Electrode Construction and Analysis

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DOE OVT Review
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Purpose of Work / Barriers

- Purpose:

  To provide a fundamental understanding of the role and limitations of the inactive material in a composite electrode in order to make a battery that may meet or exceed the performance targets for either a HEV, PHEV, or EV.

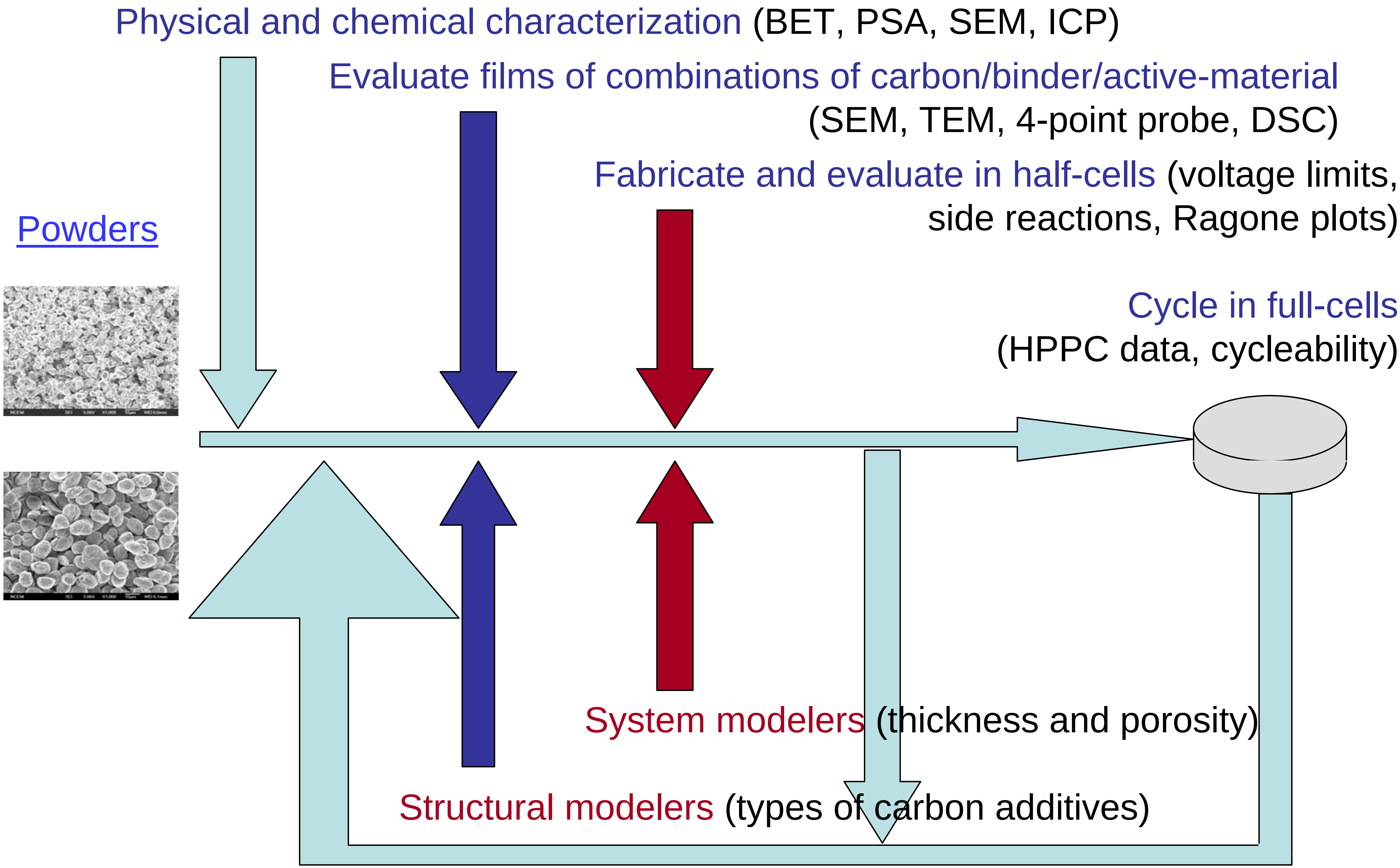
- Barriers:
  - Understanding the role the inactive materials play in a composite electrode.
  - Understanding the effects of varying the levels of inactive materials on the performance of an electrode
    - Rate performance
    - Cycle life

This work addresses OVT's performance barriers for HEVs, PHEVs, and EVs of cycleable, high energy- or power-density systems.

Responses to Previous Year Reviewers' Comments

- <u>Recommendation:</u> Mostly consisting of encouragement to continue along the same path of electrode fabrication research, e.g. "*Highly relevant and underappreciated research area*…"
- <u>Recommendation:</u> "*Collaborations with manufacturers are unclear, should be increased*."
  - Many manufacturers request copies of our presentations
  - We visit a handful of U.S. battery manufacturers every year.
- <u>Recommendation:</u> "*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



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

Experts

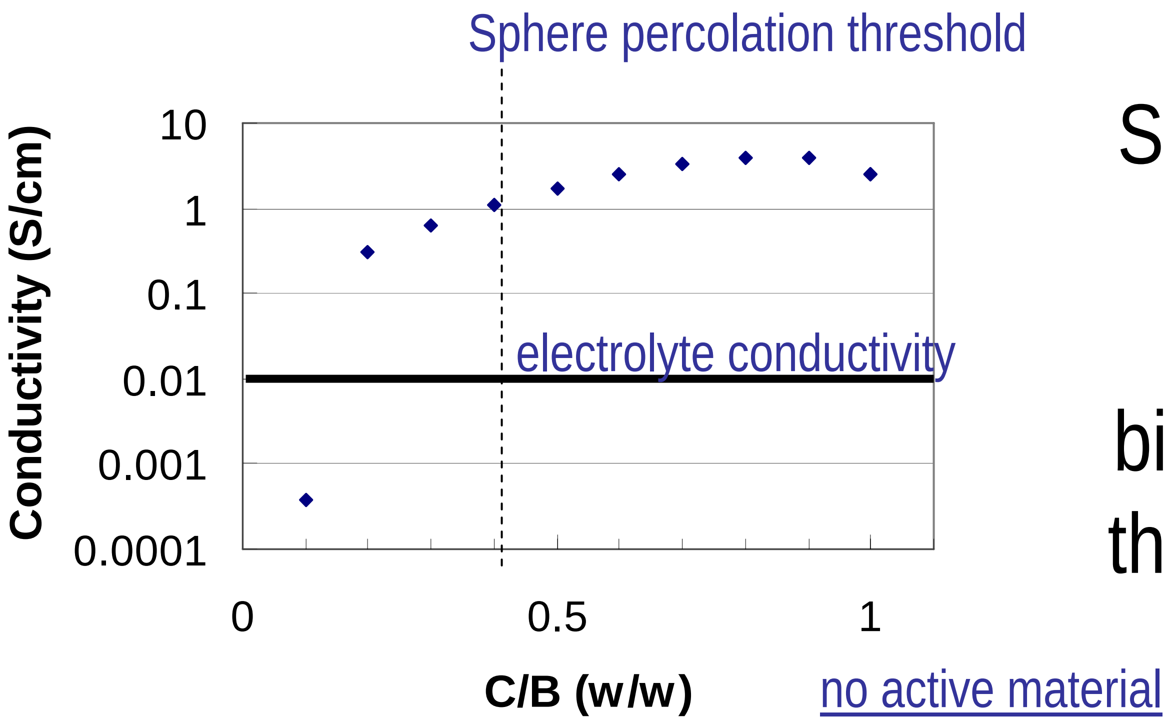
- Xiangyun Song – Microscopist/Researcher, provides SEMs and TEMs of all of our materials and all physical and chemical analyses.
- Gao Liu, Ph.D. – Polymer Chemist, studies the interactions of carbon additives / binders / active materials (C/B/A).
- Honghe Zheng, Prof. – Materials Scientist, fabricates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

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

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

Today I will present highlights of projects 1. and 4.

Project 1: Interactions of C/B/A (Carbon/Binder/Active material)



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

C – Denka black
B – KF1100

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

The percolation threshold for this system is *ca.* 1:5 C:B.

We further investigated these two extremes and points in between

Accomplishments/Progress/Results (cont.)

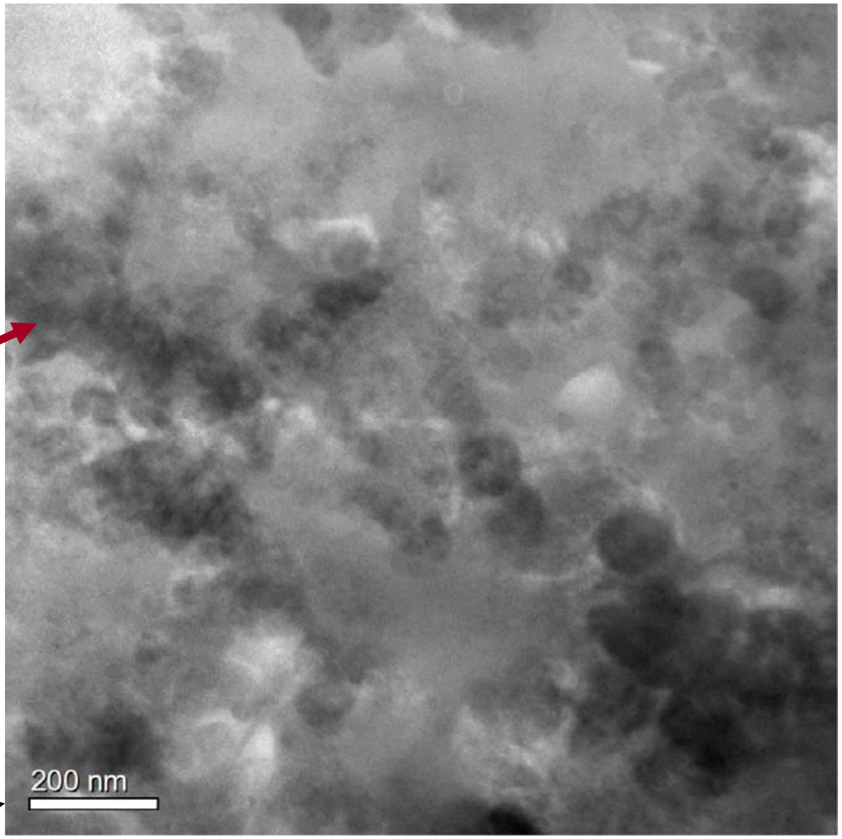
G. Liu

Project 1: C/B/A

C:B = 1:5

TEM

Strands of aggregated carbon



200 nm

The forces for carbon to aggregate are stronger than those that would lead to a uniform distribution in the binder.

