SAND2016-4879C

Exceptional service in the national interest

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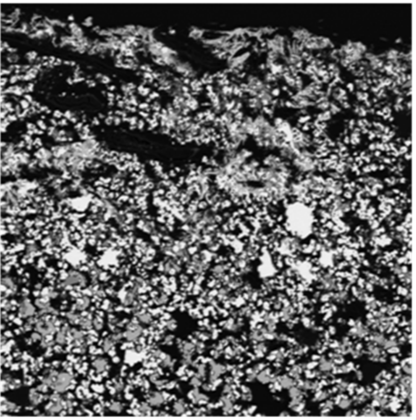

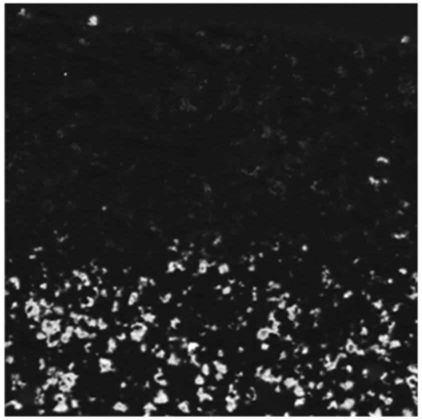

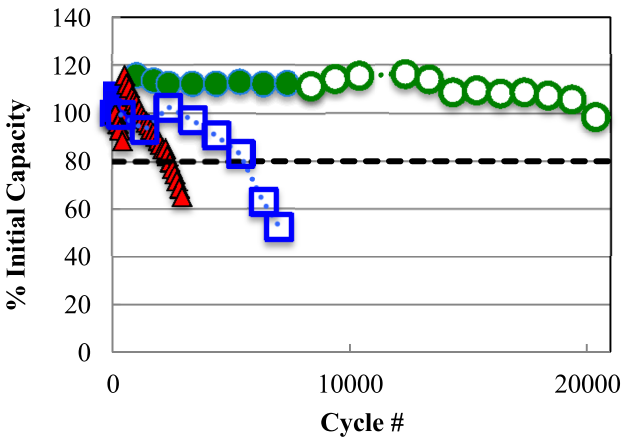

Advanced Pb-Acid Battery Performance

Summer Ferreira, David Enos, Wes Baca

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

SNL Energy Storage System Analysis Laboratory

Sandia National Laboratories

Providing reliable, independent, third party testing and verification of advanced energy technologies for cell to MW systems

Testing Capabilities Include:

- Expertise to design test plans to fit technologies and their potential applications
- OE supported testing
- CRADA opportunities
- WFO arrangements

Cell, Battery and Module Testing

- 14 channels from 36 V, 25 A to 72 V, 1000 A for battery to module-scale tests
- Over 125 channels; 0 V to 10 V, 3 A to 100+ A for cell tests

Energy Storage Test Pad (ESTP)

72 V 1000 A Bitrode (2 Channels)

System Testing

- Up to 1 MW, 480 VAC, 3 phase
- 1 MW/1 MVAR load bank

Cycling protocols employed in testing

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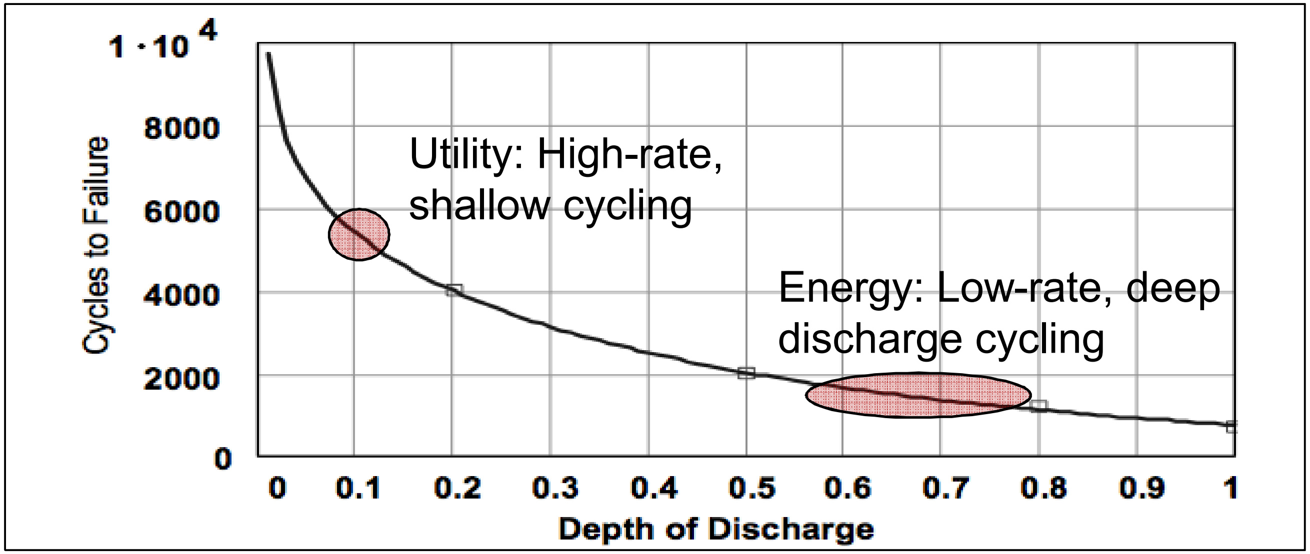
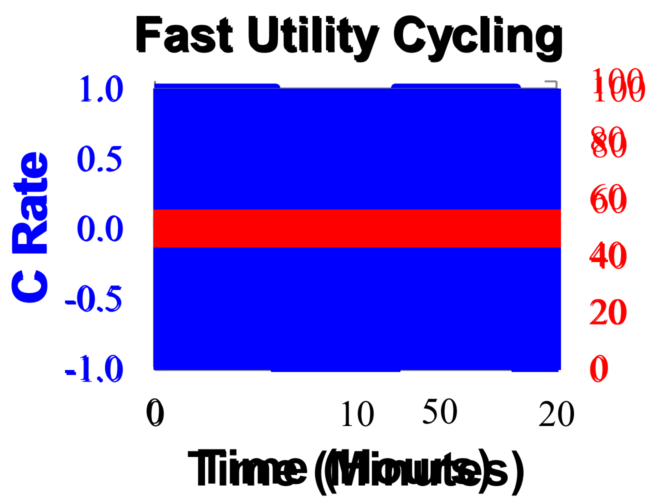
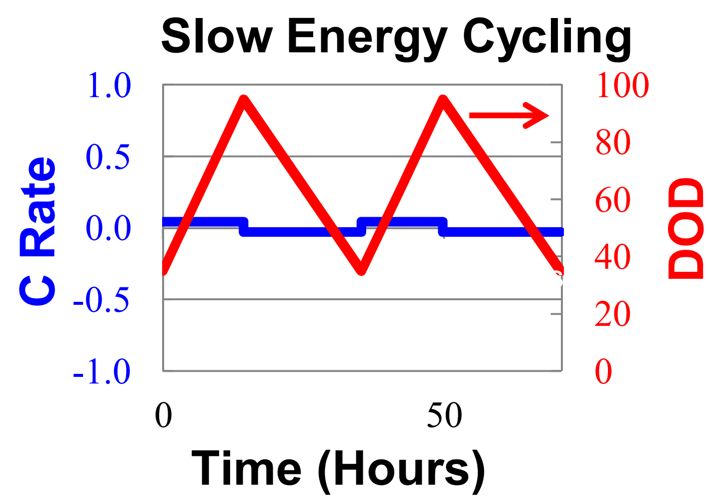


