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Energy Storage Tutorial, Part III

Lithium Ion Batteries

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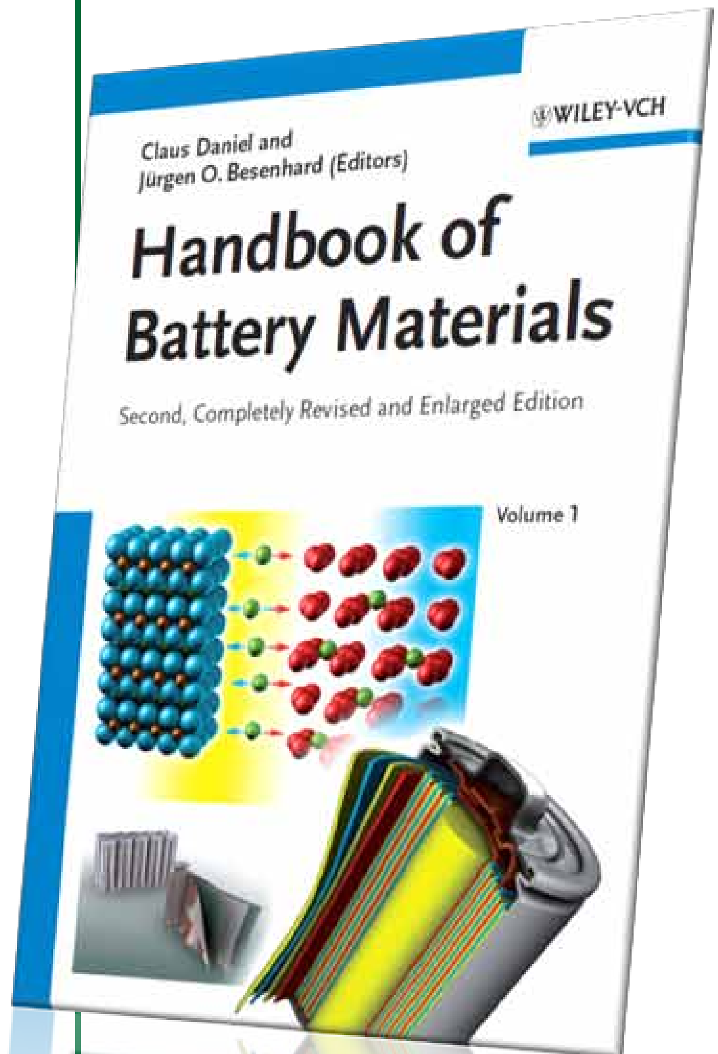
U.S. DEPARTMENT OF ENERGY



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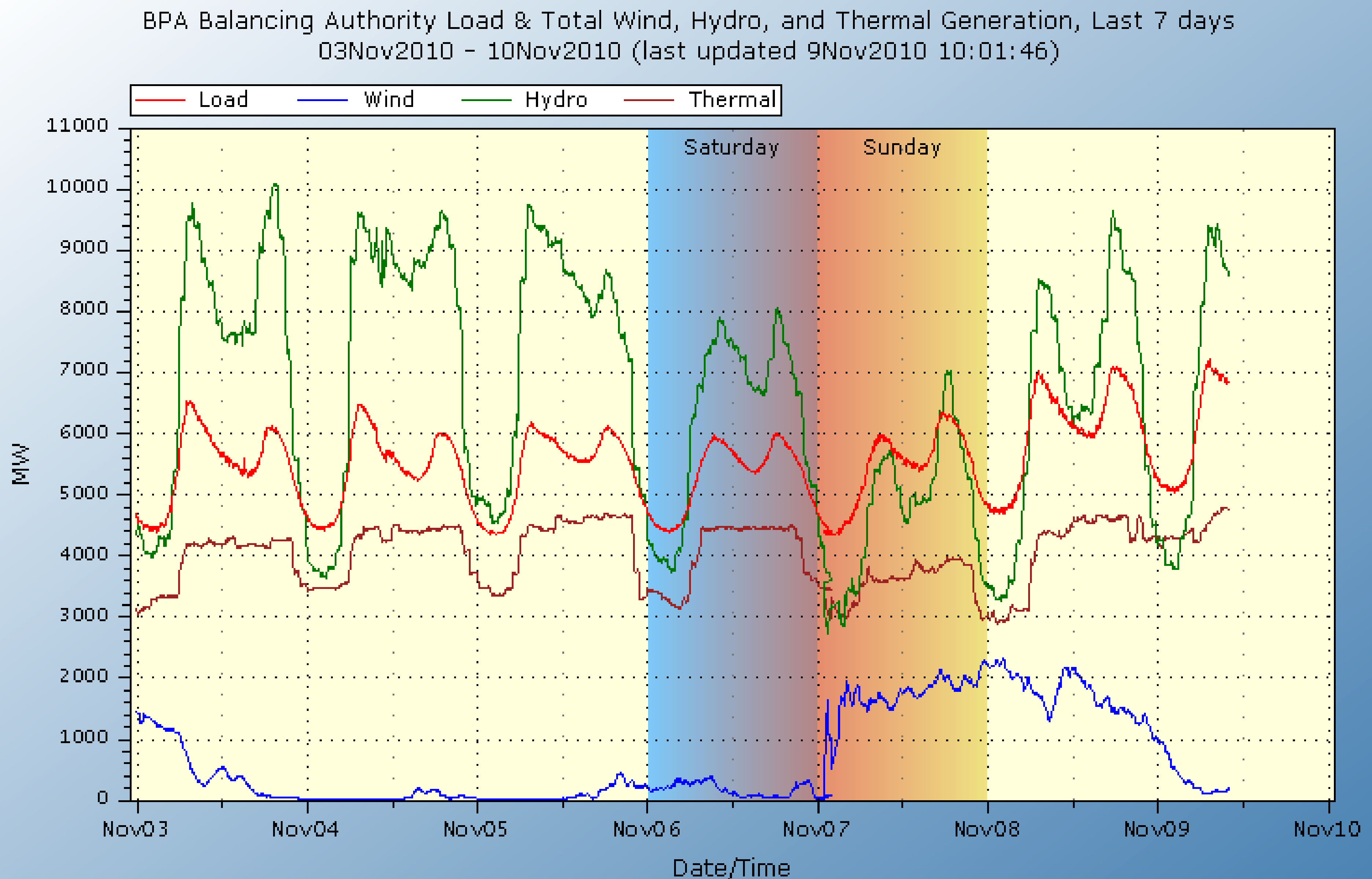
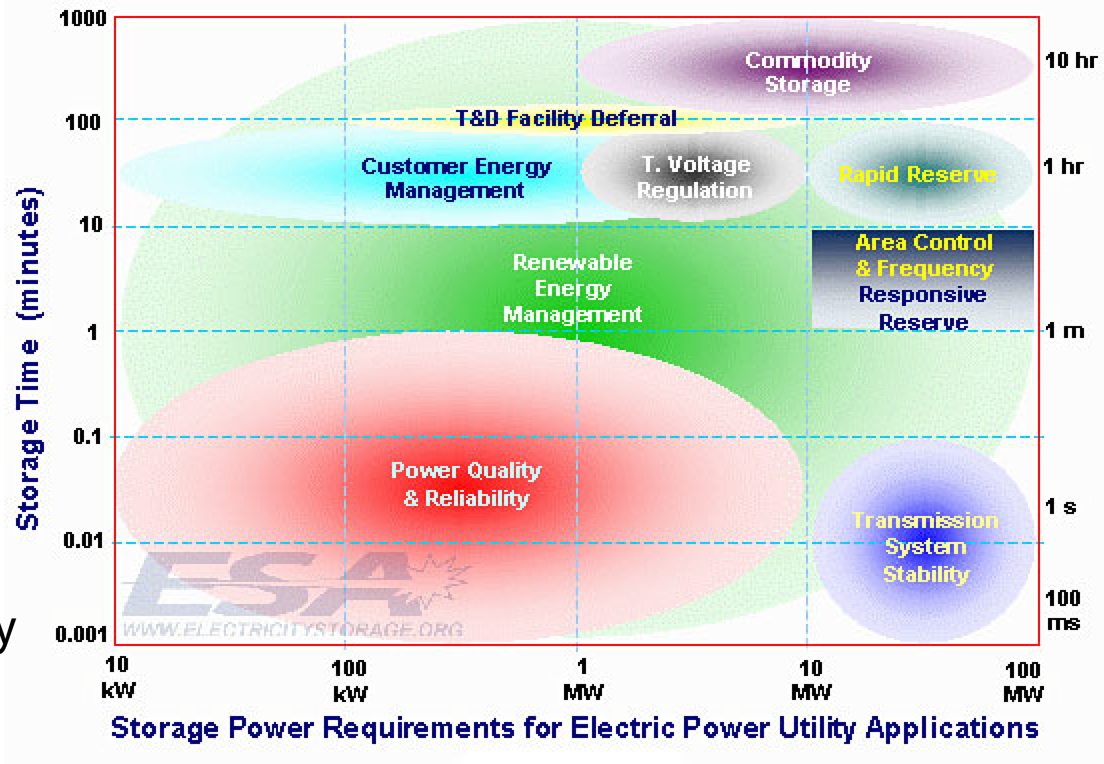


