Electrode Fabrication and Materials Evaluation

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DOE OVT Review
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This presentation does not contain any proprietary or confidential information.

Purpose of Work / Barriers

- Purpose:

  To make cells with optimum performance characteristics from a fundamental understanding of electrode construction.

- Barriers:
  - Understanding the role of each component in a composite electrode.
  - Determining the best electrode configuration for a particular application.
    - Fraction of inactive material required to make an optimized electrode.
    - Fraction of porosity.
  - Determining the cycleable voltage limits of a material.
  - Assessing electrode performance in a full-cell.

This work addresses OVT's Performance barrier,

i.e. cycleable energy density.

Responses to Previous Year Reviewers' Comments

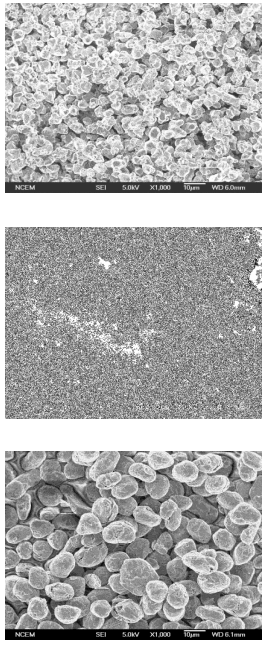
- Recommendation: Mostly consisting of encouragement to continue along the same path of electrode fabrication research, e.g. "*Highly relevant and underappreciated research area…*"
- Recommendation: "*Collaborations with manufacturers are unclear, should be increased*."
  - We do correspond and pay visits to a few U.S. manufacturers.
  - Many manufacturers request copies of our presentations at ECS meetings.
- Recommendation: "*Control water content of materials*."
  - We store all materials in a glove box; we dry all materials and laminates several times during the fabrication process. We intend to study the effect of water content.

Approach

Physical and chemical characterization (BET, PSA, SEM, ICP)

Evaluate carbon/binder/active-material interactions (SEM, TEM, DSC)

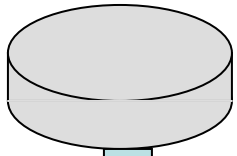
Powders



+
Binder

Fabricate and evaluate in half-cells (Voltage limits)

Cycle in full-cells
(Cycleability)



System modelers

Structural modelers

A bottom-up, comprehensive approach that combines experiments and modeling.

Experts

- Xiangyun Song – Microscopist/Researcher, provides SEMs and TEMs of materials and all physical and chemical analyses.
- Gao Liu – Polymer Chemist, studies the interactions of carbons / binders / active materials (C/B/A).
- Honghe Zheng – Materials Scientist, fabricates and tests different electrode formulations.
- Paul Ridgway – Electrochemical Engineer, evaluates the performance of materials.

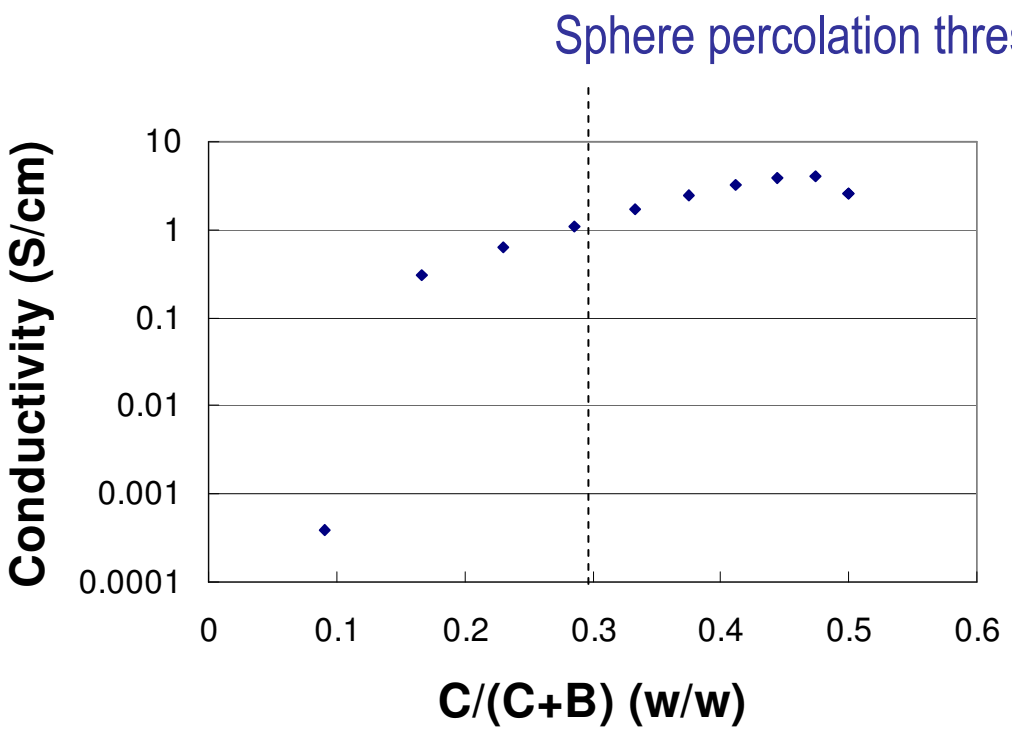
There are four major areas of study that we are presently pursuing *via* our defined Approach:

1. Assess the effects of different combinations of acetylene black / PVdF / $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ on electrode impedance.
2. Assess and compare two Mn-spinel materials for HEV applications.
3. Design and test a $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$-based electrode for PHEV applications.
4. Design and test a graphite-based electrode for PHEV applications.

Accomplishments/Progress/Results (cont.)

G. Liu

Project 1: C/B/A



Shown is the conductivity of several combinations of conductive additive and binder measured *via* the four-point probe method.

The percolation threshold for this system is *ca.* 1:5 C:B. SEM shows that carbon is bond into interlinking strands.

The maximum conductivity appears around 4:5. Beyond 5:5 there is not enough binder to maintain film integrity.

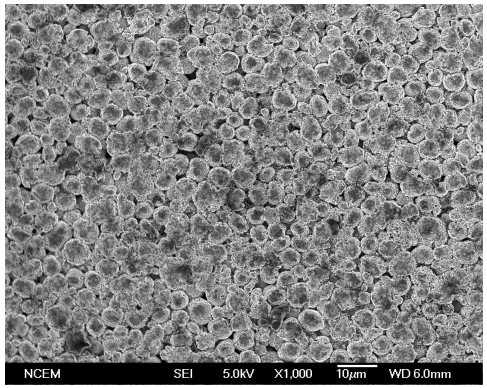
We further investigated these two extremes and points in between

Accomplishments/Progress/Results (cont.)

