



Carbon-Enhanced VRLA Batteries

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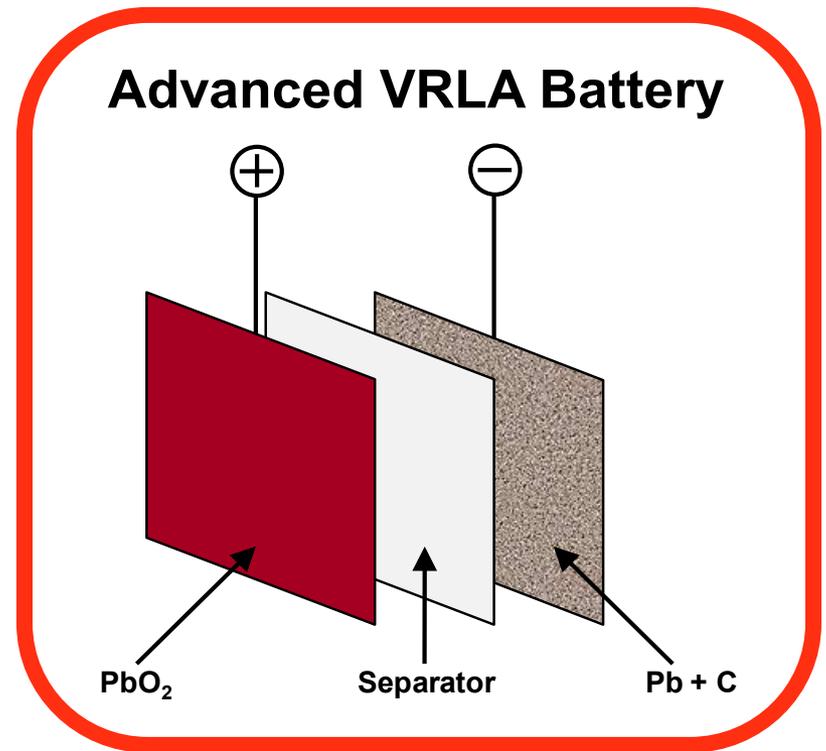
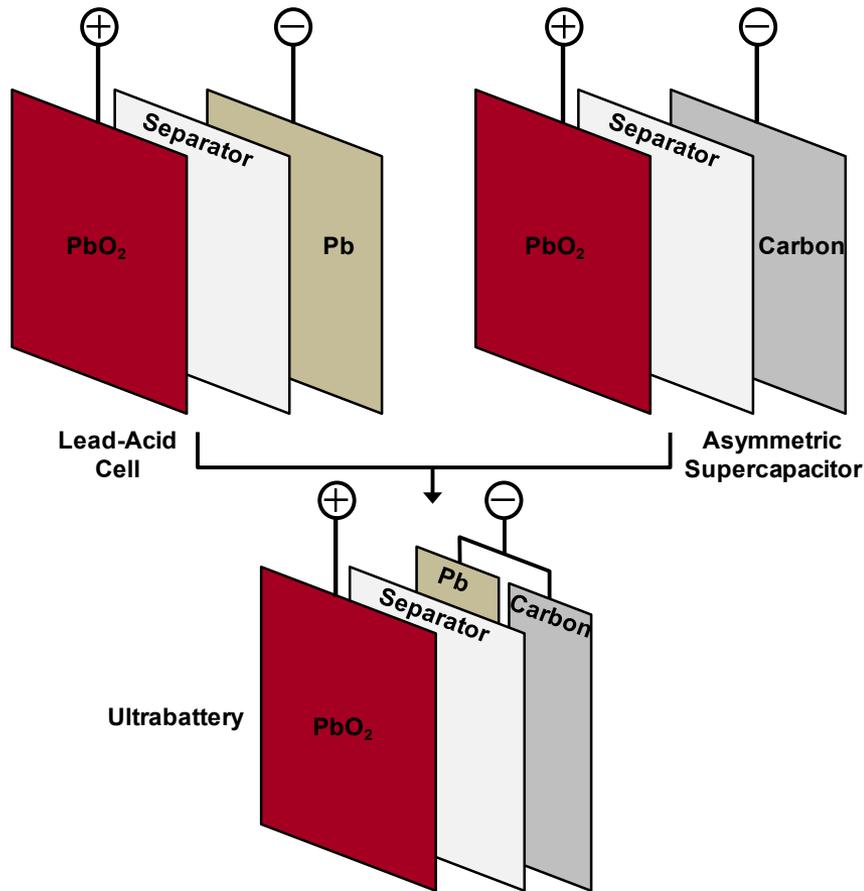
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Carbon Enhanced VRLA Batteries

- Pb-Acid batteries are inexpensive, but have a poor cycle life when subjected to high-rate, partial state of charge (HRPSoC) operating conditions.
- The addition of some carbon materials have been demonstrated to dramatically improve the cycle life, enabling use of VRLA batteries under HRPSoC conditions.
 - Some additions enhance, others detract... not clear why.
- The overall goal of this work is to quantitatively define the role that carbon plays in extending the cycle life of a VRLA battery.

The Advanced VRLA Battery

- Recently, there have been several manners in which carbon has been added to a Pb-Acid battery
 - The work presented here deals with the Advanced Battery, where carbon has been added to the negative active material