Based on 5-min readings from the BPA SCADA system for points 45583, 79687, 79682, and 79685
Balancing Authority Load in Red, Wind Gen. in Blue, Hydro Gen. in Green, and Thermal Gen. in Brown
Installed Wind Capacity=3011 MW
BPA Technical Operations (TOT-OpInfo@bpa.gov)

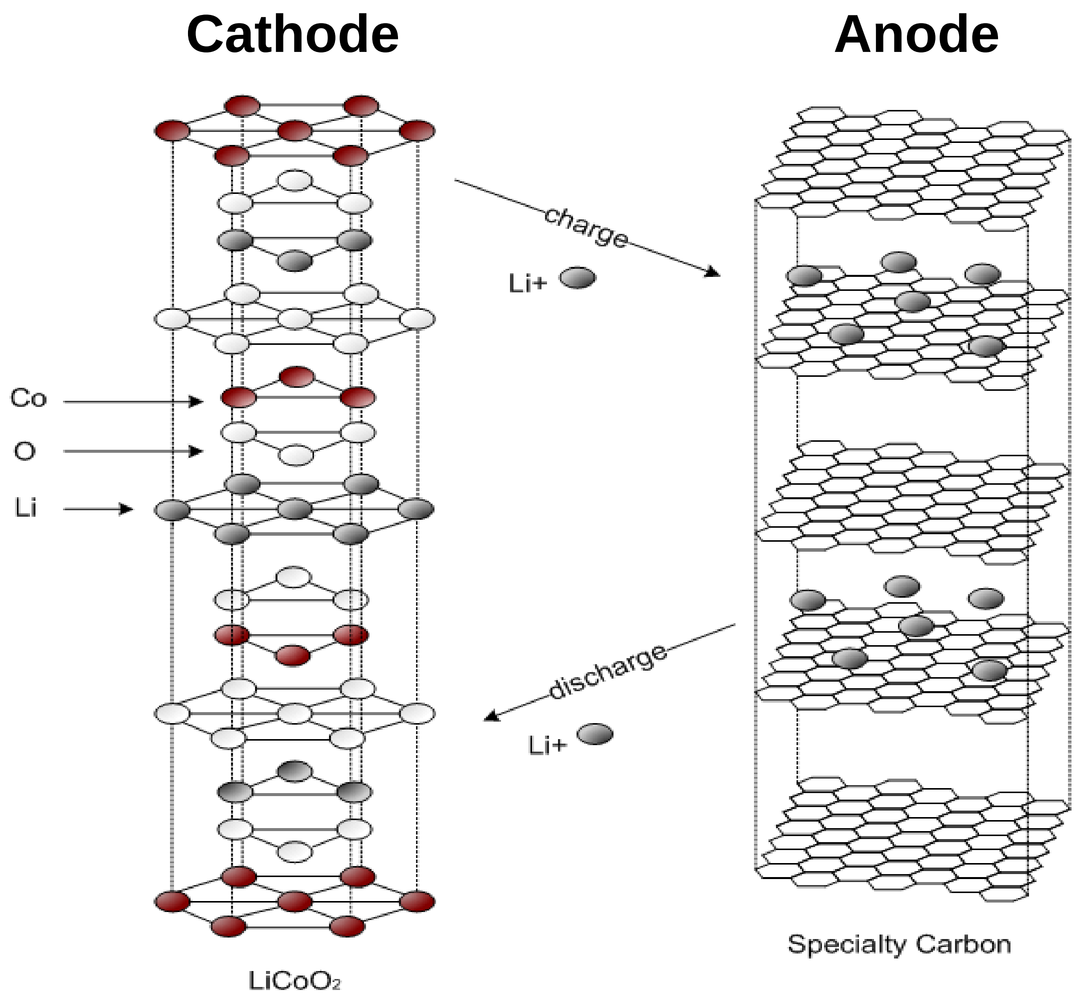


Data from Sandia Report 2002-1314

- Arbitrage
- Spinning reserve
- Transmission and distribution deferral
- Transmission support and avoidance of congestion charges
- Reduced need for generation capacity
- Substation upgrade deferral
- Load following
- Frequency regulation
- Renewables value enhancement
- Time-of-use energy cost reduction
- Demand charge reduction
- Reduced financial losses from improved electric reliability
- Reduced financial losses from improved on-site power quality
- Reduced cost for T&D losses
- T&D life extension
- T&D asset utilization
- Environment and environmental credits

Storage Technologies	Main Advantages (relative)	Disadvantages (Relative)	Power Application	Energy Application
Pumped Storage	High Capacity, Low Cost	Special Site Requirement		●
CAES	High Capacity, Low Cost	Special Site Requirement, Need Gas Fuel		●
Flow Batteries: PSB VRB ZnBr	High Capacity, Independent Power and Energy Ratings	Low Energy Density	◐	●
Metal-Air	Very High Energy Density	Electric Charging is Difficult		●
NaS	High Power & Energy Densities, High Efficiency	Production Cost, Safety Concerns (addressed in design)	●	●
Li-ion	High Power & Energy Densities, High Efficiency	High Production Cost, Requires Special Charging Circuit	●	○
Ni-Cd	High Power & Energy Densities, Efficiency		●	◐
Other Advanced Batteries	High Power & Energy Densities, High Efficiency	High Production Cost	●	○
Lead-Acid	Low Capital Cost	Limited Cycle Life when Deeply Discharged	●	○
Flywheels	High Power	Low Energy density	●	○
SMES, DSMES	High Power	Low Energy Density, High Production Cost	●	
E.C. Capacitors	Long Cycle Life, High Efficiency	Low Energy Density	●	◐

Lithium ion battery principle



Discharge reaction: $Li^+ + e^- + MeO_2 \rightarrow LiMeO_2$ $LiC_6 \rightarrow Li^+ + e^- + C_6$

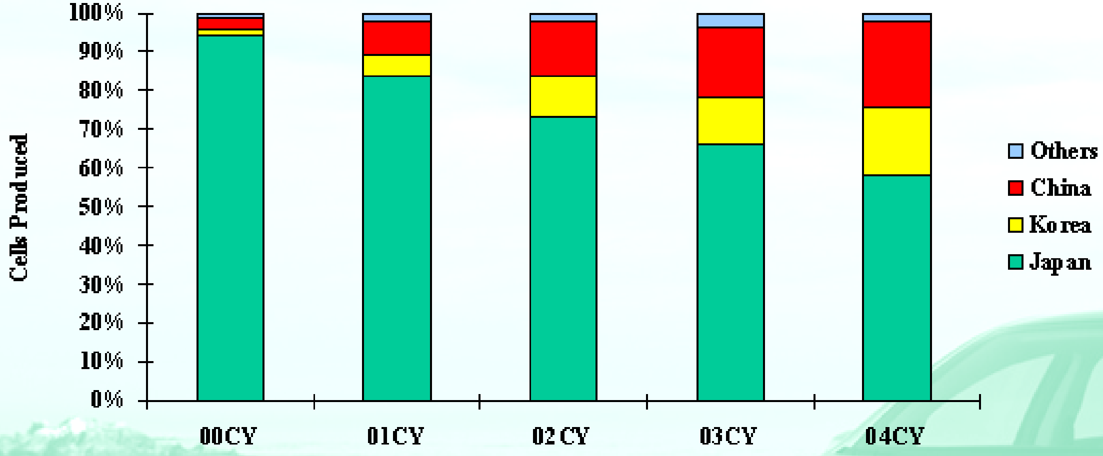
Lithium ion battery problems

- Cost
  - raw materials
  - materials processing
  - cell and module packaging
  - manufacturing
- Performance
  - discharge pulse power limitations at low temperatures
  - capacity and power fading
- Abuse Tolerance / Safety
  - short circuits
  - overcharge
  - over-discharge
  - crush
  - fire or high temperatures
  - thermal runaway
- Life
  - calendar life