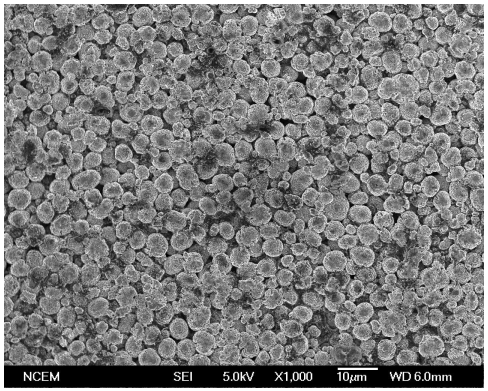
G. Liu, X. Song

Project 1: C/B/A

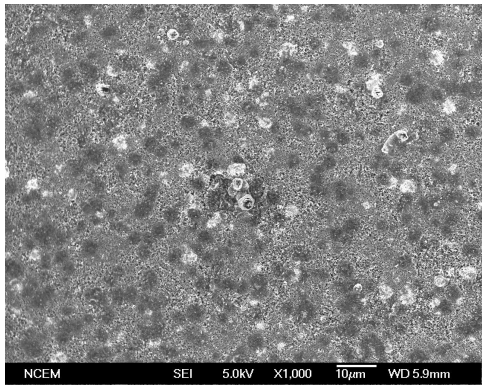
1:5 C:B SEMs



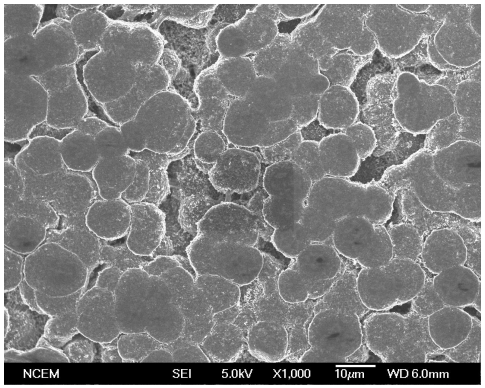
97.6% A



95.2% A



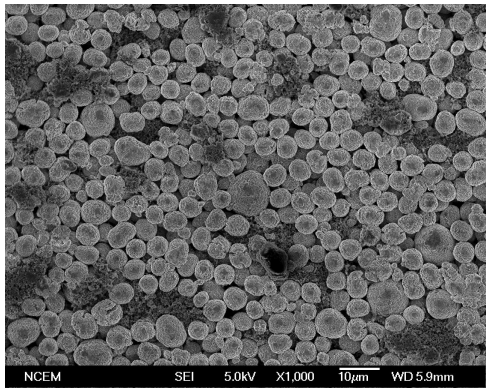
90.4% A



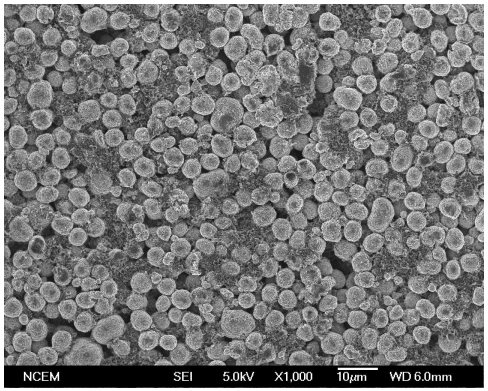
76% A

4:5 C:B

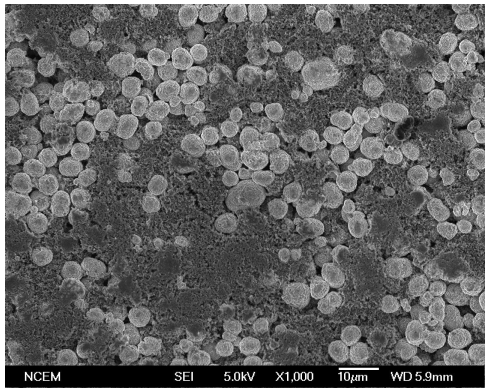
— 10 μm



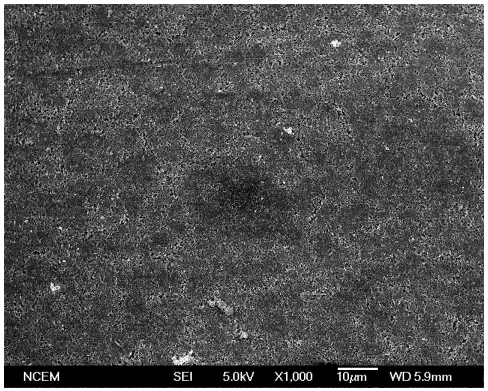
96.4% A



91% A



82% A



73% A

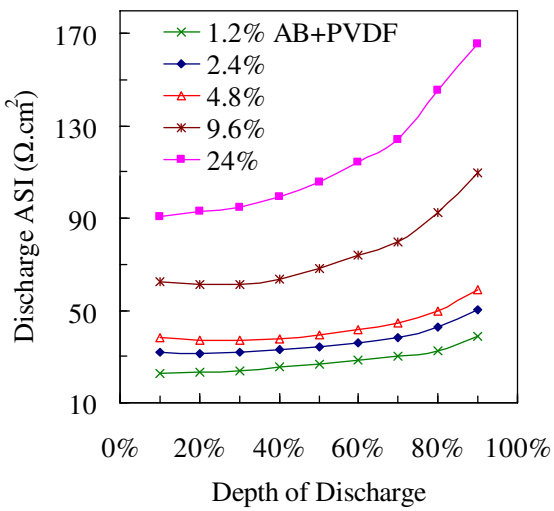
1:5 appears to form a uniform coating of carbon and binder that grows thicker on each particle.
4:5 demonstrates thin coatings and clumping of excess carbon - independent of time of mixing!

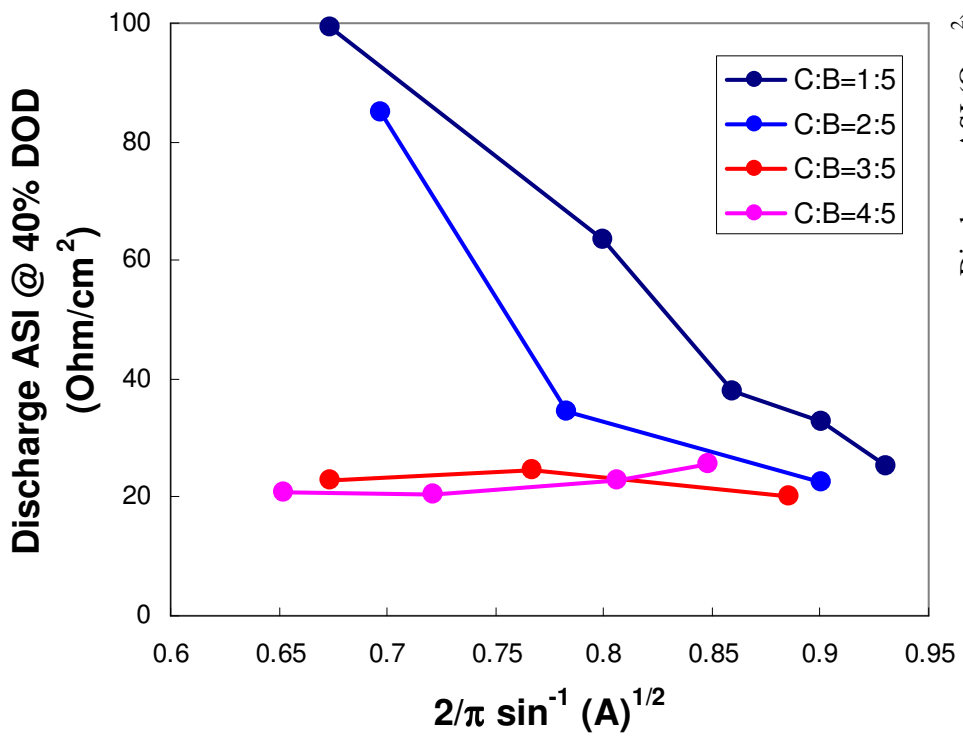
Accomplishments/Progress/Results (cont.)

