SAND2011-4417C

Recent Progress in Understanding the Performance Improvements in Carbon-Enhanced Valve Regulated Lead Acid Batteries

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Advanced Power Sources R&D

Sandia National Laboratories

Albuquerque, New Mexico, USA

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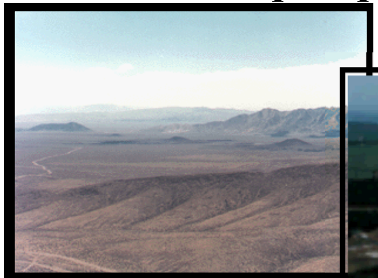
Sandia National Labs

Albuquerque, New Mexico

Tonopah Test Range, Nevada

WIPP, New Mexico

National Security Test Site, Nevada



Kauai Test Facility, Hawaii

Livermore,California

Sandia National Laboratories

Sandia — in round numbers

8,700 full-time employees

~7,800 in New Mexico

~800 in California

1185 buildings, 6.5 M sq. feet

1,550 PhDs, 2,500 Masters

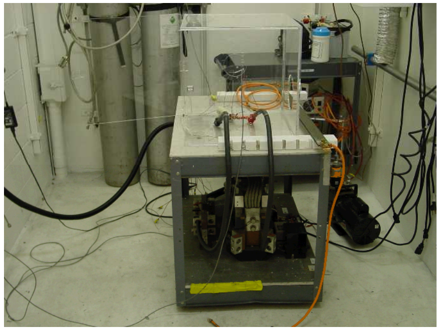
- Mechanical Engineering – 15%
- Electrical Engineering – 25%
- Other Engineering – 14%
- Other Fields – 11%
- Physics – 8%
- Chemistry – 7%
- Math – 3%
- Computing – 11%
- Other – 6%

Annual budget $2.5B

Sandia Is The Lead US Department of Energy Lab For Transportation Battery Response In Abnormal Environments

Sandia provides full range of material, cell, module and pack-level electrical and thermal characterization and abuse testing.

Overcharge

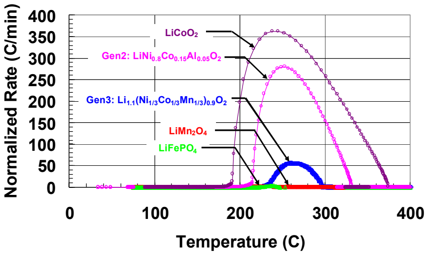


Short circuit

Over Discharge

Over Temperature

Cell Prototyping



Thermal Stability (Accelerating Rate Calorimetry)

Crush

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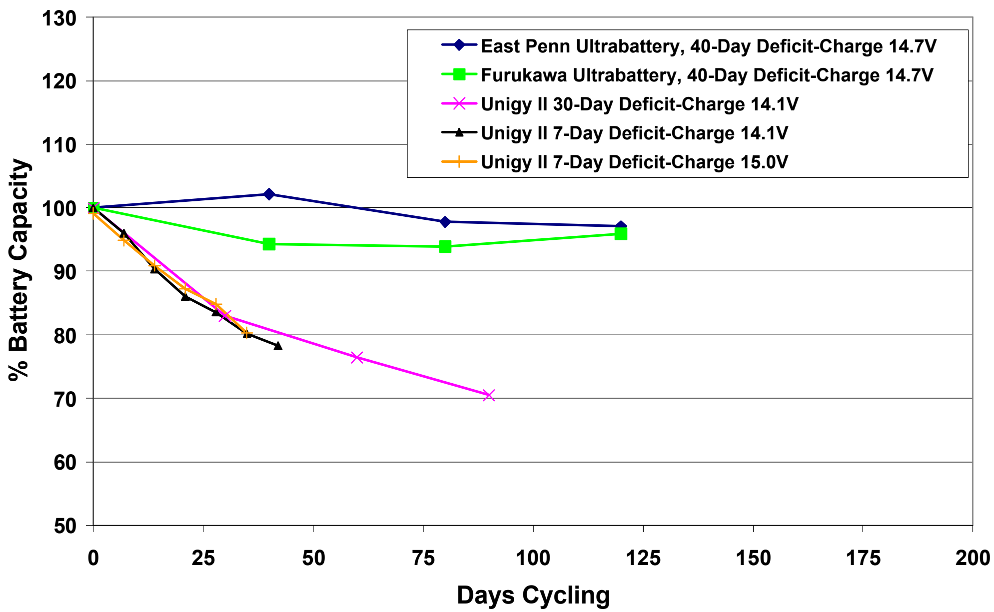
Energy Storage Testing Program

Collaborative with Industry, Utilities and States

PV Hybrid Cycle-Life Test

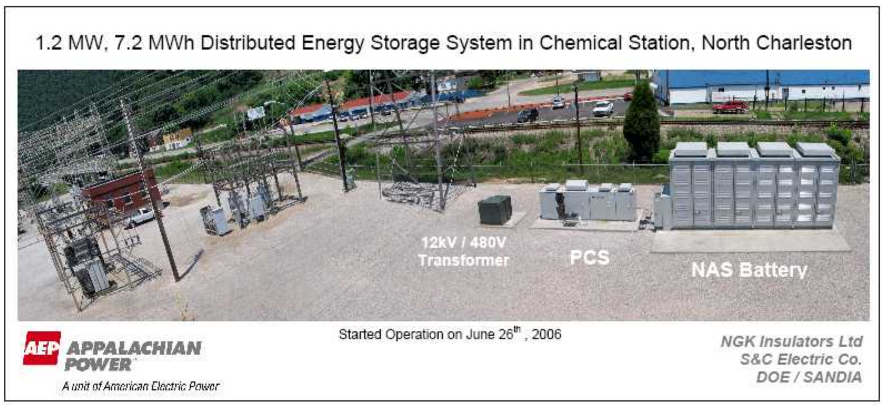


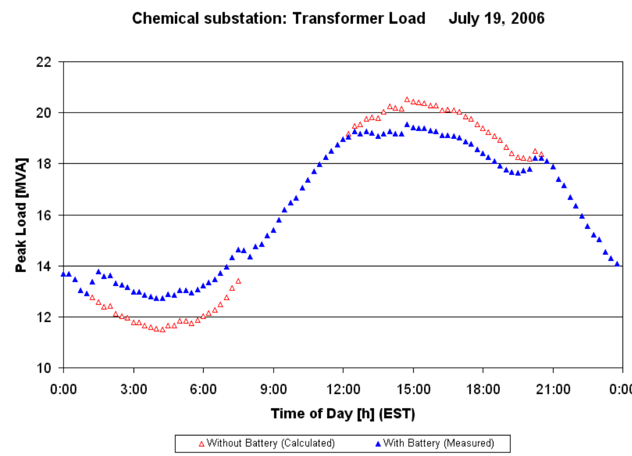
Testing in simulated PV cycle shows the carbon enhanced ‘Ultra Batteries’ maintain capacity significantly better than conventional VRLA batteries

DOE Energy Storage Program

- Dr. Imre Gyuk—DOE Program Manager
- SNL provides leadership for OE energy storage program
  - Ross Guttromson's Energy Infrastructure Department
- Power Sources Technology Group leads the electrochemical energy storage element

Large-scale storage demonstration projects

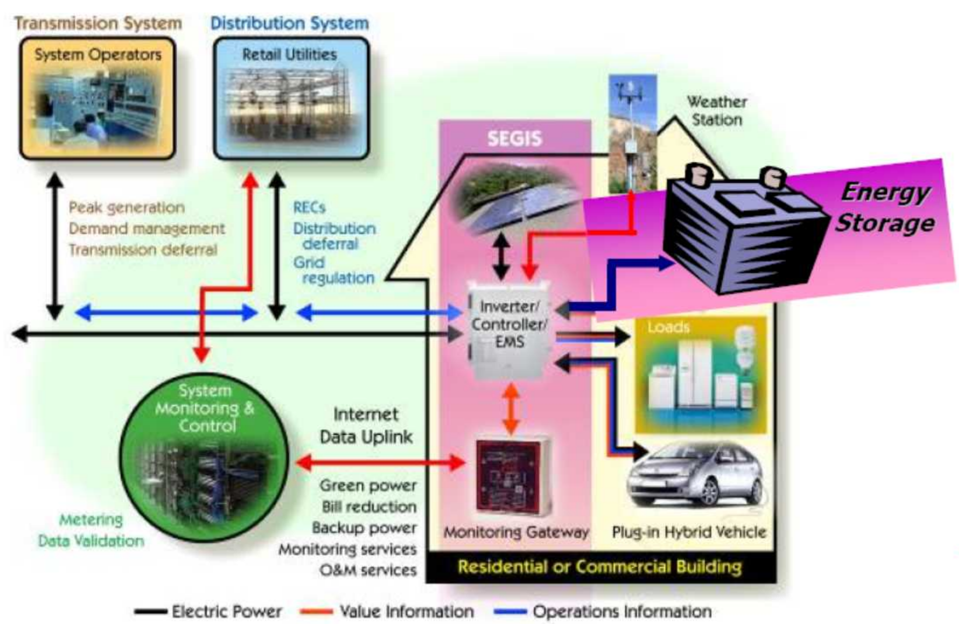




Storage battery test and evaluation
"independent, objective results"
reputation

Presentation Outline

- **Sandia National Laboratories**
- **Research at Sandia in Energy Storage**
  - Flow Batteries
  - Sodium-Based Systems
  - Flywheels
  - Testing
- **Introduction to Advanced Lead-Acid ("Lead Carbon") batteries**
  - Motivation
- **Characterization Plan**
- **Results**



