U.S. DEPARTMENT OF ENERGY

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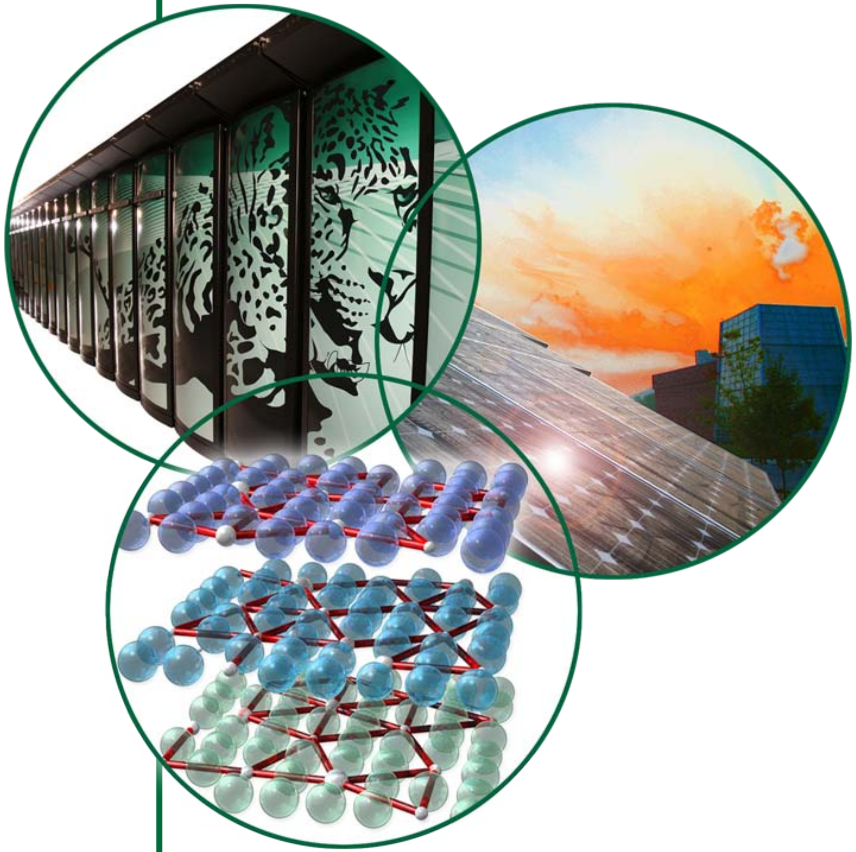
2010 U.S. Department of Energy Hydrogen Program and Vehicle Technologies Program

Project ID #ES039

In-situ characterization of fatigue behavior of electrodes



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June 10, 2010

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

- Start: Aug. 2009
- End: Sept. 2012
- 25% Complete

Budget

- Total Project Funding: $900K
- Funding for FY09: $300K
- Funding for FY10: $300K

Barriers

- Poor cycle life

Goals

- Cycle life: 5000 cycles
- Calendar life: 15 years

Objectives

In-situ characterization of fatigue behavior of electrodes

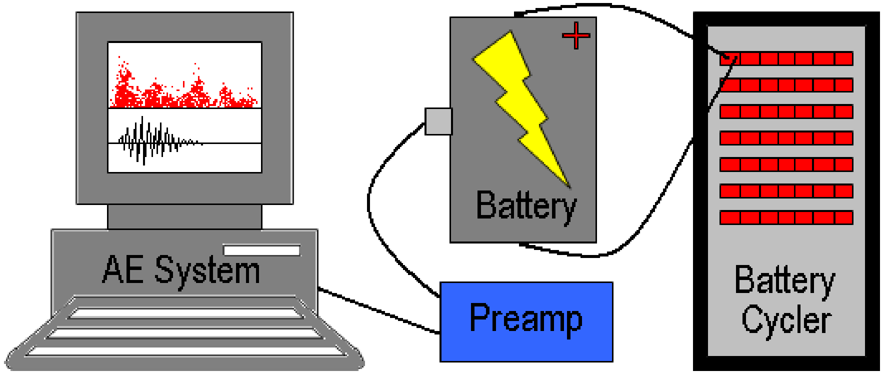
- **Development of in-situ tool to characterize mechanical degradation (crack initiation, crack growth, particle fracturing, particle loosening) during cycling.**
- **Fundamental understanding of accumulation of defects and resulting mechanical degradation.**
  - **Opportunity to develop a real life time prediction for different materials.**
  - **True quantification of mechanical degradation**
- **Importance of mechanical degradation to capacity fade.**

