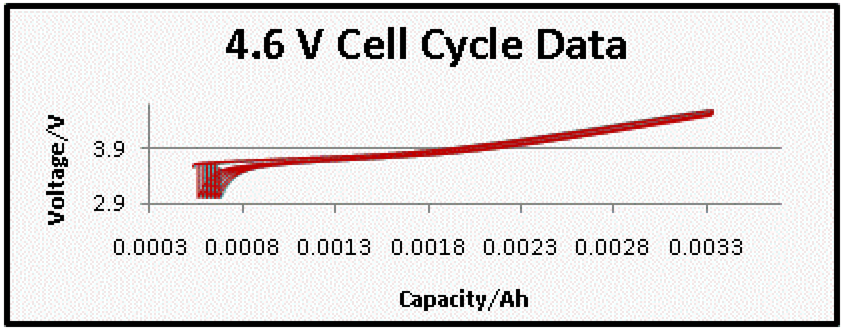
Gr./NCM in High-Voltage Electrolyte

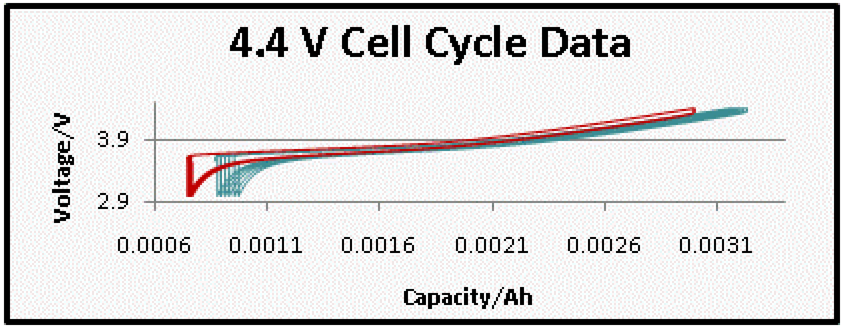


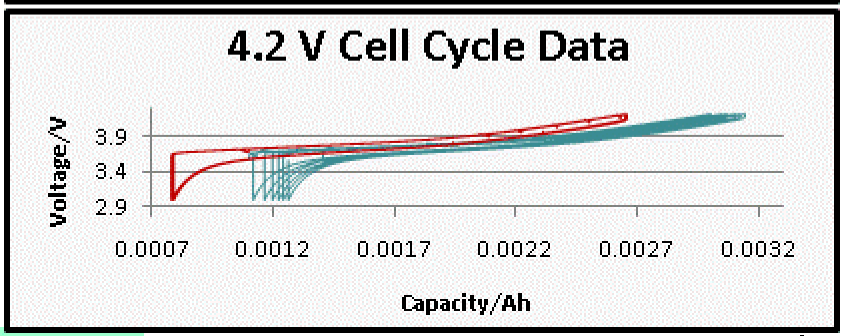
High-voltage electrolyte allows improved cycling at all voltages and allows long-term cycling of cells up to 4.4 V from 4.3 V.