G. Liu, H. Zheng

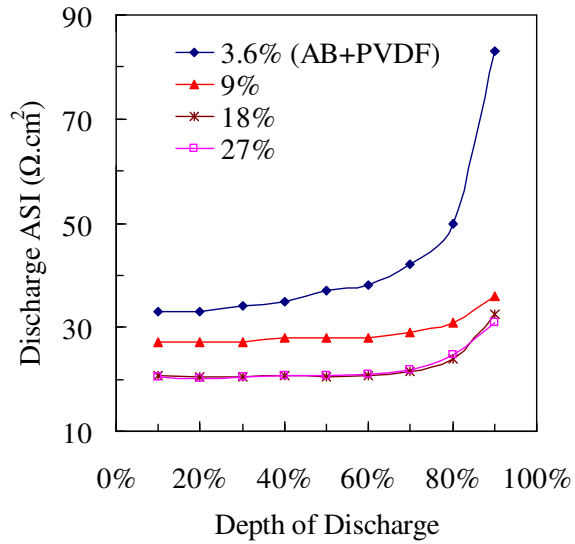
Project 1: C/B/A

1:5 C:B





4:5 C:B



Where energy is not an issue (HEV), a large fraction of C:B of 4:5 will give the lowest impedance.
Where energy density is important, a smaller fraction of C:B ~ 2-3:5 may be the best option.
We now need to evaluate the effect on cycle life.

Accomplishments/Progress/Results (cont.)

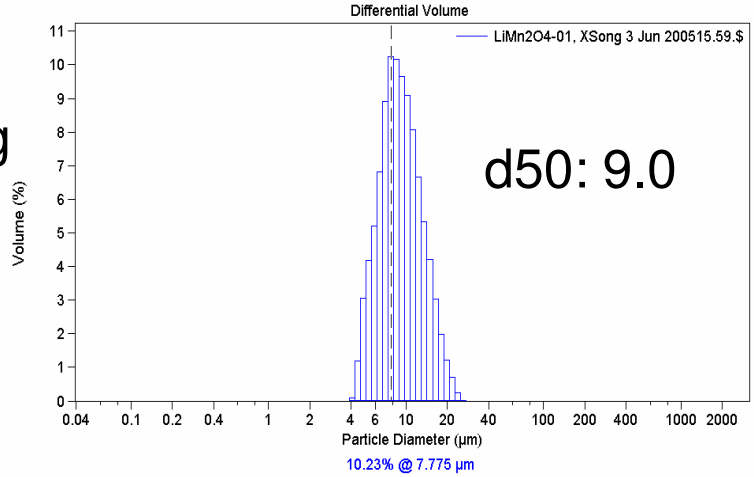
Project 2: Toda vs. BATT doped Mn-Spinel