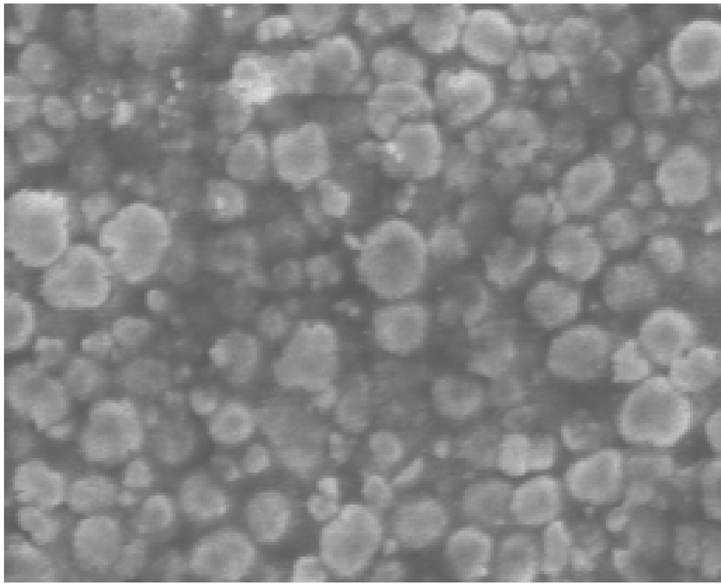
Above 1:5 the **carbon aggregation** forms a continuous **electronic network** that allows for a **lower percolation threshold** than one would expect from random ordering of the carbon.

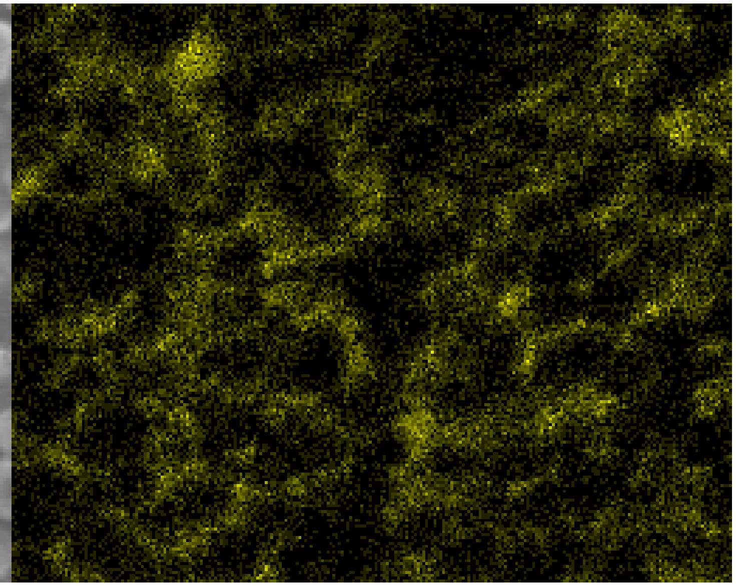
Accomplishments/Progress/Results (cont.)

G. Liu, X. Song

Project 1: C/B/A

C:B = 1:5; 4% B — SEM — EDX - C

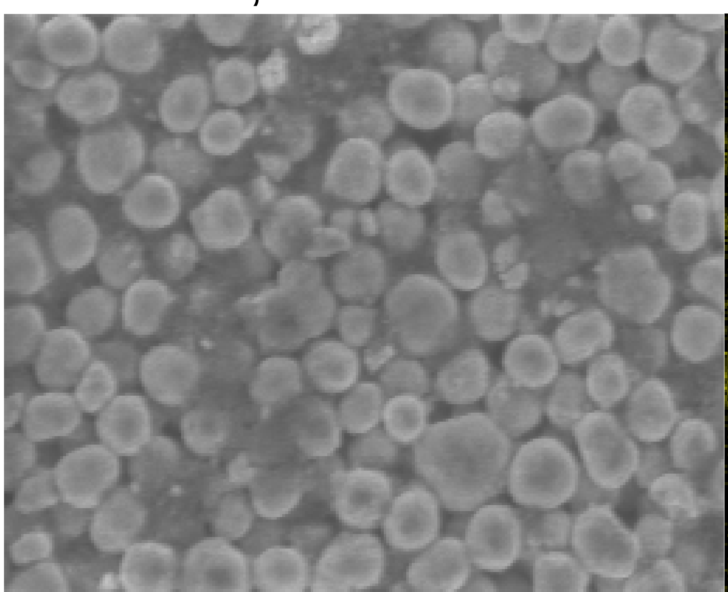


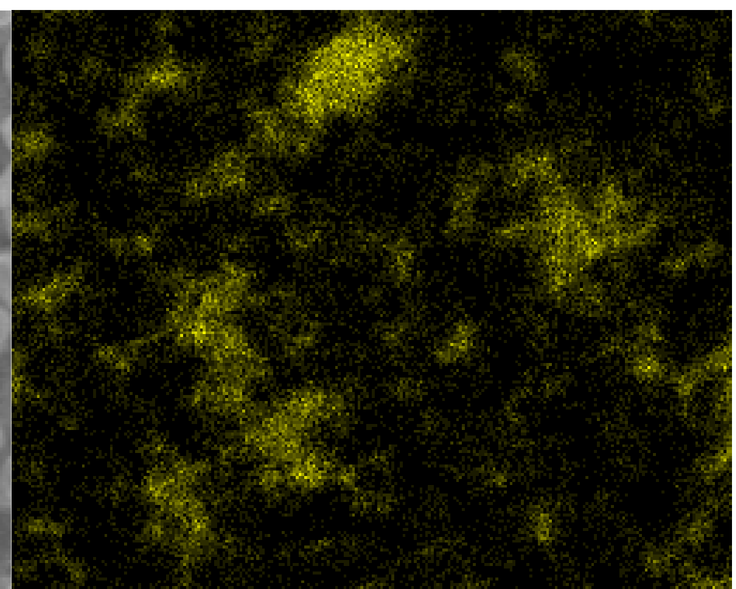


The electrode with ¼ the amount of carbon shows a much more uniform carbon distribution!

Carbon distribution is not improved with increased time of mixing.