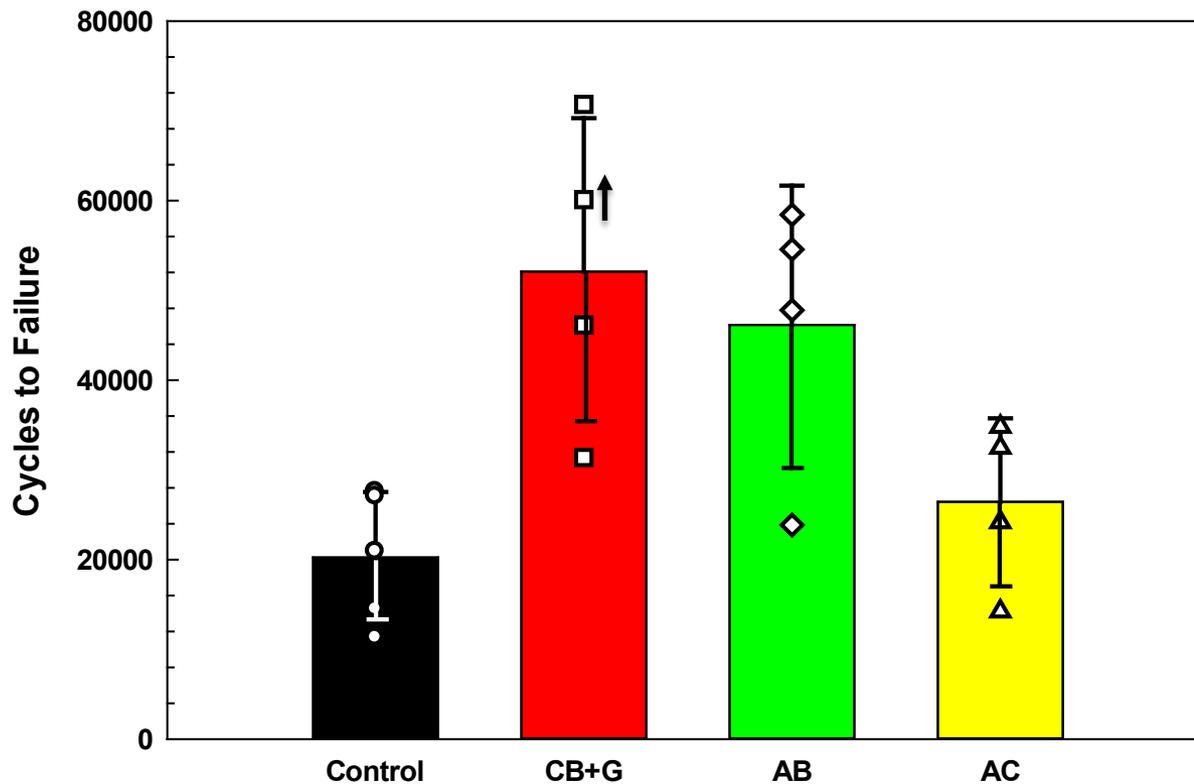


Activities in FY12

- As reported in FY11, initial efforts focused on characterizing the basic materials of construction of the carbon modified batteries, and their impact on battery plate morphology and basic functional characteristics. Initial cycle testing was also completed.
- In FY12, longer term cycle testing was completed (10k cycles and then continuing to battery death)
 - Cycle life as a function of battery type
 - Changes in battery performance as a function of cycle life
 - Morphological changes in the negative plate material as a function of cycle life

Cycle Life Under HRPSoC Conditions

- Batteries cycled until the remaining capacity was below 80% of the initial capacity
- 4 Battery types were evaluated
 - Control, Carbon Black + Graphite, Acetylene Black, Activated Carbon

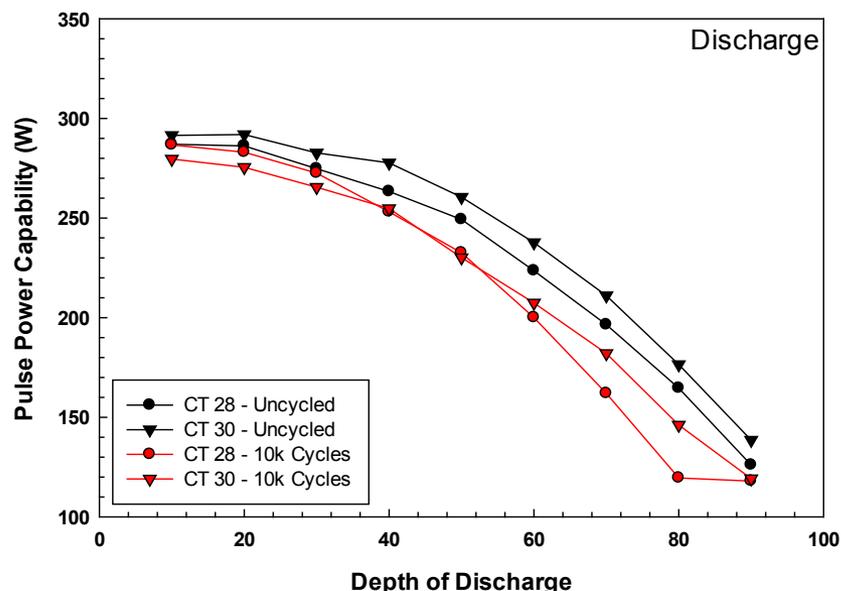
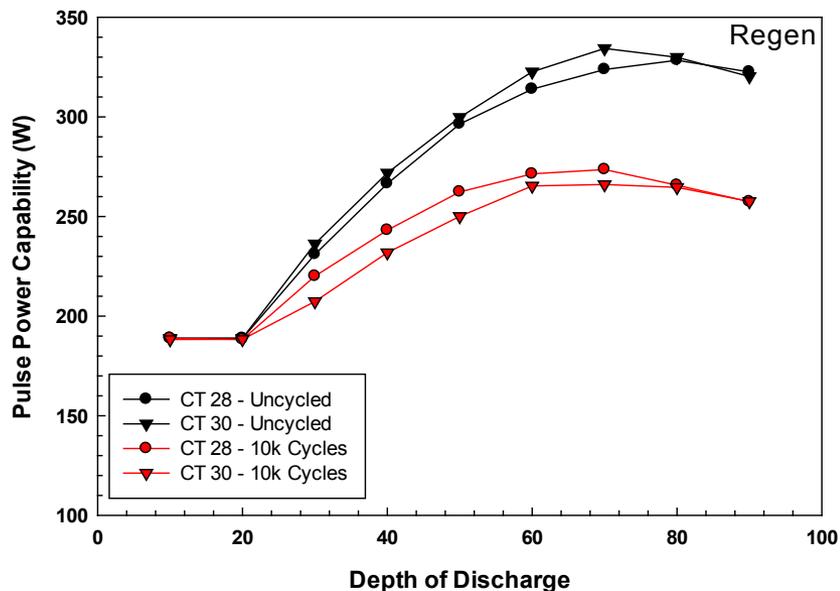