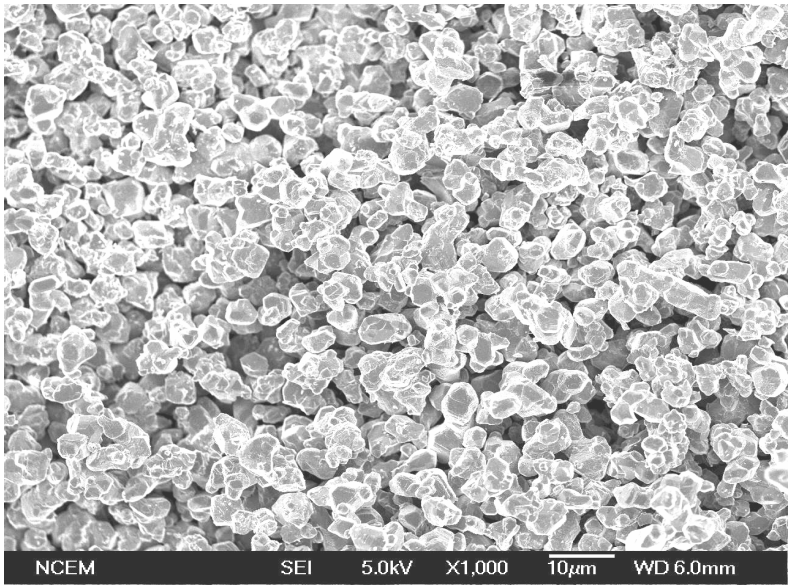
X. Song

Toda Li-doped Mn-Spinel

$LiMn_{1.85}Li_{0.15}O_4$

BET = 0.54 m^2/g

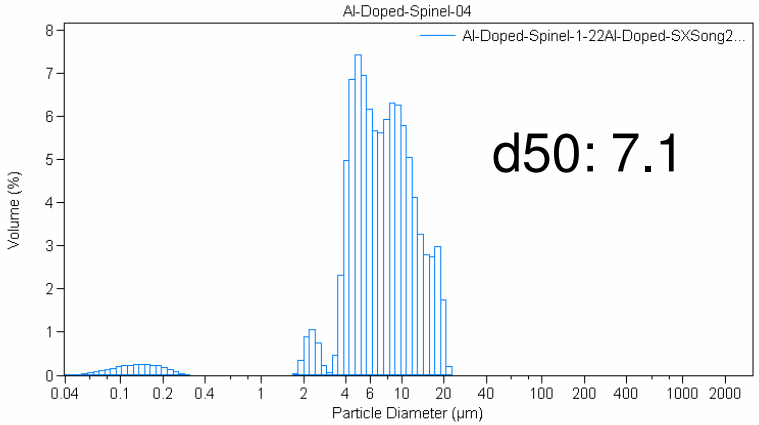


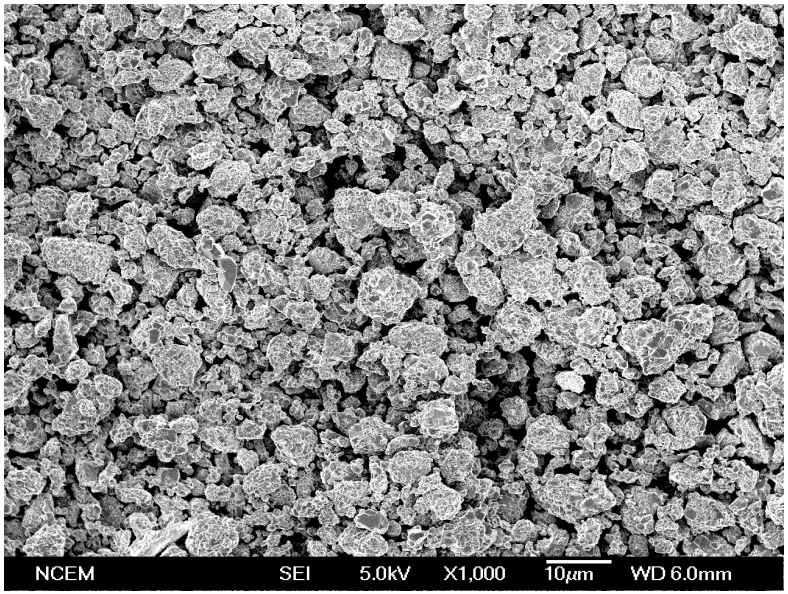


BATT Mn-Spinel

$LiMn_{1.85}Li_{0.075}Ni_{0.04}Cu_{0.035}O_4$

BET = 0.53 m^2/g

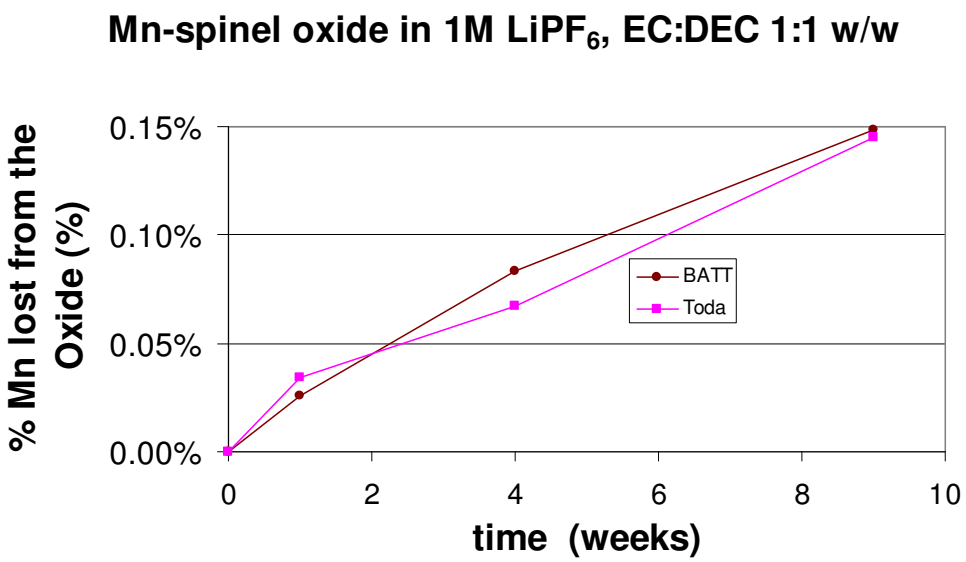




Accomplishments/Progress/Results (cont.)

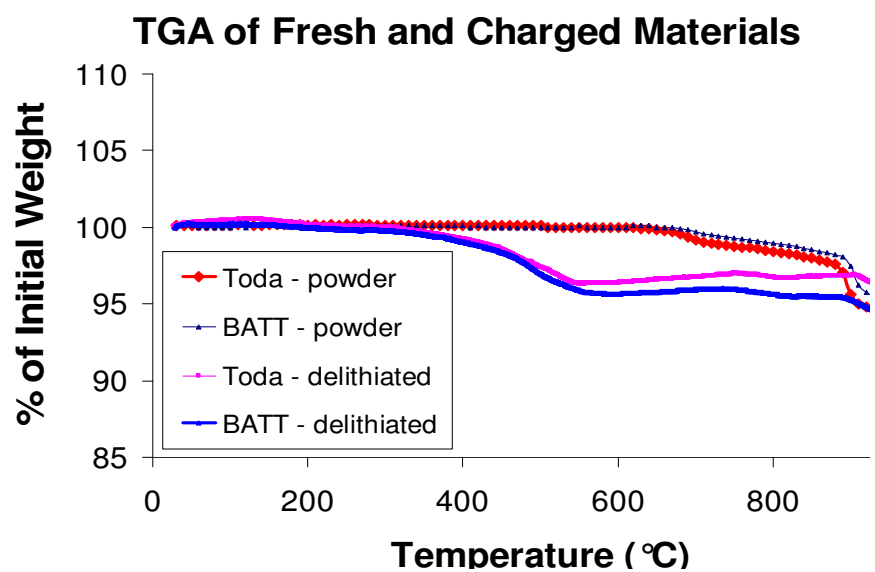
Project 2: Toda vs. BATT doped Mn-Spinel

X. Song



Materials show similar rates of loss of Mn in electrolyte.

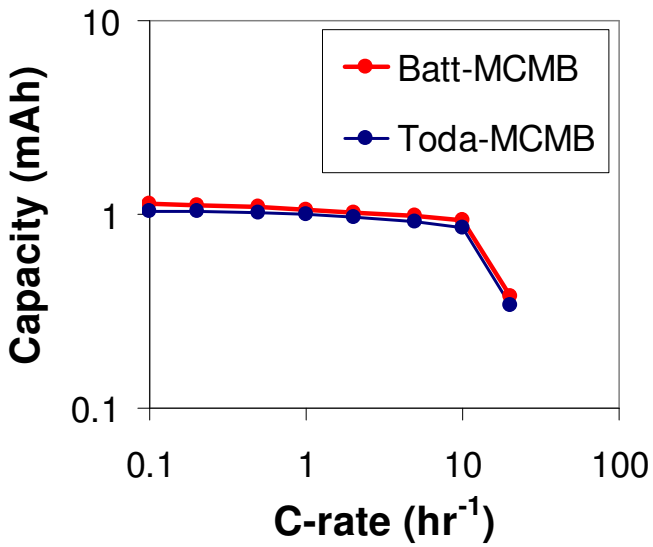
Materials show similar thermal stability properties.

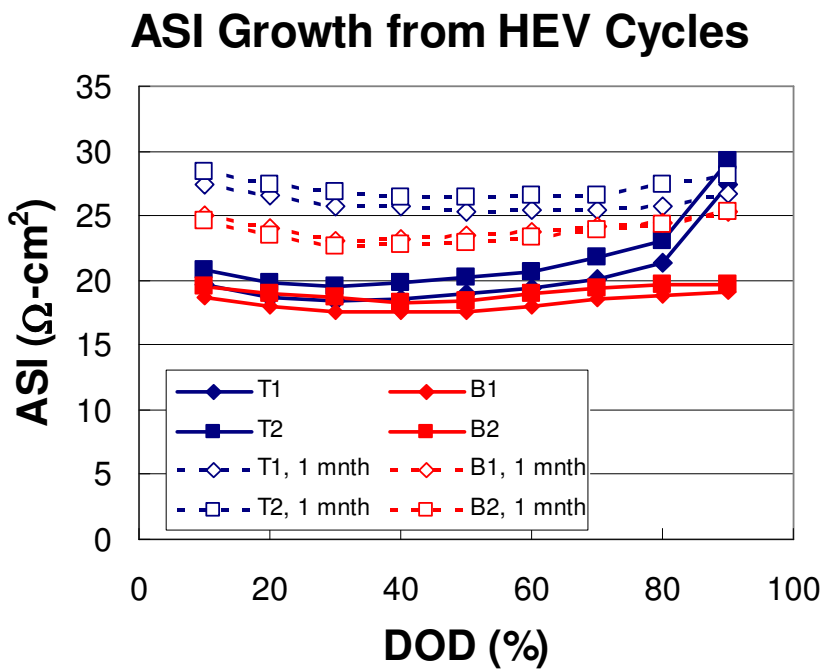


Accomplishments/Progress/Results (cont.)