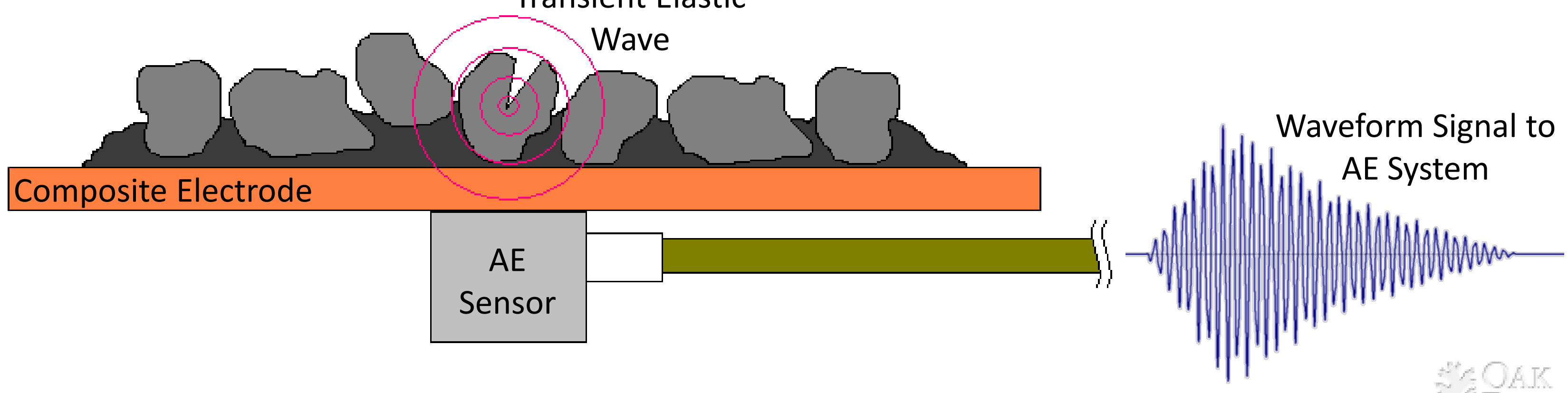
Milestones FY2010/11

Month/Year	Milestone or Go/No-Go Decision
Oct 09	Acoustic emission detection and classification of events in coin cell samples based on signal signature.
Apr 10	In-situ studies combining acoustic emission spectroscopy and X-ray diffraction
Sept 10	Establishing combination with other methods such as neutron diffraction, Raman spectroscopy, etc.
Sept 11	Understanding of physical evidence to acoustic emissions and degradation mechanisms in electrodes.
Sept 12	Development of life time prediction tools and ‘fatigue’ like models for materials behavior.