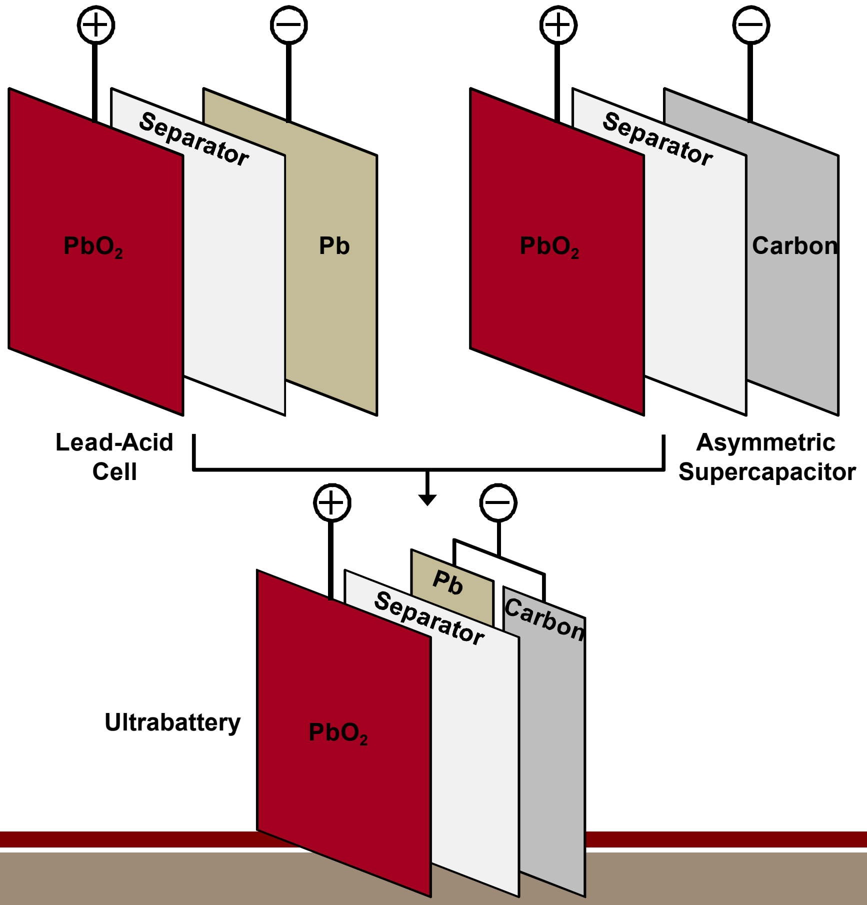
VRLA Life cycle data *S. Drouilhet, B.L. Johnson, 1997 NREL*

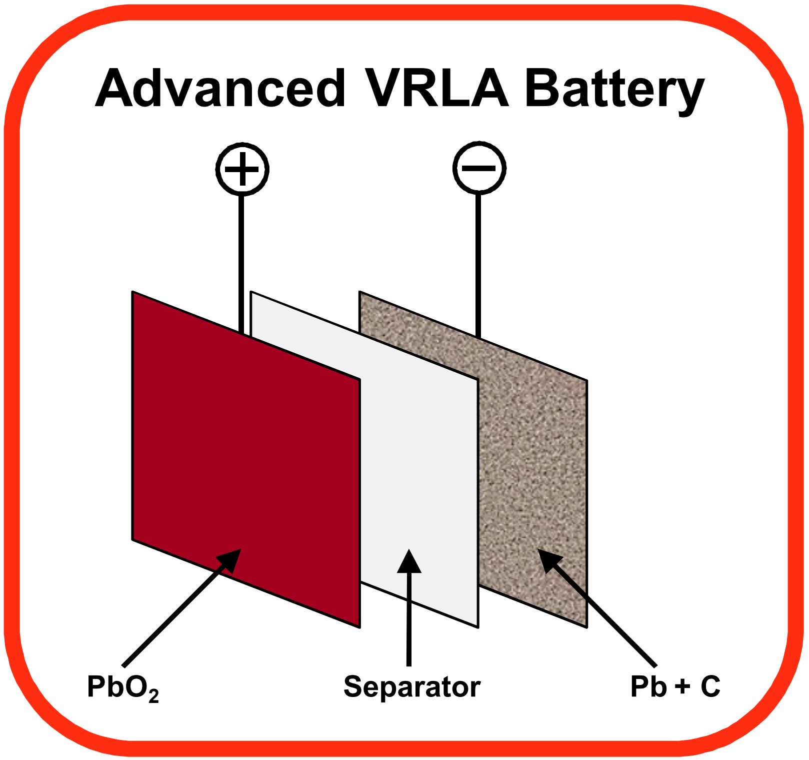




The Advanced VRLA Battery

- Recently, there are 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

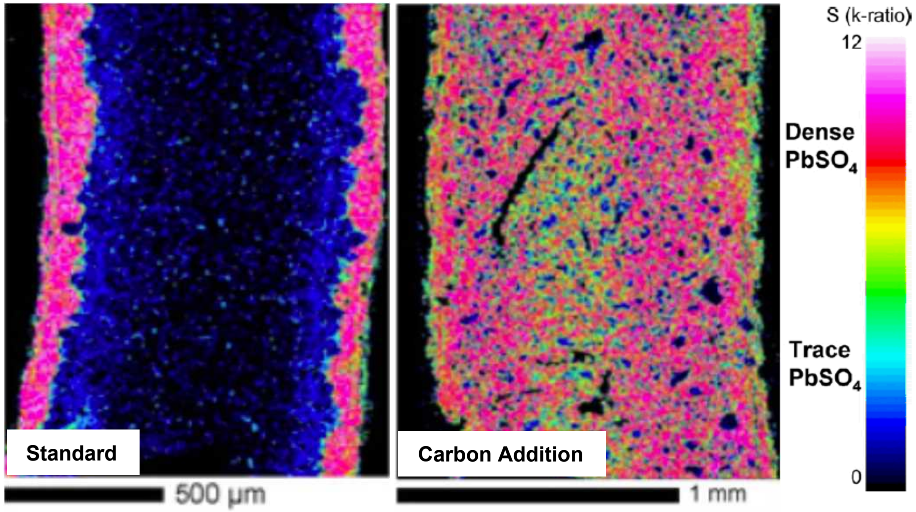




Why add excess carbon to the NAM?

