Electrode Construction and Analysis

Gao Liu and Vince Battaglia
Lawrence Berkeley National Laboratory

DOE OVT Annual Merit Review
Crystal City, VA
May 20, 2009

es_16_battaglia

Overview

Timeline

Anode fabrication and analysis
Start date: October 2007
End date: September 2010
~50 % complete

Barriers

Inadequate energy density to meet the cost target

Inadequate cycle life

Inadequate calendar life

Budget

FY08 $800 k (100% DOE)
1 Program Manager
1 Research Scientist
1 Visiting Scholar
2 Research Associates

FY09 $1016 k (100% DOE)
1 Program Manager
1 Research Scientist
3 Research Associates
1 Post doctorate

Collaborators

Researchers	Companies
V. Srinivasan	Bosch
R. Kostecki	Lockheed Martin
A.M. Sastry	Seeo
D. Wheeler	Applied Materials
K. Zaghib	Toda
P. Ross	Hitachi Chemical
	Conoco Phillips
	Veeco

Objectives / Relevance

- Overall: *To provide a fundamental understanding of the role of the inactive materials in the performance of electrodes.*

- This year: *Focus on Anode*
  - Identify a replacement carbon for MCMB.
  - Measure the effect of different conductive additive fractions and binder fractions on anode cycleability.
  - Quantify the effect of vinylene carbonate on anode performance.
  - Develop electroactive binders for Si-based anodes.

Relevance to Vehicle Technologies Program

Success in this endeavor will accelerate the path to reaching the PHEV…

specific energy target of 145 Wh/l

cycle life target of 2500 cycles

Milestones

FY2008

Cathode

- Complete the electrode performance characterization of NCM-based cathodes for PHEV-40, (Jun. ’08).

Graphite

- Complete the electrode performance characterization of graphite based anodes for PHEV-40, (Sep. ’08).

Cathode

- Complete the chemical characterization of NCM, (Sep. ’08).

FY2009

Graphite

- Determine the reduction and oxidation potentials of VC against a Pt electrode (May ’09).

Graphite

- Select a new baseline graphite to replace MCMB (June ’09).

Cathode

- Distribute electrodes cycled to different cut-off voltages to other members of the BATT program (June ’09).

Silicon

- Construct several electrodes of Si-based active material with PVdF and test their performance, (January ’09).

Silicon

- Develop an new binder for Si-based anodes (Sept. ’09).

Approach

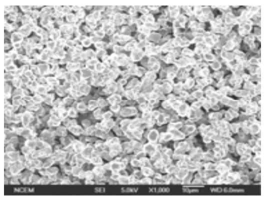
Physical and chemical characterization (BET, PSA, SEM, ICP)

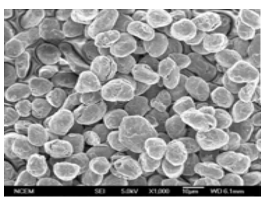
Evaluate films of combinations of carbon/binder/active-material (SEM, TEM, 4-point probe, DSC)

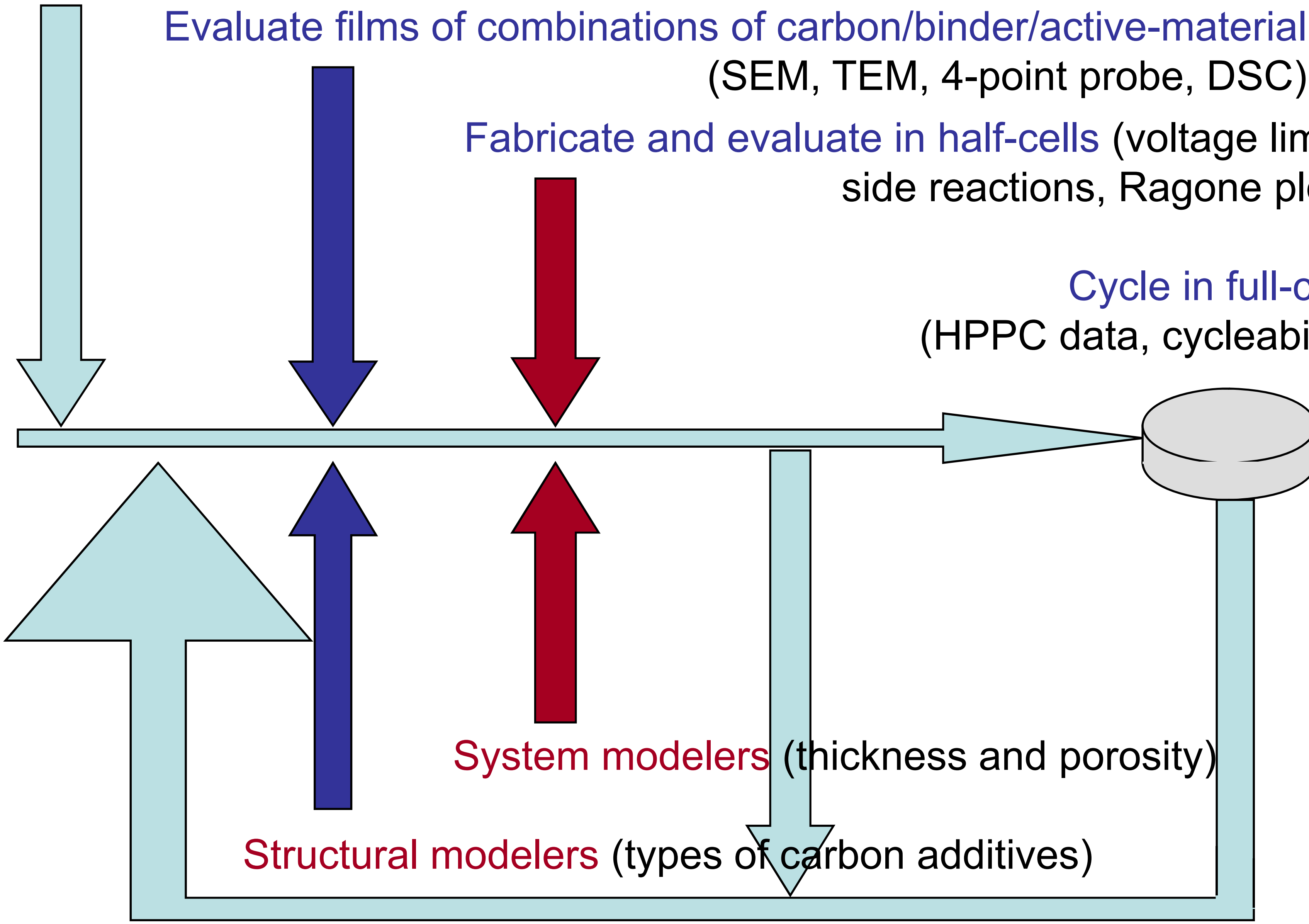
Fabricate and evaluate in half-cells (voltage limits, side reactions, Ragone plots)