- ALABC PSoC cycle test
- 50% SoC
 - 1 Minute charge/discharge at 2C rate
 - 10s pause between cycles
 - 2.45V high cutoff
 - 1.75V low cutoff

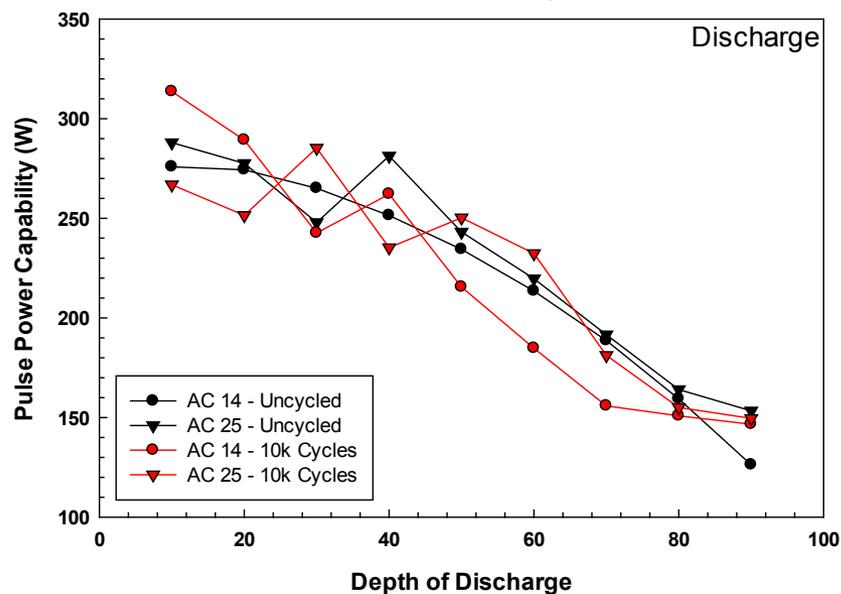
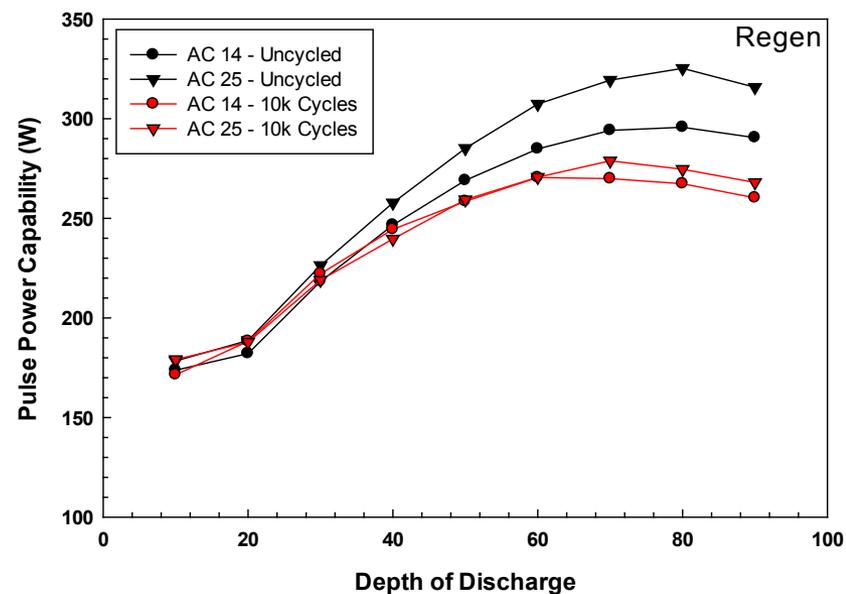
- With Recovery Charges
- Control: 61116
 - CB+G: 103923+
 - AB: 85271+
 - AC: 79675

HPPC Performance

Control

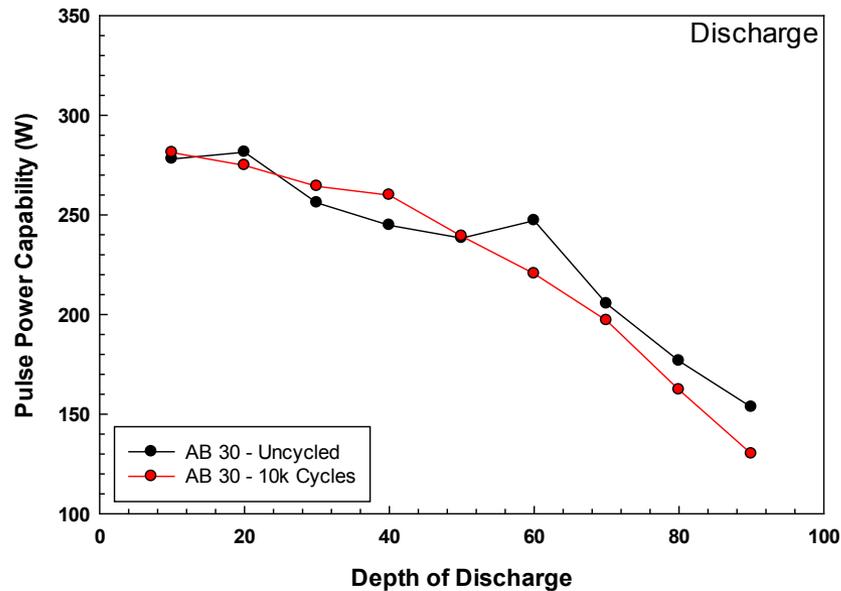
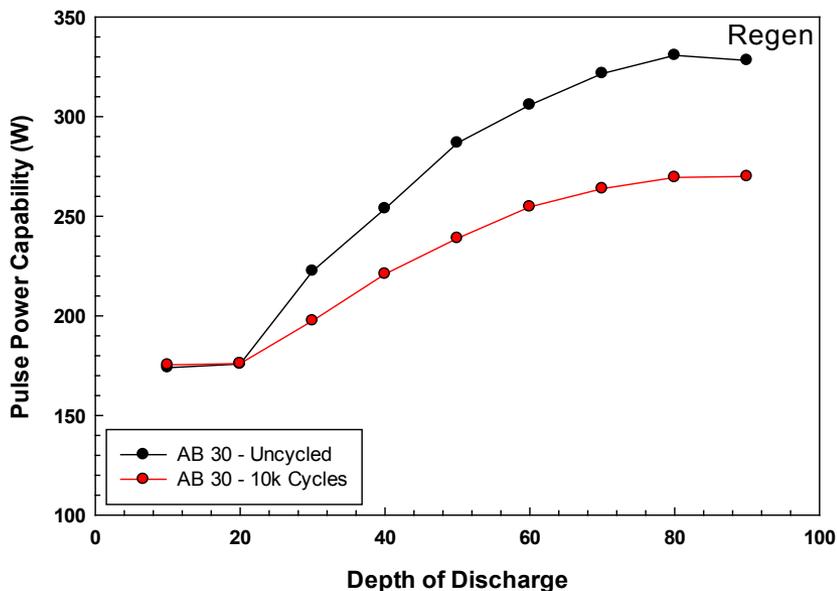