- Carbon additions to the negative active material (NAM) can substantially reduce hard sulfation

➢ **Fernandez, 2010***



*M.Fernandez, J.Valenciano, F.Trinidad, N. Munoz, Journal of Power Sources, Vol. 195 (2010), pp. 4458-4469.

Research Goals

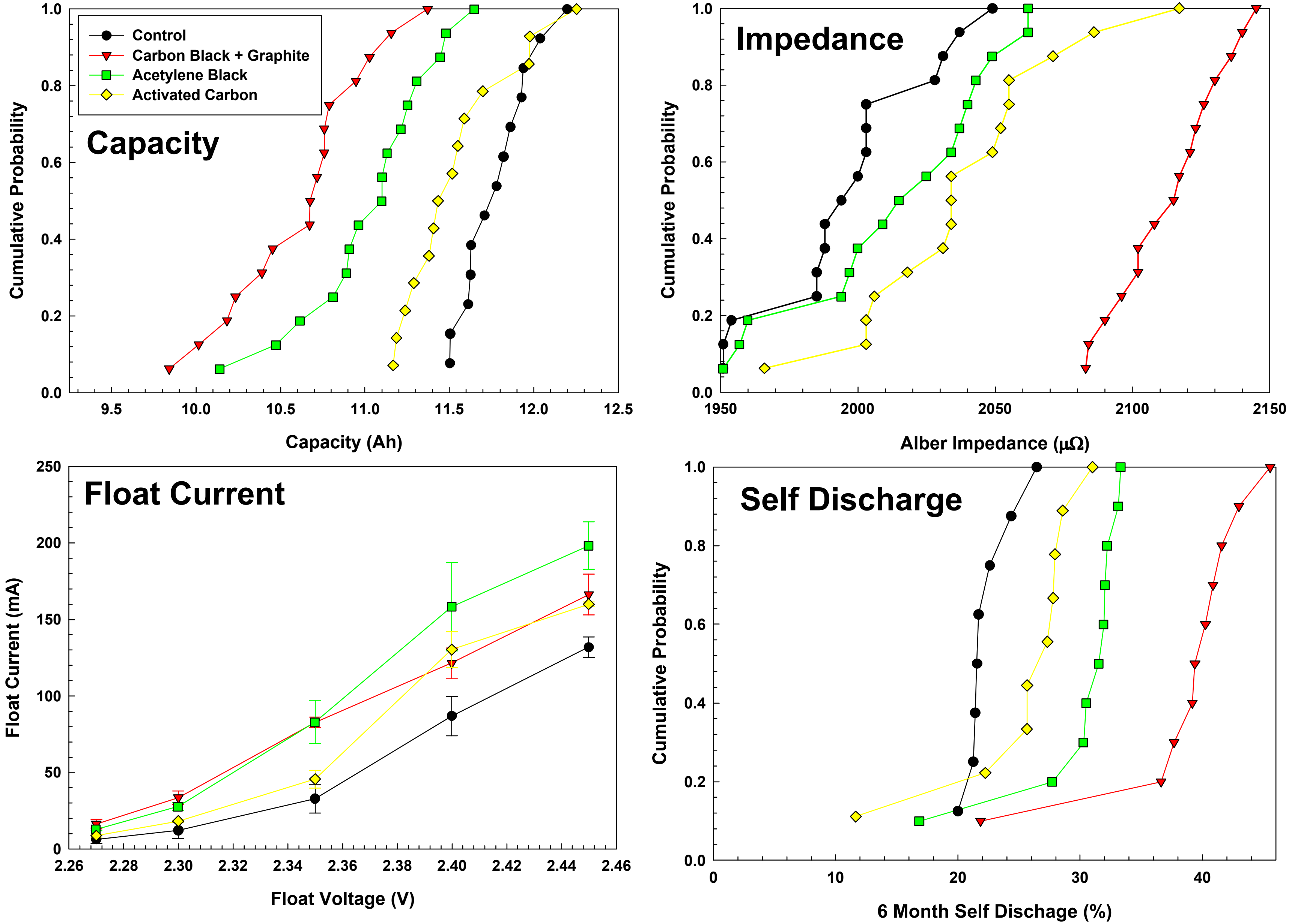
- The overall goal of this work is to quantitatively define the role that carbon plays in the electrochemistry of a VRLA battery.
  - What reactions/changes take place on the surface of the carbon particles?
  - What processes govern the increase and then eventual decrease in capacity with increasing # of cycles?
  - Are the kinetics of the charge/discharge process different when carbon is present vs. when it is not?
  - Why are some carbons effective additions while others are not? Are there any distinguishing characteristics of effective additions? Is the effectiveness controlled by aspects of the plate production method? etc.

Constituent Material Analysis

- **Given the limited understanding of what characteristics yield an effective carbon addition, a broad spectrum approach is being taken to quantify the carbon particle properties**.

	Carbon Black	**Graphite**	**Actetylene Black**	**Activated Carbon**
Particle size	20 nm	20+ µm	20 nm	100+ µm
Effective surface area (BET)	75 m^2/g	6 m^2/g	75 m^2/g	>2000 m^2/g
Structure (XRD)	Semicrystalline	Crystalline	Semicrystalline	Amorphous
Acid Soluble Contamination	Clean	Clean	Very Clean	Na, PO_4

Performance Testing Shows Some Differentiation between Control and Carbon Modified Batteries



Performance Testing Shows Similarities Between Control and Carbon Modified Batteries

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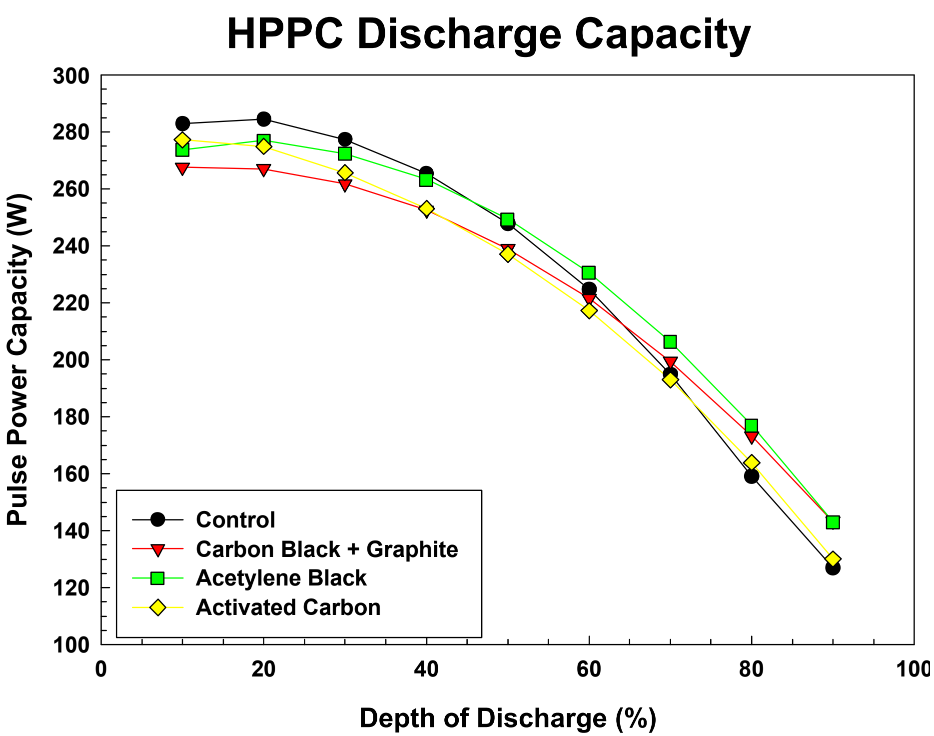