C:B = 4:5; 4% B



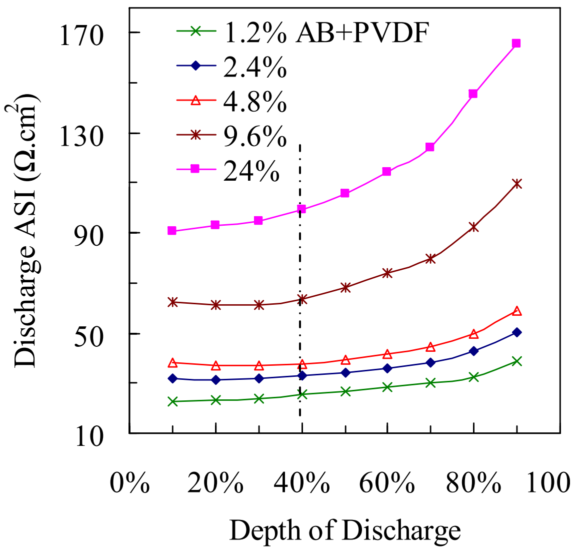


Denka black
KF1100
NCA

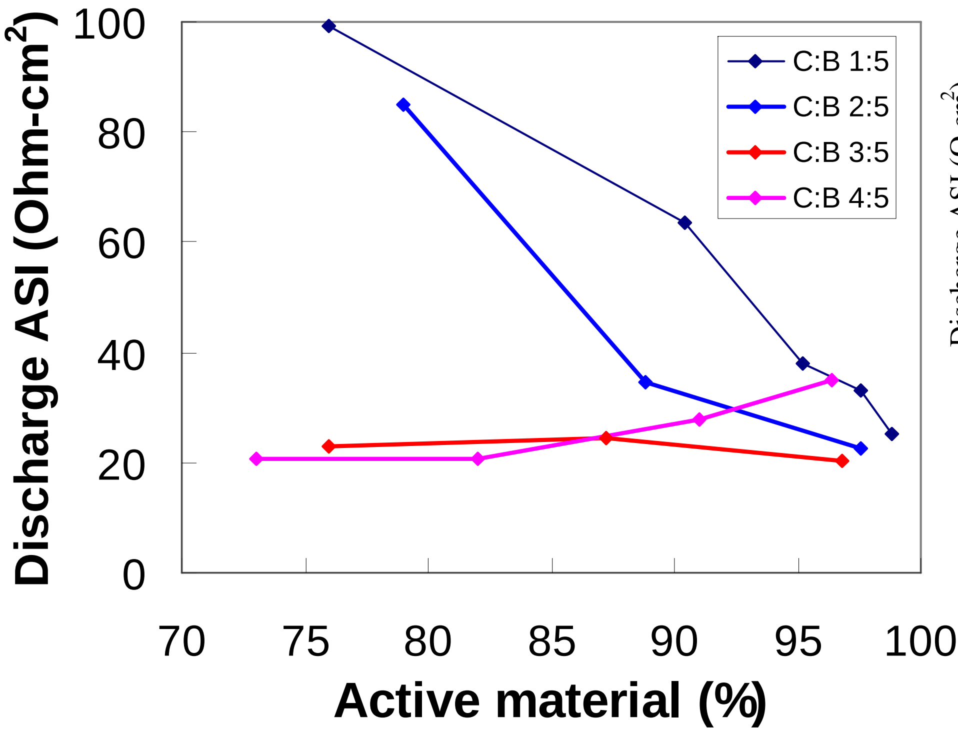
G. Liu, H. Zheng

Project 1: C/B/A

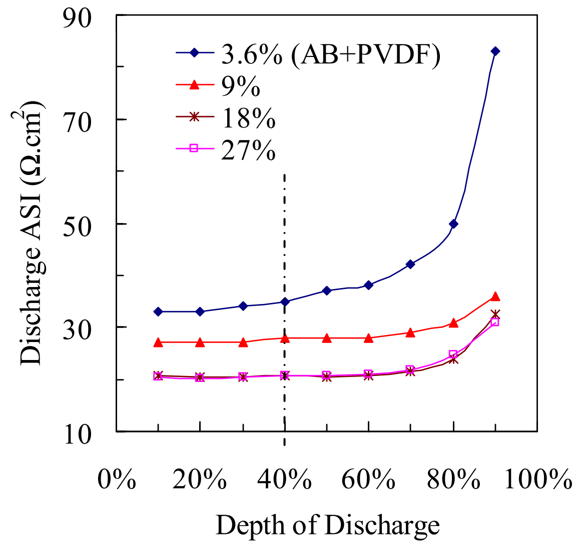
1:5 C:B



~ 50 μm thick



4:5 C:B



vs. MCMB 10-28

Where energy is not an issue (HEV), a large fraction of C:B at 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.

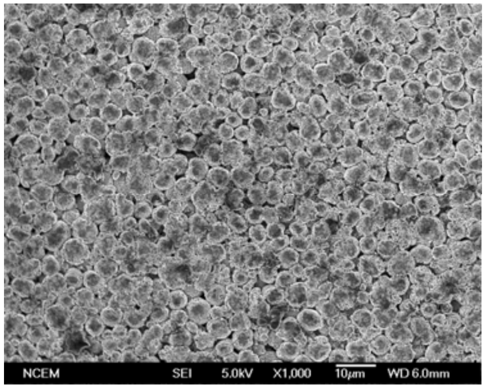
Accomplishments/Progress/Results (cont.)

G. Liu, X. Song

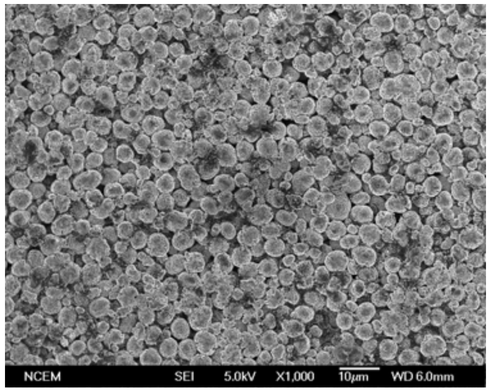
Project 1: C/B/A

1:5 C:B

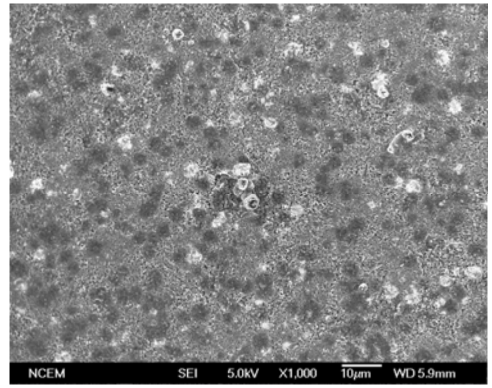
SEMs



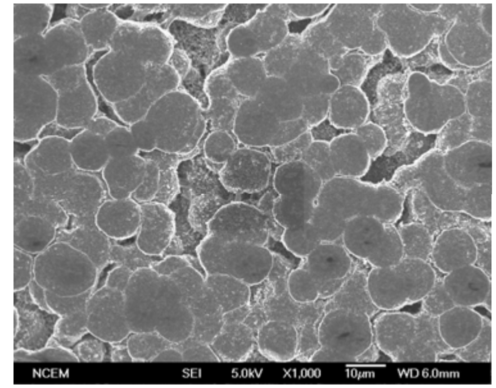
97.6% A



95.2% A



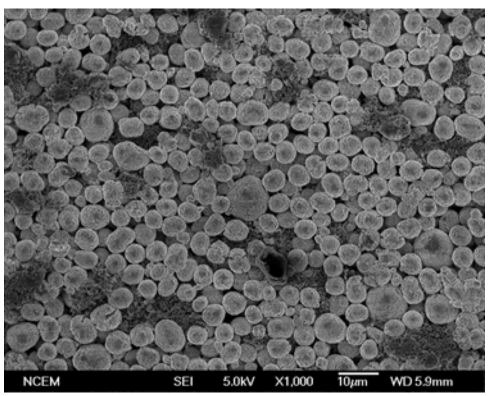
90.4% A



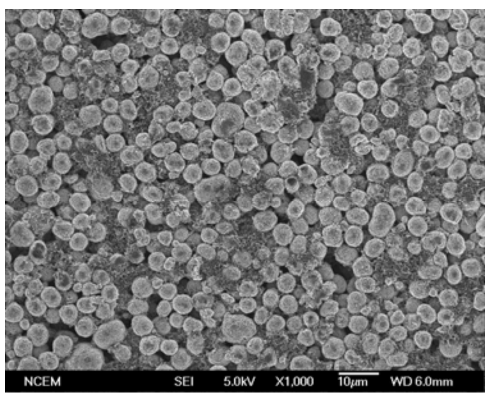
76% A

4:5 C:B

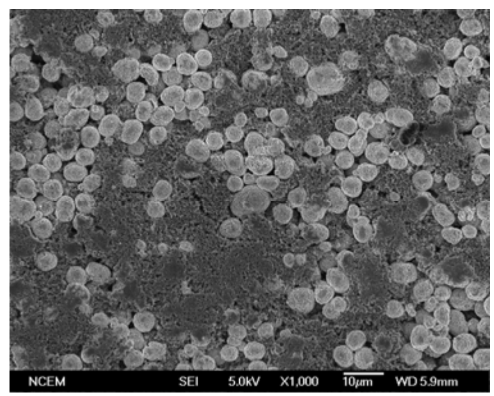
– 10 μm



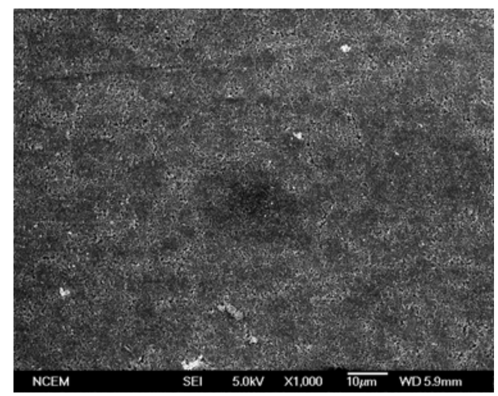
96.4% A



91% A



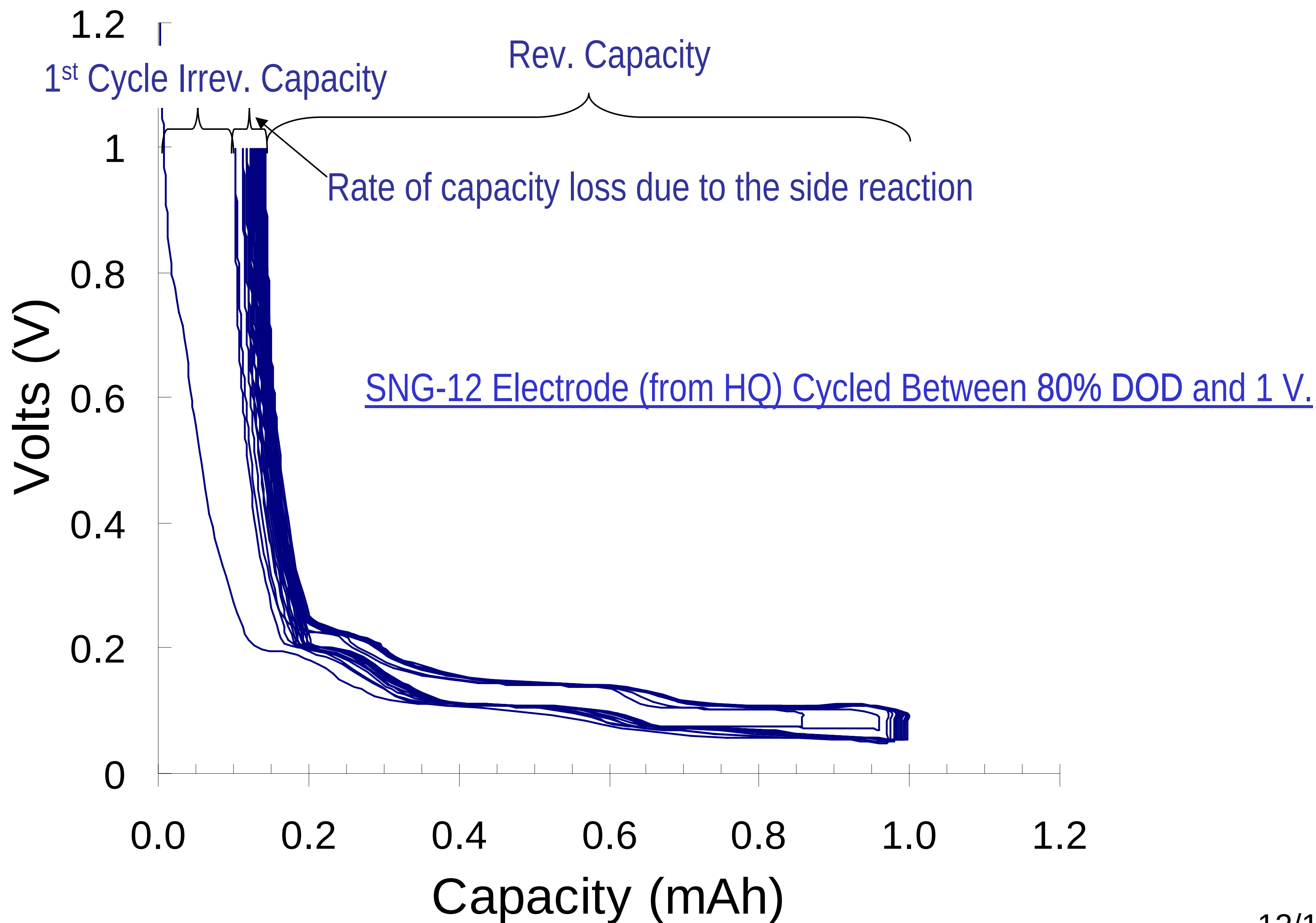
82% A



73% A

1:5 appears to form a coating on the active material particles that grows thicker with addition.
4:5 shows the active material in a sea of agglomerated carbon.
These results are for *these* materials for 50 μm thick electrodes. We now need to evaluate cycling capability.