Approach

- 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



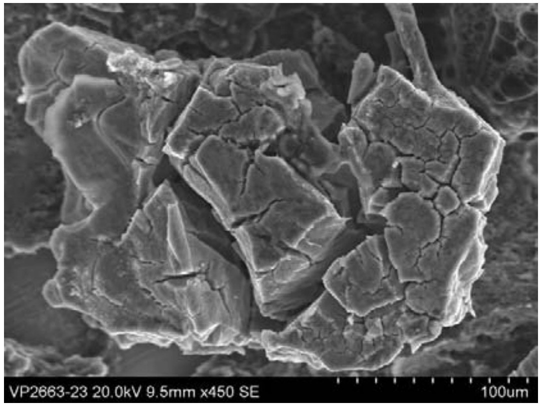


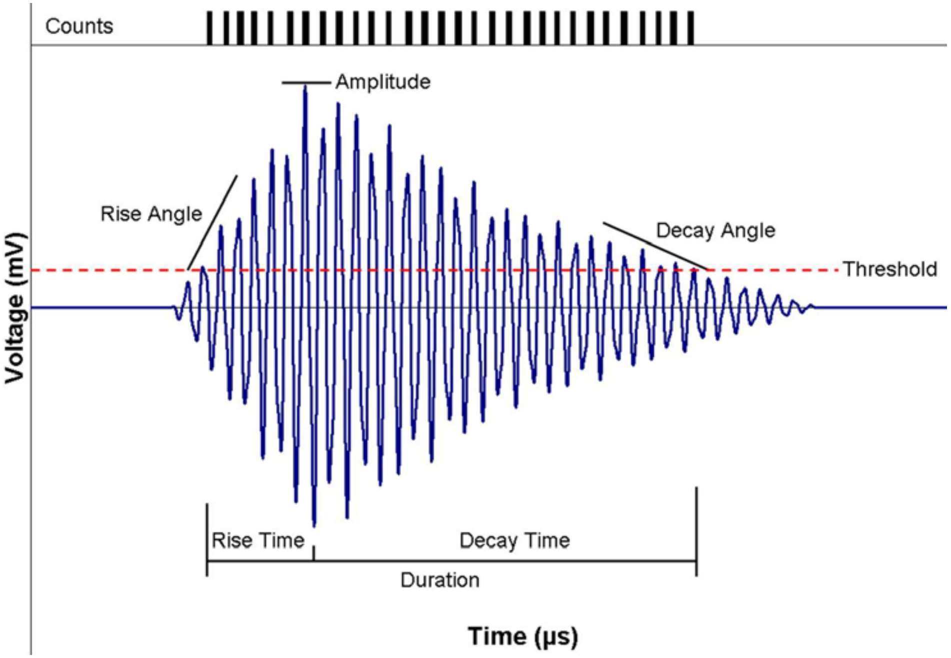
Subject specific optimized sample configuration and testing with standard recipes

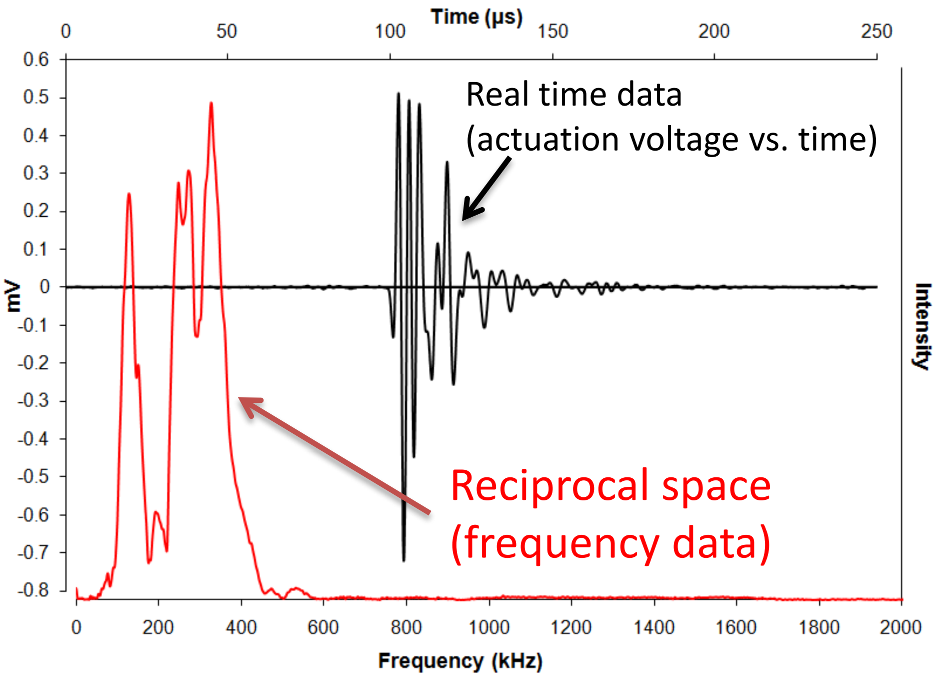
- Composite Electrodes
  - Silicon or carbon
  - PVDF, Super S Carbon (8:1:1 by wt)
  - NMP solvent
  - Cu current collector
- Cell Assembly
  - Weigh & assemble in glove box
  - Components
    - Li foil
    - Composite electrode
    - 2325 Celgard
    - 1.2M $LiPF_6$ in EC:DMC (3:7 by wt)
  - 2032 coin cell hardware