Technical Accomplishments: Cell Failure

Half-cell Evaluation of High-Voltage Electrolyte from Daikin

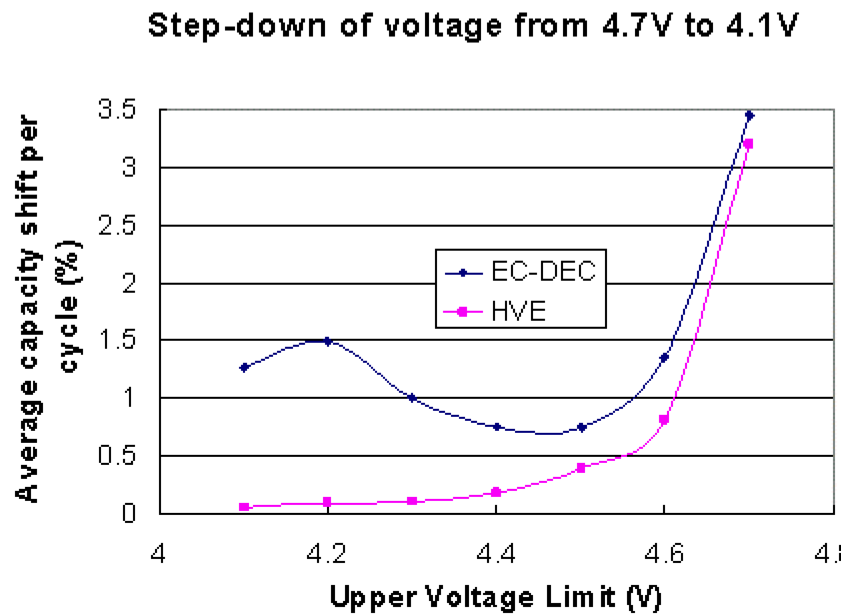






D. Cheung

Speed: C/10



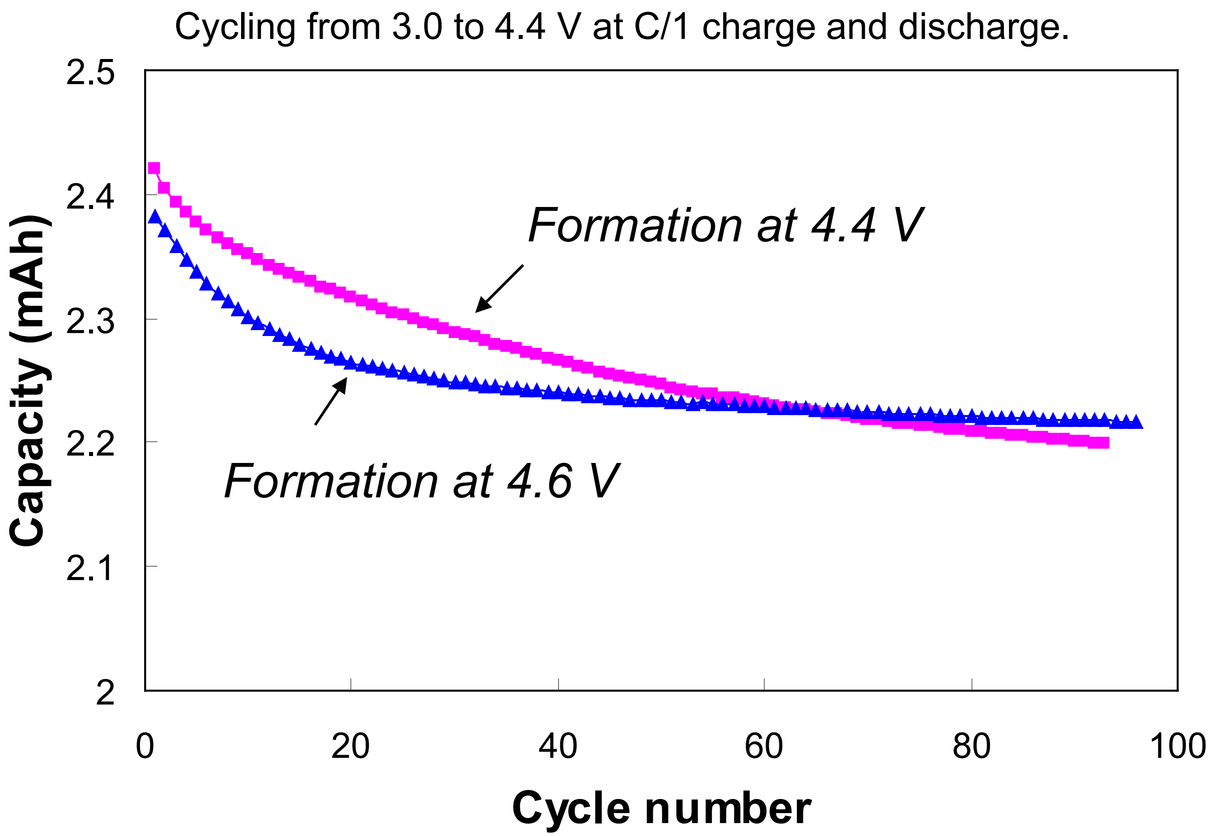
Step down in Voltage

HVE

EC:DEC

- When starting from a high voltage and stepping down, the shifting at 4.7 V is larger then when stepping up to 4.7 V.
- This suggests that the surface has changed by the time one reaches 4.7 V.
- The change with the HVE is protective at lower voltages.

Formation at Different Voltages



Electrodes first cycled 7 times at C/10 to indicated upper cut-off voltage

Electrodes sent to Diagnostics for analysis.

Collaborations

Investigator	Institution	Interaction	Investigator	Institution	Interaction
V. Srinivasan	LBNL	Made Si-based electrodes and half cells	K Zaghib	HQ	Supplier of materials
J. Newman	LBNL	Showed how to make electrodes and cells	J.-W. Park	UCD	Supplied cells.
J. Cabana-Jimenez	LBNL	Made electrodes of his material	L. Chunzeng	Veeco Instruments	Supplied aged laminates
T. Richardson	LBNL	Showed how to make electrodes and cells	M. Isaacs	Lockheed Martin	Showed how to make electrodes and cells
R. Kostecki	LBNL	Provided aged electrodes	R. Axelbaum	Wash. Univ.	Showed how to make electrodes and cells
			M. Koh	Daikin	Supplied HVE

Acknowledgment

The majority of this work was carried out by Honghe Zheng, Xiangyun Song, and Paul Ridgway.

Always in Pursuit of Better Electrodes

- Rest of this year
  - Electrode Processing
    - Evaluate other process parameters and materials including
      - Time of mixing
      - Lamination speed
      - Calendering temperature
      - Binders (SBR-CMC)
    - Work with Modeling group to figure out where stress is most important
  - Cell Failure Analysis
    - Work with Diagnostics Group to identify key features of high-voltage electrolyte:
      - The electrolyte shows less reactivity with cathode surface
        - » Does the electrolyte form a film?
        - » Is it simply an issue of reactivity?
    - Will measure the dissolution of NCM in high-voltage electrolyte.

Ahead of schedule on Milestones; none outstanding!

Summary

- Mixing order matters
  - Difficult to discern quality from initial characterization studies.
  - Clearly affects long-term cycleability.
  - Possible that catastrophic cell failure a result more of stress in electrode than in active material particles.

- High-voltage electrolyte from Daikin shows promise
  - Baseline electrolyte shows catastrophic failure at 4.4 V after 500 cycles.
  - Less side reaction with new electrolyte.
  - New electrolyte may create a protective film when cathode is taken to 4.7 V.
  - Pre-formation may lead to improved cycle life.
  - Hope to identify key properties of electrolyte in coming months.