DOE, Energy Storage Research and Development Annual Progress Report 2008

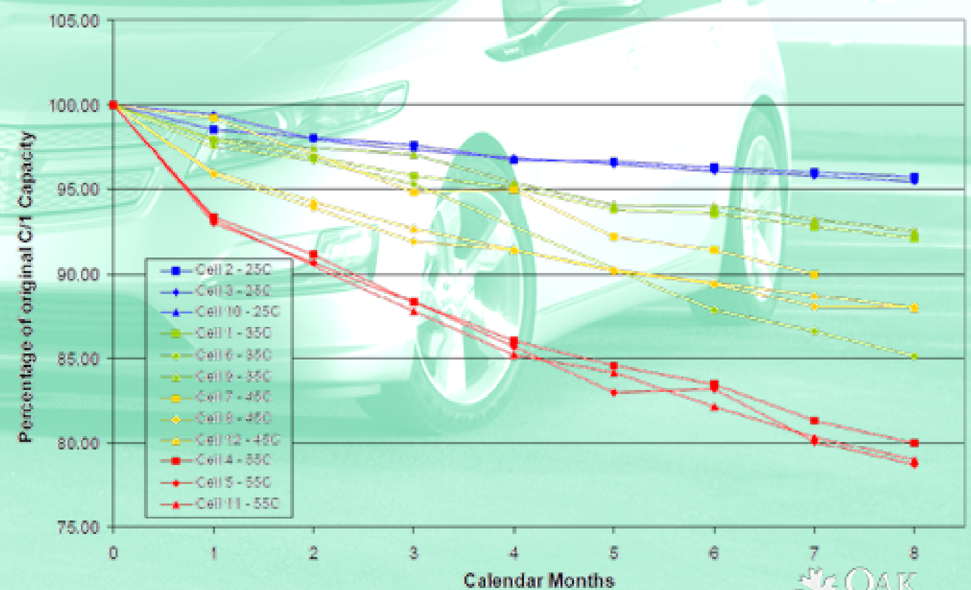
ORNL is addressing two problems:

1. Batteries not being manufactured in the U.S.
2. Batteries not lasting long enough or performing well enough



Work with U.S. battery manufacturers together to make them competitive with their U.S. operations

Study degradation mechanisms and develop new materials and concepts for batteries



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OAK RIDGE National Laboratory

DOE Energy storage targets

Characteristics	Minimum value	Maximum value
Pulse discharge power (kW)	25 (for 10 seconds)	40 (for 10 seconds)
Maximum regenerating pulse (10 s; kW)	20 (50 Wh pulse)	35 (97 Wh pulse)
Total available energy (kWh)	0.3	0.5
Round trip efficiency (%)	>90–25 Wh cycle	>90–50 Wh cycle
Cycle life (cycles)	300k 25-Wh cycle (7.5 MWh)	300k 50-Wh cycle (15 MWh)
Cold-cranking power at −30°C (three 2-sec pulses, 10-s rests between; kW)	5	7
Calendar life (years)	15	15
Maximum weight (kg)	40	60
Maximum volume (liters)	32	45
Production price @ 100k units/year ($)	500	800
Maximum operating voltage (Vdc)	<400 maximum	<400 maximum
Minimum operating voltage (Vdc)		
Maximum self-discharge (Wh/d)		
Operating temperature (°C)		
Survival temperature (°C)		

HEV

PHEV

Characteristics at EOL (End of Life)		High Power/Energy Ratio Battery	High Energy/Power Ratio Battery
Reference Equivalent Electric Range	miles	**10**	**40**
Peak Pulse Discharge Power (2 sec/10 sec)	kW	**50/45**	**46/38**
Peak Regen Pulse Power (10 sec)	kW	**30**	**25**
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	**3.4**	**11.6**
Available Energy in CS (Charge Sustaining) Mode	kWh	**0.5**	**0.3**
CD Life / Discharge Throughput	Cycles/ MWh	**5,000 / 17**	**5,000 / 58**
CS HEV Cycle Life, 50 Wh Profile	Cycles	**300,000**	**300,000**
Calendar Life, 35°C	year	**15**	**15**
Maximum System Weight	kg	**60**	**120**
Maximum System Volume	Liter	**40**	**80**
System Recharge Rate at 30°C	kW	**1.4 (120V/15A)**	**1.4 (120V/15A)**
Unassisted Operating & Charging Temperature	°C	**-30 to +52**	**-30 to +52**
Survival Temperature Range	°C	**-46 to +66**	**-46 to +66**
Maximum System Production Price @ 100k units/yr	$	**$1,700**	**$3,400**

DOE, Energy Storage Research and Development Annual Progress Report 2008

Battery production prize for vehicles

Targets*

- HEV (0.3-0.5kWh)
  - $1.6 – 1.7/Wh
- PHEV (3.4-11.6kWh)
  - $0.3 – 0.5/Wh (charge depleting mode)

State of the art

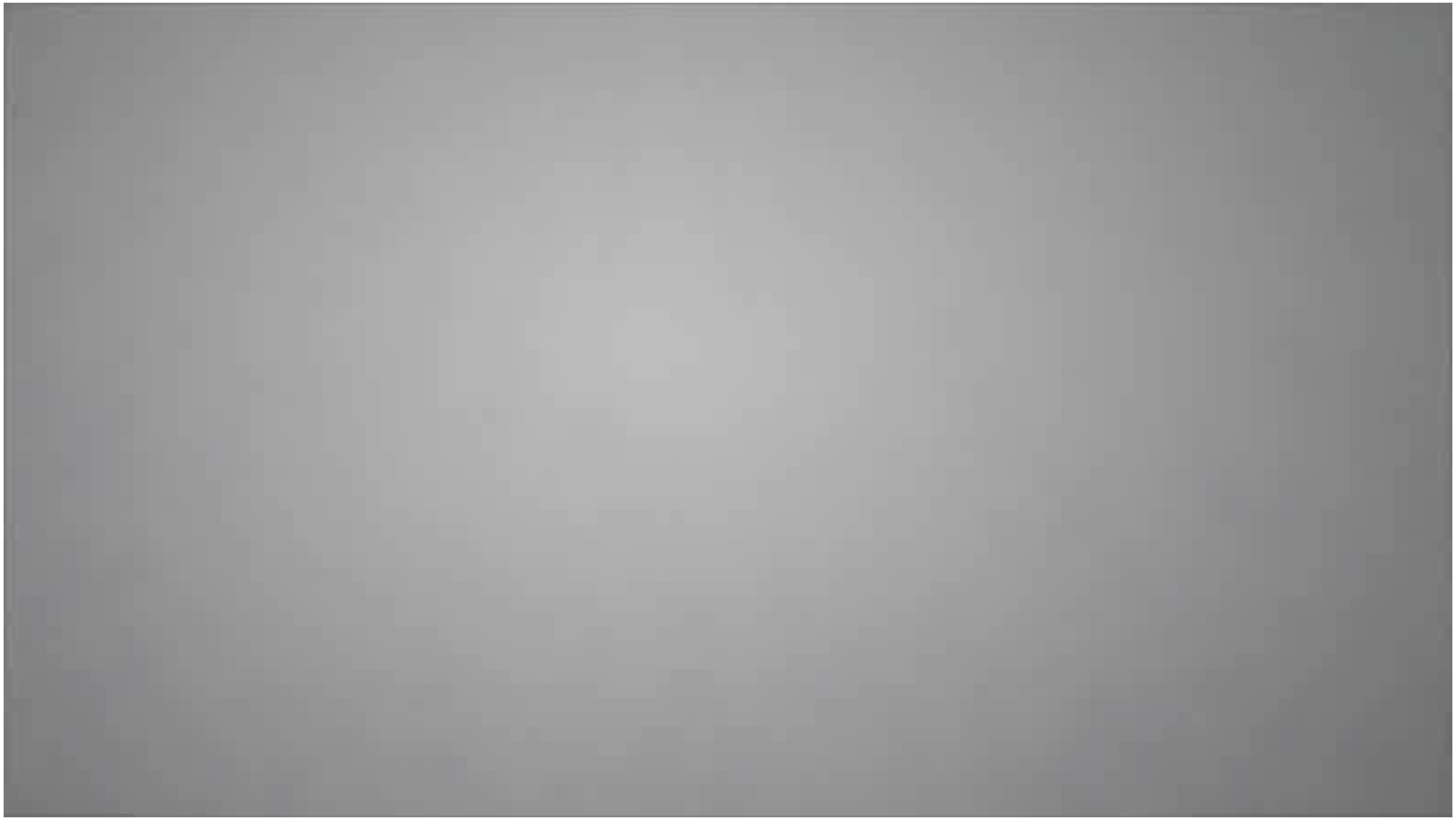
- HEV (0.3-0.5 kWh)
  - High quality materials: $1.28-1.33/Wh
  - Max. processing and manufacturing: $0.32-0.37/Wh
  - State of the art low cost materials can potentially save 25%.

Processing and Manufacturing together between $0.32 and $0.64 per Wh!
That's just $100-190 for a 25kW unit!