Project 4: Graphite Electrode for PHEVs



Accomplishments/Progress/Results (cont.)

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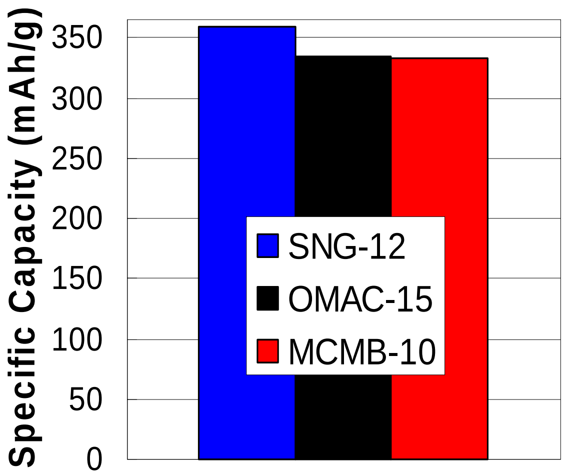
Merit Review

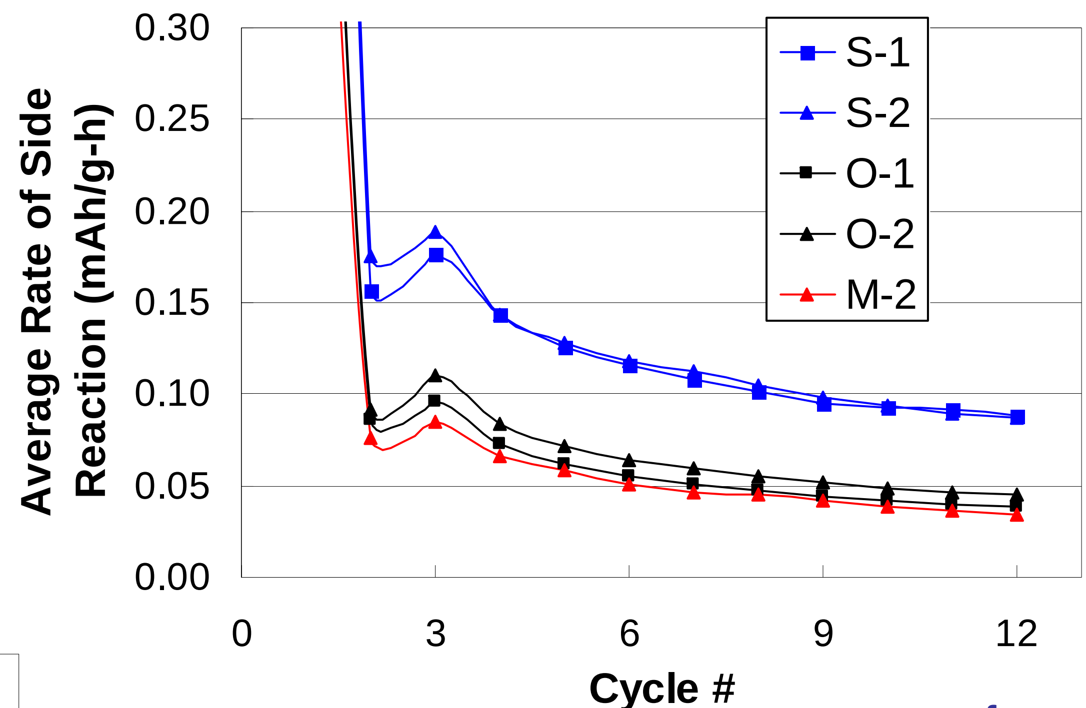
Project 4: Graphite Electrode for PHEVs

P. Ridgway

Reversible Capacity
1V to 5mV cycle limits

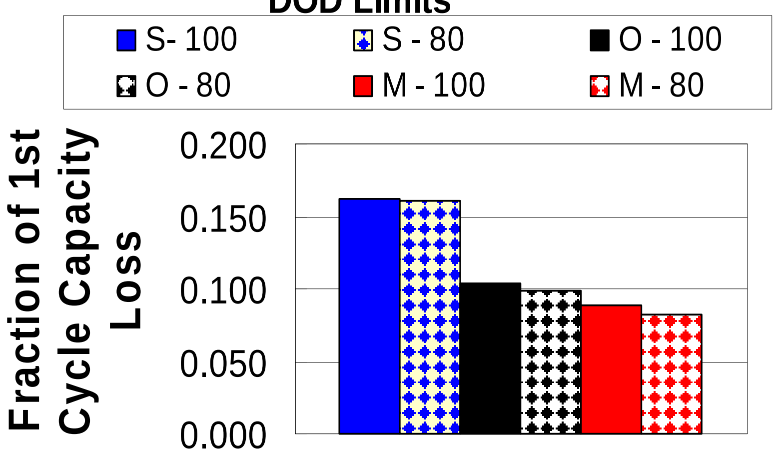


Average rate of Side Reaction when Discharged to 80% DOD



from HQ

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

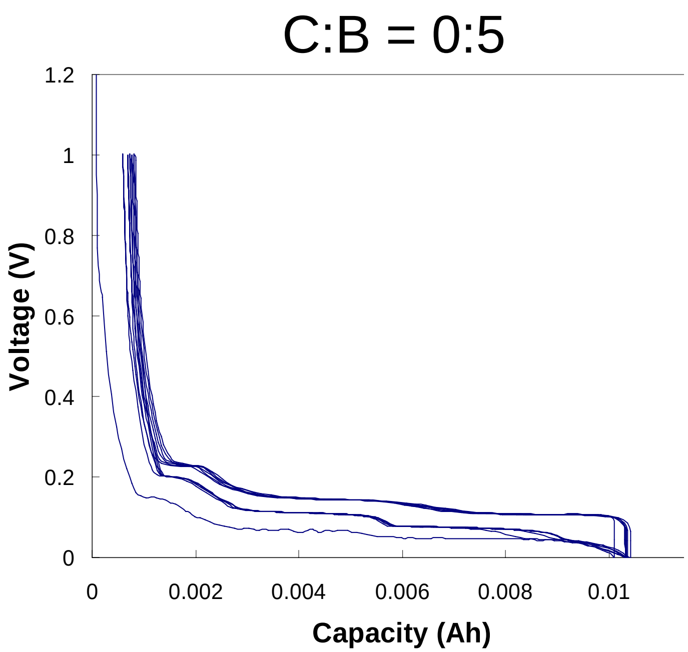


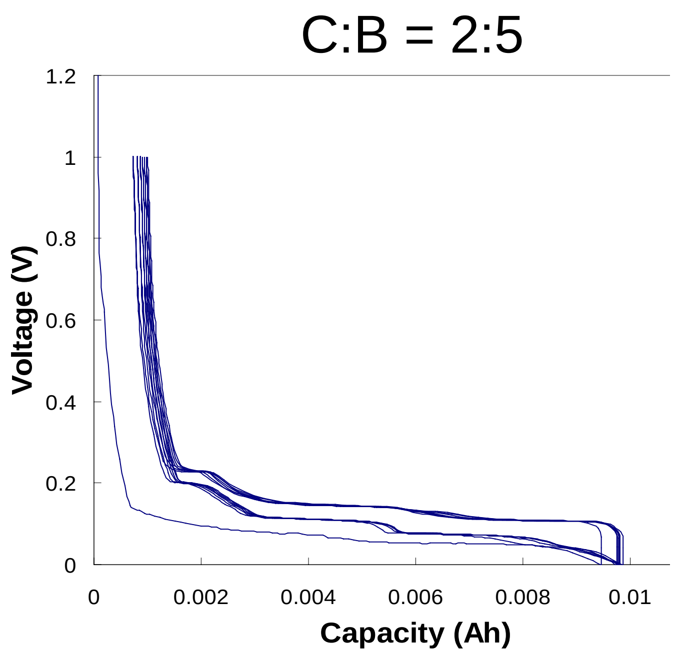
$$\frac{330\,\mathrm{mAh/g}}{0.05\,\mathrm{mAh/g\cdot h}}\bullet\frac{1\,\mathrm{day}}{24\,\mathrm{h}} = 275\,\mathrm{days};\,230\ \mathrm{cycles}$$

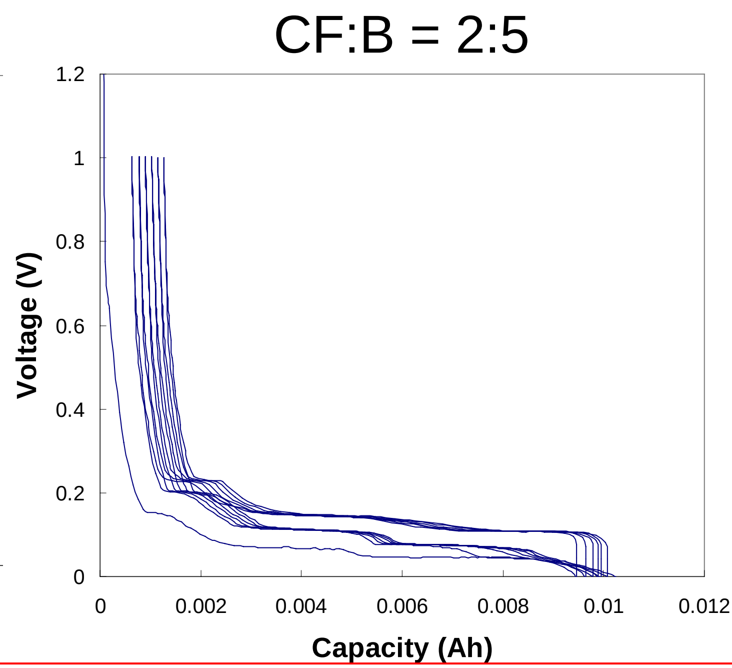
We have selected OMAC to continue with our anode optimization.