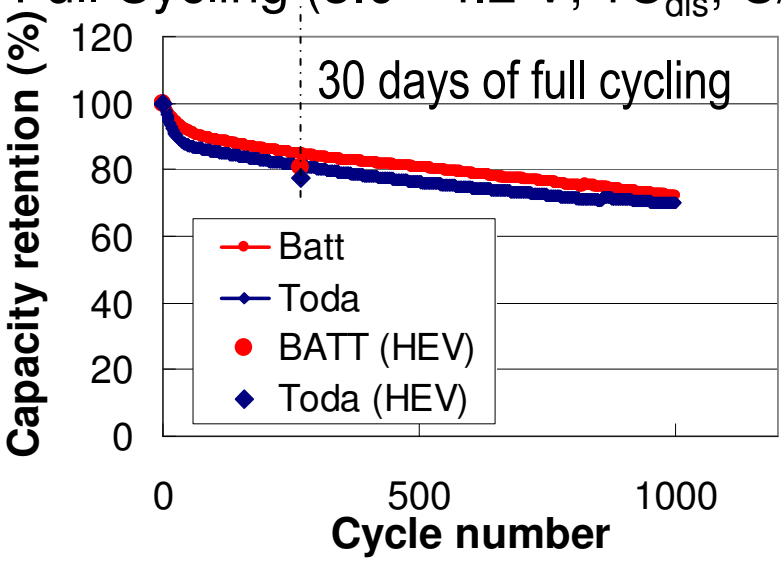
Project 2: Toda vs. BATT doped Mn-Spinel

H. Zheng





Full Cycling (3.0 - 4.2 V; $1C_{dis}$, $C/2_{chg}$)



Overall, performance of these two equally-doped materials is remarkably similar; although, the BATT material has 6% more cycleable capacity.

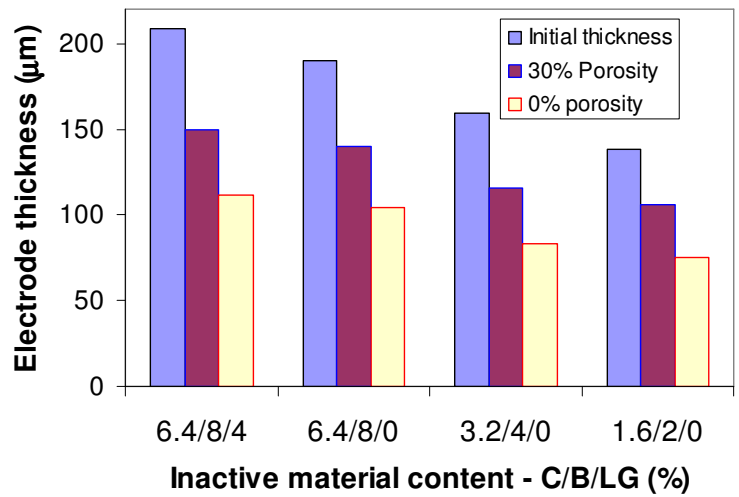
Accomplishments/Progress/Results (cont.)

Project 3: Optimized Cathode for PHEV

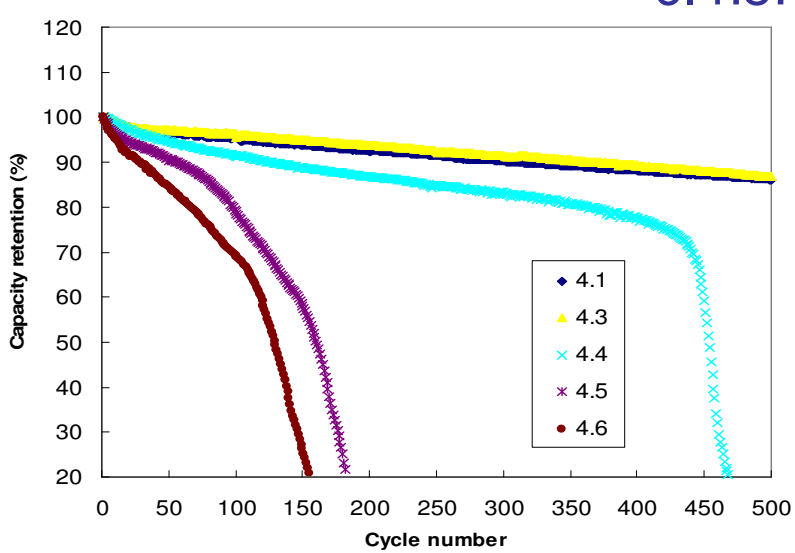
H. Zheng

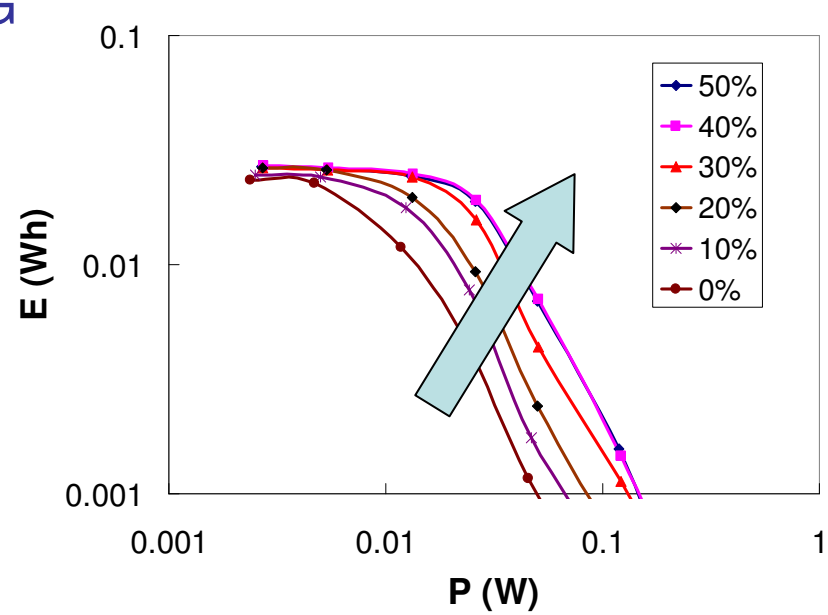
Make electrodes with the same ratio of C:B (4:5) but:

1. with different fractions of active material
   - 81.6, 85.6, 92.8, and 96.4%
2. calendered to different porosities
   - 50, 40, 30, 20, 10, and 0%



6.4:8:4 C:B:LG



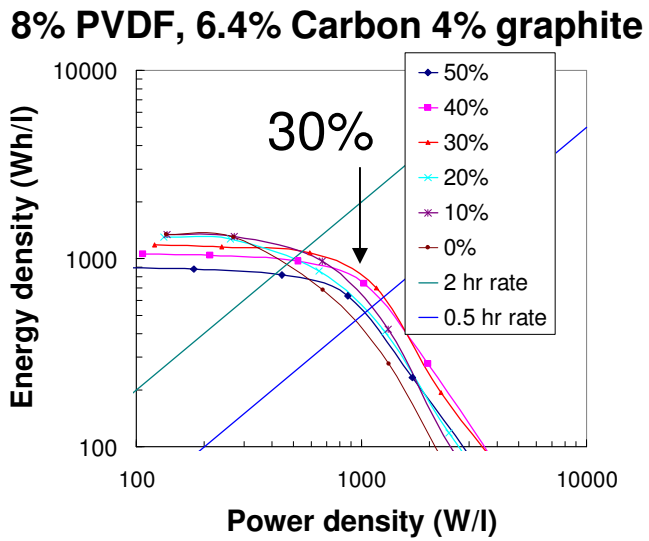


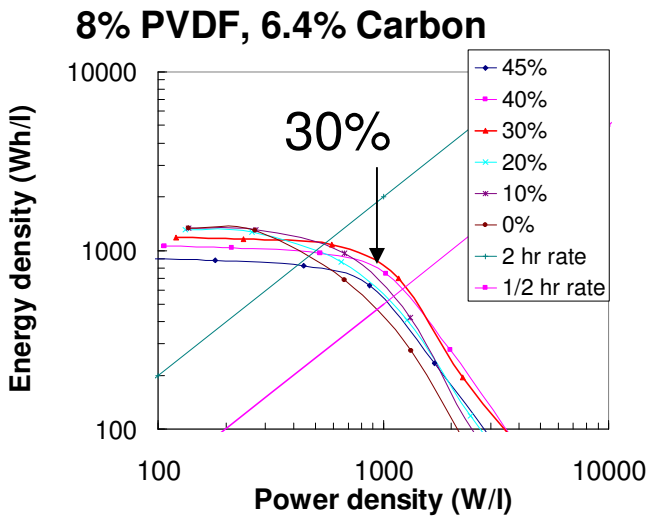
The less the inactive material, the less the volume change; 4.3 V cycleable upper-voltage limit; A spread in performance is seen with electrodes with a high level of inactive material.