***based on 100k units per year**

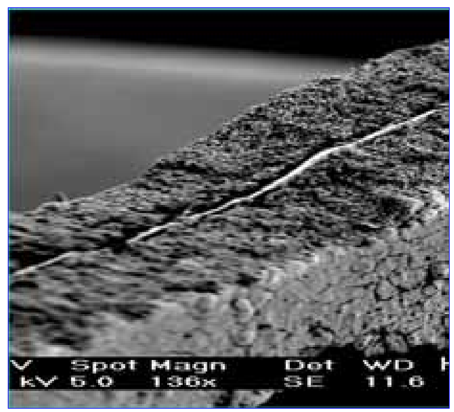
DOE, Energy Storage Research and Development Annual Progress Report 2008
G.L. Henriksen et al., Materials Cost Evaluation Report for High power Li-ion HEV Batteries, ANL

Battery manufacturing

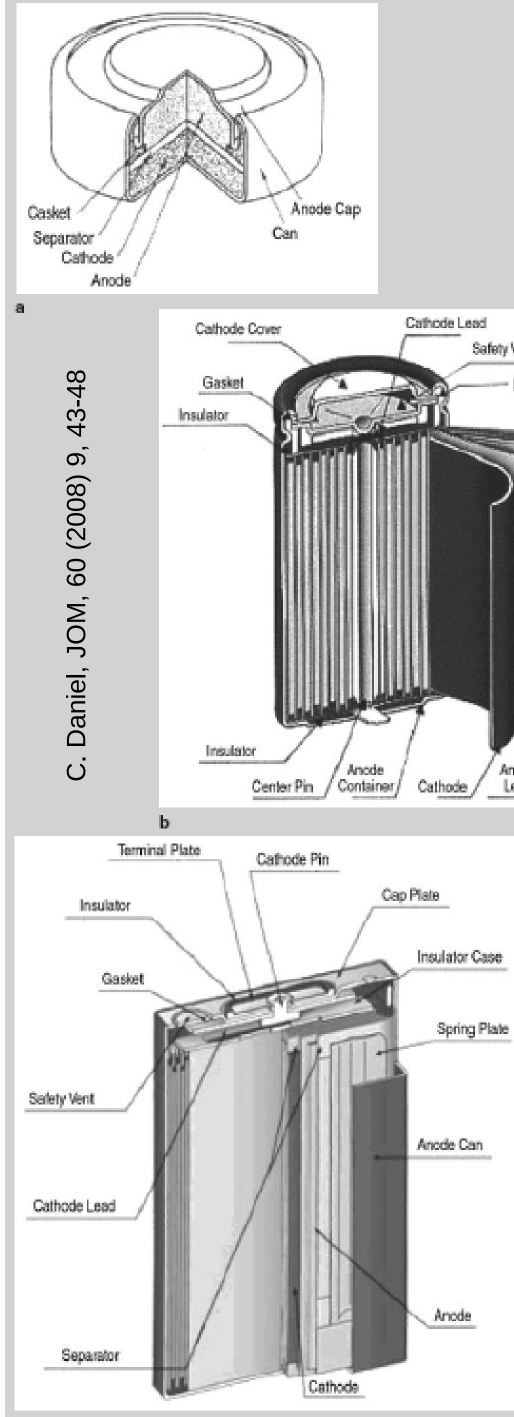


Materials and processing R&D

- Reduction of solvent recovery (N-Methyl-2-pyrrolidone)
- In-line quality control
- Drying mechanisms
- Reducing formation cycling
- thermal processing of electrodes without affecting polymers or temperature sensitive substrates
  - photonic processing for annealing, sintering, solidification of surfaces
- 3D-electrode/battery design
  - battery foam materials, flexible chemically bonded layer structure



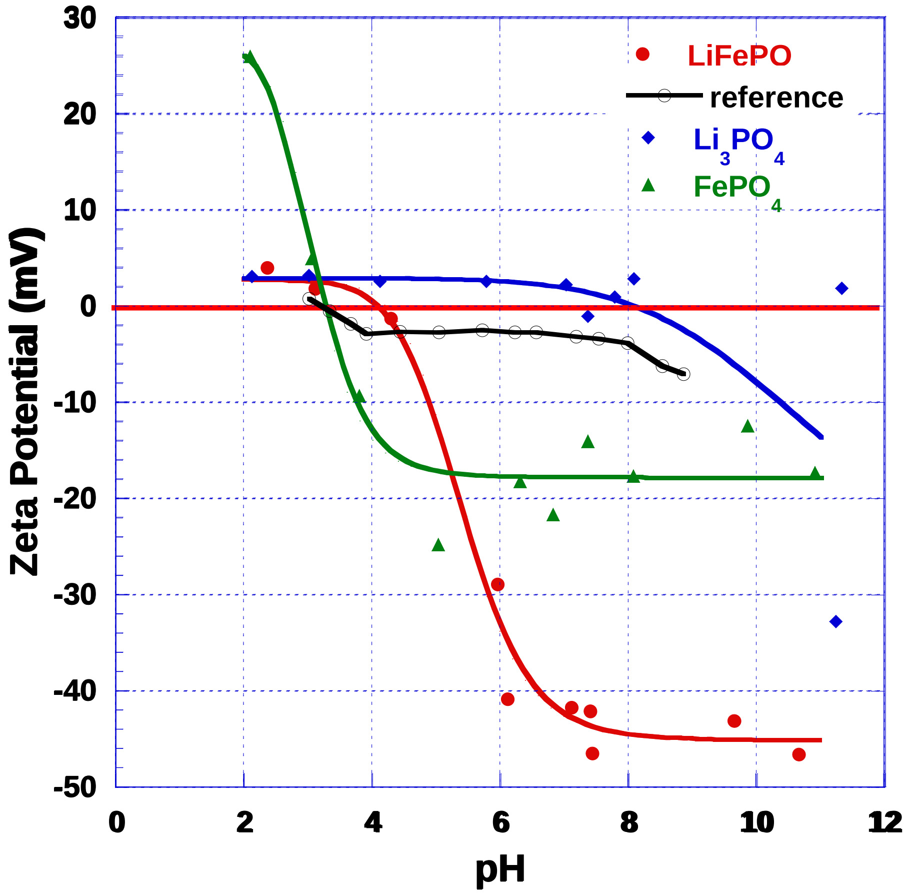
- All solid state batteries
- ORNL capabilities
  - Ink-jet, tape casting, slot dying, screen printing, direct manufacturing, vacuum processing (PVD, CVD), drying, reel to reel, machining, rolling, calendaring, heat treatment, photonic processing, sealing, joining, infrared imaging, X-ray diffraction



C. Daniel, JOM, 60 (2008) 9, 43-48

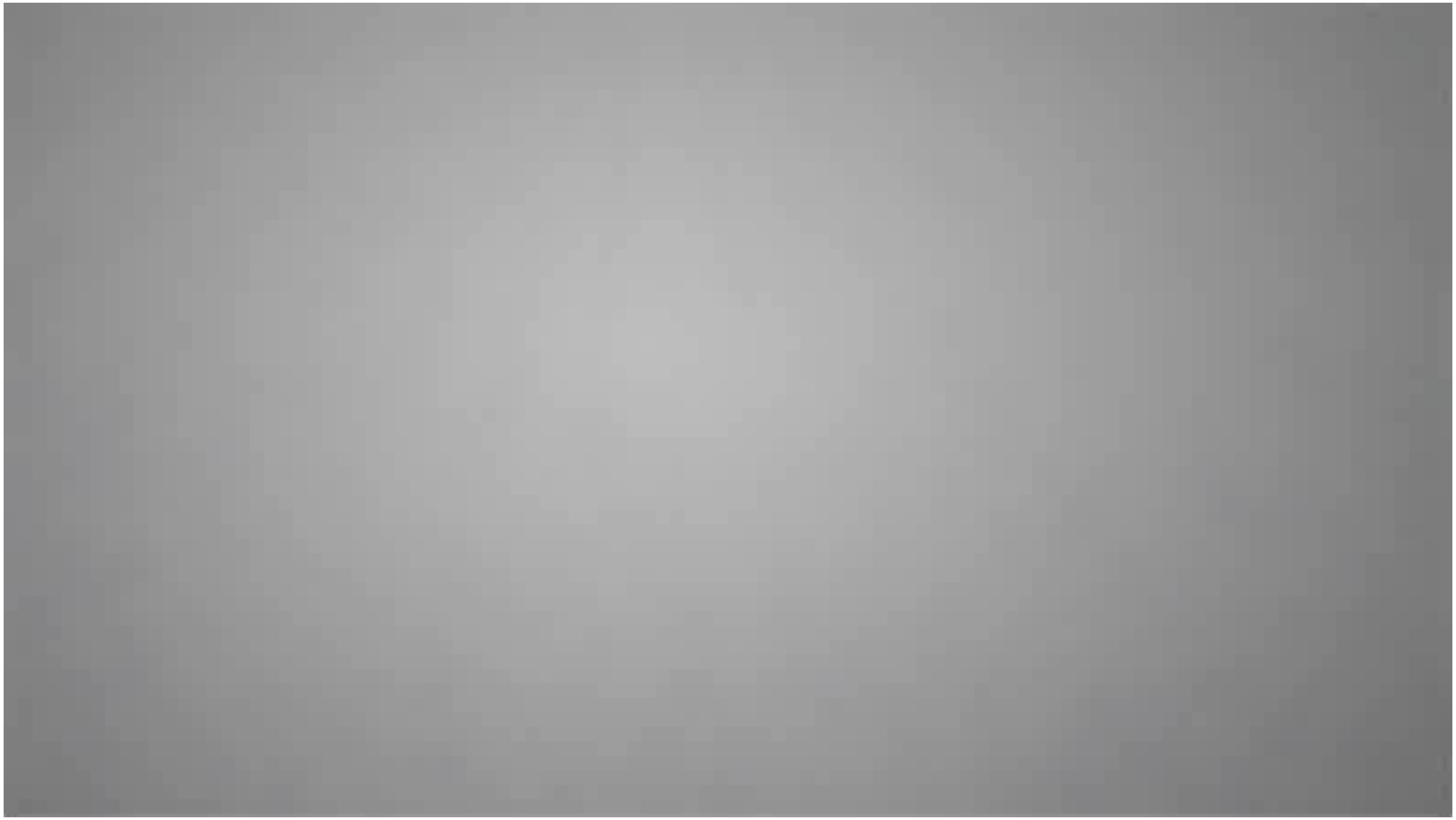
Figure 3. A schematic of cell forms as found from a multitude of sources:[6-8] (a) button cell, (b) cylindrical cell, and (c) prismatic cell.