Cycle in full-cells (HPPC data, cycleability)

Start with Powders







Work with Modelers

System modelers (thickness and porosity)

Structural modelers (types of carbon additives)

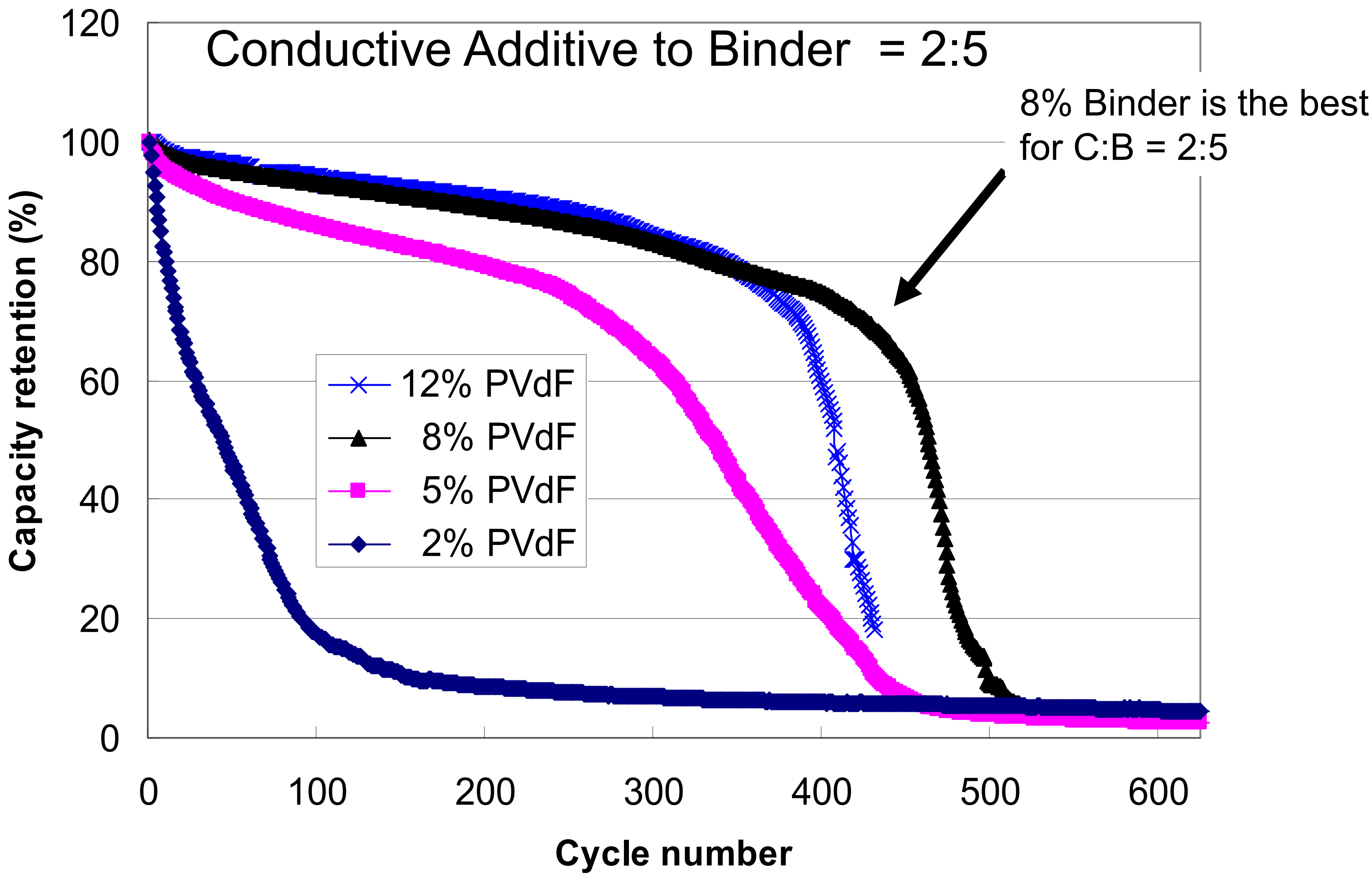
A bottom-up, comprehensive approach that combines experiments and modeling.