Highly Leveraged State and Utility Energy Storage Collaborations

- California Energy Commission (CEC)
- New York State Energy Research and Development Authority (NYSERDA)
- Clean Energy States Alliance (CESA)
- Utility Field Tests for new technologies and Applications

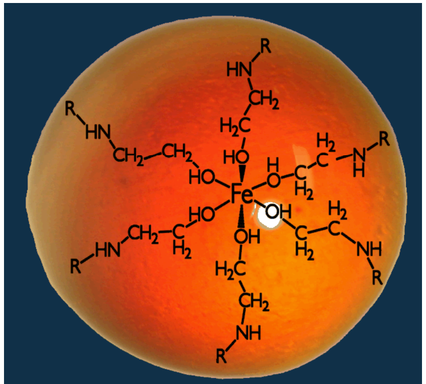
DOE and its Labs provide technical expertise to aid State Energy Agencies in determining and managing energy storage projects appropriate to local state requirements

Sandia National Laboratories

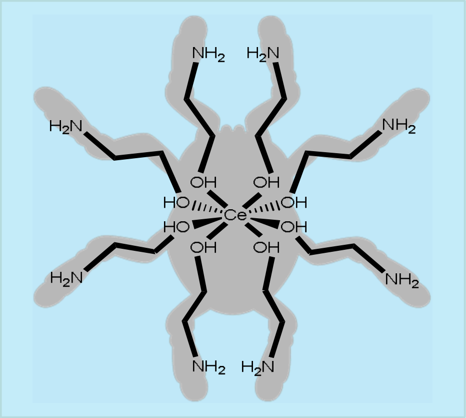
New Redox Couples for Flow Batteries

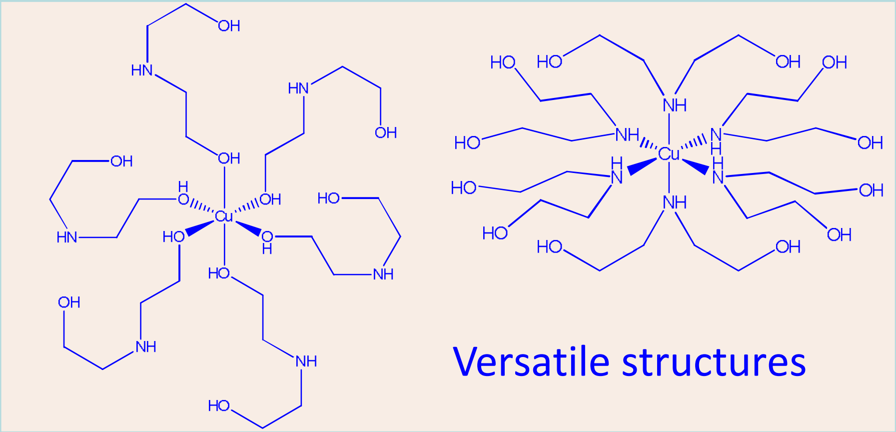
Materials research and development for:

- Higher energy density because materials acts as both the electrolyte and storage medium
- Low cost, improved safety, environmentally benign, cost effective scale-up option

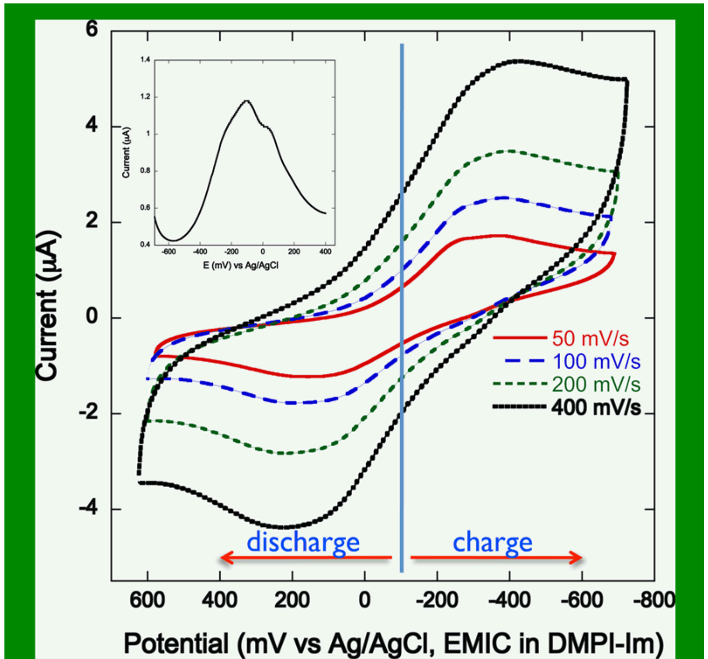


Photomicrograph of a Fe^{3+} (iron) coordination cation ionic liquid prepared in a single-step reaction





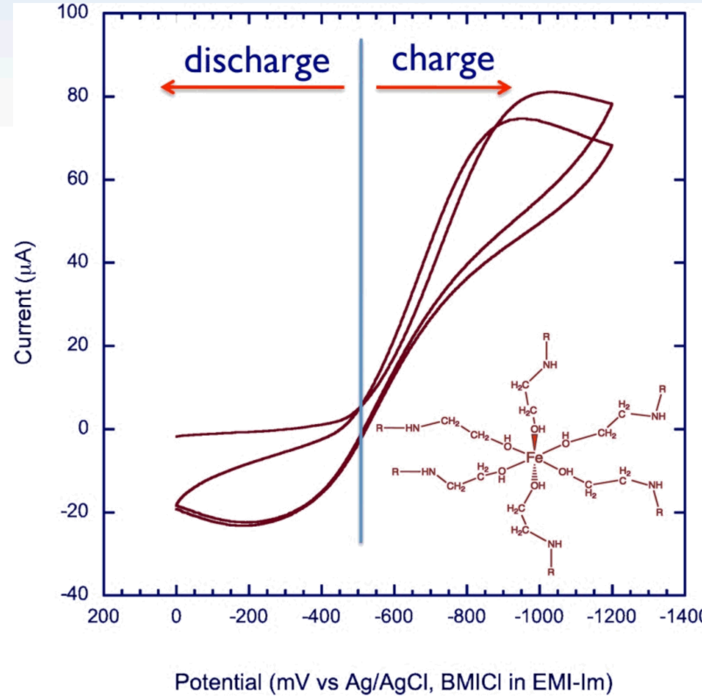
Versatile structures



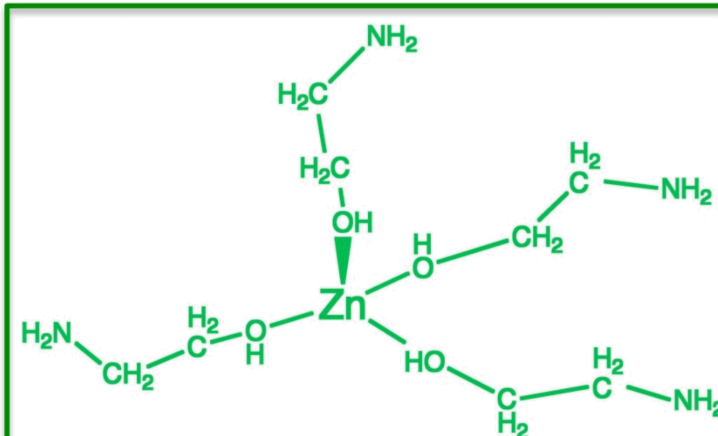
Electrochemical behavior of iron coordination ionic liquid. Voltammetry and Osteryoung square wave (inset).