Challenges with aqueous processing



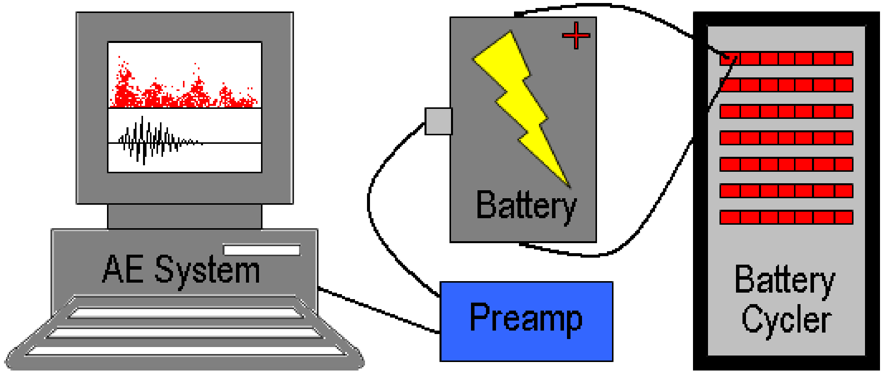
- Goal is to develop aqueous route processing for various active cathode materials such as $LiFePO_4$ or $Li(Ni_xMn_yCo_z)O_2$.
- Colloidal chemistry optimization becomes important when NMP is replaced with water.

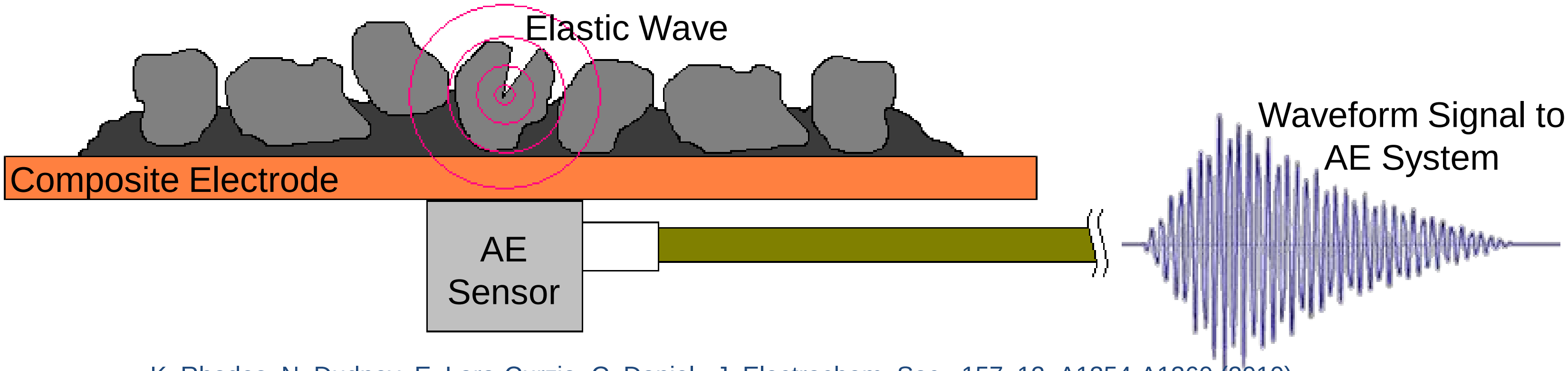
Degradation studies
Acoustic emission and other methods to understand degradation mechanisms



Acoustic Emission Spectroscopy

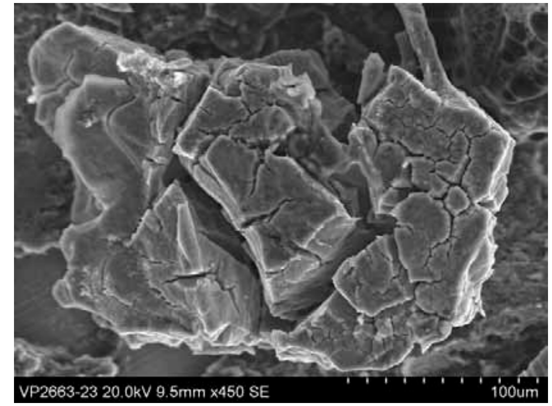
- Utilizing acoustic emissions stemming from mechanical events to probe degradation
- Cells are cycled while acoustic emissions are recorded and analyzed
- Acoustic emissions are classified according to a set of 28 parameters in standard data analysis procedures
- Additional characterization techniques such as XRD, neutron diffraction, optical microscopy, Raman spectroscopy are applied simultaneously in order to validate understanding