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

1. Assessing the effects of different combinations of acetylene black / PVdF / MCMB on electrode performance.
2. Comparing the performance of electrodes designed for PHEV applications.
3. Assessing the effect VC has on the anode and the cathode performance.
4. Developing a new binder for Si-based electrodes.

Today I will focus on 1. and 2. and present <u>highlights</u> of 3. and 4.

Task 1 – Testing graphite with different amounts of binder and conductive additive

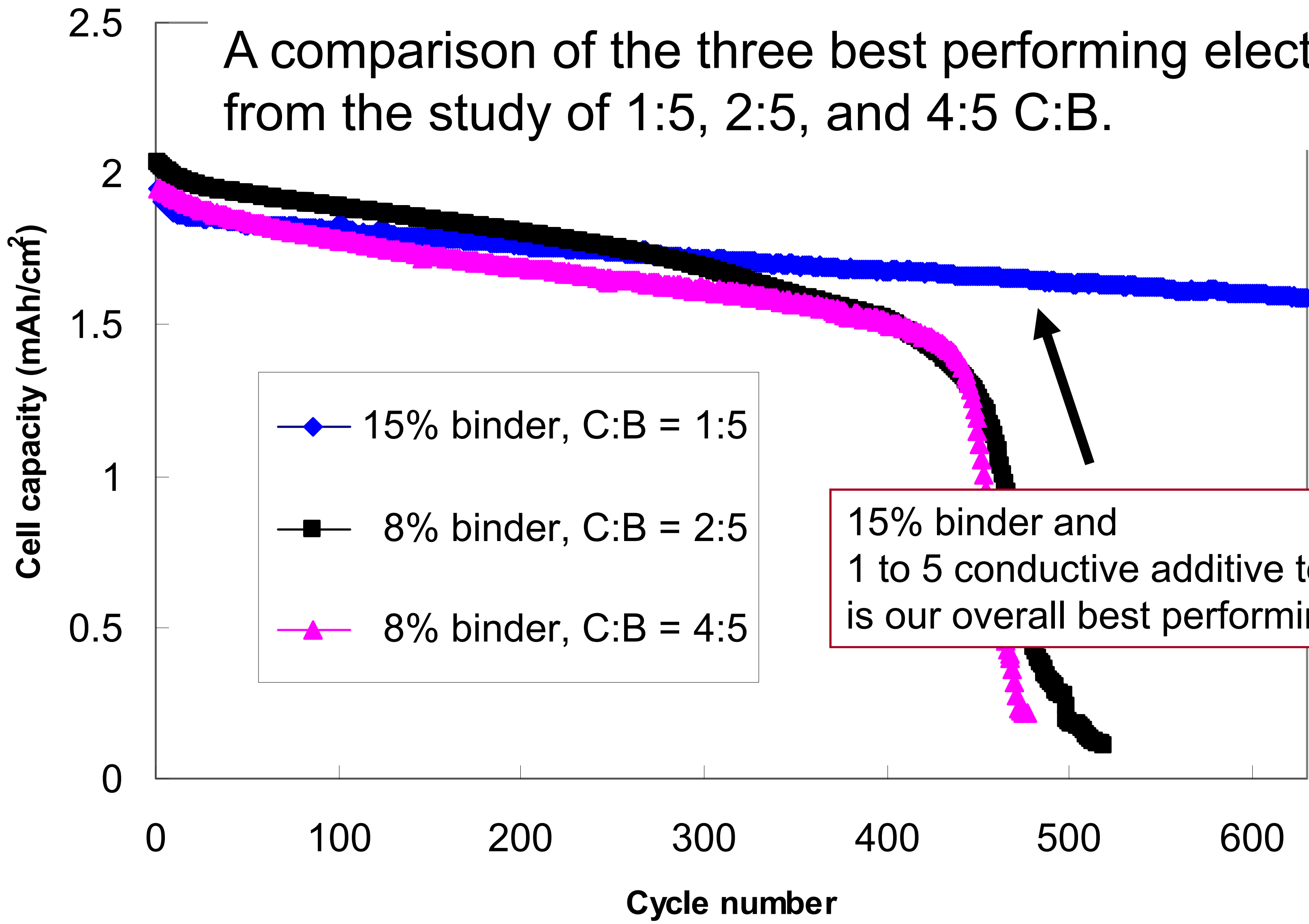


Anodes cycled against a cathode from the ABR program.

Technical Accomplishments / Progress / Results

Task 1 – Testing graphite with different amounts of binder and conductive additive.

A comparison of the three best performing electrodes from the study of 1:5, 2:5, and 4:5 C:B.



15% binder and
1 to 5 conductive additive to binder
is our overall best performing anode.

Anodes cycle against a cathode from the ABR program.

Simultaneously, we found delamination of the anode to be a major problem!