New Redox Couples for Flow Batteries

- Materials research and development for:
  1. Higher energy density materials
  2. Multi-functional materials – acts as both the electrolyte and energy storage medium
     - Multi-functionality engenders high energy density
  3. Low cost
  4. Safety
  5. Environmentally benign
  6. Cost effective scale-up options



Four different transition metal ionic liquids

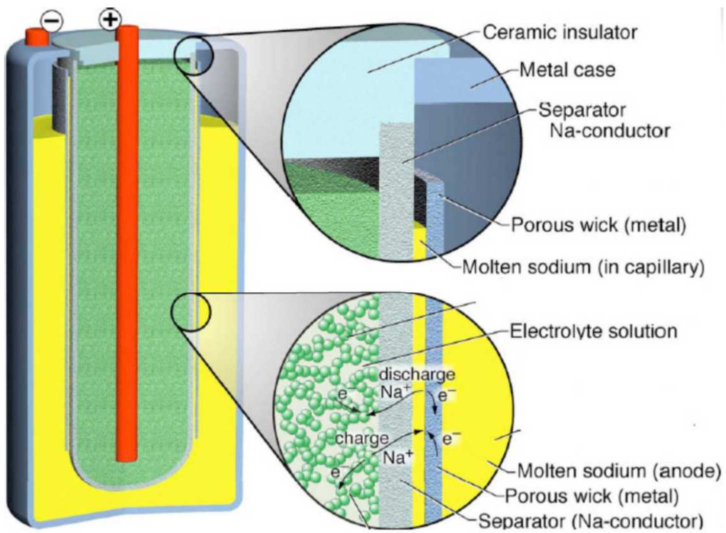


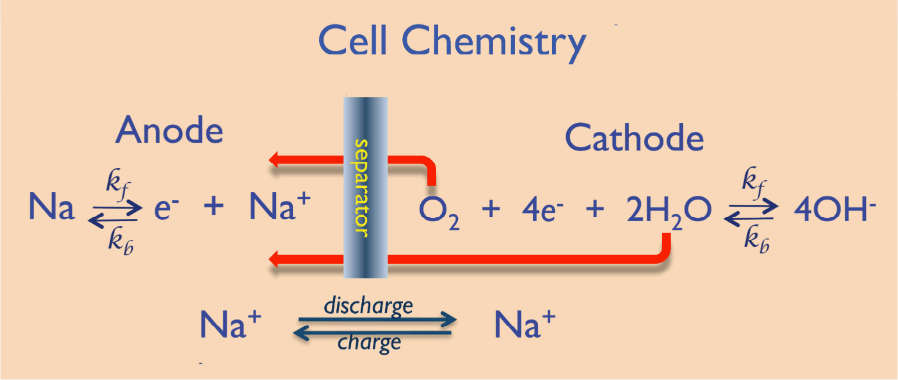
Zinc-based ionic liquid

(cation shown)

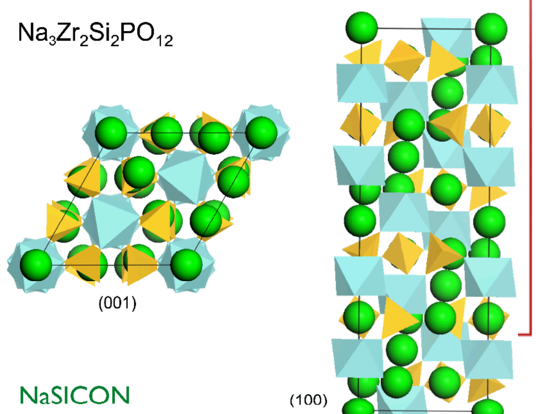
Sodium-Air and Sodium-based Chemistries

- Why Sodium based systems
  - high energy content
  - U.S. has large reserves of sodium commodities
  - very low cost
  - sodium has few health issues
  - a perm-selective sodium ion conductor is available
- Why air (oxygen)
  - high energy content
  - widely available and "free"
  - can be coupled with NaSICON
- Why other cathodes
  - to fill the multiple application needs for electrical storage – a suite of solutions



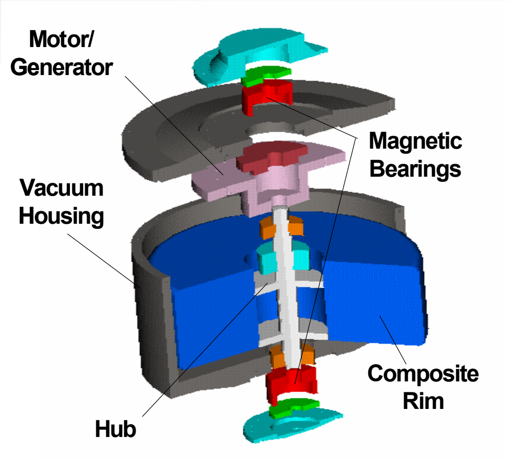


- NaSICON, ceramic sodium (Na) Super Ion Conductor discovered decades ago
- room temperature conductivities on the order of 10^{-2} S/cm
- stable against molten sodium
- stable against aqueous alkaline solutions
  - beta"-alumina is not stable against H_2O
- highly complex structures can be fabricated, necessary for:
  - ensuring mechanical integrity
  - maximizing rate of mass transfer by minimizing mass transfer distances and maximizing surface area
  - sealing/joining



Laboratories

Increasing the strength of the rim of the flywheels is critical to higher spin speeds and more stored energy



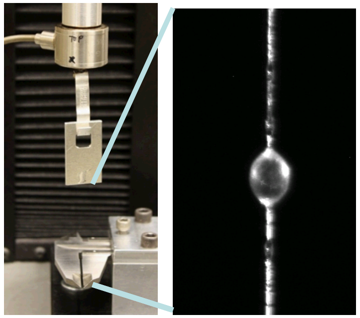
- Kinetic energy depends on speed of wheel which is limited by the tensile strength of the rim material

$$E_k = \frac{1}{2} \cdot I \cdot \omega^2$$

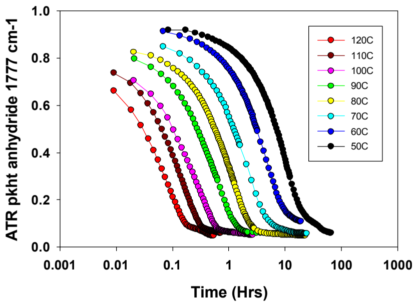
$$\sigma_t = \rho r^2 \omega^2$$

Our approach is to introduce nanoceramic fillers into the resin to increase the strength of the rim material. These nanoparticles will not significantly increase the weight of the rim but should allow for faster spin speeds and thus more stored energy

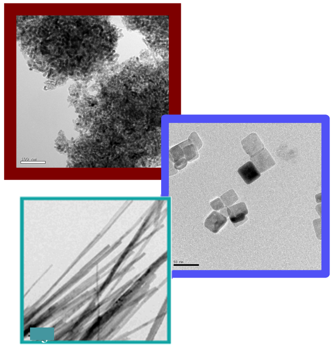
Approach is to initially determine the properties of the 'state-of-the-art' commercial system (Beacon Power) through (i) mechanical and (ii) chemical testing. With this baseline information, we can then introduce well-characterized nanoparticles - both in (iii) physical (i.e., size,shape) and (iv) chemical properties (i.e., solubility) to elucidate/optimize changes.



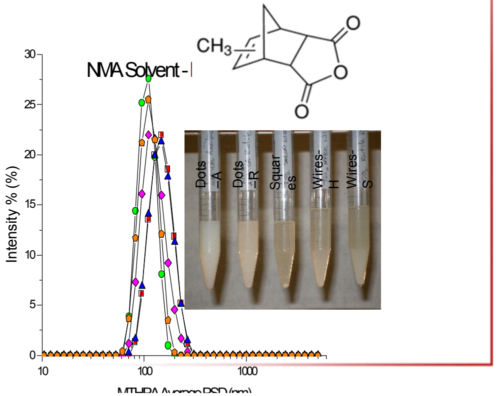
(i) Microdroplet testing of epoxy-fiber strength



(ii) Isothermal cure kinetics determined by IR spectroscopy



(iiii) nanoceramic filler materials



(iv) Optical scattering of different curative agents

Sandia's Energy Storage Test Pad

- **Evaluate large scale ~ 100KW - 1MW electrical energy storage (EES) systems:**
  - Test for reliability, efficiency, operability at the system level
  - Evaluate compliance with various standards i.e., IEEE 1547
  - Test EES systems for performance to the various storage applications
- **Test leading-edge technology in a safe, controlled laboratory environment**

Capabilities of ESTP at the Distributed Energy Storage Test Lab (DETL)

- Enable vendors of large scale battery systems (≤1MW AC) and electrical utilities to obtain an un-biased performance evaluation
  - UL/NRTL certification or label not required
- Utility-connected EES tests can be performed in a controlled environment
- Islanded tests can be performed utilizing DETL's microgrid
- Test EES performance to various power and energy applications – time shift, load following, regulation, power quality/reliability
- Use of sub-cycle metering for transient analysis
- Develop improved energy storage models using gathered field measured data
- Enhance control algorithms

Introduction to Lead-Carbon Batteries

- The addition of certain forms of carbon to the negative plate in valve regulated lead acid (VRLA) batteries has been demonstrated to increase the cycle life of such batteries by an order of magnitude or more under high-rate, partial-state-of-charge operation. Such performance will provide a significant impact, and in some cases it will be an enabling feature for applications including hybrid electric vehicles, utility ancillary regulation services, wind farm energy smoothing, and solar photovoltaic energy smoothing

- There is a critical need to understand how the carbon interacts with the negative plate and achieves the aforementioned benefits at a fundamental level. Such an understanding will not only enable the performance of such batteries to be optimized, but also to explore the feasibility of applying this technology to other battery chemistries

- In partnership with East Penn Manufacturing, Sandia will investigate the electrochemical function of the carbon and possibly identify improvements to its anti-sulfation properties

- CRADA between Sandia National Laboratories and East Penn Manufacturing, initiated August, 2010.