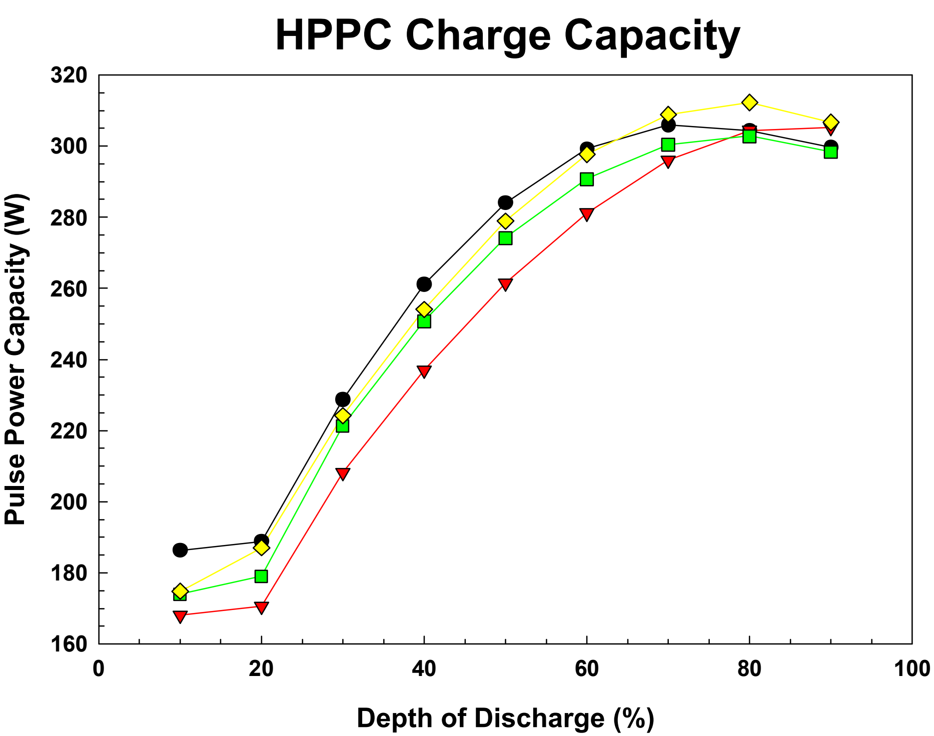

Note: These HPPC data are for new cells

More Dramatic Differentiation Observed as the Batteries are Cycled

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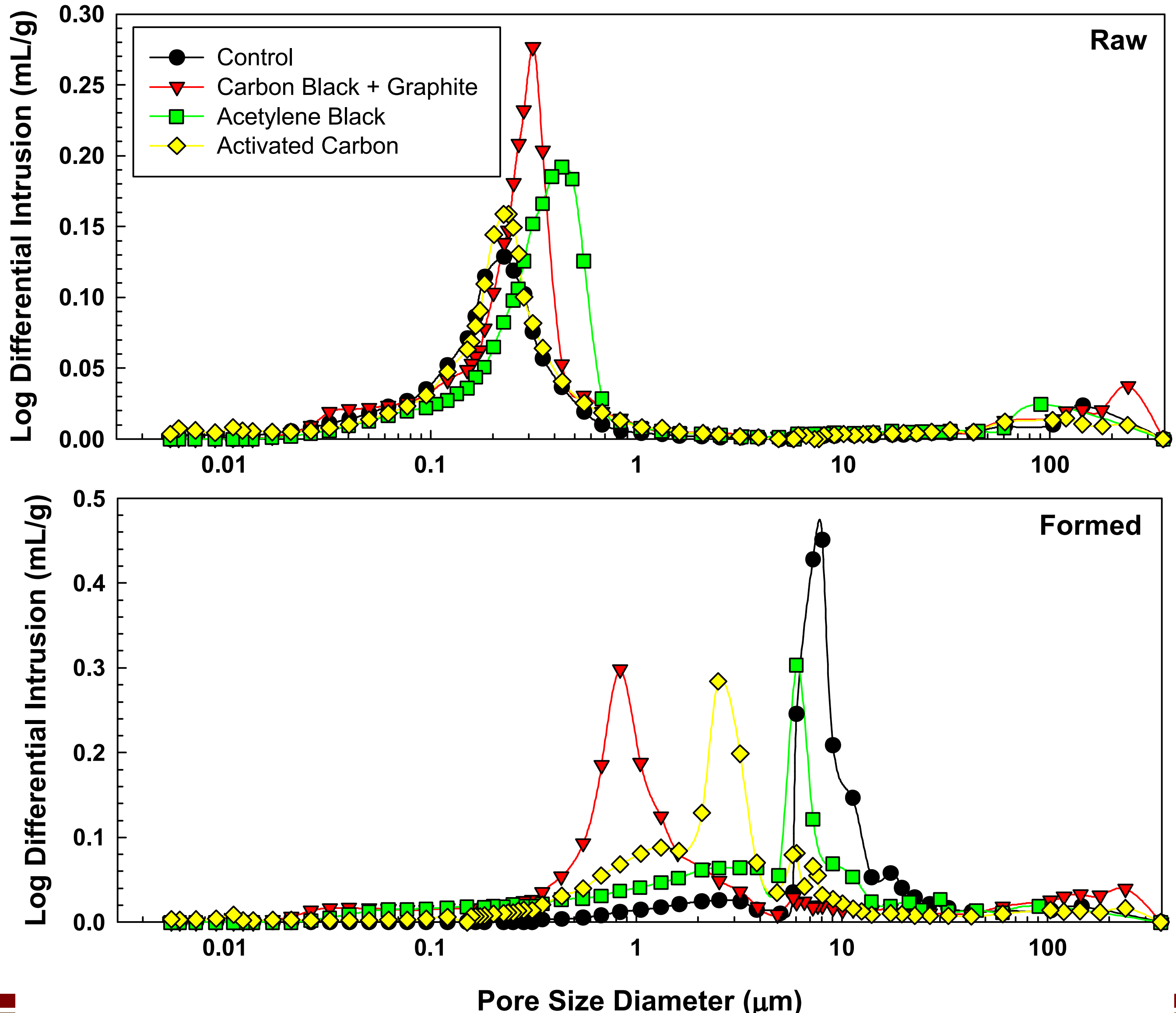
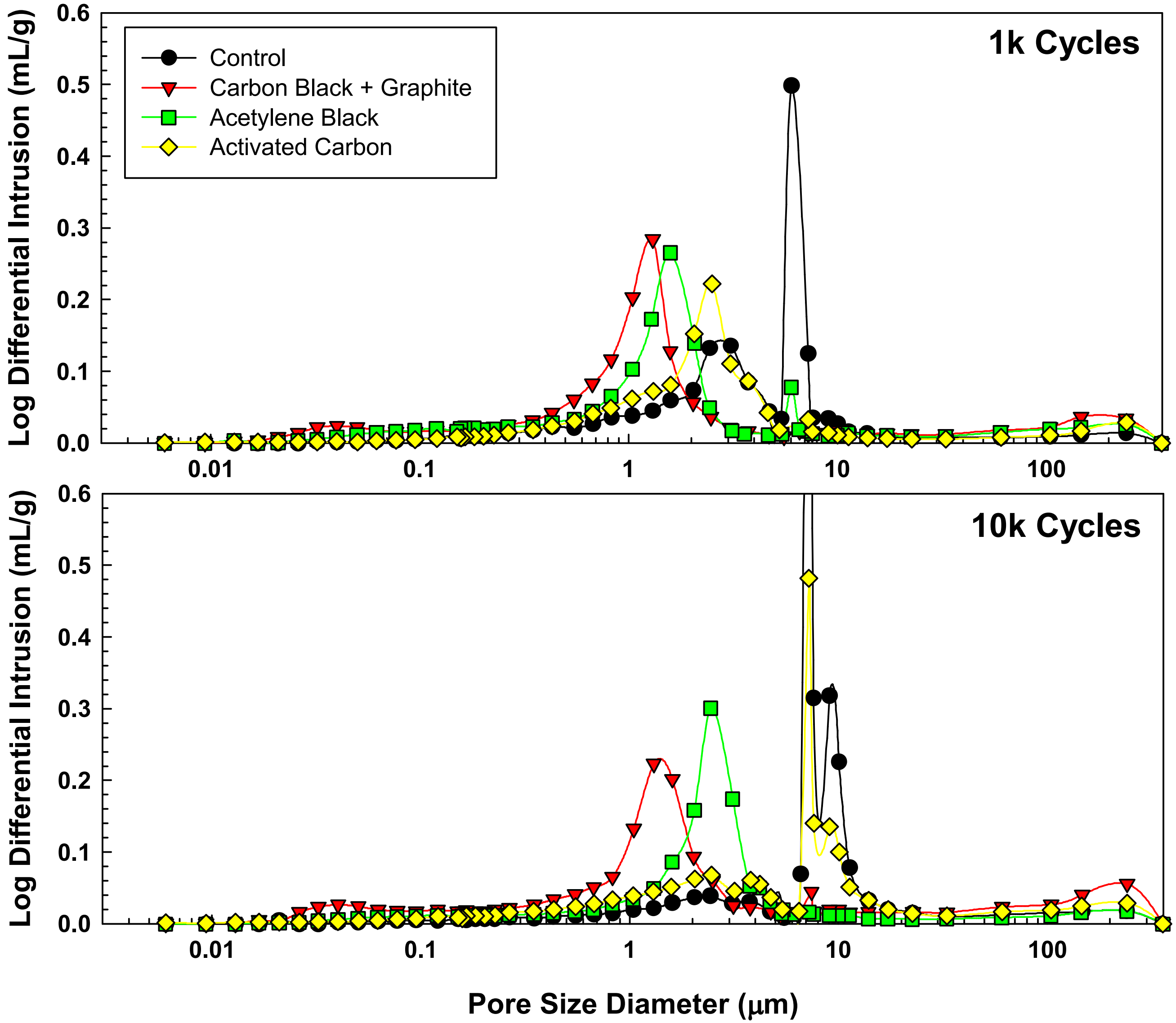
- Comparable behavior observed for all four battery types at 1k cycles
- At 10k cycles, capacity loss was evident in the control, acetylene black, and activated carbon batteries (but not in the carbon black + graphite cell)
- Control battery failed at 11,292 cycles
  - Failure defined as a capacity loss of greater than 20% after three discharge/charge cycles in an attempt to recover.