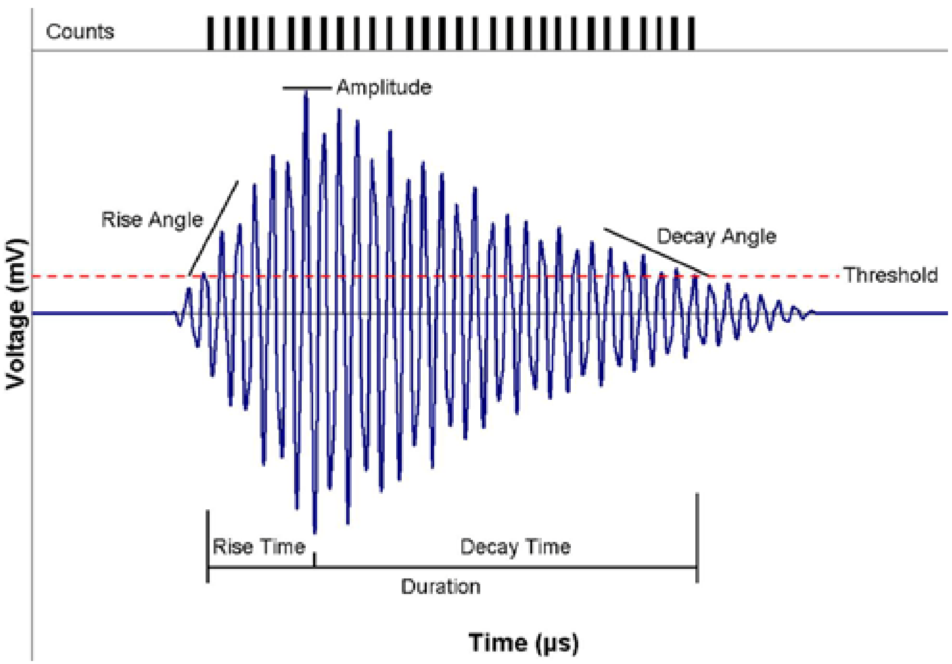


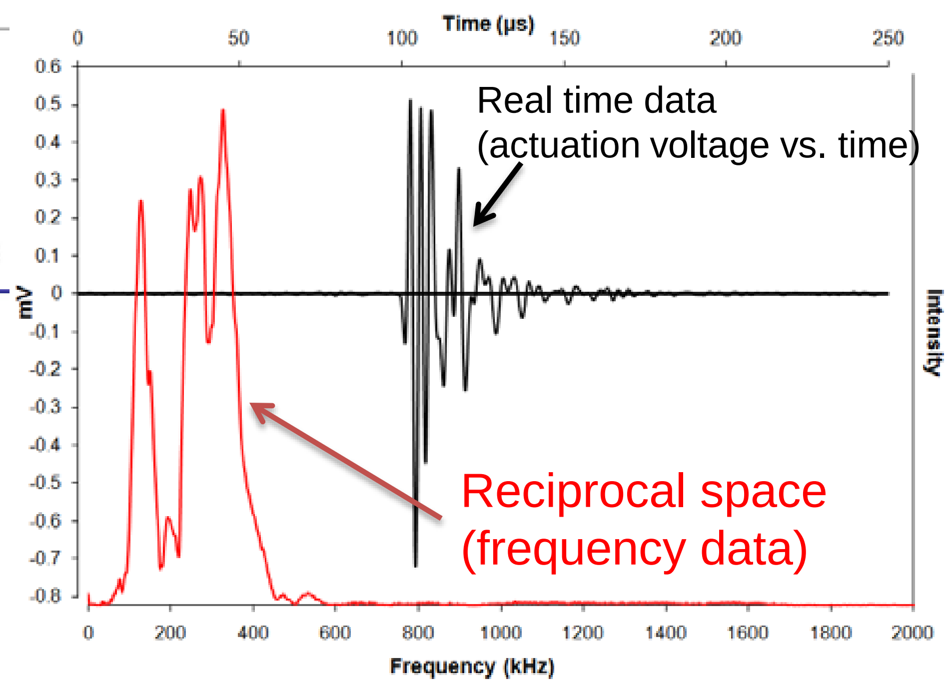


K. Rhodes, N. Dudney, E. Lara-Curzio, C. Daniel,, J. Electrochem. Soc., 157, 12, A1354-A1360 (2010)

Acoustic emissions are analyzed in real and reciprocal space

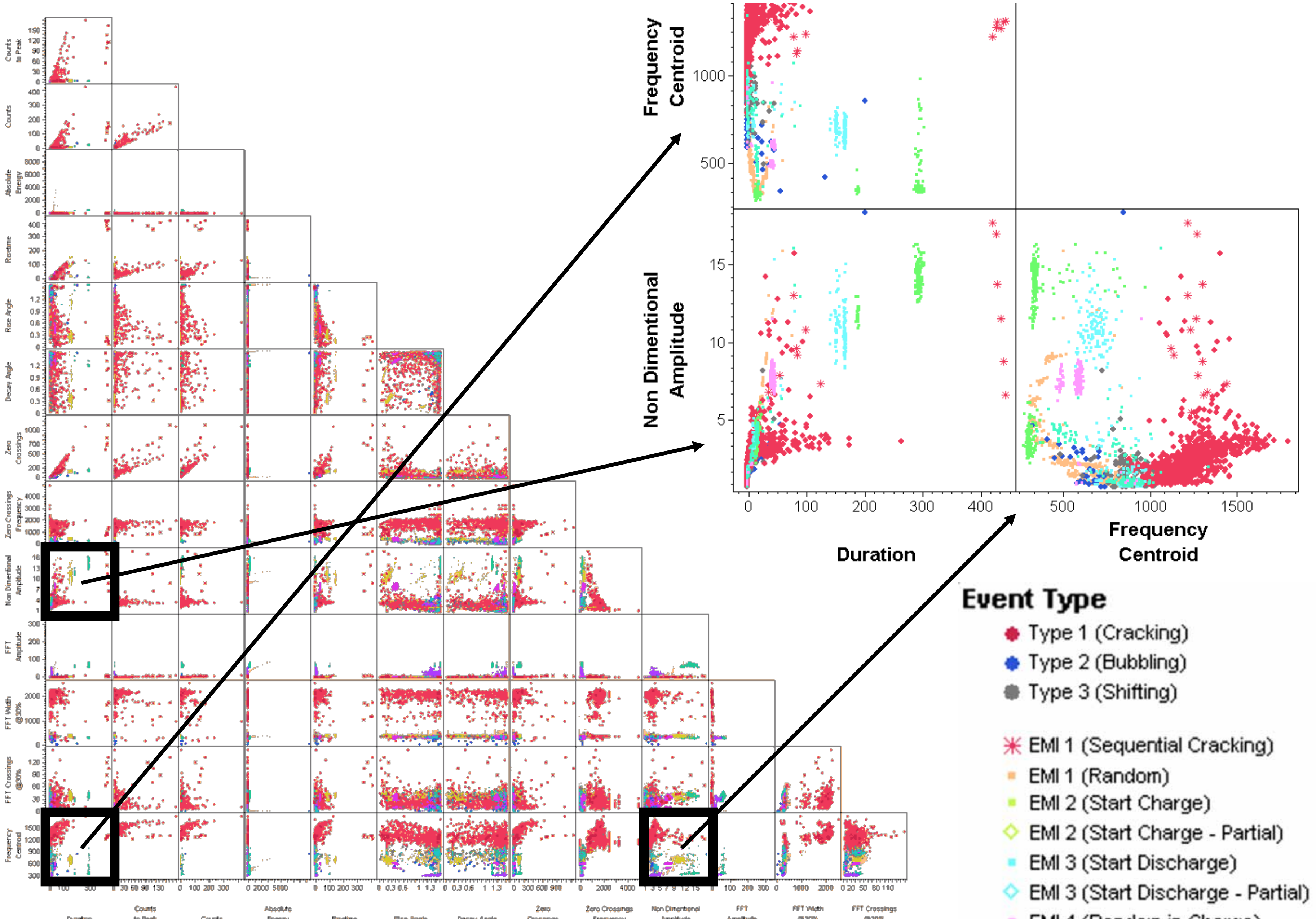






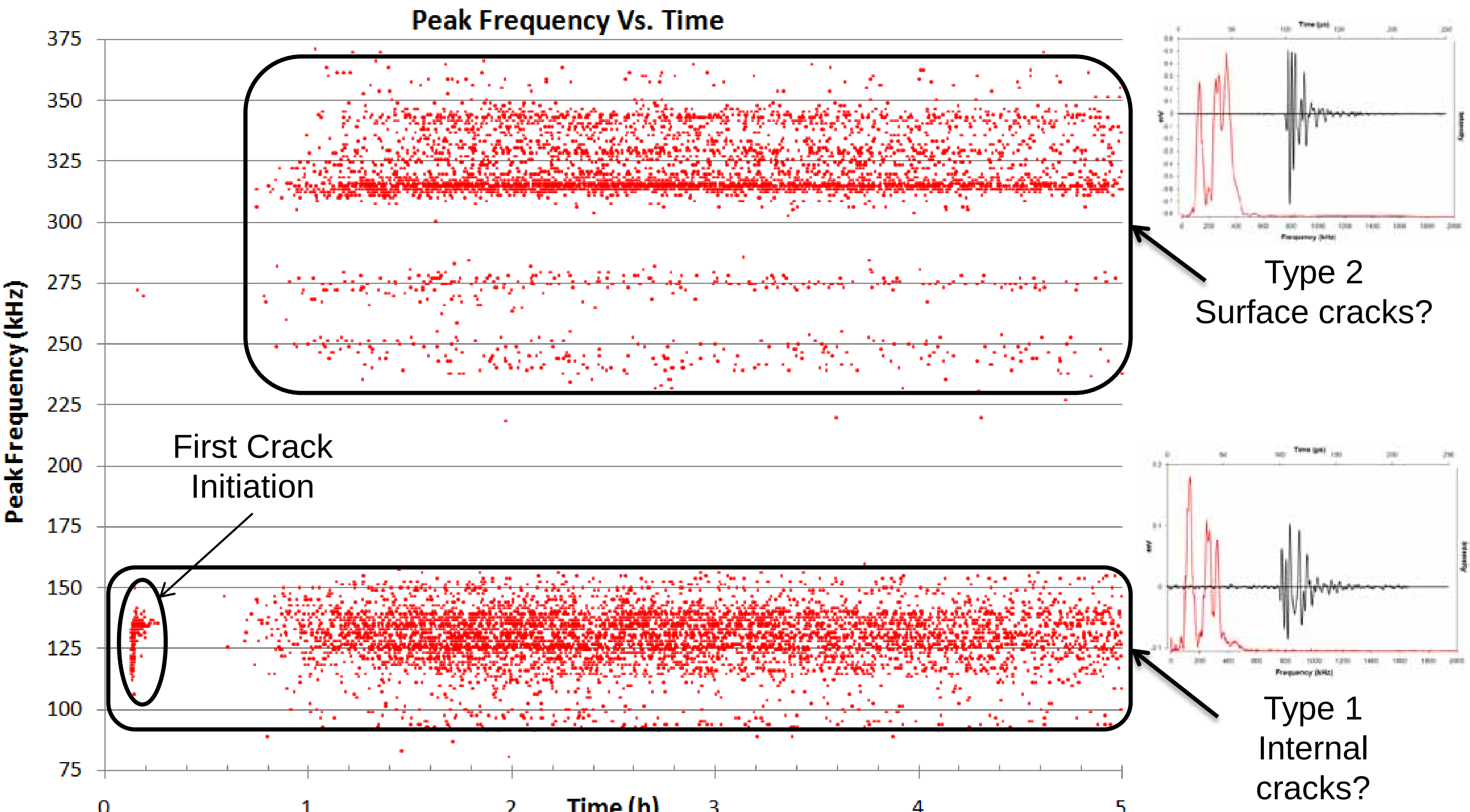
K. Rhodes, N. Dudney, E. Lara-Curzio, C. Daniel,, J. Electrochem. Soc., 157, 12, A1354-A1360 (2010)

Data is prepared in training sets to train software for automatic event classification, background and noise are classified and removed