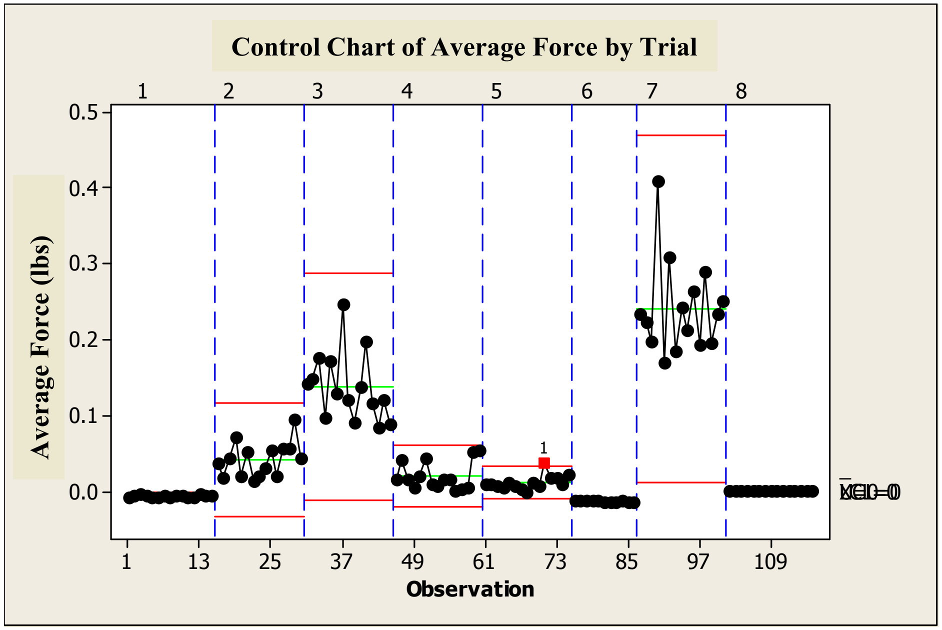
We investigated 7 parameters in a partial factorial, resolution III, eight-experiment (2^{7-4}), test matrix where peel strength was measured

1. Binder type
2. Binder to carbon ratio
3. Binder fraction
4. Laminate thickness
5. Heating lamps
6. Calendering
7. Collector thickness

Level	x1: Binder Type	x2: Conductive Carbon to Binder Ratio (C:B)	x3: Binder Fraction	x4: Doctor Blade Height	x5: Heating Lamps	X6: Calendering	x7: Collector Thickness
-	KF1700	No Conductive Carbon	5% PVDF	55 micron	Off	20% Porosity	Thick Copper
+	KF1100	C:B = 3:5	12% PVDF	420 micron	On	Freestanding	Thin Copper

Technical Accomplishments / Progress / Results

Run Order	1	2	3	4 12	5 13	6 23	7 123
8	-	-	-	+	+	+	-
6	+	-	-	-	-	+	+
2	-	+	-	-	+	-	+
4	+	+	-	+	-	-	-
7	-	-	+	+	-	-	+
3	+	-	+	-	+	-	-
5	-	+	+	-	-	+	-
1	+	+	+	+	+	+	+



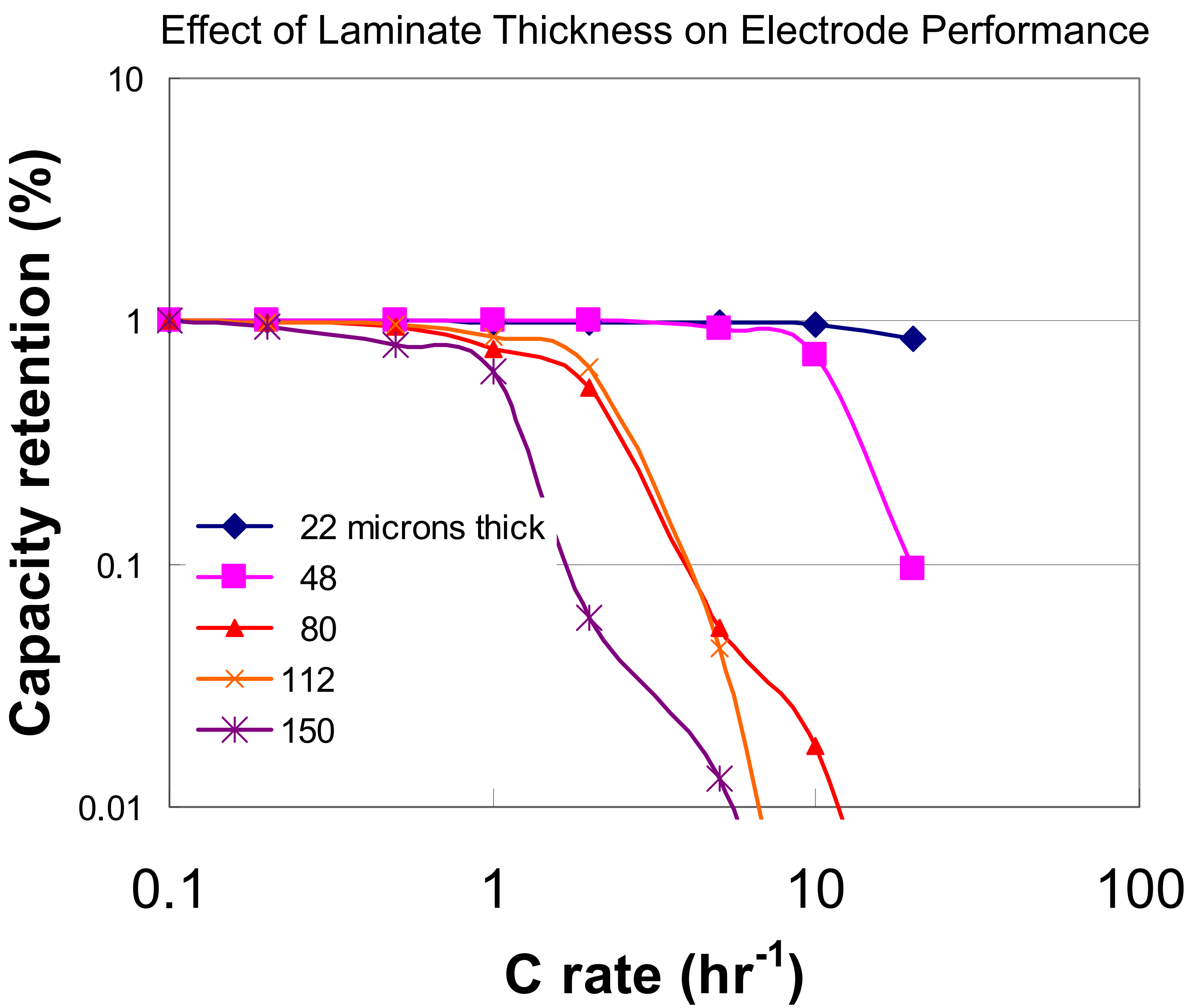
Variables	Effect
1. Binder Type	-0.03878
2. C:B	-0.07463
3. Binder Fraction	0.08367
4. Thickness	0.01902
5. Lamps	-0.02138
6. Calendering	-0.11213
7. Collector thickness	0.02342