Porosity and Pore Size Distribution



Porosity and Pore Size Distribution



Minimal Sulfation at 1k Cycles

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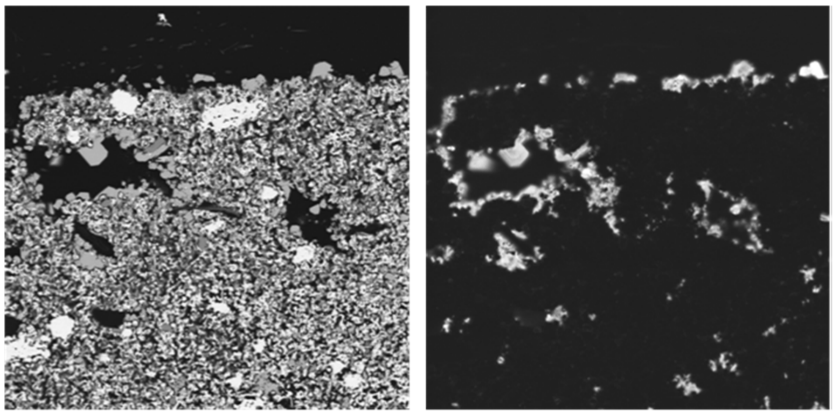
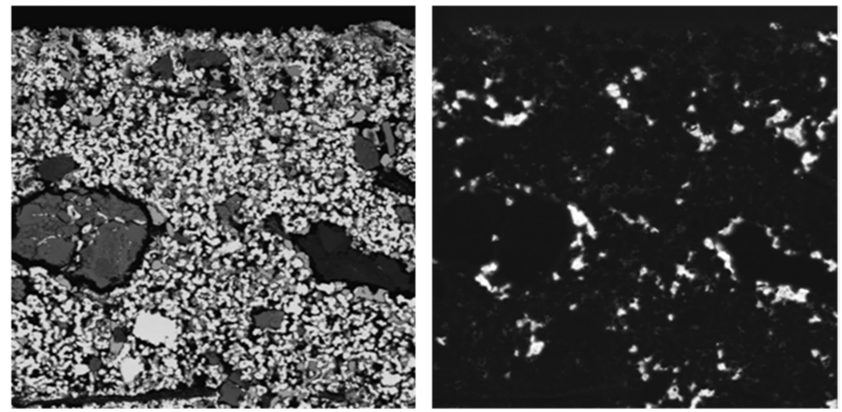
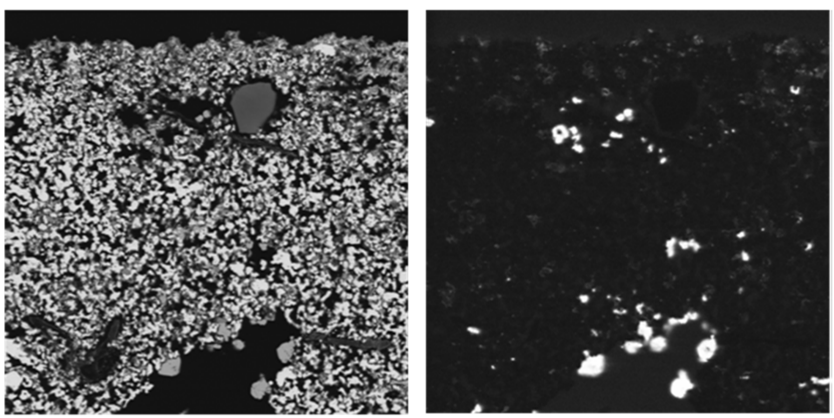
Control