Project 4: Graphite Electrode for PHEVs

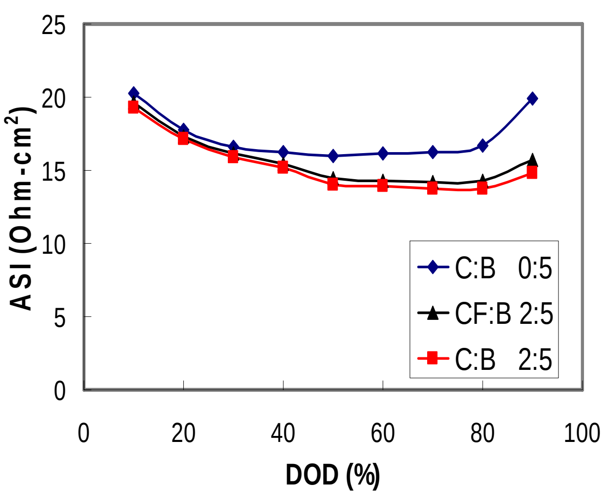
H. Zheng

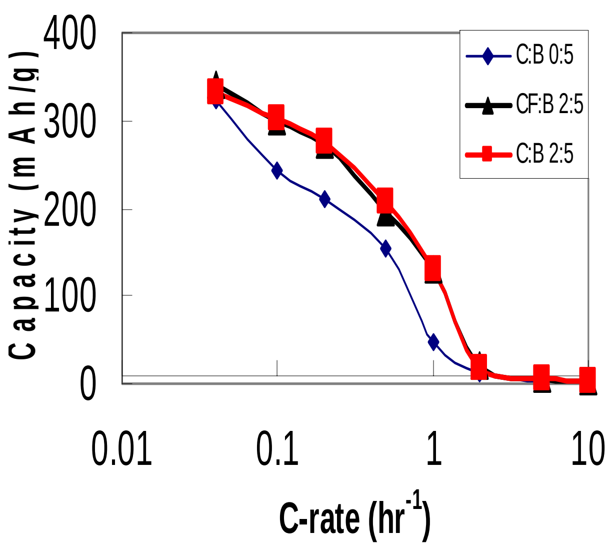






~175 μm thick





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

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

We've got another problem!

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. Repeat the analysis for a $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.
   3. Study binders typically used for anodes and electronically conducting binders.
2. Mn-spinel Study
   1. Complete HEV cycling and discern capacity and power fade mechanisms.
3. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Study
   1. Assess cycle performance against a graphite electrode; will require a DOEx. Milestone – June: <u>On schedule</u>
   2. Assess dissolution properties. Milestone – September: <u>On schedule</u>
   3. Discern high voltage limitation.
4. Graphite Study
   1. Complete evaluation of C/B/A interactions following the same approach as the cathode study. Milestone – August: <u>On schedule</u>
   2. Assess effect of VC as an electrolyte additive.
   3. Assess cycle and charge capability against a cathode (3.1) for PHEV.

Summary

- Potential for petroleum displacement
  - Significant progress in the displacement of petroleum will come about through finding the limits of electrodes for different hybrid and electric vehicle applications.
- Approach to research
  - A comprehensive, bottom-up approach of electrode design, construction, and analysis.
- Technical Accomplishments and timeliness thereof
  - Carbon/binder/active-material interactions suggest high C:B for HEVs and lower C:B for PHEVs and EVs.
  - Mn-spinel evaluation indicates that BATT material is as good or better than commercial material.
  - Cathode designs of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ suggest electrode configurations of >500 Wh/l.
  - 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 for different binders and active materials with DSC and other techniques.
  - Mn-spinel HEV testing to be completed.
  - Evaluate electrode cycle performance by constructing a complete 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.

End

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

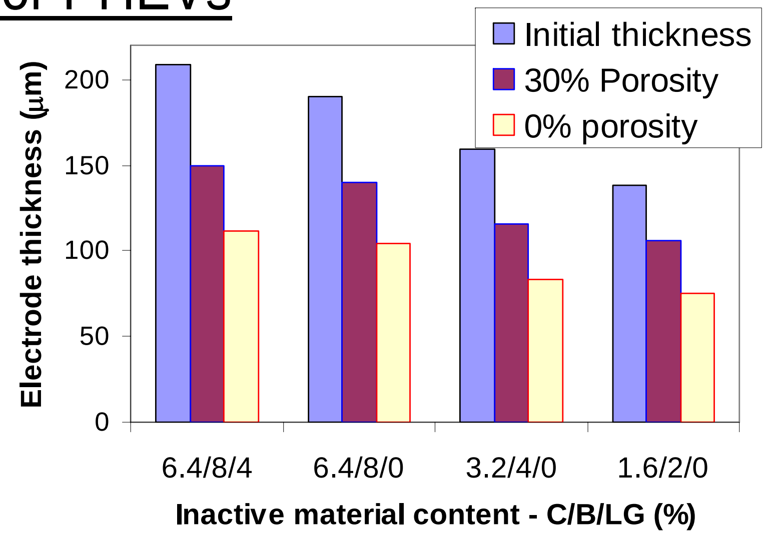
Accomplishments/Progress/Results (cont.)

H. Zheng

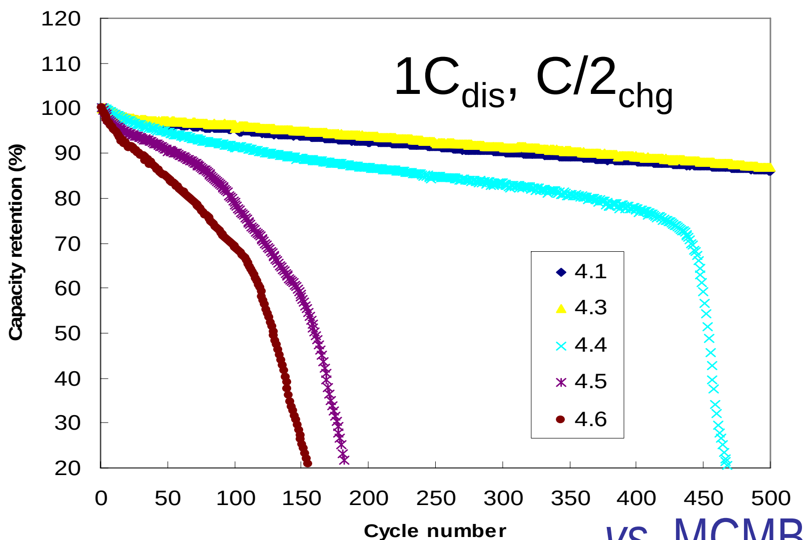
Project 3: Cathode for PHEVs

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

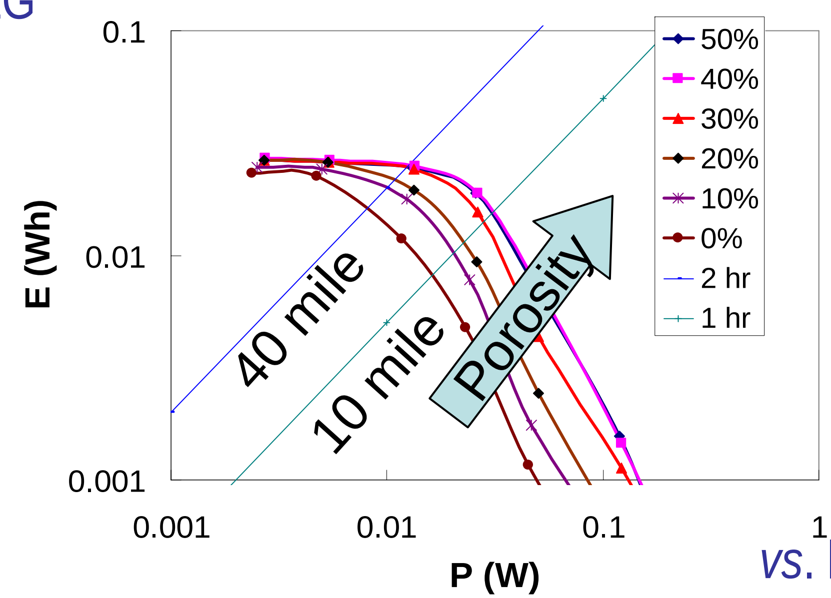
1. with different fractions of active material
   - 81.6, 85.6, 92.8, and 96.4%
2. calendered to different porosities
   - 50, 40, 30, 20, 10, and 0%



6.4:8:4 C:B:LG



vs. MCMB-10



vs. lithium

The less the inactive material, the thinner and less the volume change; 4.3 V cycleable upper-voltage limit; For C:B:LG= 6.4:8:4 electrodes of porosity $\geq$ 30% may work for 40-mile PHEVs .

Accomplishments/Progress/Results (cont.)