Activated Carbon



HPPC Performance

Acetylene Black



Carbon Black + Graphite

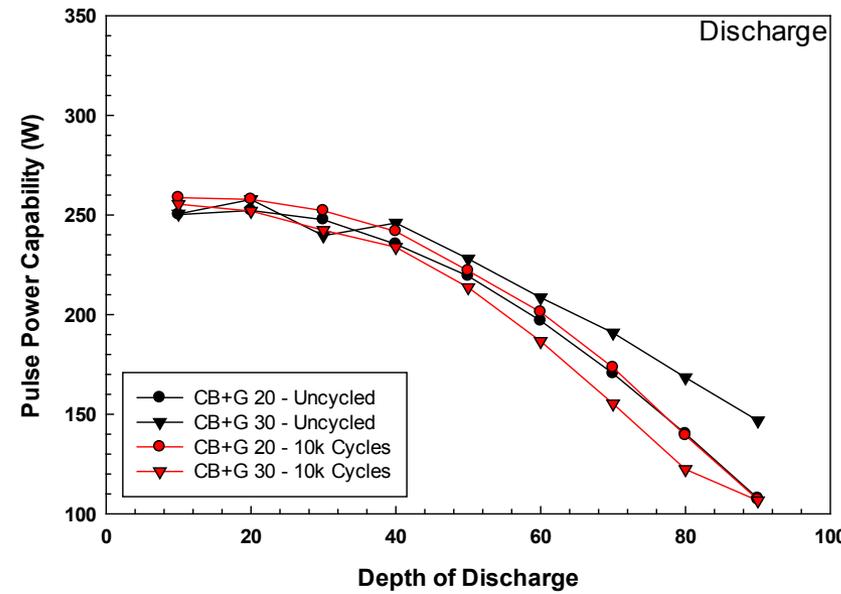
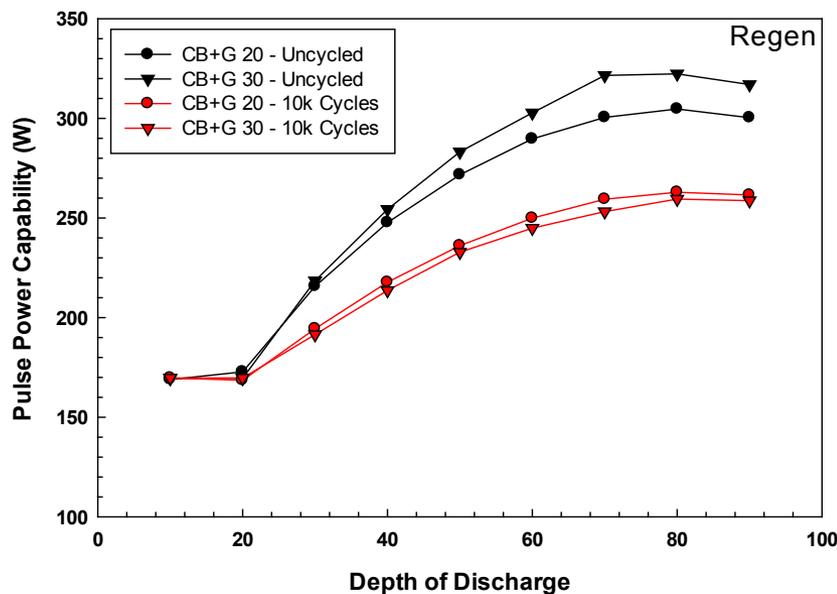
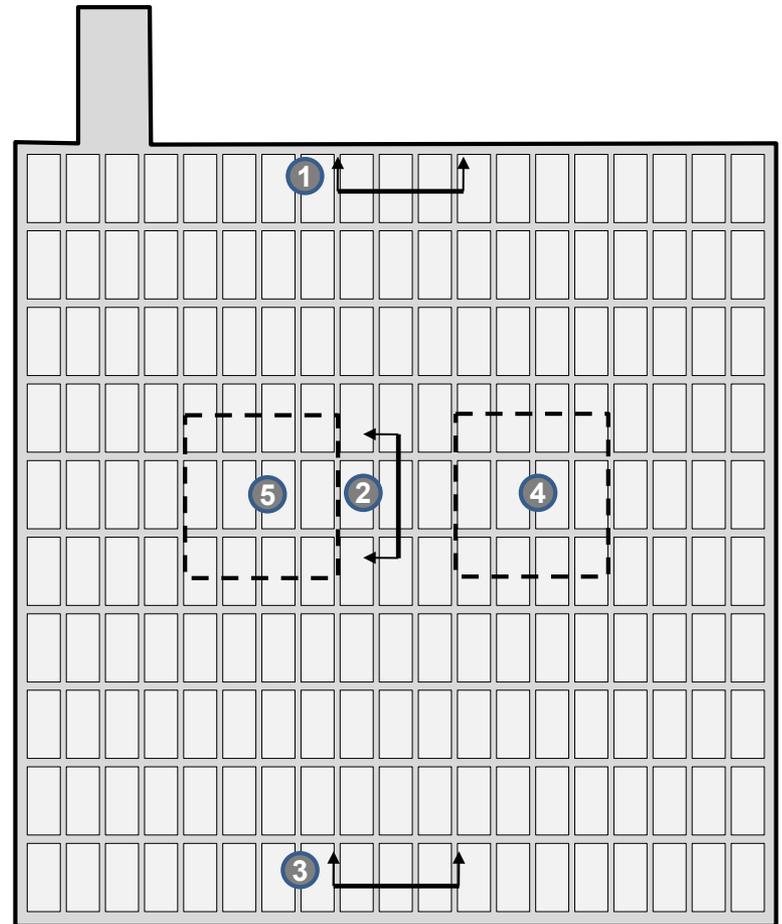