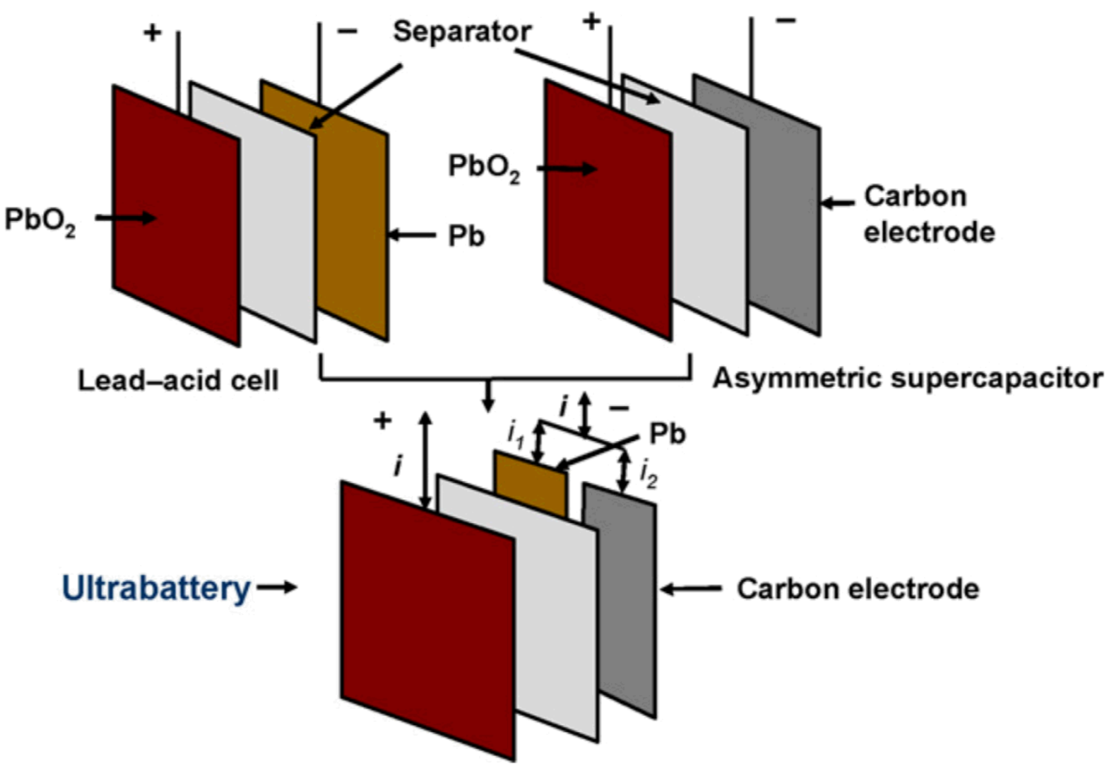
How does carbon impact battery performance?

- Previous work by Pavlov et al. (2010)*, Boden et al. (2010)** and others, funded by the ALABC arrived at a series of preliminary conclusions:
  - Not all carbon additions provide beneficial effects
  - Carbon appears to enhance nucleation and retard recrystallization of lead sulfate
    - Smaller crystallite size -> increased Pb^{2+} concentration
    - Increased Pb^{2+} enhances the charging process within the NAM
  - Carbon particles adsorb onto the lead crystallites within the NAM
    - Carbon exposed to electrolyte (rather than buried in the electrode)
  - The carbon increases the electrochemically active surface area of the NAM.
  - The increased specific surface area of the NAM
    - Lower current density on the electrode as it is being charged
    - Lower polarization experienced by the electrode for a given charging current
    - Enhanced charge acceptance/efficiency

*D. Pavlov, P. Nikolov, T. Rogachev, Journal of Power Sources, Vol. 195 (2010), pp. 4444-4457.
**D.P. Boden, D.V. Loosemore, M.A. Spence, T.D. Wojcinski, Journal of Power Sources, Vol 195 (2010), pp. 4470-4493.

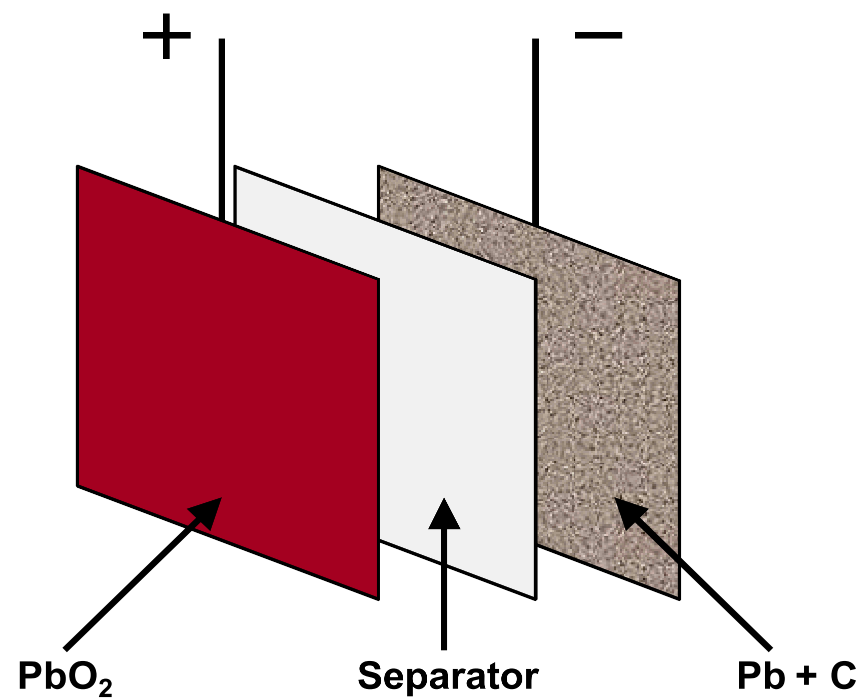
Carbon Modified Pb-Acid Batteries

- **Two different mechanisms through which Pb-acid batteries are being modified – one is a hybrid device, often called the Pb-Acid Ultrabattery**