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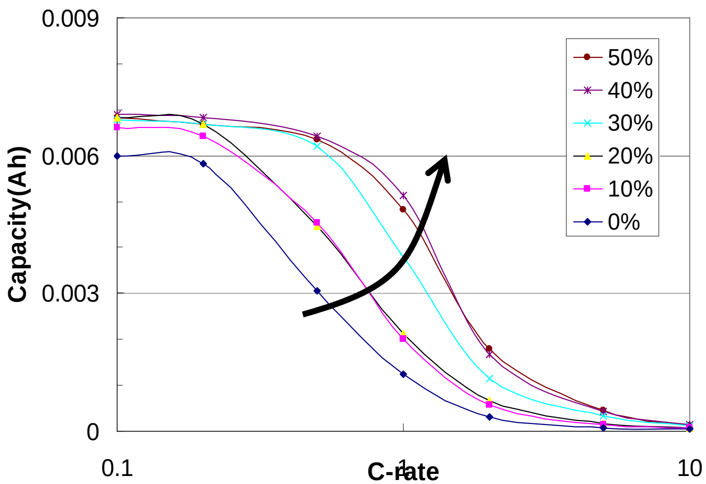
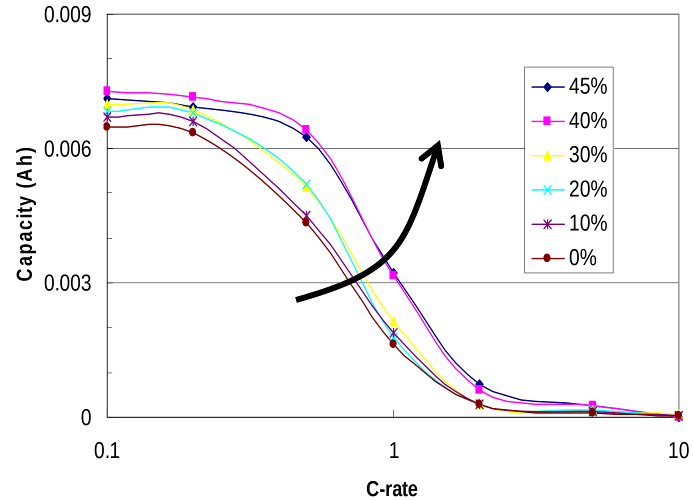
Project 3: Cathode for PHEVs

H. Zheng

8% PVDF, 6.4% Carbon 4% graphite

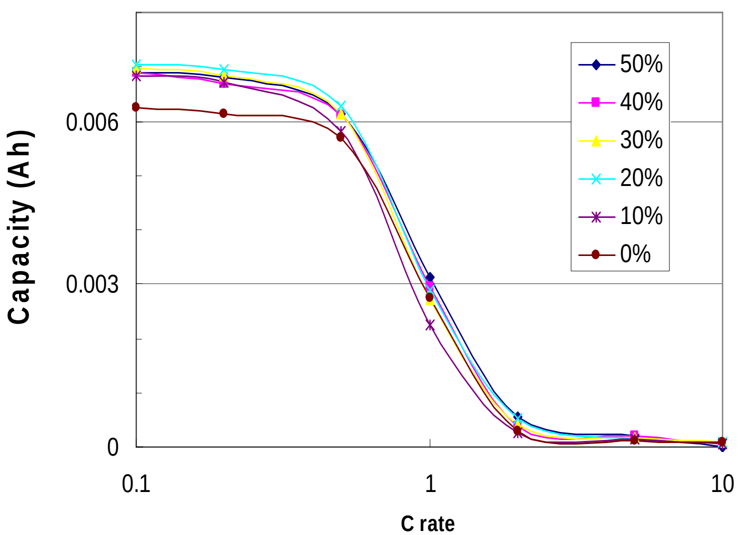


8% PVDF, 6.4% Carbon

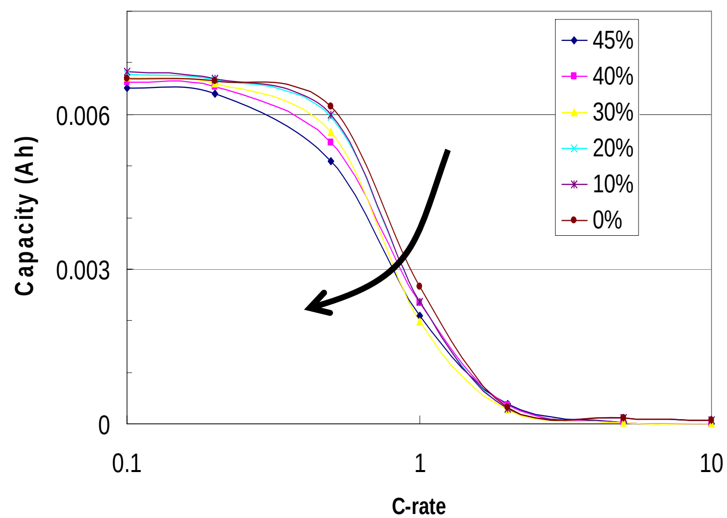


Electrodes with a large fraction of inactive material show the greatest variation in performance.

4% PVDF, 3.2% Carbon



2% PVDF, 1.6% Carbon



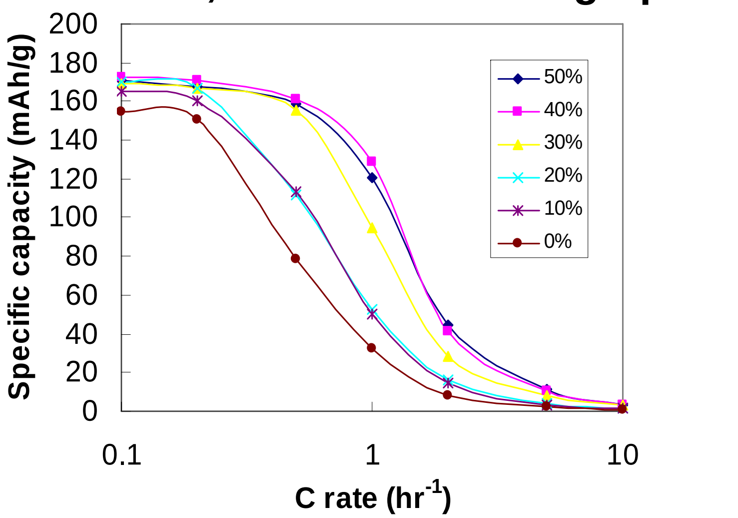
Li counter electrode used where the impedance of concentration overpotential is minimized.

Accomplishments/Progress/Results (cont.)