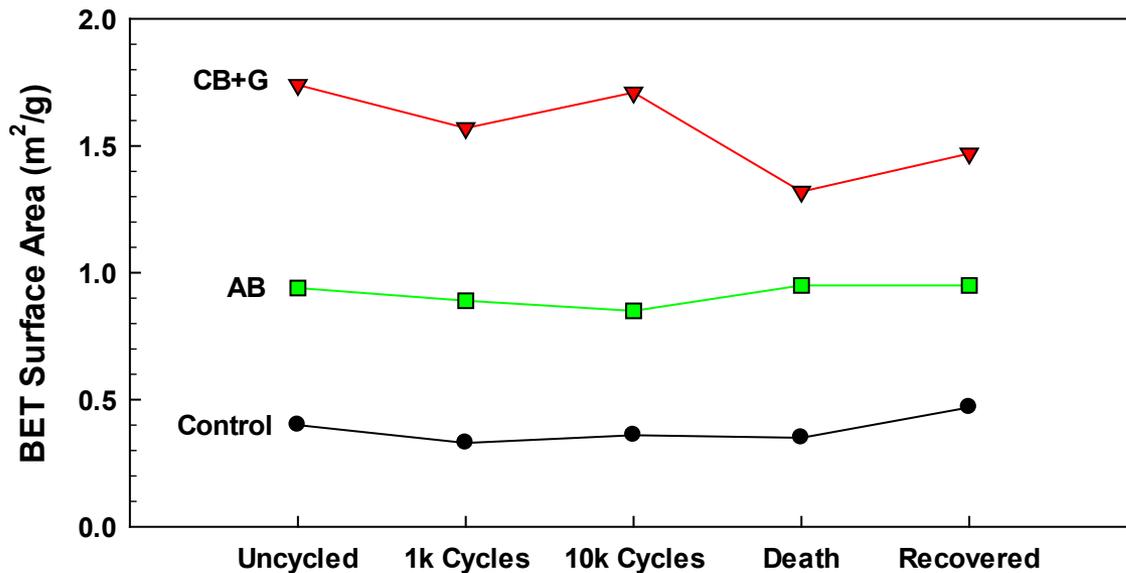
Plate Morphology

- Cross sectional analysis (SEM)
- Cathodoluminescence
- BET surface area
- Hg porosimetry



Surface Area as a Function of Cycles

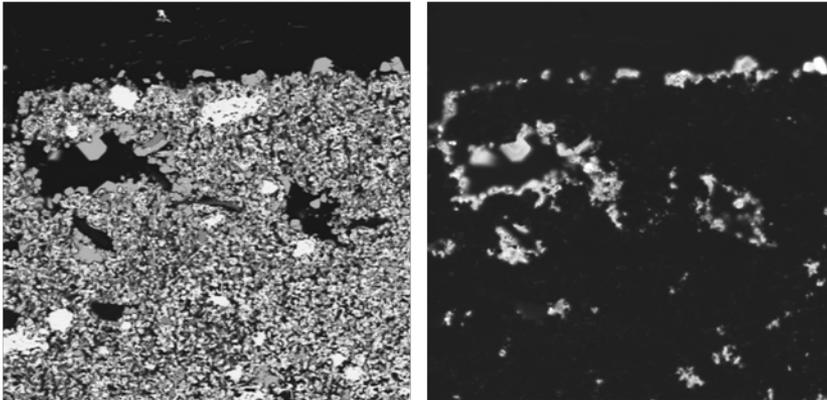
- BET surface area measurements (in m^2/g) for all four battery types as a function of HRPSoC Cycles
- Recovered battery was cycled to death with periodic recovery charges



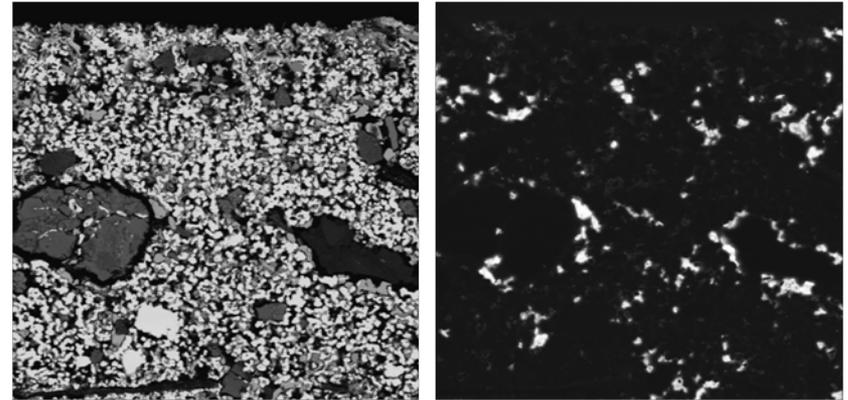
	Uncycled	1k Cycles	10k Cycles	Death	Recovered
Control	0.40	0.33	0.36	0.35	0.47
CB+G	1.74	1.57	1.71	1.32	1.47
AB	0.94	0.89	0.85	0.95	0.95
AC	9.30	6.46	8.45	4.21	