To improve lamination to the copper current collector:

- More binder is good.
- Less conductive additive in the binder is good.
- Calendering may be important.

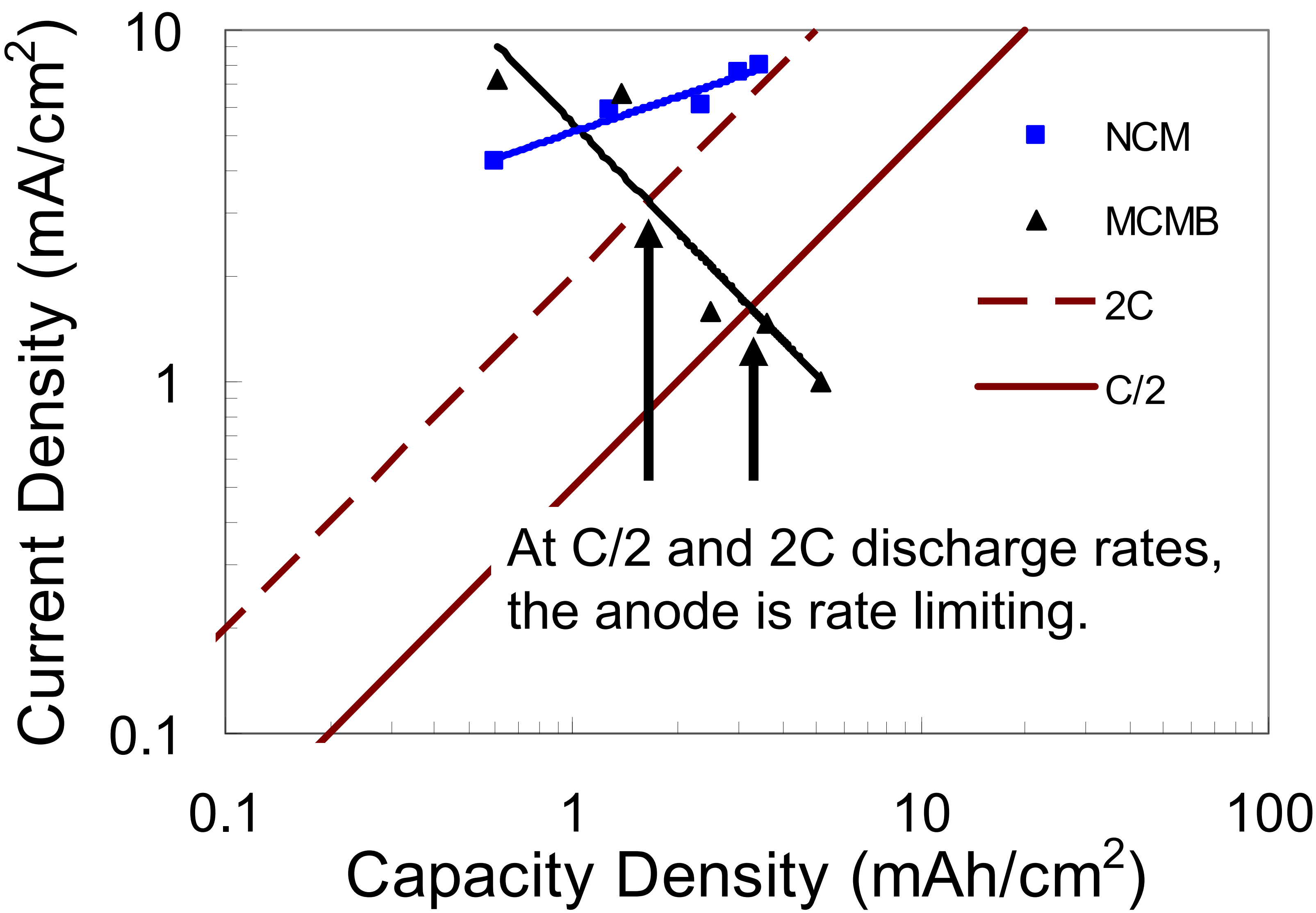
Correlates very well with our best electrode design.