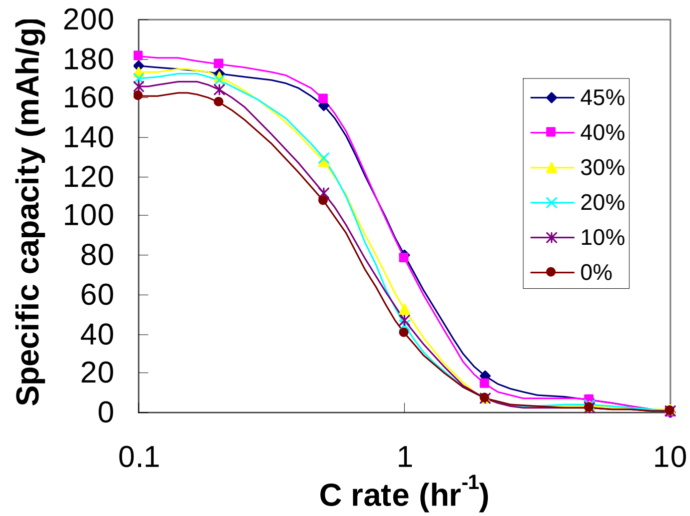
Project 3: Cathode for PHEVs

H. Zheng

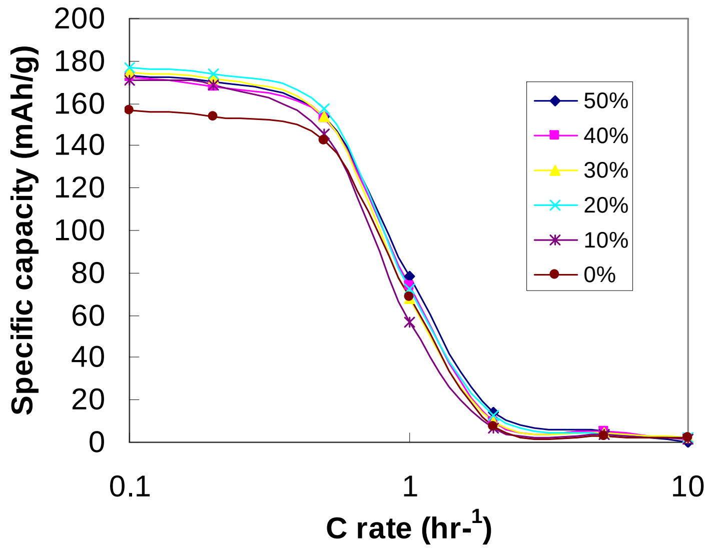
8% PVDF, 6.4% Carbon 4% graphite



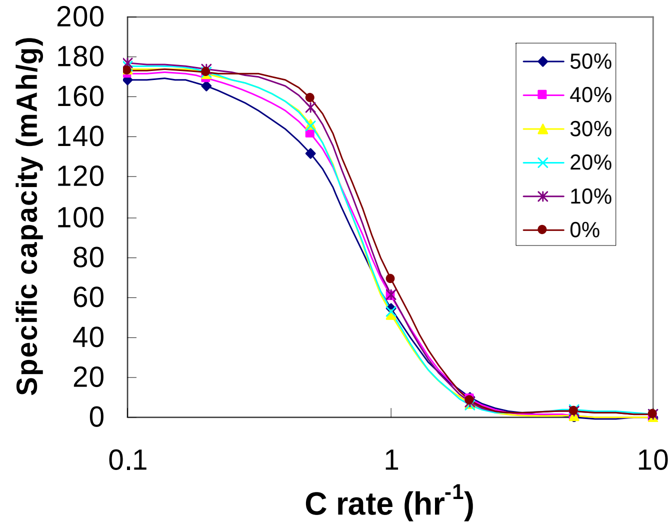
8% PVDF, 6.4% Carbon



4% PVDF, 3.2% Carbon



2% PVDF, 1.6% Carbon



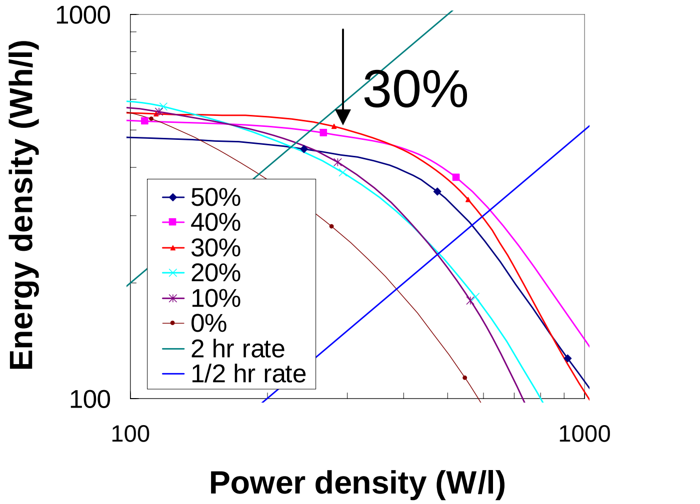
Electrodes with a large fraction of inactive material show the greatest variation in performance.

Accomplishments/Progress/Results (cont.)

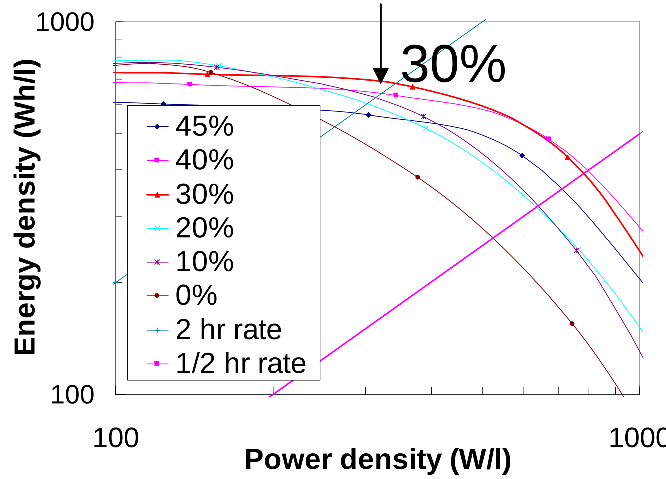
Project 3: Cathode for PHEVs

H. Zheng

8% PVDF, 6.4% Carbon 4% graphite

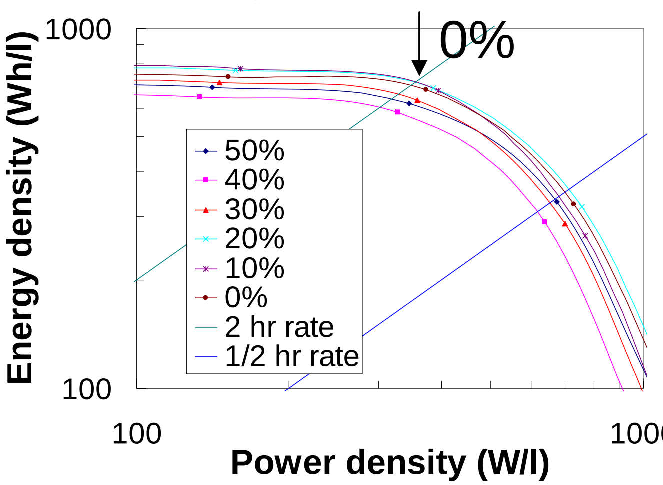


8% PVDF, 6.4% Carbon

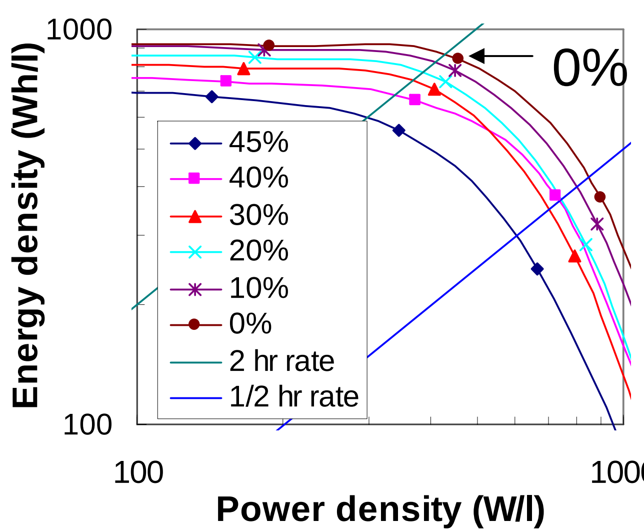


Although the <u>energy density</u> increases substantially with the removal of inactive material, the true test will be cycleability!

4% PVDF, 3.2% Carbon



2% PVDF, 1.6% Carbon



Also, one should not forget the need to meet the pulse power capability, therefore, HPPC data against graphite is another critical metric.

Data obtained against lithium counter electrode but energy density based on 155 micron graphite electrode.

Accomplishments/Progress/Results (cont.)

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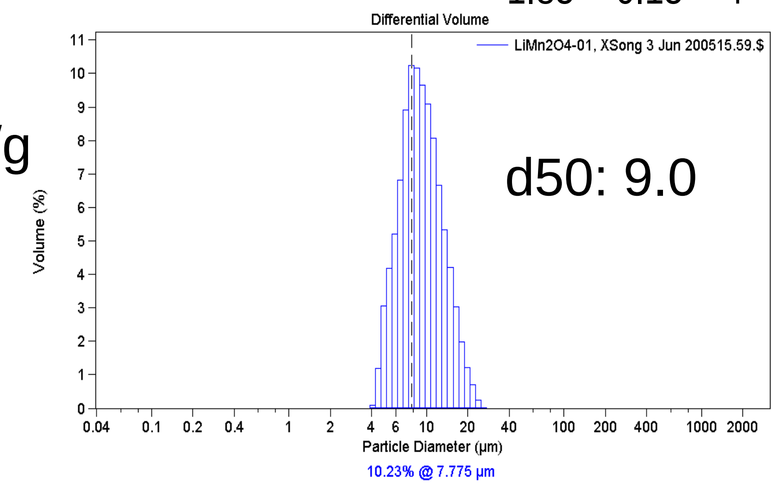
Project 2: Toda vs. BATT doped Mn-Spinel