Structural Evolution: 1k Cycles

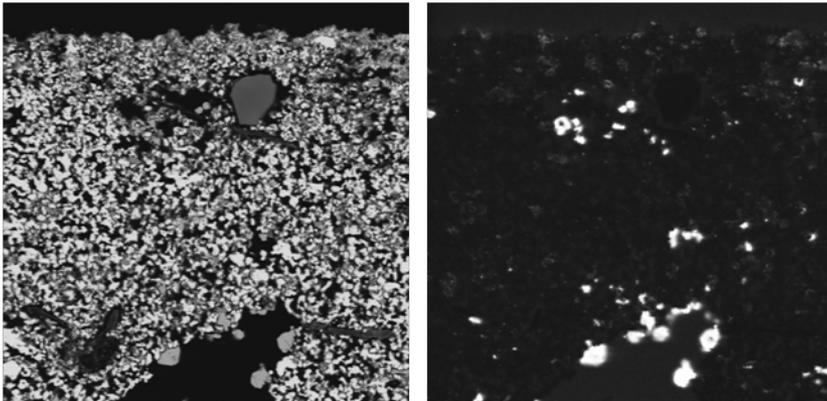
Control



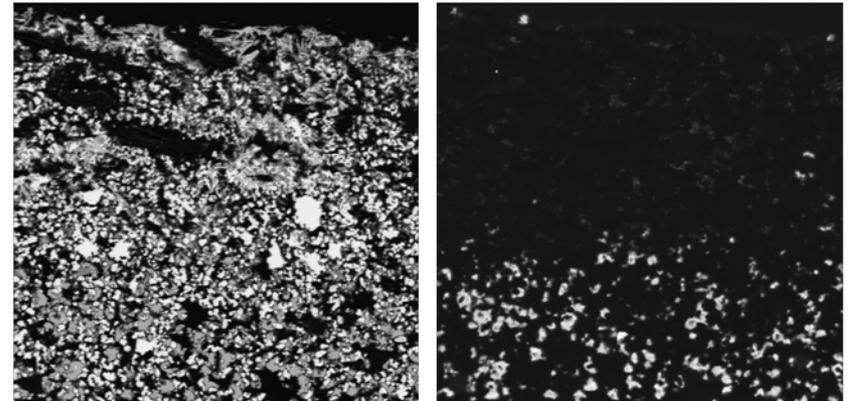
Activated Carbon



Acetylene Black



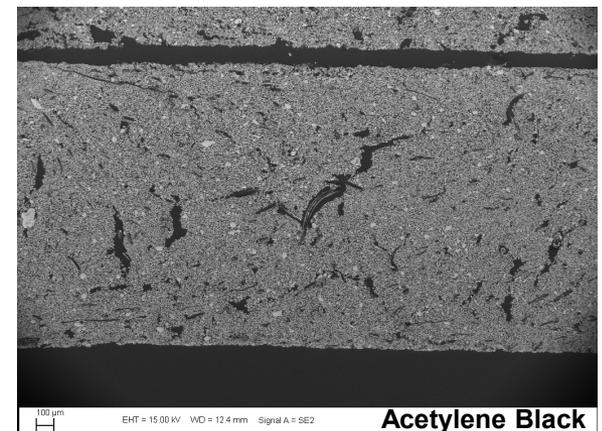
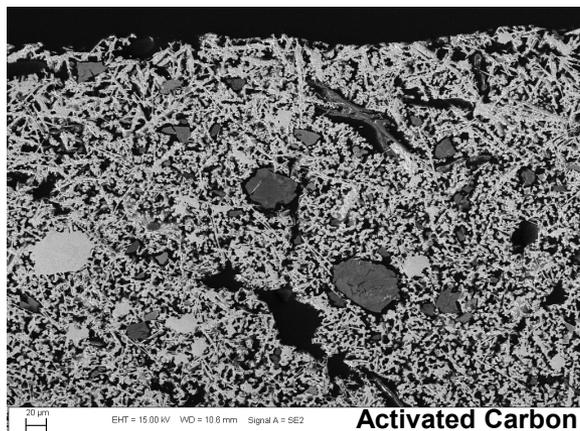
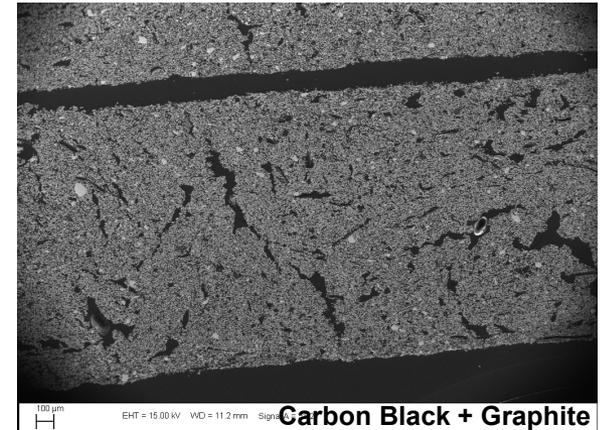
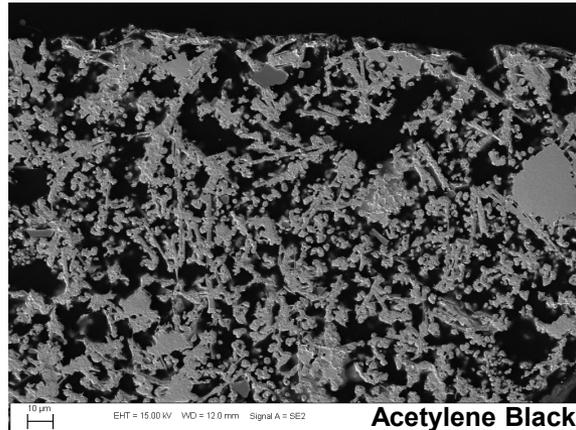
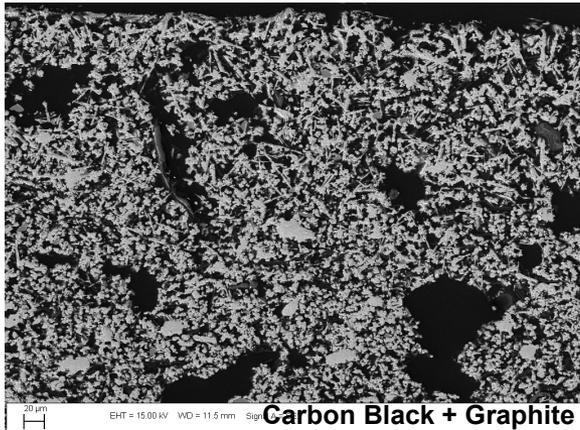
Carbon Black + Graphite