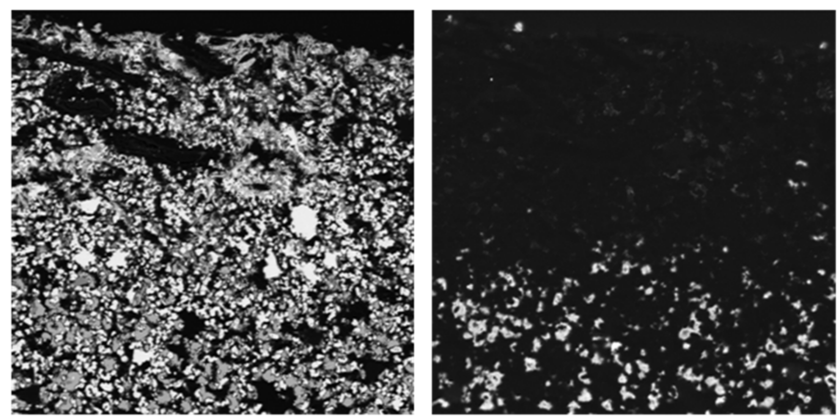
Activated Carbon



Acetylene Black

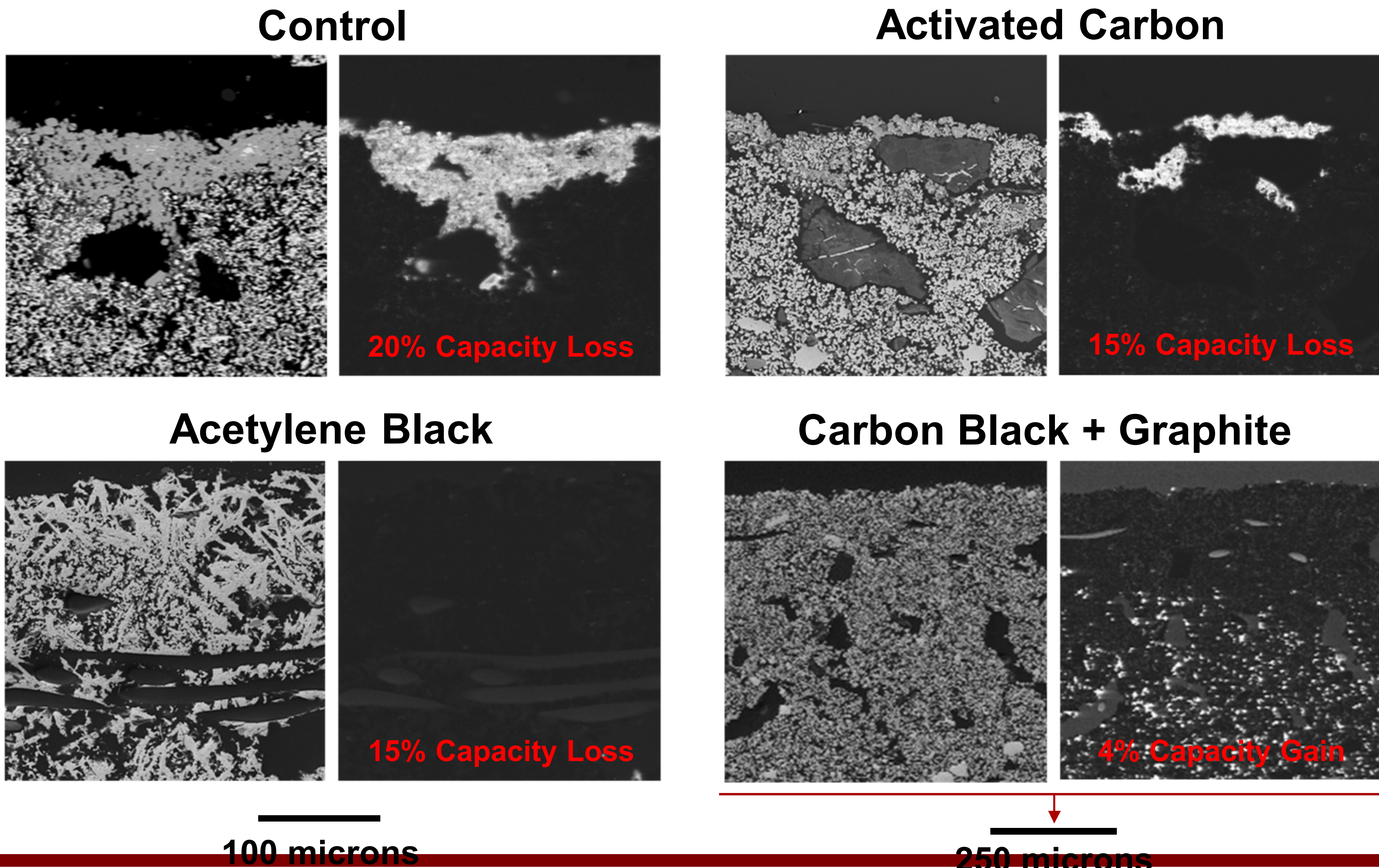


Carbon Black + Graphite



100 microns

Significant Sulfation at 10k Cycles for Two of the Batteries



FY11 Testing of Ultrabattery® modules

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East Penn

- Both Ultrabattery® designs incorporate a supercapacitor in parallel with the negative electrode in a VRLA 12 cell, 1,000 Ah, 24V battery module.
- Tested with both a 'PV' and 'utility' cycle.