Task 2. Designing a Cell for a 40-Mile PHEV



Technical Accomplishments / Progress / Results

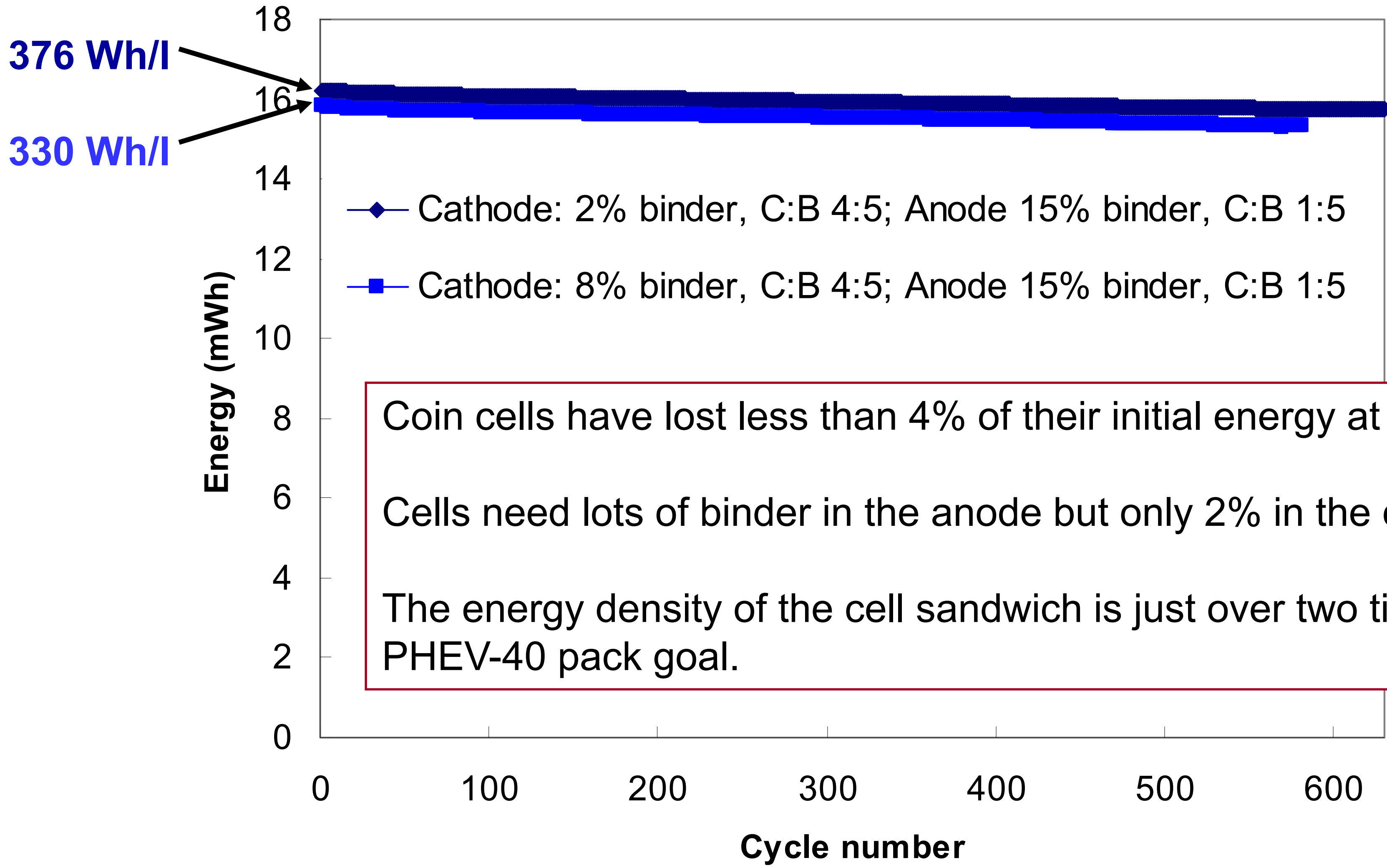
The current at which an electrode of a given capacity begins to show mass transfer resistance.



Technical Accomplishments / Progress / Results

Task 2 – Next iteration: Look at cycling performance of our cathodes against our best anode where both are designed for PHEV 40-mile systems.

Constant power cycles to 70% of cell's initial full discharge capacity, P/2 discharge, P/4 charge, with an upper charge voltage of 4.3 V