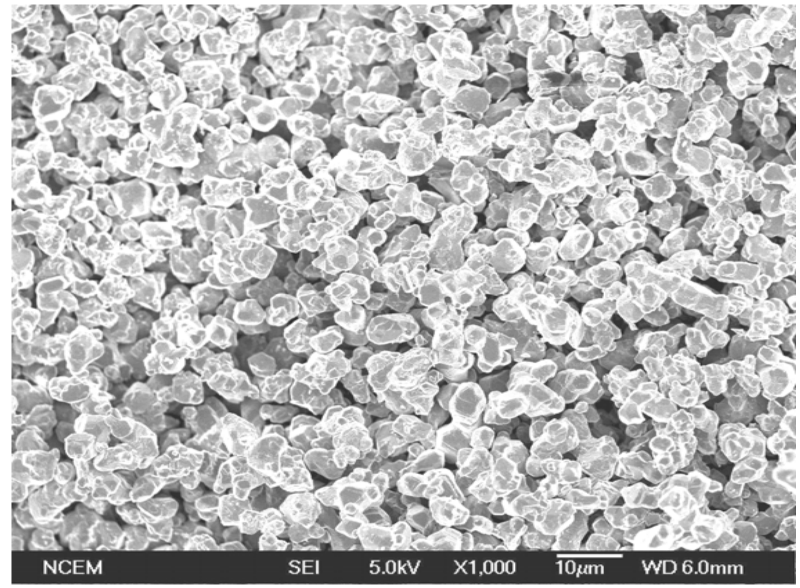
X. Song

Toda Li-doped Mn-Spinel

$LiMn_{1.85}Li_{0.15}O_4$

BET = 0.54 m^2/g

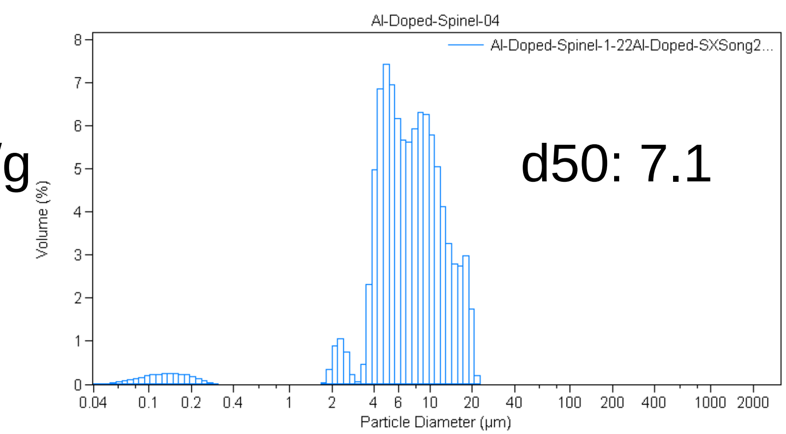


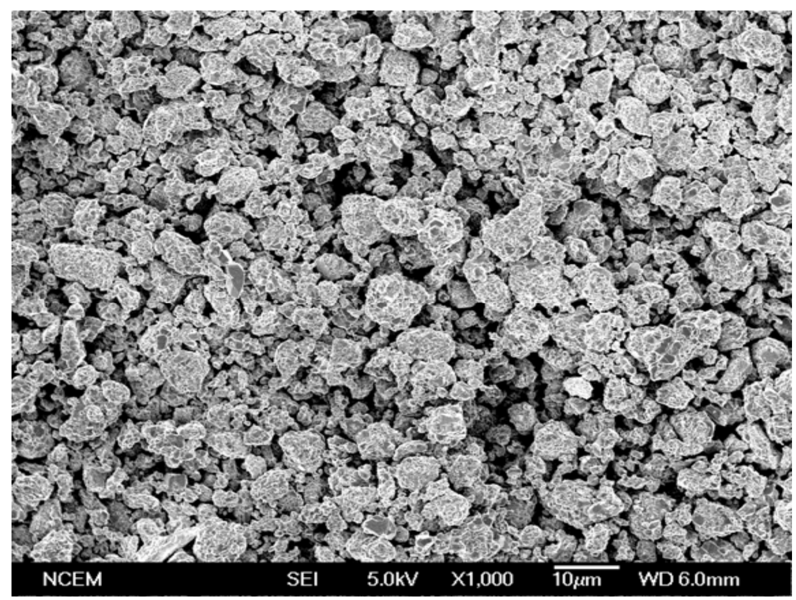


BATT Mn-Spinel

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

BET = 0.53 m^2/g

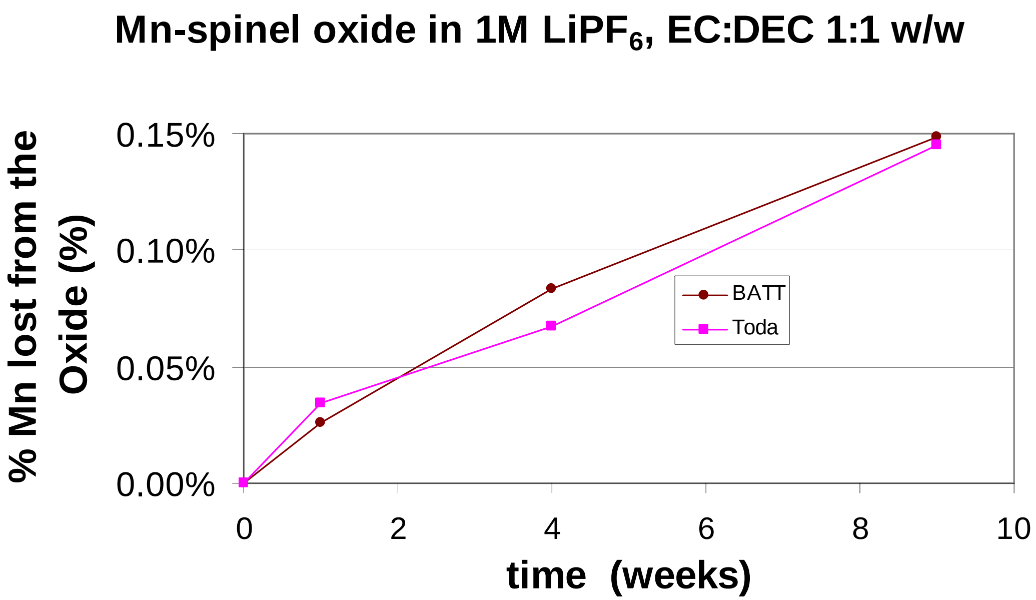




Accomplishments/Progress/Results (cont.)

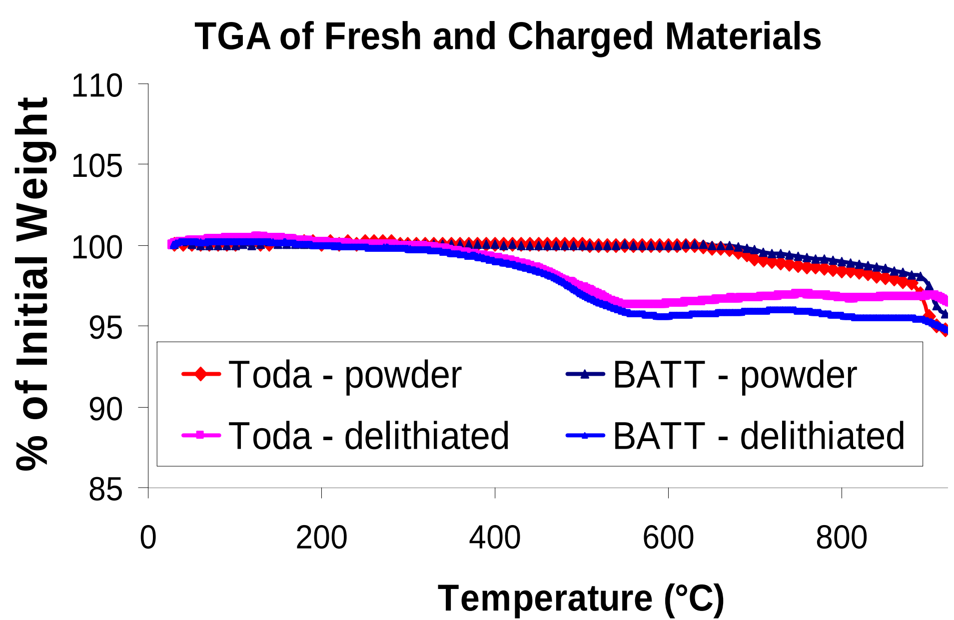
Project 2: Toda vs. BATT doped Mn-Spinel

X. Song



Materials show similar rates of loss of Mn in electrolyte.

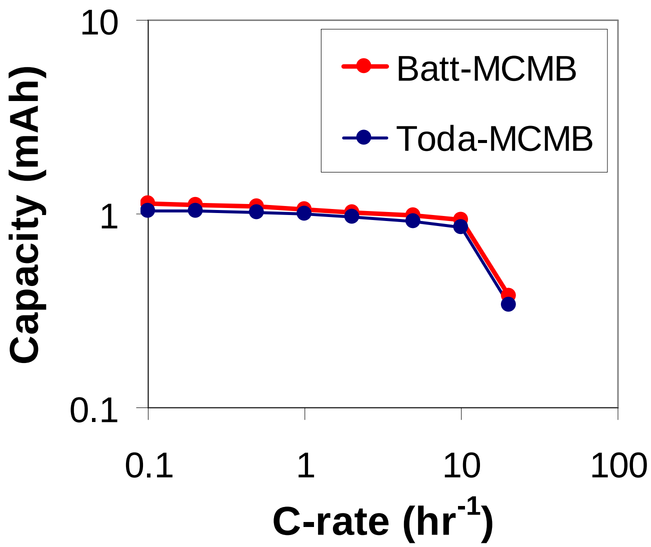
Materials show similar thermal stability properties.

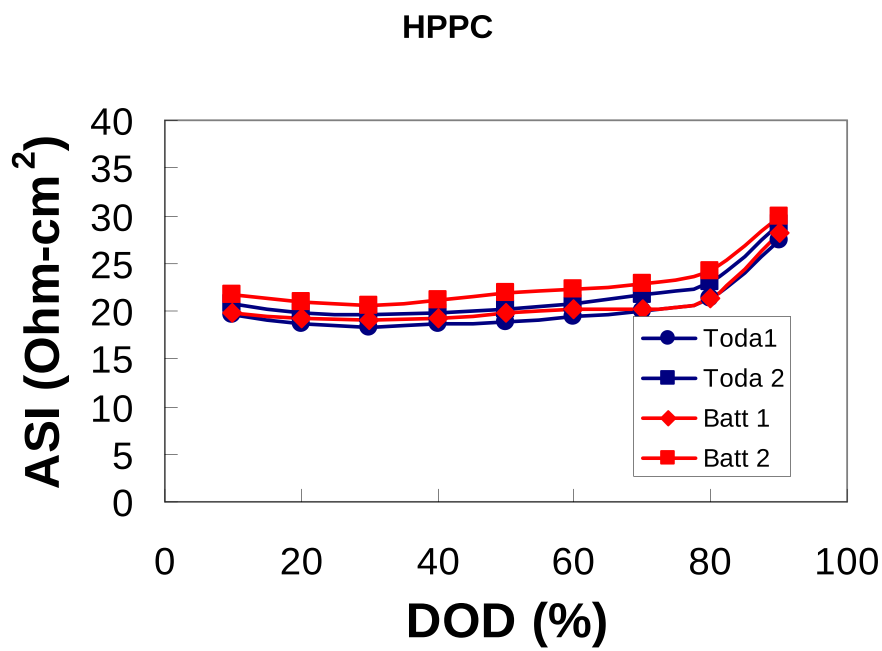


Accomplishments/Progress/Results (cont.)

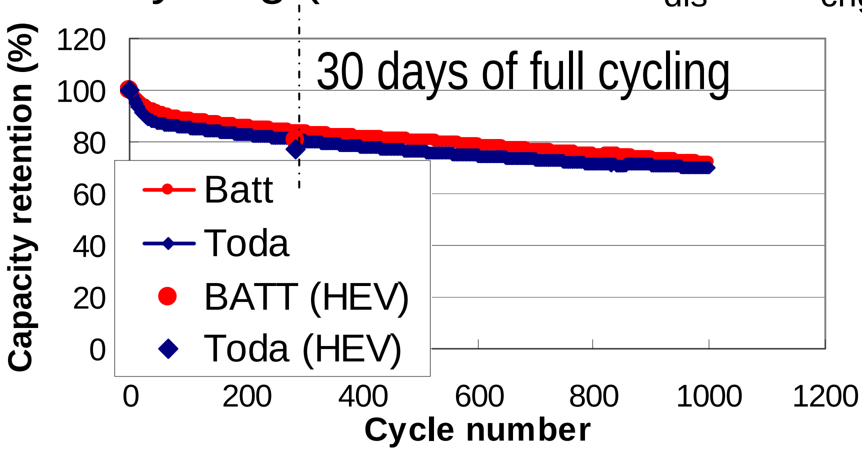
Project 2: Toda vs. BATT doped Mn-Spinel

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 accessible capacity.