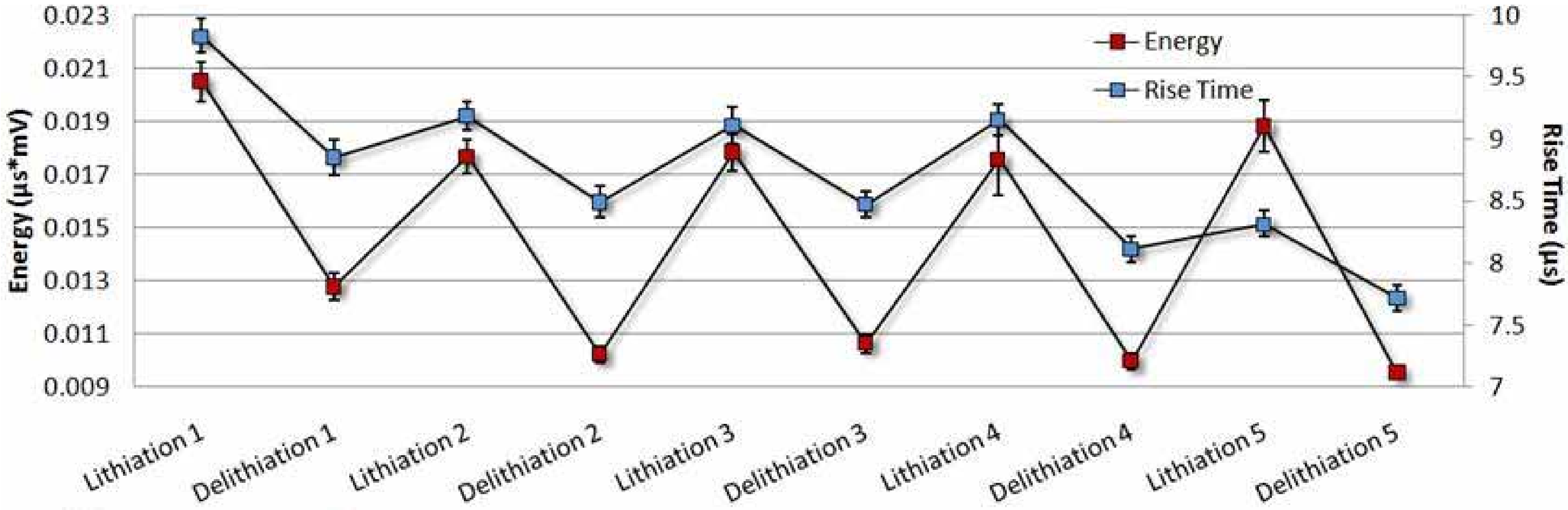
K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, J. Electrochem. Soc. (submitted).

How to cracks form and propagate?



AE from Cycling silicon – CCCV – 50mV-1.3V @ C/20

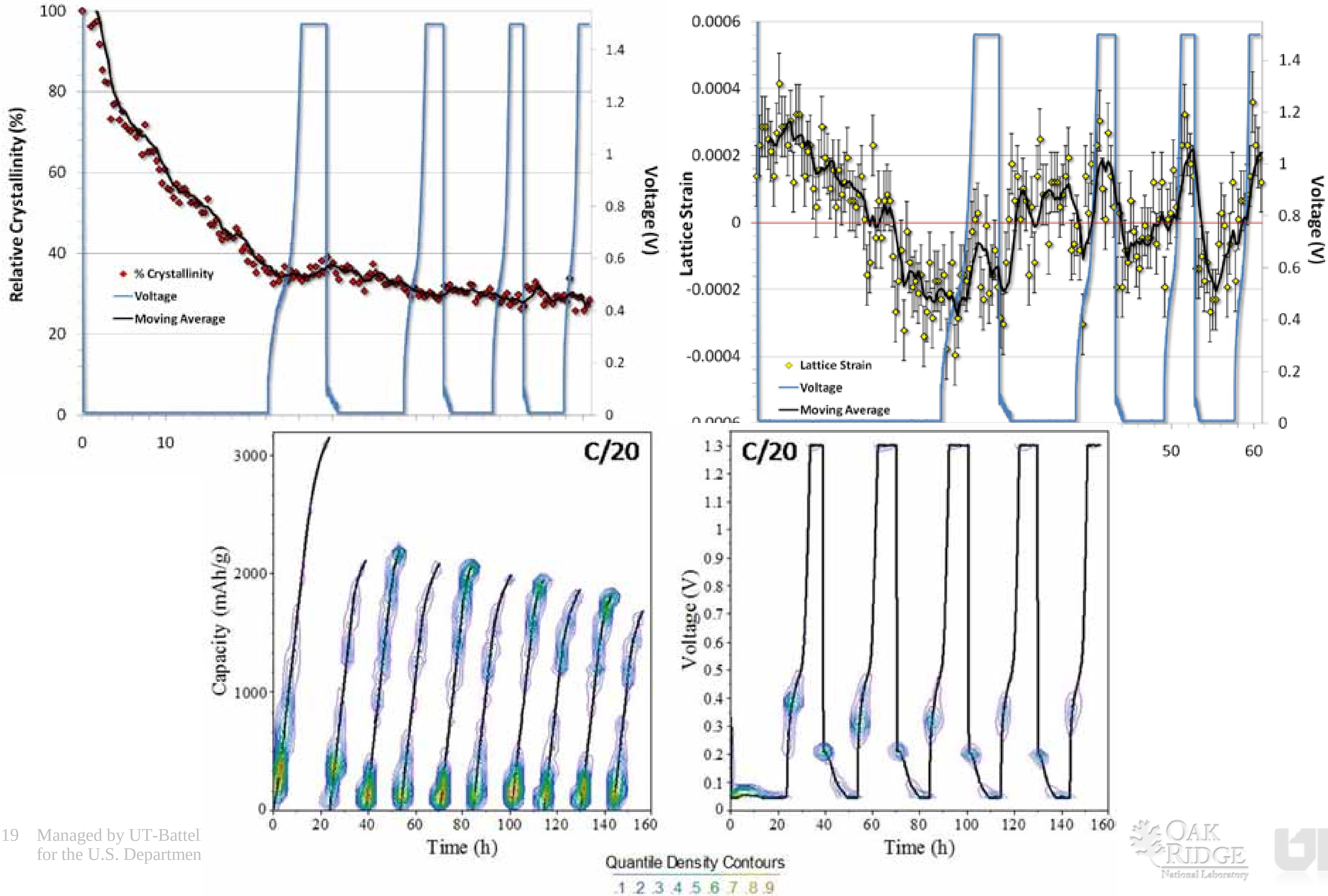
When do batteries degrade most?



silicon

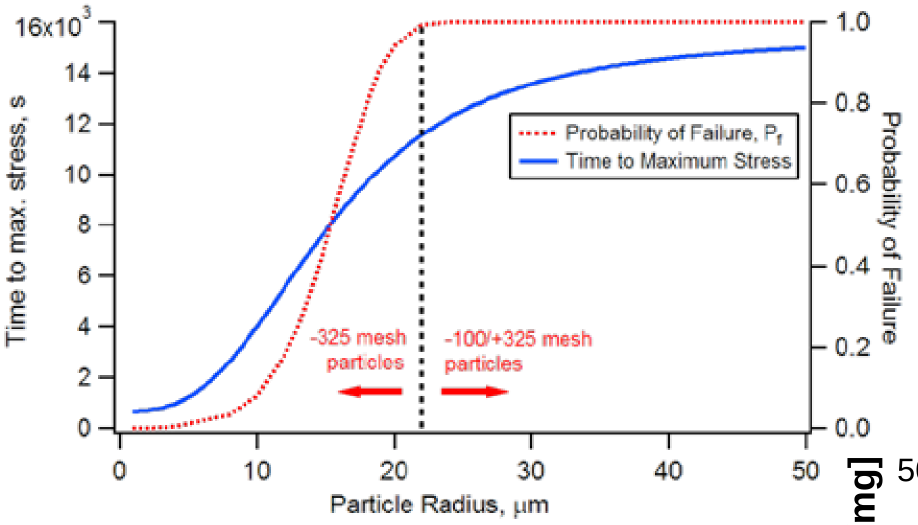
K. Rhodes, N. Dudney, E. Lara-Curzio, C. Daniel,, J. Electrochem. Soc., 157, 12, A1354-A1360 (2010)

How do phase transformations and fractures influence behavior?