100 microns

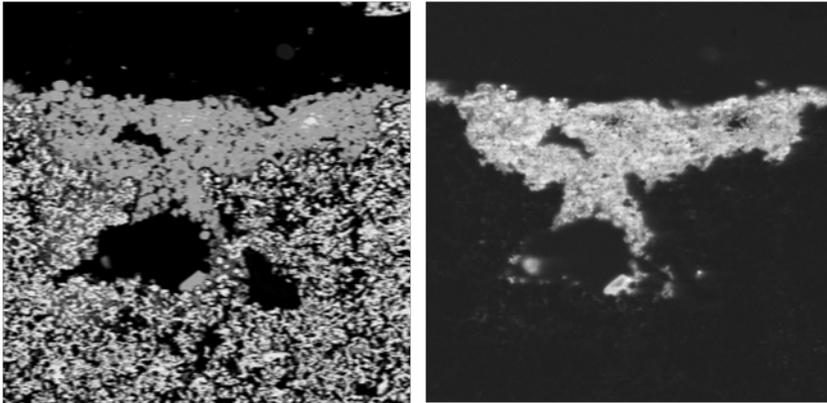
Differences at 1k Cycles

- Begin to see development of a dendritic structure in the near surface regions (top 50-100 microns) of carbon containing cells
- Fissures visible in carbon containing cells, most prominent in CB+G

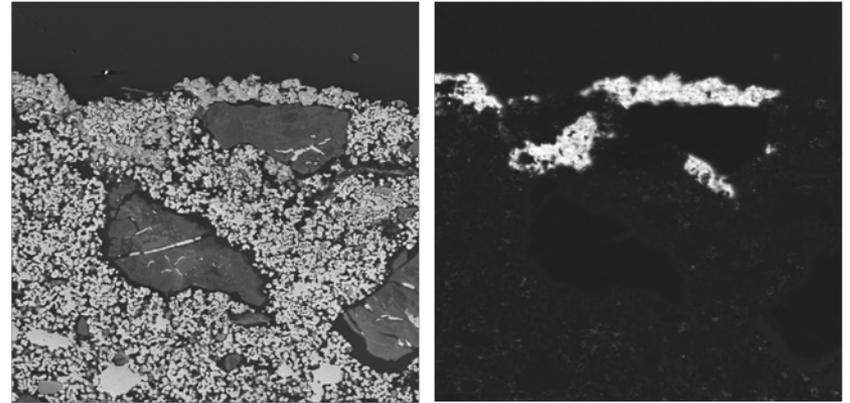


Structural Evolution: 10k Cycles

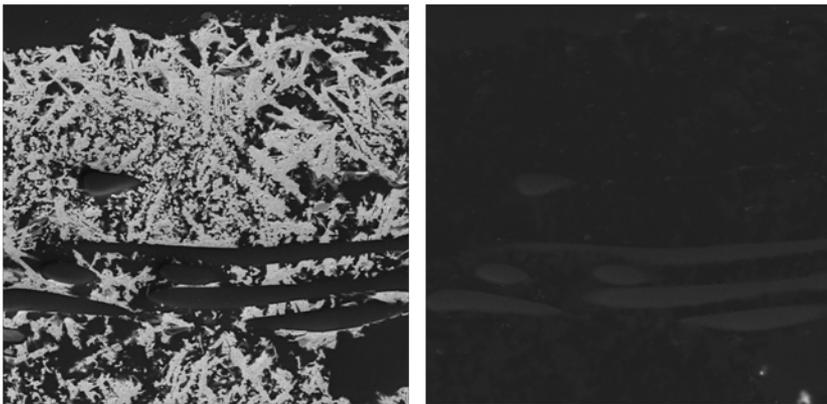
Control



Activated Carbon

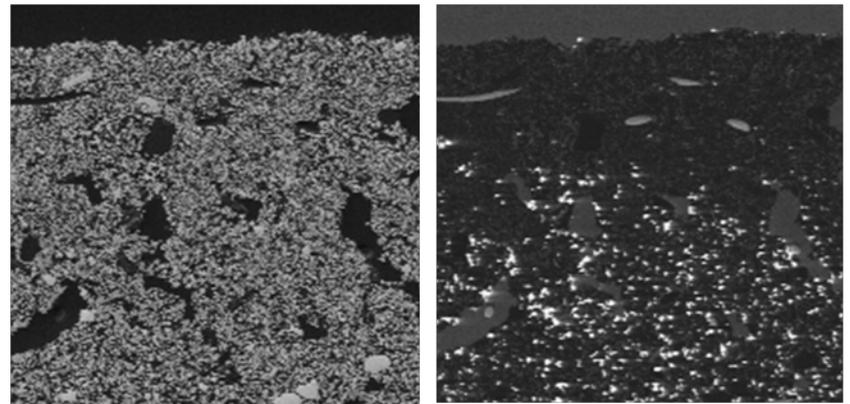


Acetylene Black



100 microns

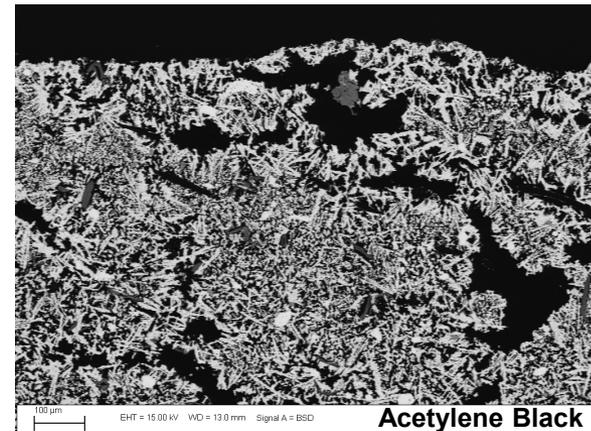
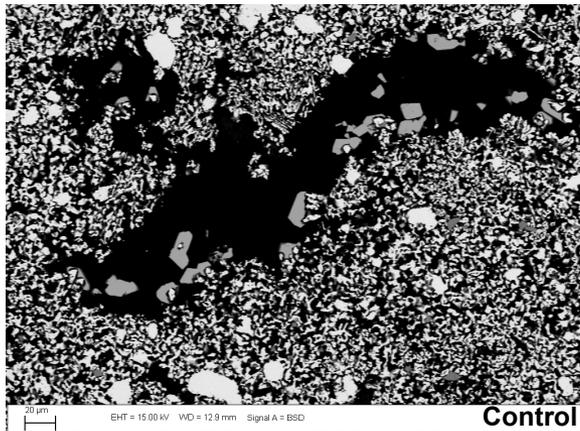
Carbon Black + Graphite