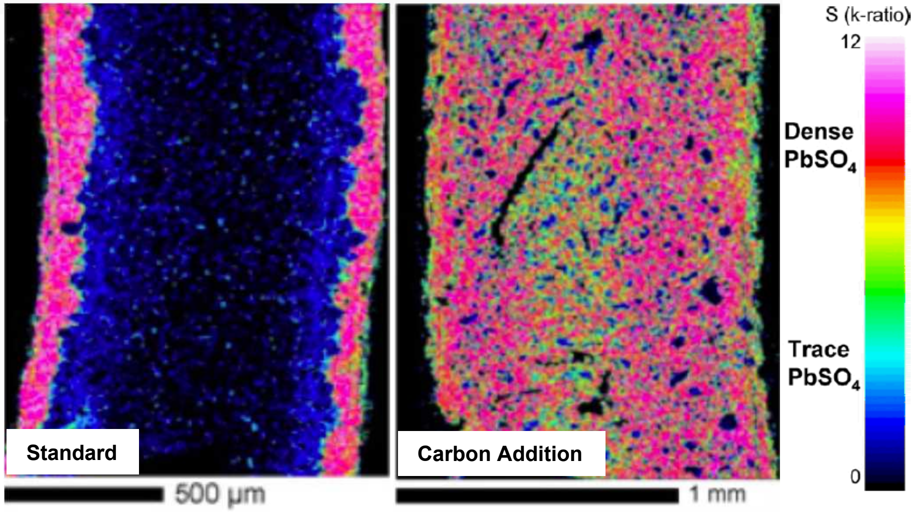
Carbon Modified Pb-Acid Batteries

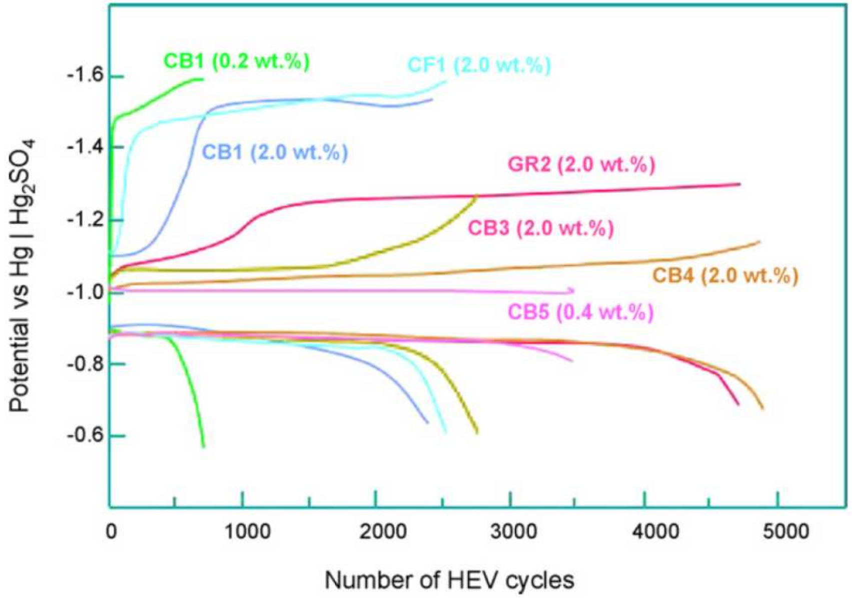
- **Second method is through the direct addition of carbon to the negative active material (in quantities greater than normally found). This is currently called the “Advanced Battery”**



Impact of carbon on performance

- **Sulfation process is significantly altered by the carbon additions**
  - Fernandez, 2010*



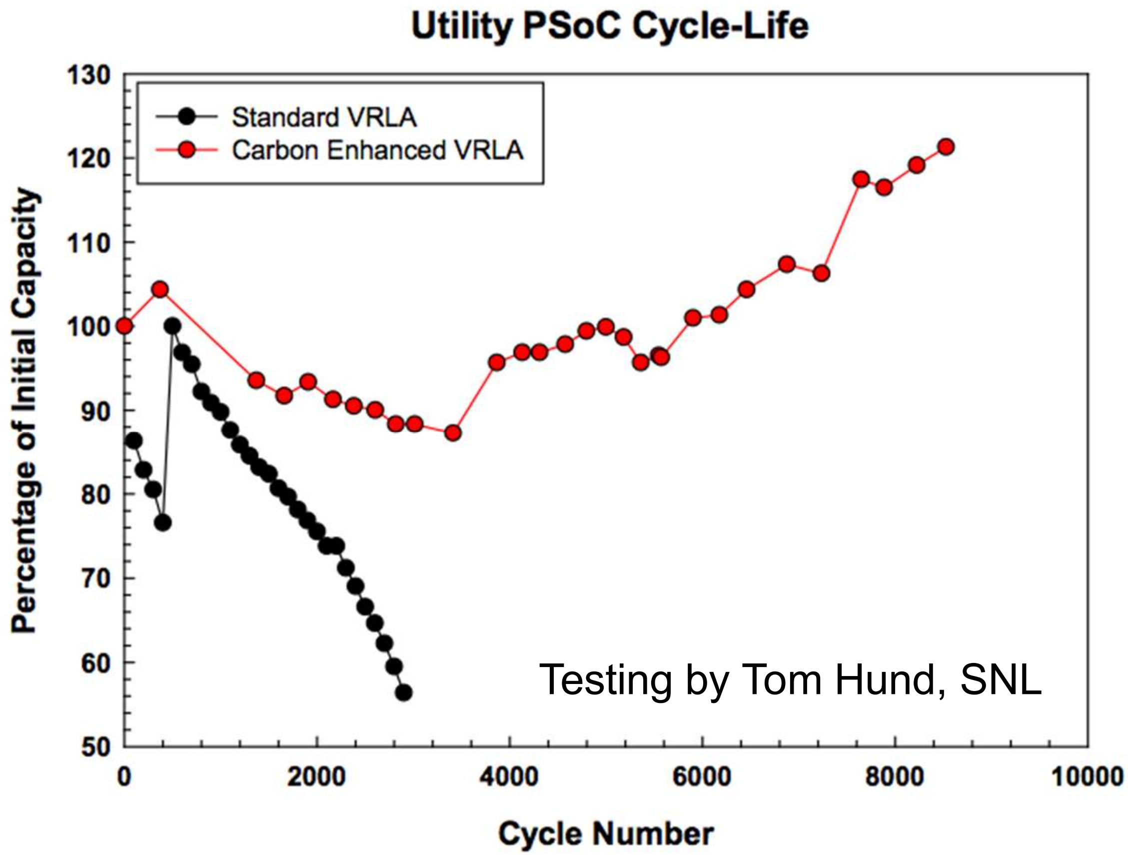


- Different results are achieved with different carbon additions (quantity and type)
  - Moseley, 2009**

*M.Fernandez, J.Valenciano, F.Trinidad, N. Munoz, Journal of Power Sources, Vol. 195 (2010), pp. 4458-4469.
**P.T. Moseley, Journal of Power Sources, Vol. 191 (2009), pp.134-138.

Performance of a Representative "Advanced" Battery

- **Cycle life of a carbon modified VRLA is dramatically improved over a conventional VRLA battery.**



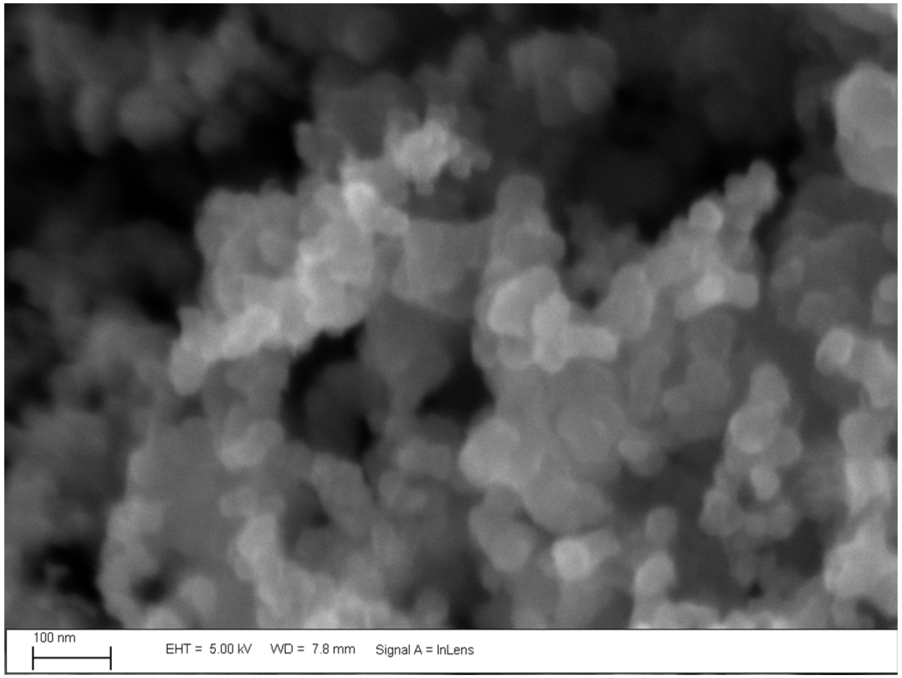
CRADA Research Goals

- **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.

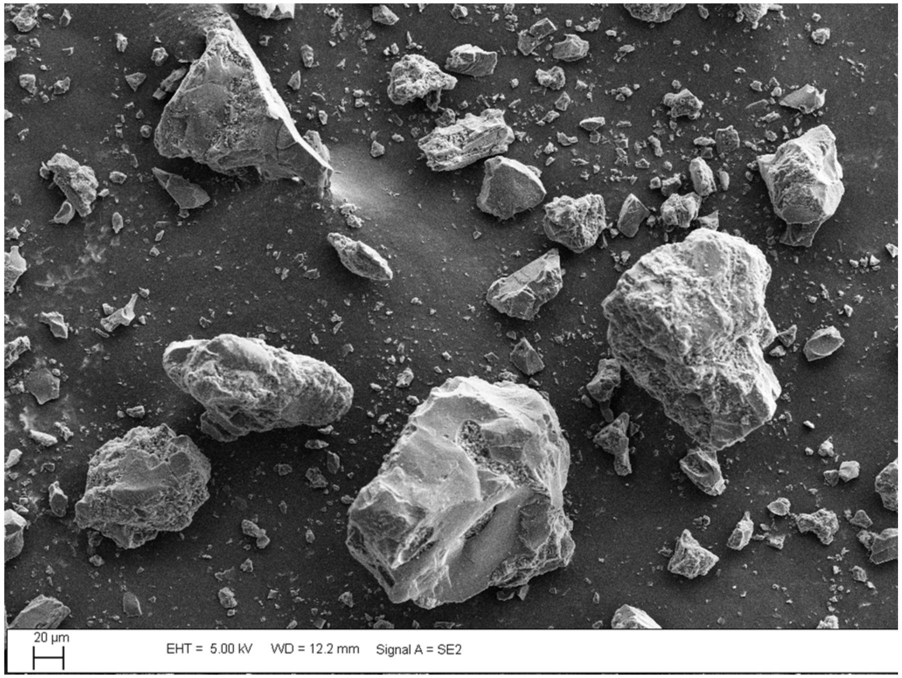
Constituent Material Analysis

- **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**.
  - Particle size and size distribution
  - Effective surface area (BET)
  - Structure/composition (XRD)
  - Acid soluble contaminant concentration
  - Surface electrochemical activity (Boehm)