K. Rhodes, N. Dudney, E. Lara-Curzio, C. Daniel,, J. Electrochem. Soc., 157, 12, A1354-A1360 (2010)

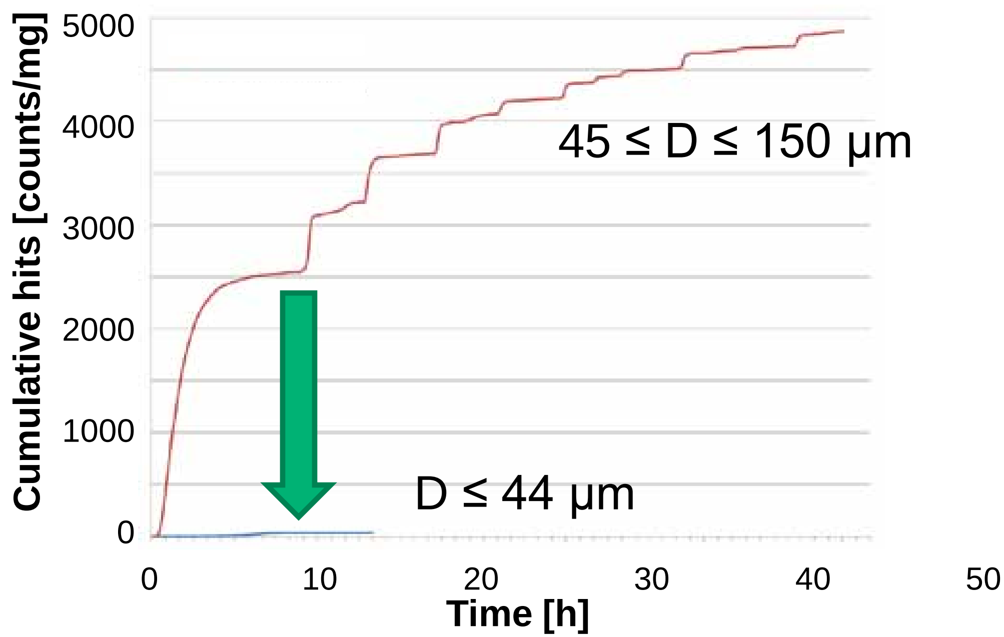
Theory of probability of failure allows for particle engineering to minimize degradation!



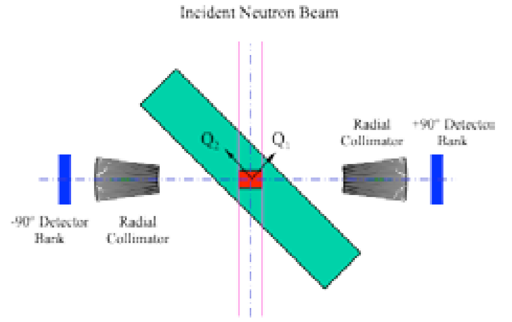
S. Kalnaus, K. Rhodes, C. Daniel, Eng. Fract. Mech. (submitted)

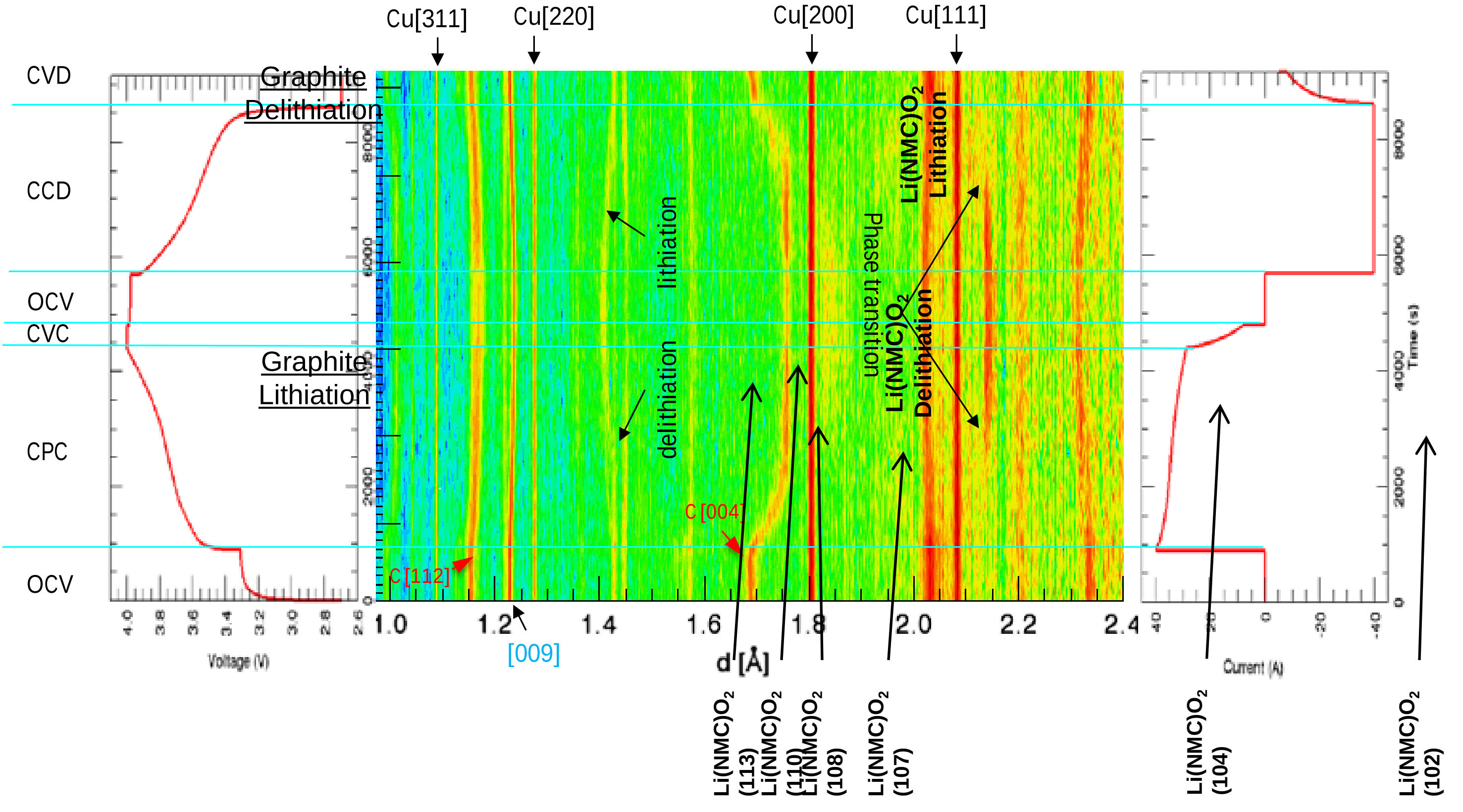
Theory:
Particle sized below **44µm**
should have no or little cracking

Experiment:
Confirms that those particles show more than 2 orders of magnitude less emissions



Neutron science for large battery cells





CVD-constant voltage discharge, CCD-constant current discharge, OCV open circuit voltage
CVC-constant voltage charge, CPC-constant power charge

Summary

- Lithium ion batteries are the most likely enabler to the electrification of the drivetrain and the utilization of intermittent renewable energy sources
- Problems with safety, cycle life and performance still exist – particular in large scale up applications
- New in situ characterization is needed to develop the knowledge of failures and limitations
- New processing routes are promising and enable new and advanced battery design
- New battery chemistries and technologies will follow Li-ion

Acknowledgements

Contributors

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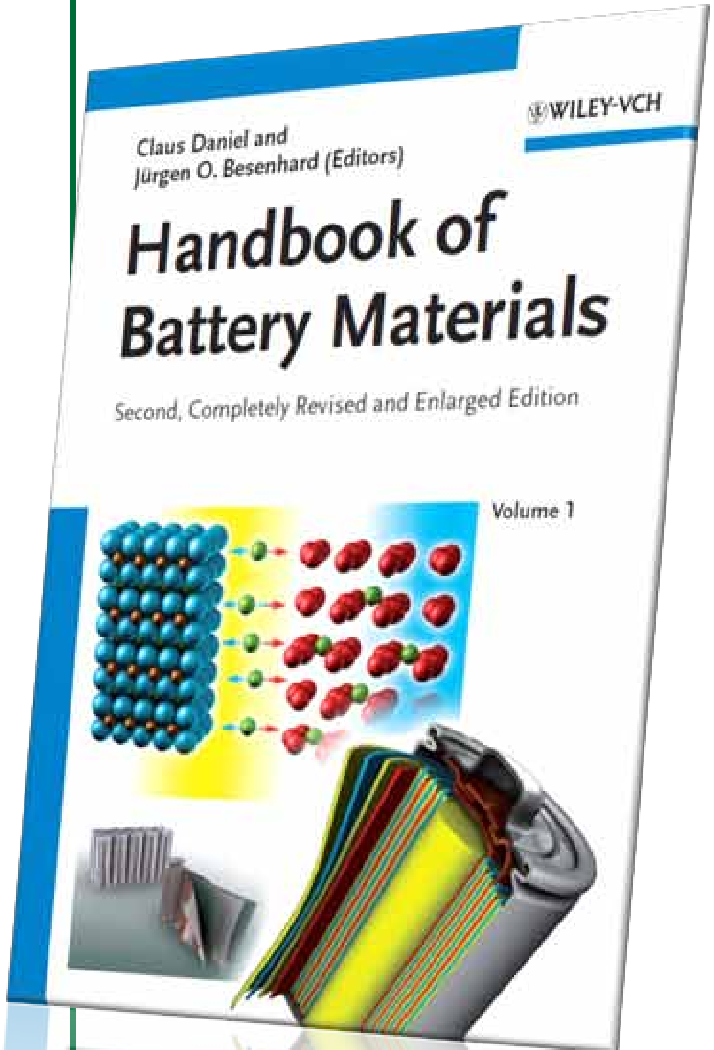

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