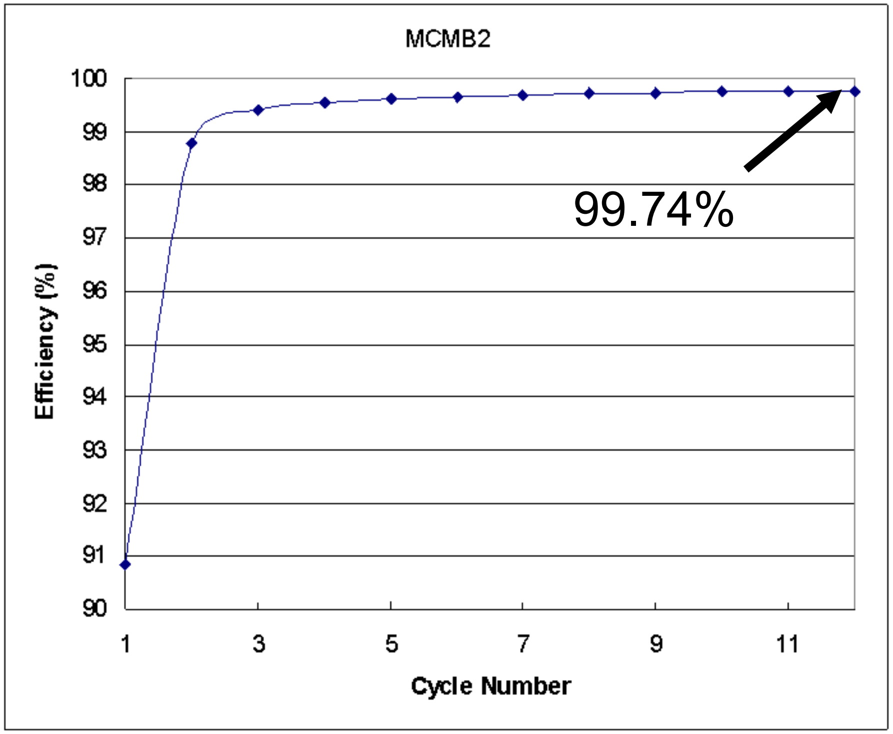
Coin cells have lost less than 4% of their initial energy at 600 cycles.

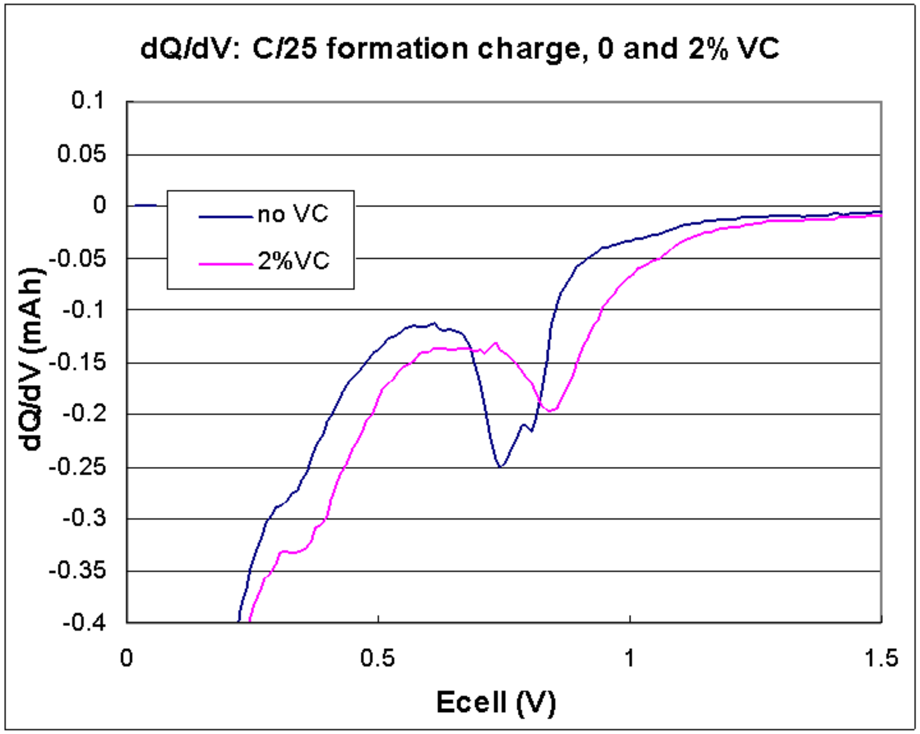
Cells need lots of binder in the anode but only 2% in the cathode.

The energy density of the cell sandwich is just over two times the PHEV-40 pack goal.

Energy density calculations include ½ of curr. coll., electrodes, and separator.

- Task 3 – Effect of VC on coulombic efficiency.