Carbon Structure



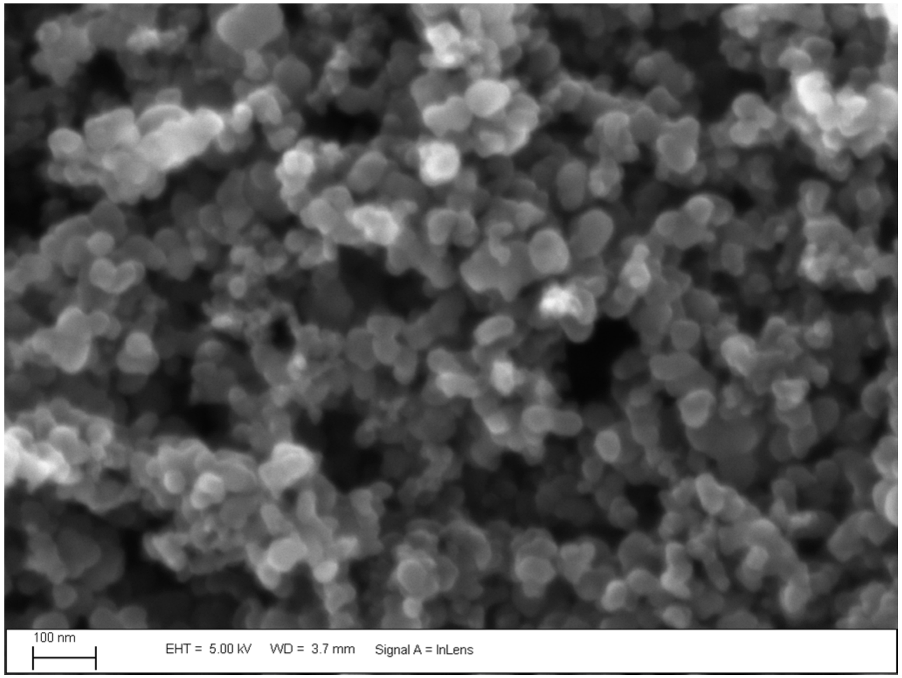
Acetylene Black



Activated Carbon

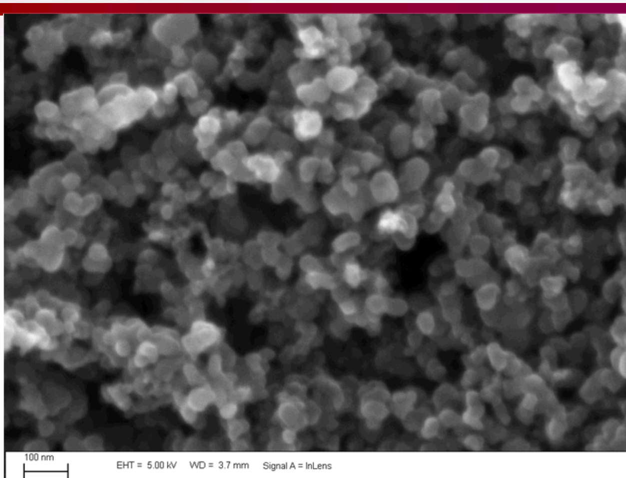
Carbon Structure

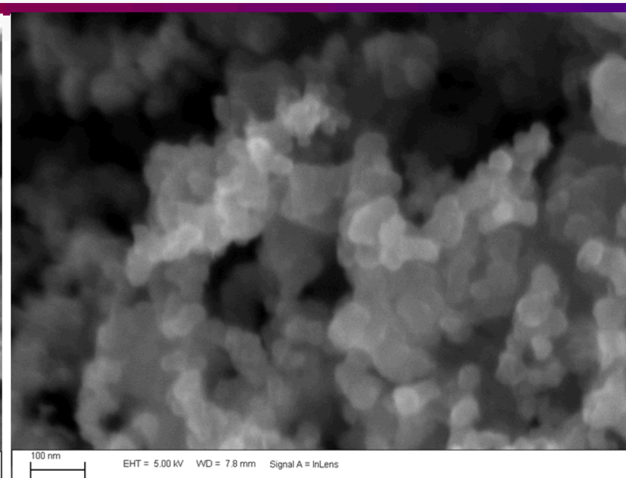
Graphitic Carbon



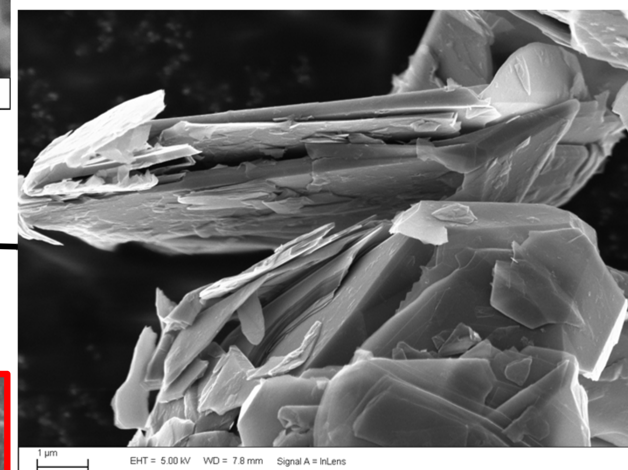
Carbon Black

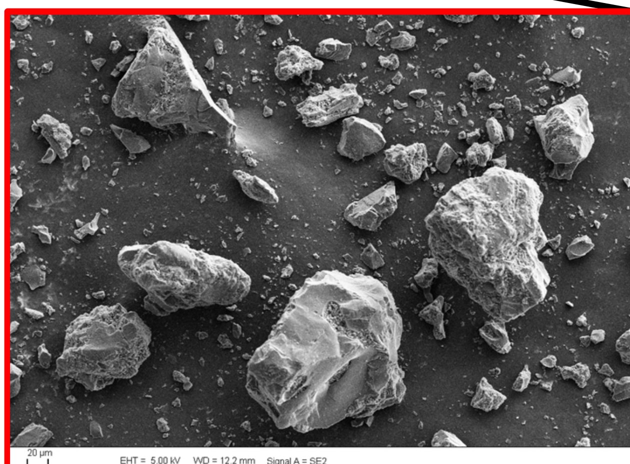
BET Surface Area (Carbons)