Furukawa

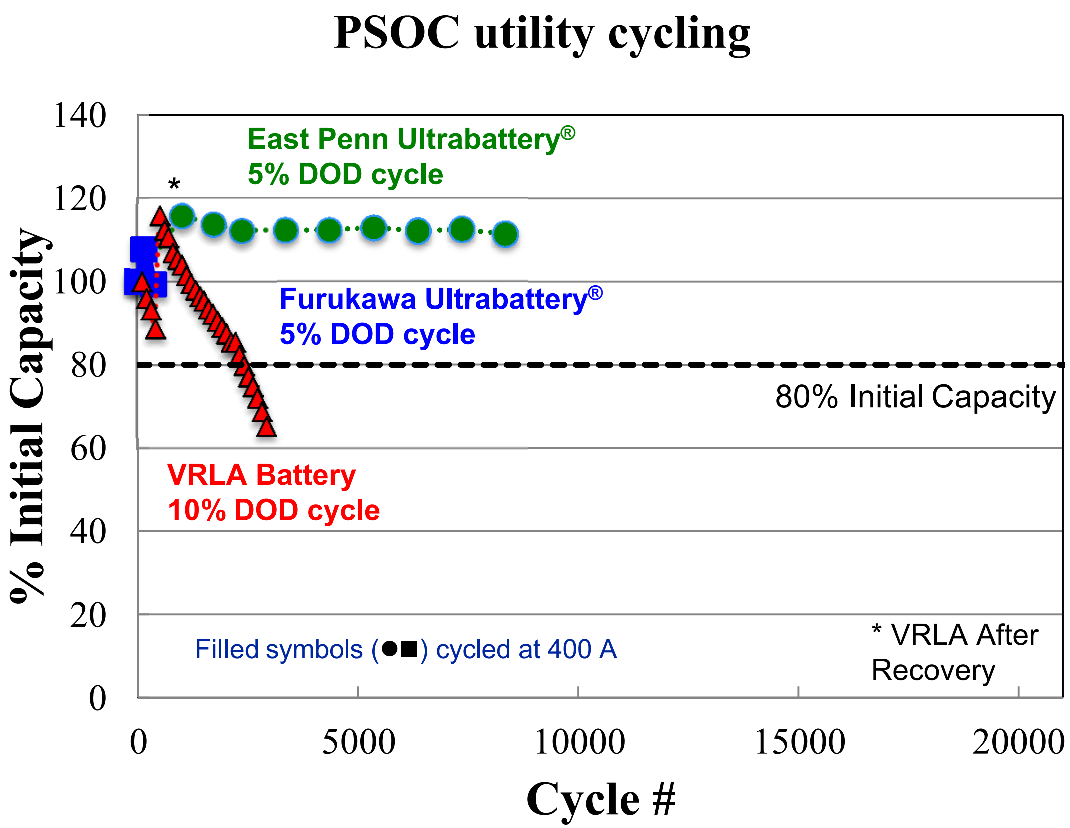
Summary of completed testing activities

East Penn Ultrabattery® Module
20,347 10% PSOC utility cycles
422 Days and 229 PV deep discharge cycles

Furukawa

FurukawaUltrabattery® Module
7,012 10% PSOC utility cycles
498 Days and 280 PV deep discharge cycles

East Penn Ultrabattery® performs much longer than VRLA



Furukawa Ultrabattery® ran for 147 cycles at 400 A PSOC current

East Penn Ultrabattery® ran for over 8,000 cycles at 400 A PSOC current

- Ultrabatteries® 1,000 AH, 400 A and 300 A 5% PSOC cycling
- VRLA 30 AH, 1C 10% PSOC cycling
- Temperature rise in Ultrabattery® modules required reducing current for further testing

East Penn Ultrabattery® performs much longer than VRLA

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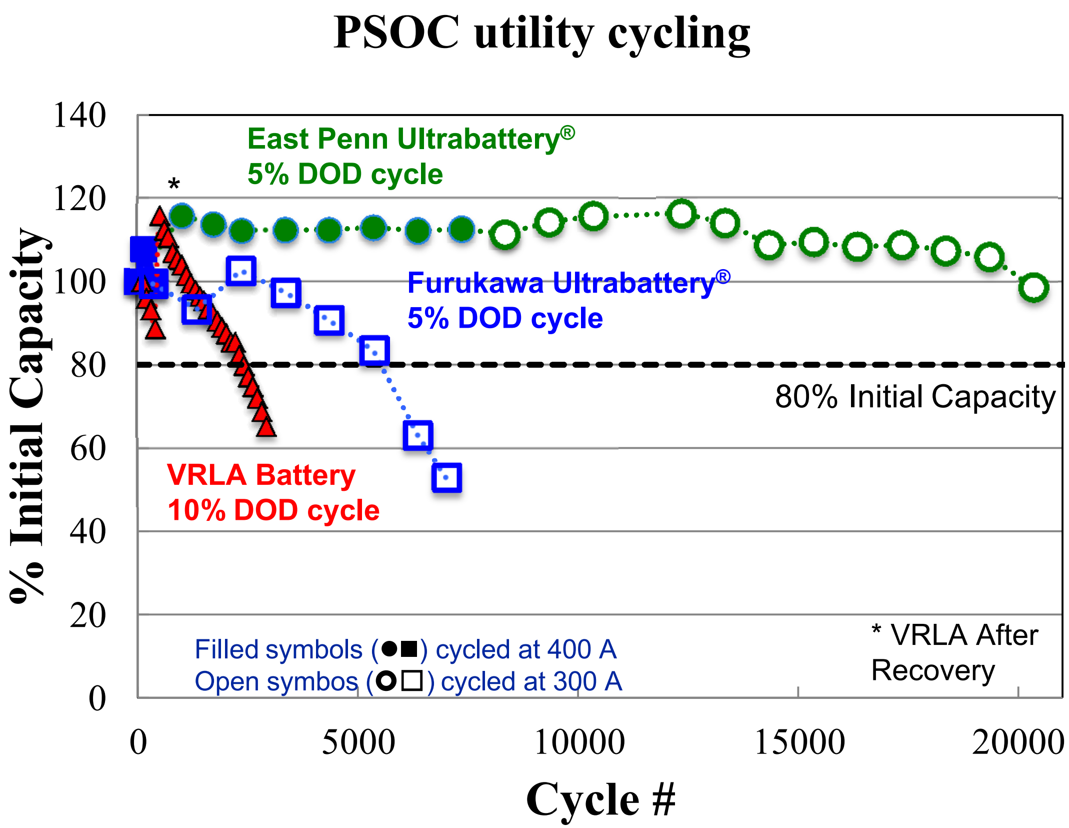

Furukawa Ultrabattery® operated at elevated temperatures, likely leading to thermally activated degradation

East Penn Ultrabattery® ran for more than 20,000 cycles without recovering the battery

- Ultrabatteries® 1,000 AH, 400 A and 300 A 5% PSOC cycling
- VRLA 30 AH, 1C 10% PSOC cycling
- Temperature rise in Ultrabattery® modules required reducing current for further testing