Accomplishments/Progress/Results (cont.)

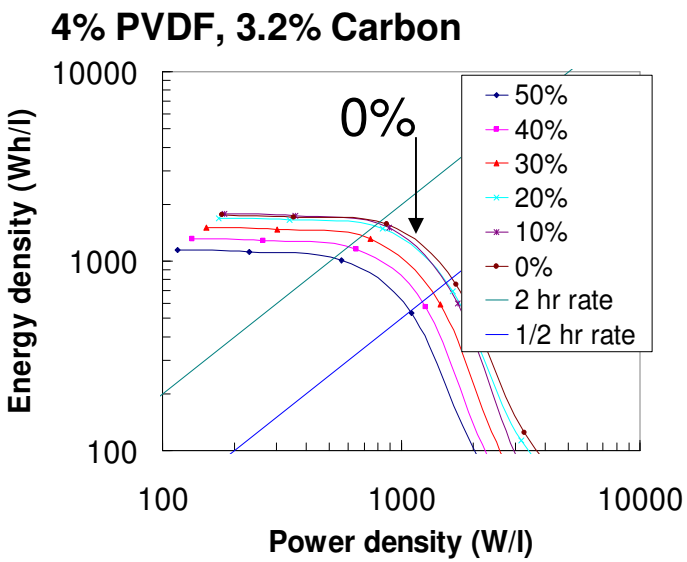
Project 3: Optimized Cathode for PHEV

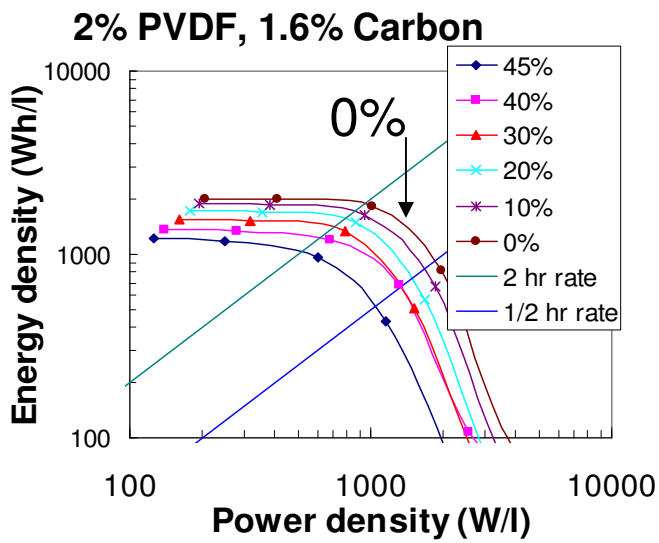
H. Zheng





Performance reductions with calendering are only seen with electrodes with lots of inactive material



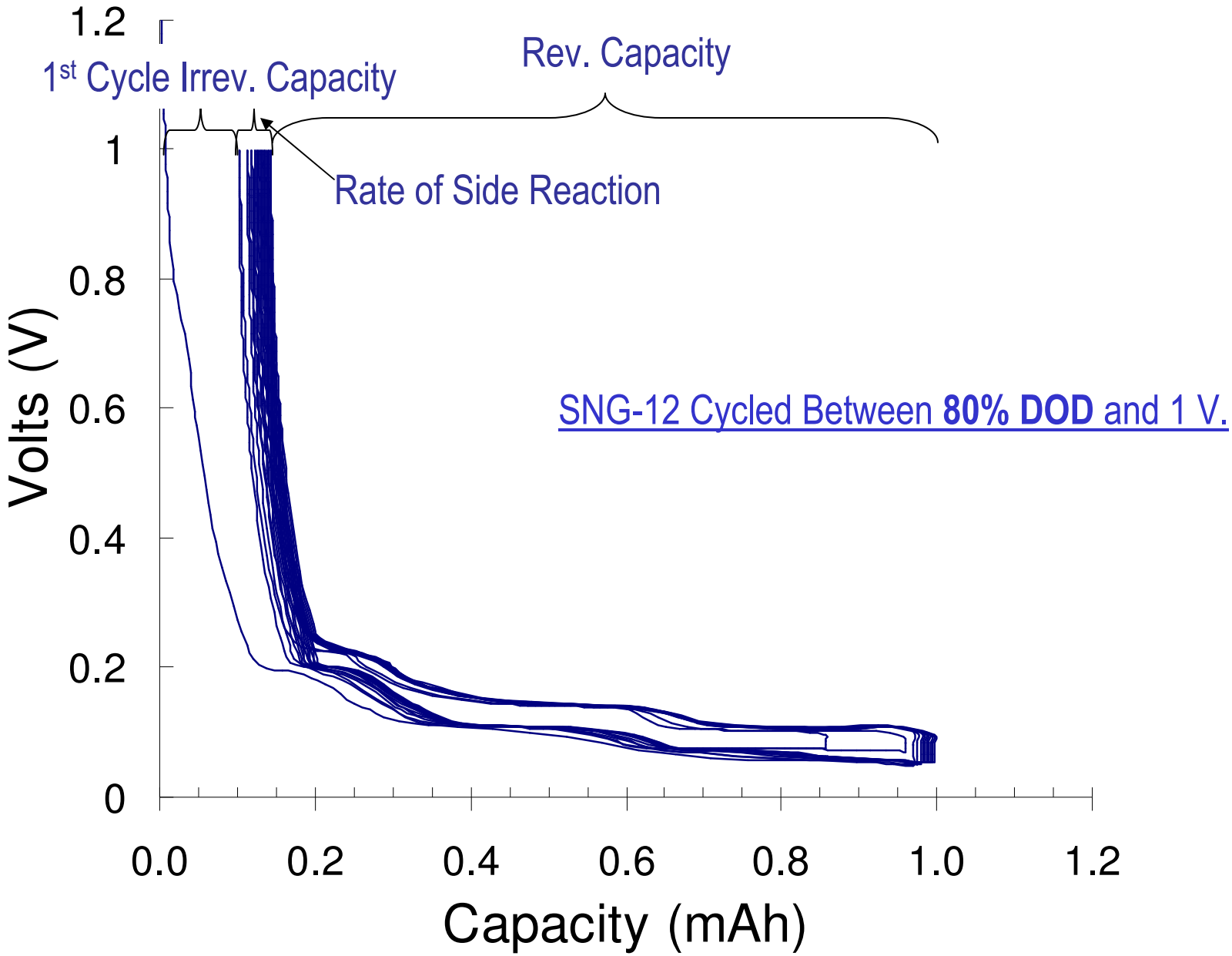


Although the energy density increases with removal of inactive material, the true test will be cycle life!

Accomplishments/Progress/Results (cont.)