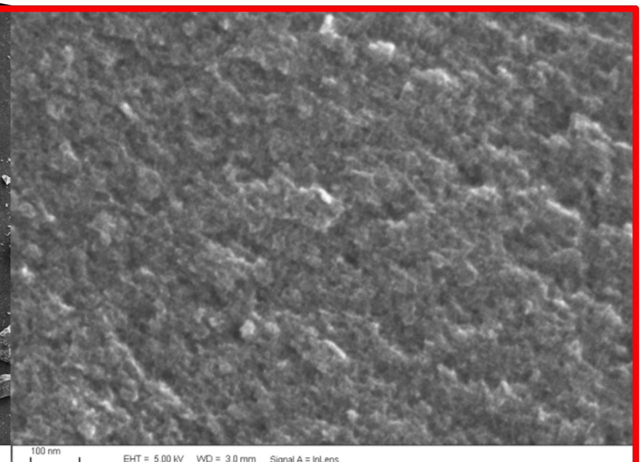




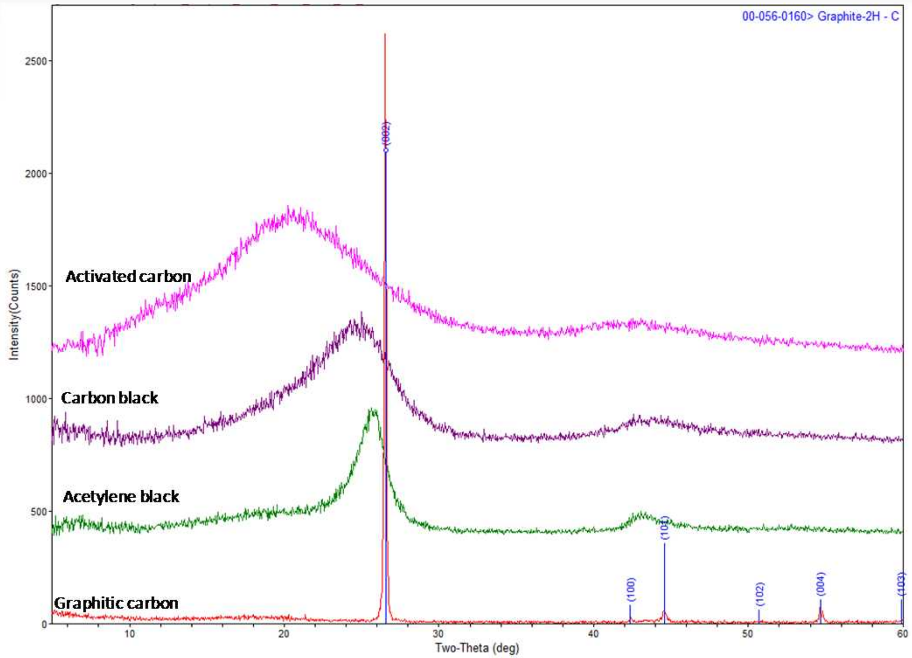
	Activated Carbon	Carbon Black	Acetylene Black	Graphitic Carbon
sample 1	2077.9754 ± 7.9393 m²/g	74.2100 ± 0.2129 m²/g	75.0488 ± 0.4638 m²/g	6.5482 ± 0.0289 m²/g
sample 2	2052.7406 ± 9.1734 m²/g	73.2207 ± 0.2193 m²/g	74.6294 ± 0.4196 m²/g	7.2968 ± 0.0478 m²/g
sample 3	2048.5571 ± 6.5117 m²/g	73.7229 ± 0.1845 m²/g	75.3409 ± 0.4351 m²/g	6.6581 ± 0.0182 m²/g







Carbon XRD Characterization



Sample	Main peak - pseudo (002) peak					Broad peak – amorphous signature				
	2θ (°)	d-spacing (Å)	FWHM (°)	Xtal size* (Å)	Relative Peak Area	2θ (°)	d-spacing (Å)	FWHM (°)	Xtal size* (Å)	Relative Peak Area
Graphite	26.538(1)	3.3560(1)	0.095(2)	>1000	100	18.1(2)	4.9(1)	5.7(5)	14(2)	17.1
Acetylene Black	25.84(4)	3.45(1)	2.26(6)	37(2)	100	19.3(7)	4.6(3)	10.7(8)	8(2)	56.3
Carbon Black	24.8(1)	3.59(4)	5.3(1)	16(1)	100	19.7(6)	4.5(3)	6.6(6)	12(2)	35.8
Activated Carbon						20.5(1)	4.33(1)	11.3(2)	7(1)	100

*Crystallite size estimates are based on Scherrer equation – values less than 10 Å strongly suggests amorphous characteristics

Carbon contamination

Acid Soluble Contamination

	Al	B	Ba	Ce	Fe	K	La	Mg	Mn	Mo	Na	Ni	Pb	Sr	Ti	Zn	Zr
Carbon Black	10.5 ± 0.6				6.24 ± 0.79	123 ± 8	2.48 ± 0.19	287 ± 12	0.57 ± 0.09		89.9 ± 5.7				0.51 ± 0.09		
Acetylene Black						0.96 ± 1.07											
Activated Carbon	28.3 ± 0.8	2.35 ± 1.21	1.03 ± 0.03		91.6 ± 5.8	13.4 ± 2.5		12.5 ± 0.3	1.83 ± 0.15		2450 ± 30	1.65 ± 0.62		1.04 ± 0.14	15.2 ± 0.7	2.54 ± 1.00	
Graphite				0.85 ± 0.03						0.95 ± 0.08			2.96 ± 1.02		7.3 ± 0.31		3.04 ± 0.21

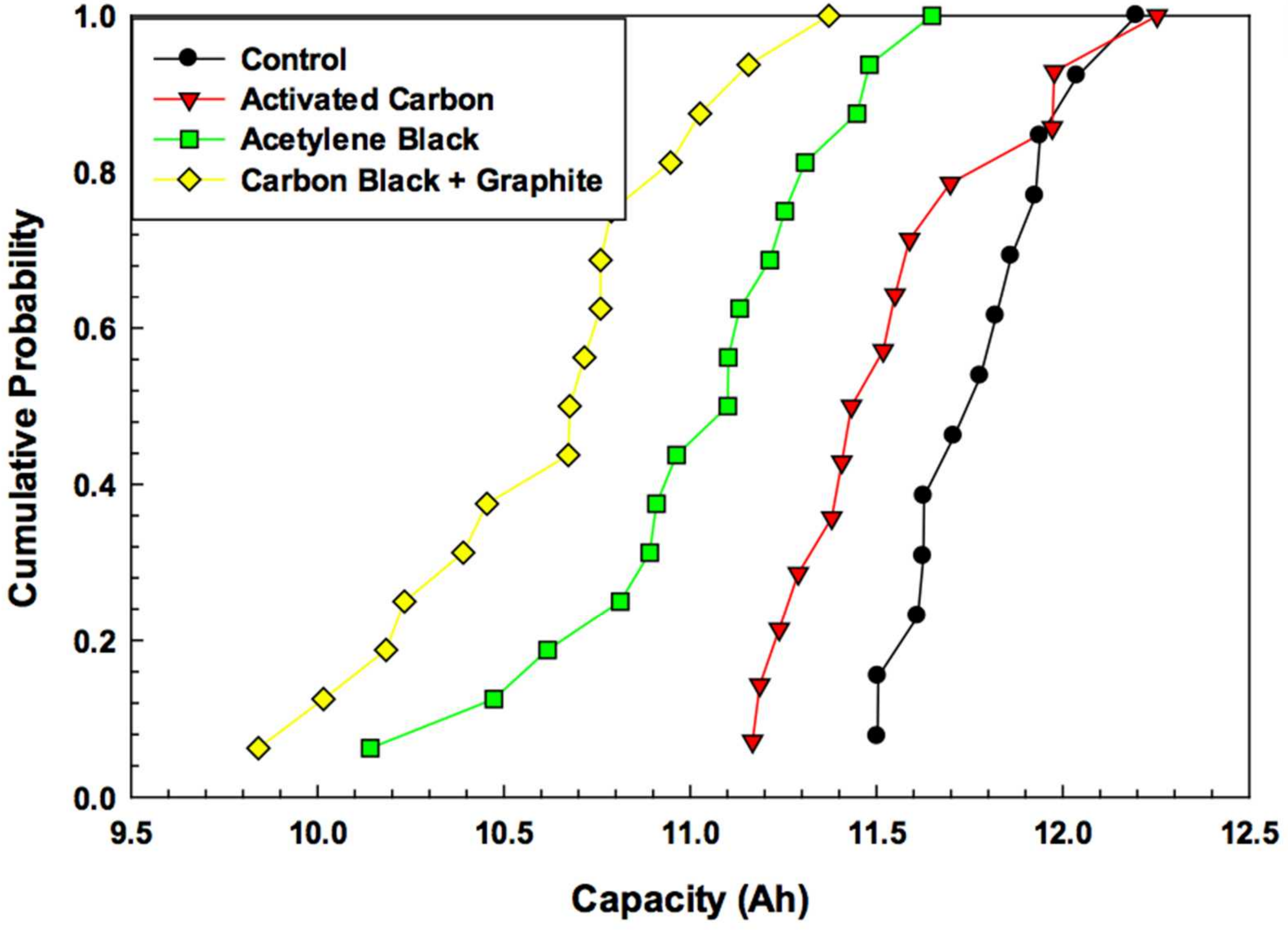
Anions

	Sulfate	Nitrate	Phosphate	Chloride	Fluoride
Carbon Black	3920	trace		trace	trace
Acetylene Black					
Activated Carbon	94.1	71.1	11929		
Graphite					