250 microns

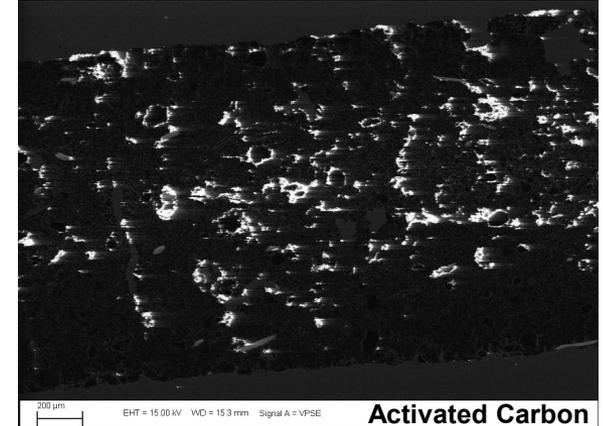
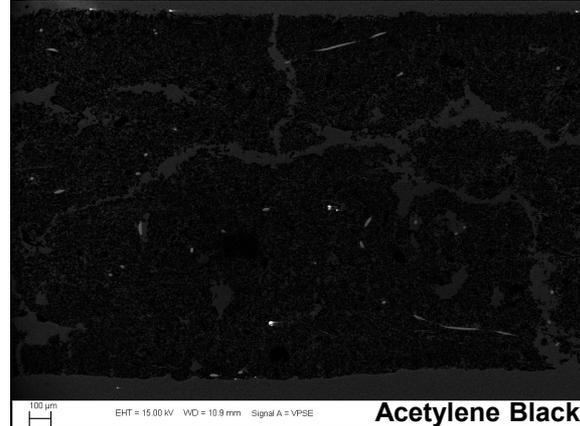
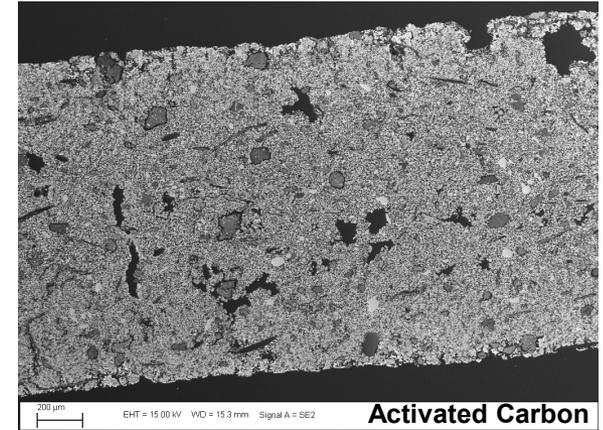
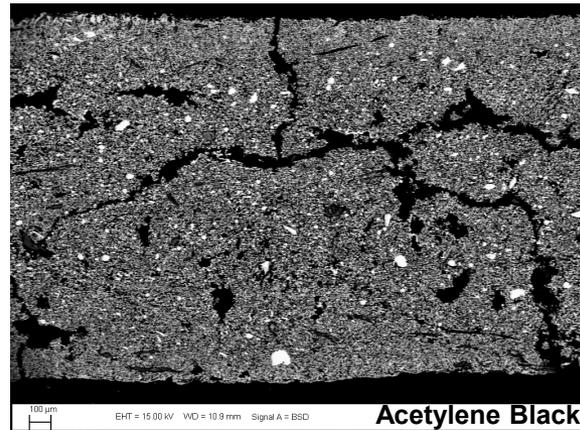
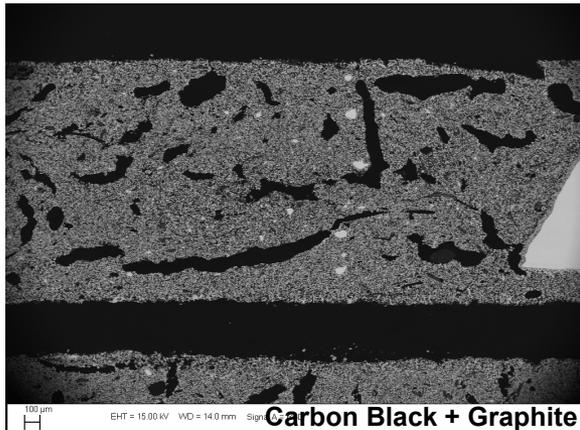
Differences at 10k Cycles

- In control and AC containing cells, sulfation took place along the surface of interior voids as well as the exterior surface
- In carbon black containing cells, appeared similar to 1k, though with a more pronounced dendritic structure



Differences at End of Life

- In most cases, just more of what was observed at 10k cycles
- Large pores/voids in carbon containing plates (esp. carbon black) become more prominent
- Sulfation ranged from almost complete/through thickness to almost none visible in some of the carbon black containing cells



Summary/Conclusions

- Batteries of all 4 chemistries have been subjected to HRPSoC cycling and evaluated as a function of cycle life
- Carbon additions increase the active area within the negative active material and are clearly electrochemically active, but surface area isn't everything
- All of the carbon modified batteries exhibited an increased cycle life. Suggests production methodology may be of comparable importance to the nature of the carbon additive.
- Carbon black additions provided most significant improvement, but also result in internal damage to the plate
- Failure mechanism for the conditions evaluated here may be tied to positive plate degradation

Future Tasks

- Evaluation of the positive plates from select batteries to establish if that is dominating failure
- Hg Porosimetry of NAM as a function of cycle life
- Wrap up of experimental program by December 2012.

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