Project 4: Optimizing a Graphite Electrode

P. Ridgway

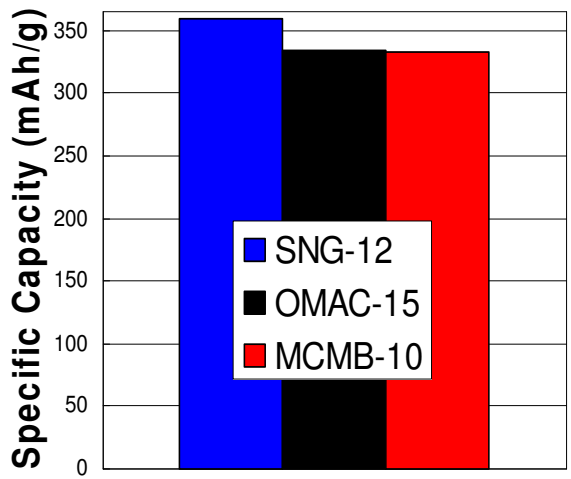


Accomplishments/Progress/Results (cont.)

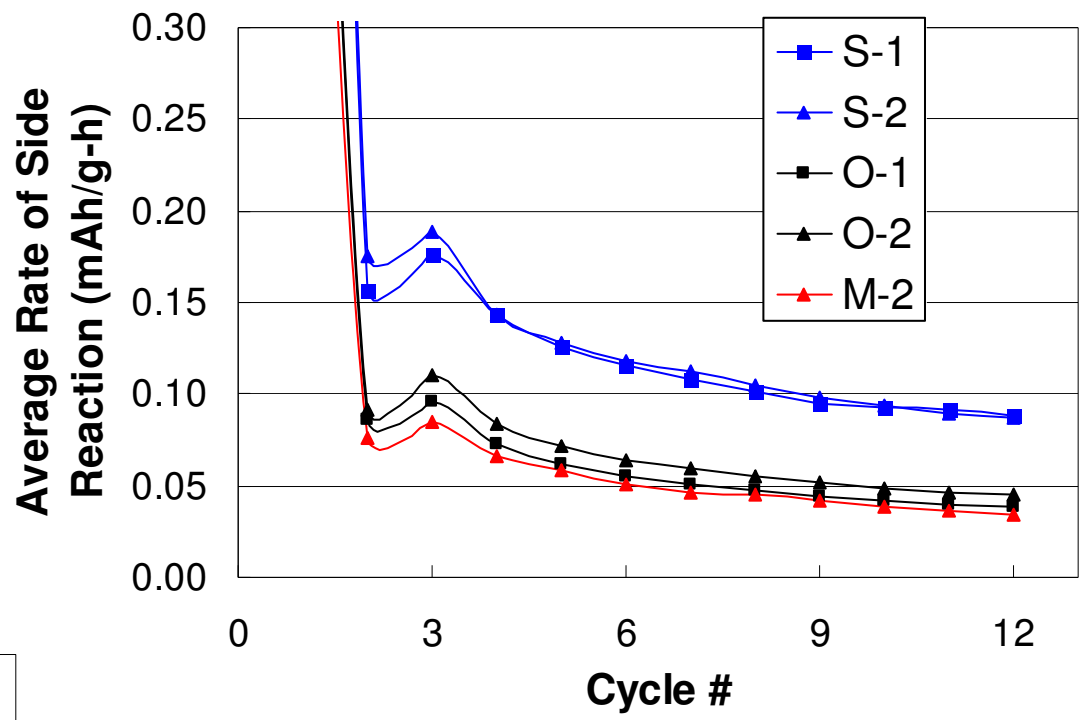
Project 4: Optimizing a Graphite Electrode

P. Ridgway

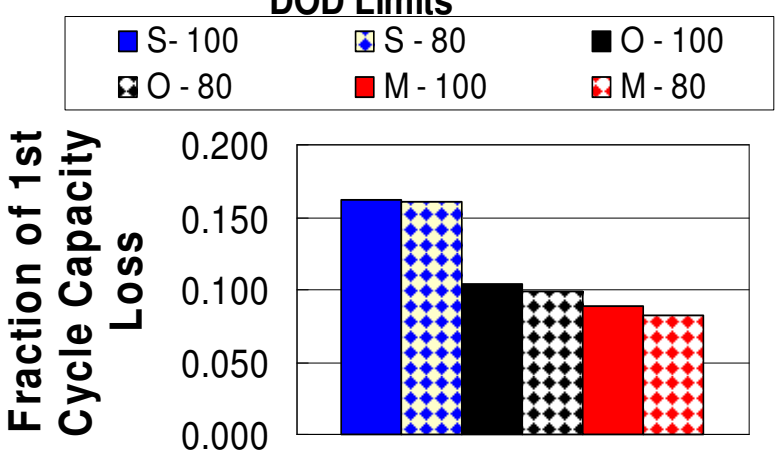
Reversible Capacity 1V to 5mV cycle limits



Average rate of Side Reaction when Discharged to 80% DOD



Comparison of of 1st Cycle Irreversible Capacity Loss Cycled to 80 and to 100% DOD Limits



$$\frac{330\,\text{mAh/g}}{0.05\,\text{mAh/g}\cdot\text{h}} \bullet \frac{1\,\text{day}}{24\,\text{h}} = 275\,\text{days}$$

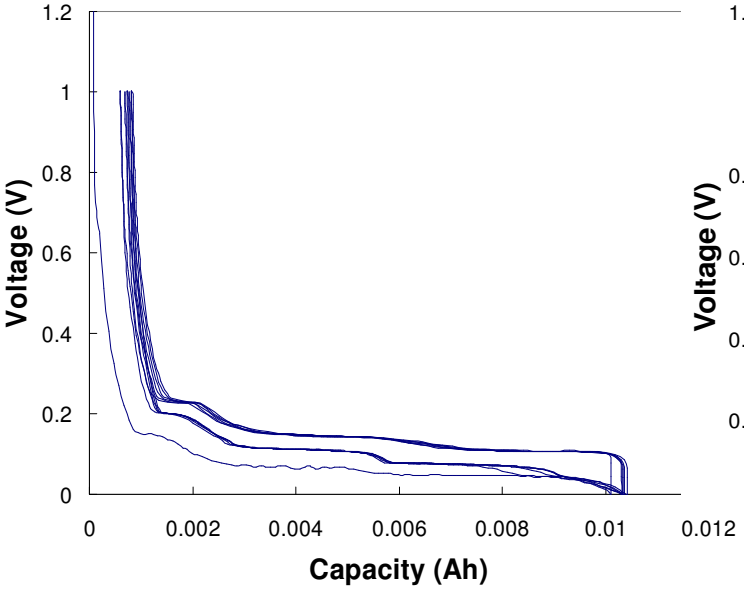
We have selected OMAC to continue with our anode optimization.

Accomplishments/Progress/Results (cont.)