East Penn Ultrabattery® performs much longer than VRLA

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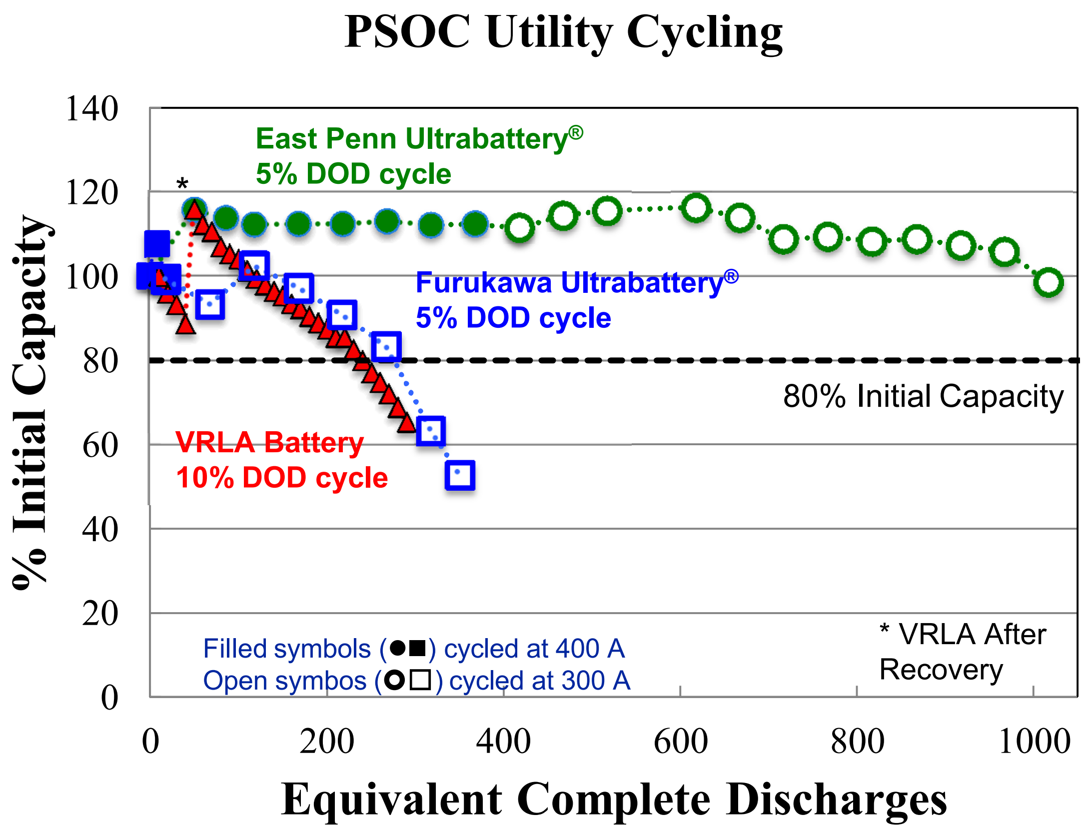
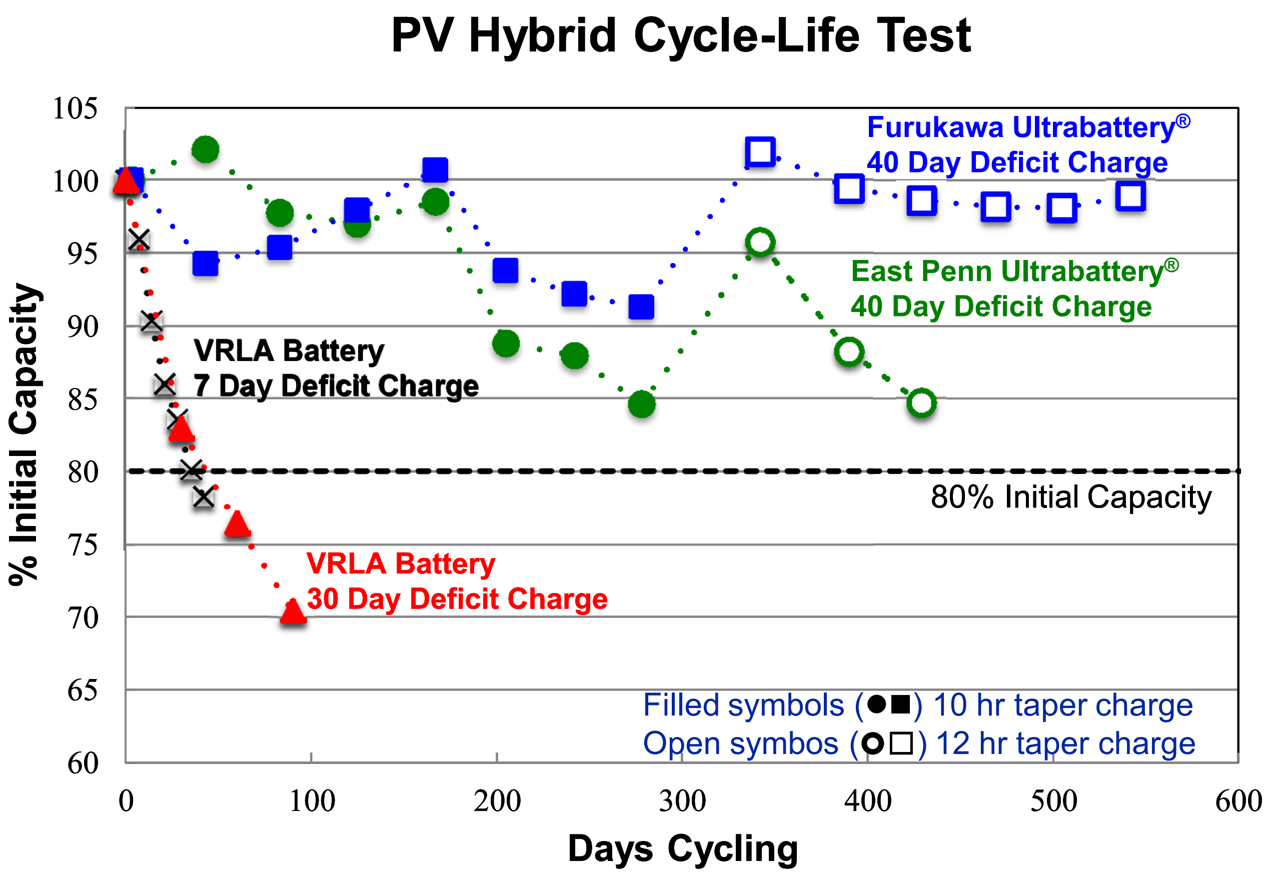


Furukawa Ultrabattery® operated at elevated temperatures, likely leading to thermally activated degradation; capacity dropped below 80% of initial by 6,300 cycles.

East Penn Ultrabattery® ran for more than 20,000 cycles without recovering the battery; cycling ended when temperatures rises prevented operation.

- Ultrabatteries® 1,000 AH, 400 A and 300 A 5% PSOC cycling
- VRLA 30 AH, 1C 10% PSOC cycling
- Temperature rise in Ultrabattery® modules required reducing current for further testing

Ultrabatteries® also perform much longer in PV cycling than VRLA



Even at 40 day deficit charge, Ultrabatteries® have performance far surpassing traditional VRLA batteries even with as low as a 7 day deficit charge (without recovery by taper charge).

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Summary/Conclusions to Date

- Battery performance
  - Pb-C batteries had lower initial capacity, higher initial internal resistance, higher float current, comparable HPPC performance, and superior HRPSoC cycling performance
  - Hybrid batteries had far longer cycle life than conventional Pb-acid batteries
- Material Characterization
  - Pore structure in Pb-C batteries notably smaller (order of magnitude), but comparable in overall volume
  - Hard sulfation becoming significant after 10k cycles with the control battery and activated carbon battery

Outlook

- Bipolar or simultaneous charge/discharge designs offer further areas of Pb-acid design.
- Further advancement of Pb-acid chemistries may be a reasonable part of a multipronged approach to designing the ‘beyond Li’ portfolio to meet current and future needs in stationary storage.