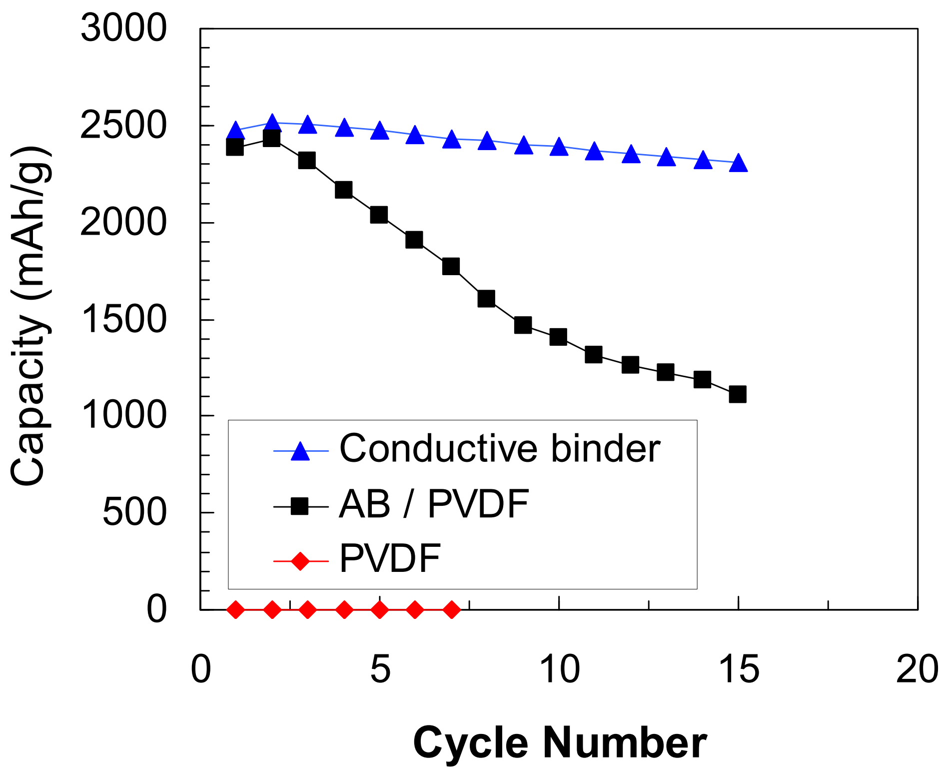


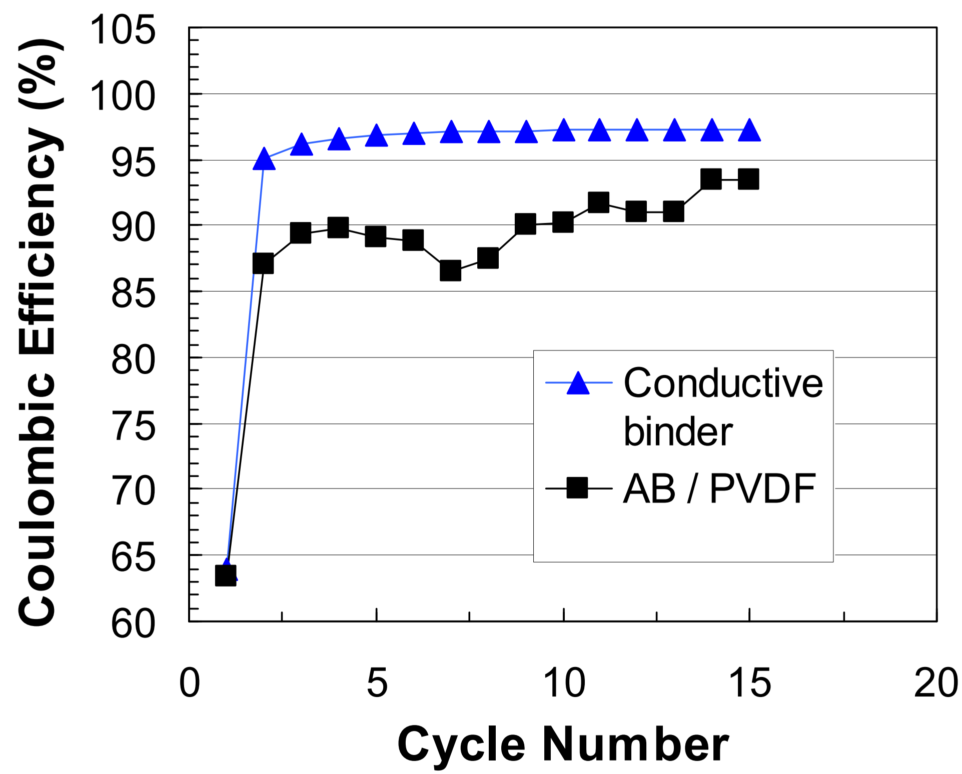
To get to 2500 cycles with just 20% capacity loss, we need coulombic efficiencies of

$(1-0.2) = \eta^{2500}$ or $\eta = 99.991\%$

We are investigating different formation scenarios with VC as an additive with the intent to improve the coulombic efficiency.

Task 4 – A new conductive binder for Si-metal anode particles.





Preliminary results obtained in the last three months.

Future Work

Task:

1. Anode development
    1. Assess two more carbons and recommend a new baseline carbon for the BATT program. June '09 Milestone
    2. Assess the performance of graphite anodes made with SBR and CMC binders.
2. PHEV study
    1. Investigate the effects of constant power cycling versus constant current cycling
    2. Look at effects of dynamic stress testing
    3. Build sealed cells with a reference electrode
    4. Investigate upper cut-off voltage on cycleability. June '09 Milestone
    5. Evaluate potential of new materials developed in the BATT program to meet PHEV targets.
3. Additive study
    1. Determine oxidation and reduction potentials of VC. May '09 Milestone
    2. Develop a list of formation processes for VC and determine which leads to improved coulombic efficiency
        1. Initial charge rate
        2. Intermittent voltage holds
    3. Test other additives
4. Binder development
    1. Develop additional formulations to improve cycleability of Si. September '09 Milestone
        1. Enhanced flexibility
        2. Improved particle adhesion

Other:

Sensitivity analysis of the different processing steps on electrode performance

- Order and weight ratio by which materials are added to the slurry.
- Slurry viscosity and doctor blade speed.
- Rate of calendering
- Calendering temperature
- Electrode drying temperature and duration

Summary

Key take-away points

- We are making cells that last several months and cycle hundreds of cycles. This provides us an excellent platform for studying
  - Effects of electrode processing on cell performance and cycle life
  - Effects of the non-active-materials on cycle life
  - New active materials
  - Additives
  - Long term affects of upper voltage cut-off limits
- Incorporating design of experiments into our fabrication methodology.
- We have developed a binder that is showing great promise and hope to improve upon its cycleability.
  - This will not necessarily make Si a viable electrode as there are still unresolved issues such as
    - First cycle irreversible capacity loss.
    - Round-trip coulombic inefficiency
    - High polarization during charge and discharge.