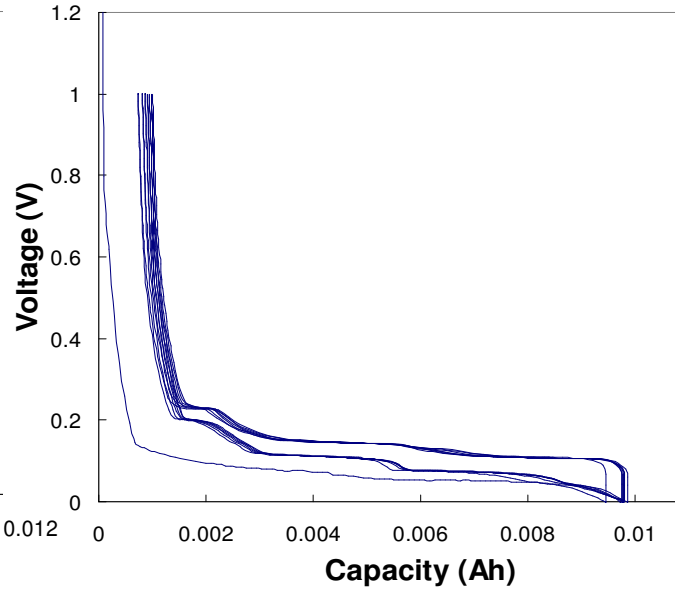
Project 4: Optimizing a Graphite Electrode

H. Zheng

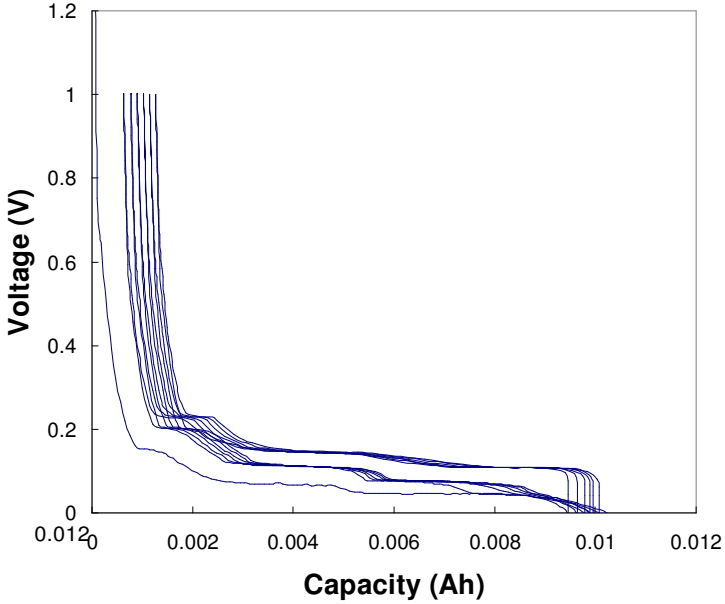
C:B = 0:5



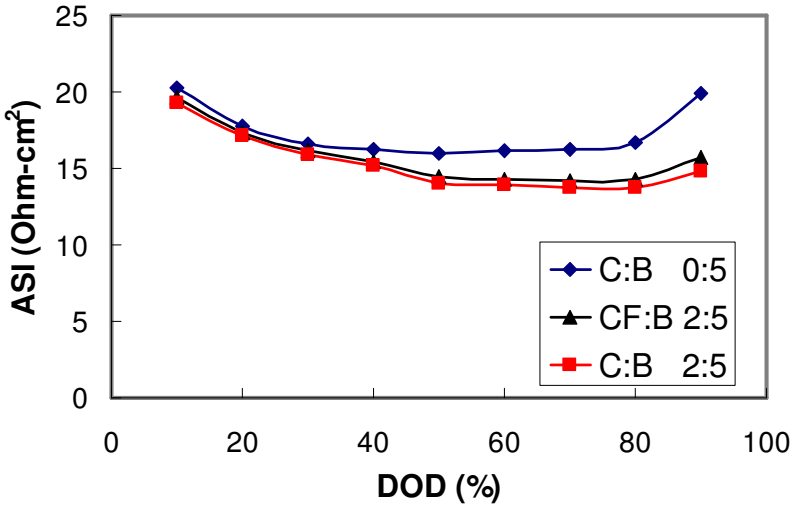
C:B = 2:5



CF:B = 2:5



~175 µm thick



The addition of carbon reduces the impedance of the electrode by *ca.* amount, independent of the type of carbon.

If the carbon is a carbon fiber, the cycleable side reaction is increased by nearly a factor of 3.

Technology Transfer

By studying electrode formulations, different electrode designs, and newly developed materials, battery developers, automakers, and the DOE will have an increased knowledge of the limits of classes of technologies.

This knowledge should accelerate the implementation of the “right” technology into the marketplace.

This information is distributed by visits to US developers and through presentations and publications.

Activities for Next Fiscal Year

Project:

1. Carbon/Binder/Active Material Study
    1. Quantify carbon/binder and binder/active material interactions from DSC experiments.
    2. Evaluate copolymer binders typically used for anodes.
2. Mn-spinel Study
    1. Complete HEV testing.
3. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Study
    1. Evaluate cycle performance using an optimized graphite electrode; will require a DOEx. Milestone – June: On schedule
    2. Evaluate dissolution properties. Milestone – September: On schedule
4. Graphite Study
    1. Optimize electrode design following the same path as the cathode study. Milestone – August: On schedule
    2. Evaluate cycle performance using an optimized cathode electrode (3.1).

Summary

- Potential for petroleum displacement
  - Significant progress in the displacement of petroleum will come about through finding cell chemistries optimized for particular hybrid and full electric applications.
- Approach to research
  - A comprehensive, bottom-up approach to cell making and testing
- Technical Accomplishments and timeliness thereof
  - Carbon/binder/active material interactions suggest different ratios for different applications
  - Mn-spinel evaluation indicates that BATT material is as good or better than commercial material
  - Optimized cathode design suggests cells of 500 Wh/l possible
  - OMAC 15 from Osaka Gas appears to be a suitable replacement for MCMB-10
- Technology Transfer
  - Working with some developers
  - Publications and presentations
- Plans for Next Fiscal Year
  - Carbon/binder/active-material interactions studied with DSC and other techniques
  - Mn-spinel HEV testing to be completed
  - Designing and cycling of an optimized PHEV cell

Publications, Presentations, Patents

- Publications:
  - Y. H. Chen, C. W. Wang, G. Liu, X. Y. Song, V. S. Battaglia, and A. M. Sastry, *J. Electrochem. Soc.* **154** (10), A978 (2007).
  - Gao Liu, Honghe Zheng, Vince Battaglia, Amanda S. Simens, Andrew M. Minor, and Xiangyun Song, *ECS Trans.* **6** (14), 45 (2007).
  - G. Liu, H. Zheng, A. S. Simens, A. M. Minor, X. Song, and V. S. Battaglia, *J. Electrochem. Soc.* **154** (12), A1129 (2007).

- Presentations:
  - Honghe Zheng, Gao Liu, Xiangyun Song, Vince Battaglia, *ECS meeting*, Washington D C., Oct. 13, 2007.
  - Gao Liu, Honghe Zheng, and Vince Battaglia, *ECS meeting*, Washington D C., Oct. 13, 2007.
  - Gao Liu, Honghe Zheng, and Vince Battaglia, *ECS meeting*, Washington D C., Oct. 13, 2007 .
  - Yen-Hung Chen, Chia-Wei Wang, Gao Liu, Xiangyun Song, Vince Battaglia, and Ann Marie Sastry, *ECS meeting*, Chicago, IL May 2007
  - Gao Liu and Vince Battaglia, *ECS meeting*, Chicago, IL May 2007.

Relevant DOE Goals

- Energy density
  - EV:
    - 230 Wh/l minimum goal for long-term commercialization
    - 300 Wh/l long-term goal
  - PHEV
    - 10-mile: 121 Wh/l if only 70% is available for charge depletion
    - 40-mile: 207 Wh/l if only 70% is available for charge depletion