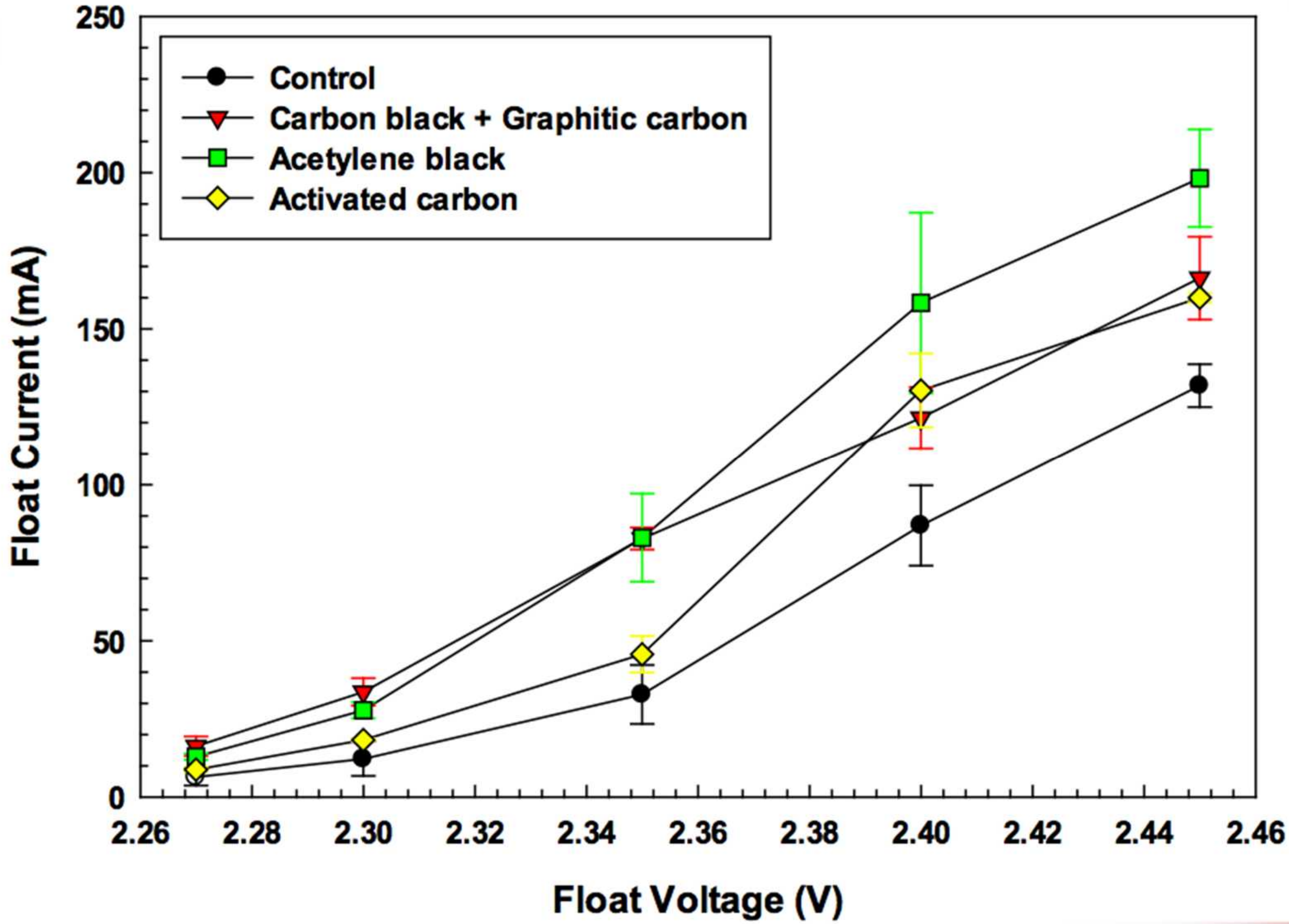
Battery Performance Testing

- **Performance characteristics of carbon enhanced cells will be compared to those of a standard cell of nominally identical construction.**
  - Mass measurement of all batteries prior to cycling
  - Initial capacity testing
  - Initial DC ohmic resistance
  - Cell float current test
  - Hybrid pulse power charge test (HPPC)
  - ALABC Hybrid cycle test (0, 1k, 10k, 50k, 100k cycles plus to end of life)
  - Electrochemical Impedance Spectroscopy at key cycles
  - Mass measurement of all batteries upon completion of cycling (water loss)

Initial Capacities



Float Current



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Battery Materials Evaluation

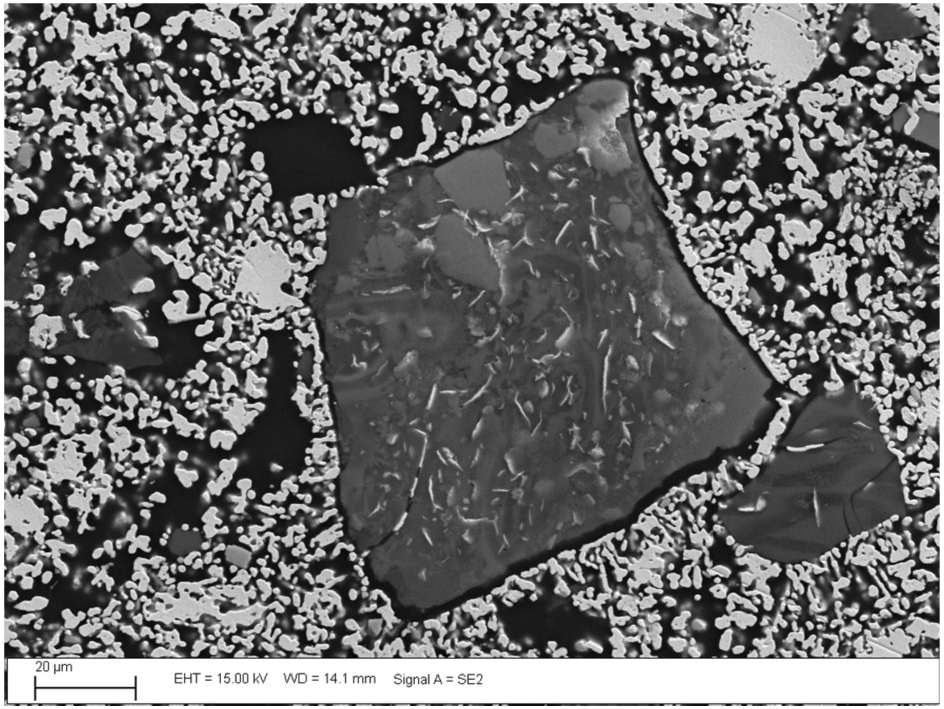
- **Characterize the chemical and structural properties of the positive and negative plates as a function of cycle life.**
  - NAM Visual assessment
  - NAM Structure (SEM)
  - NAM porosity (Hg porosimetry)
  - NAM Surface area (BET)
  - NAM Carbon content and distribution/uniformity (cross sectioning + backscatter SEM)
  - NAM Sulfation (XRF)
  - PAM Visual assessment

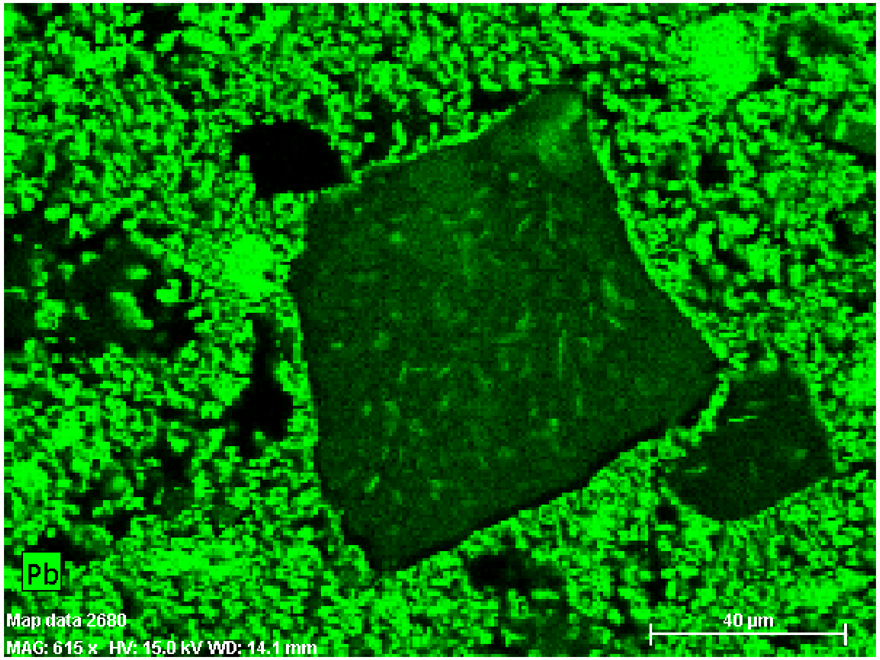
Mercury Porosimetry of Negative Plates

	% Porosity	
	Raw	Formed
Control	36.7	59.2
Acetylene back	44.8	55.8
Graphitic carbon + Carbon black	45.7	59.5
Activated carbon	37.1	55.8

Carbon Likely Electrochemically Active in Some Cases

- **Formed negative plate containing activated carbon**
  - Activated carbon has considerable internal structures (very high porosity, numerous fissures)
  - Internal structure filled with metallic Pb





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Summary

- **Sandia's efforts in energy storage spans the gamut from basic research and development to large scale demonstrations**
- **Ongoing research into the fundamental mechanism of performance enhancement in Advanced Lead-Acid technology may enable optimization of performance**
- **Research results may also be applicable to other battery chemistries to improve lifecycle capabilities**

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