- Testing procedure
  - Cycling
    - Cyclic voltammetry (CV)
    - Constant current-constant voltage (CCCV)
  - Acoustic Emission
    - 22dB Threshold
    - Filter < 3 counts
    - Complimentary sensor for background AE
  - Microscopy, diffraction, spectroscopy

Acoustic emissions are analyzed in real and reciprocal space

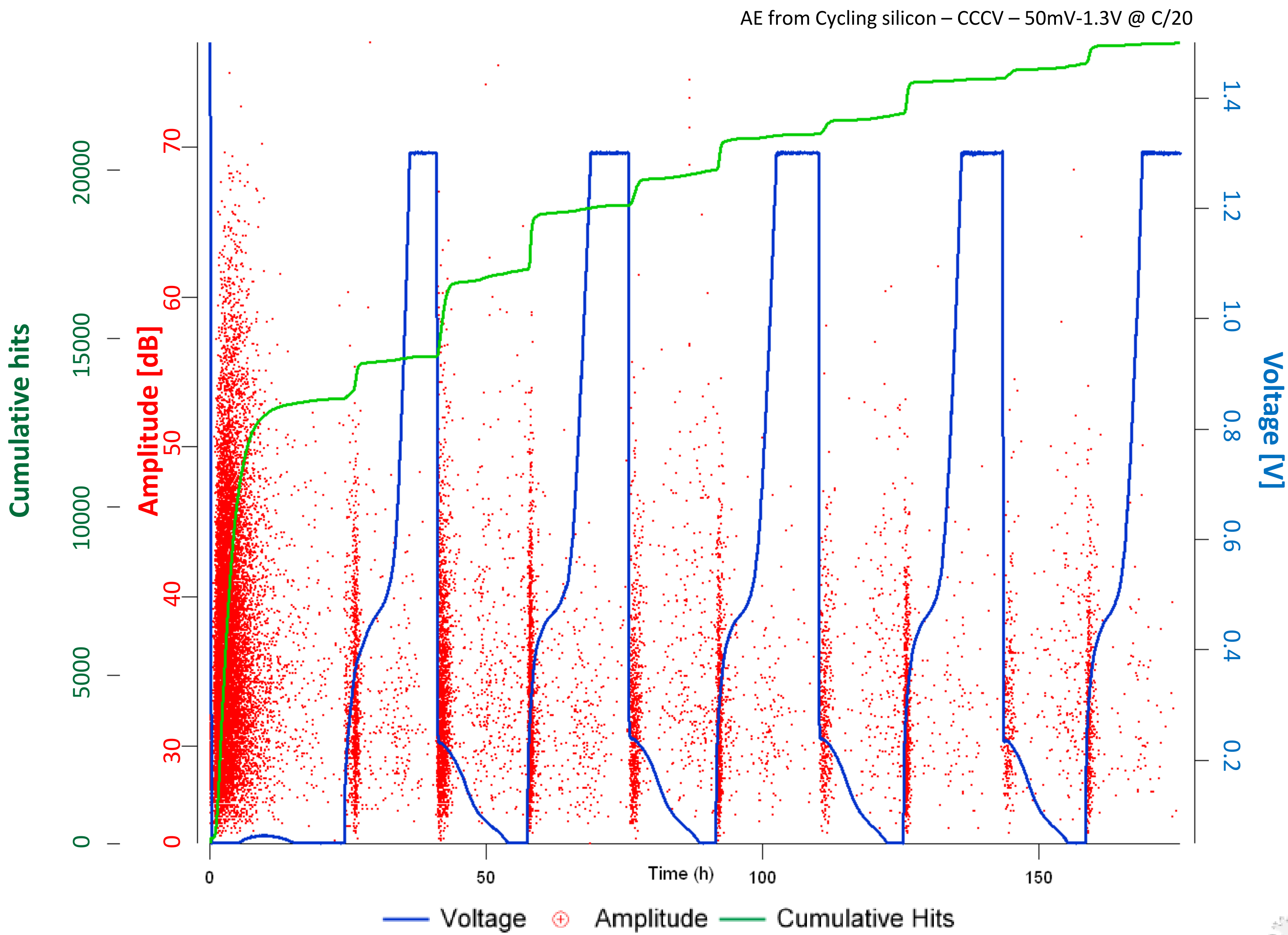






Technical accomplishments

Acoustic emissions are recorded while electrochemical cycling of samples



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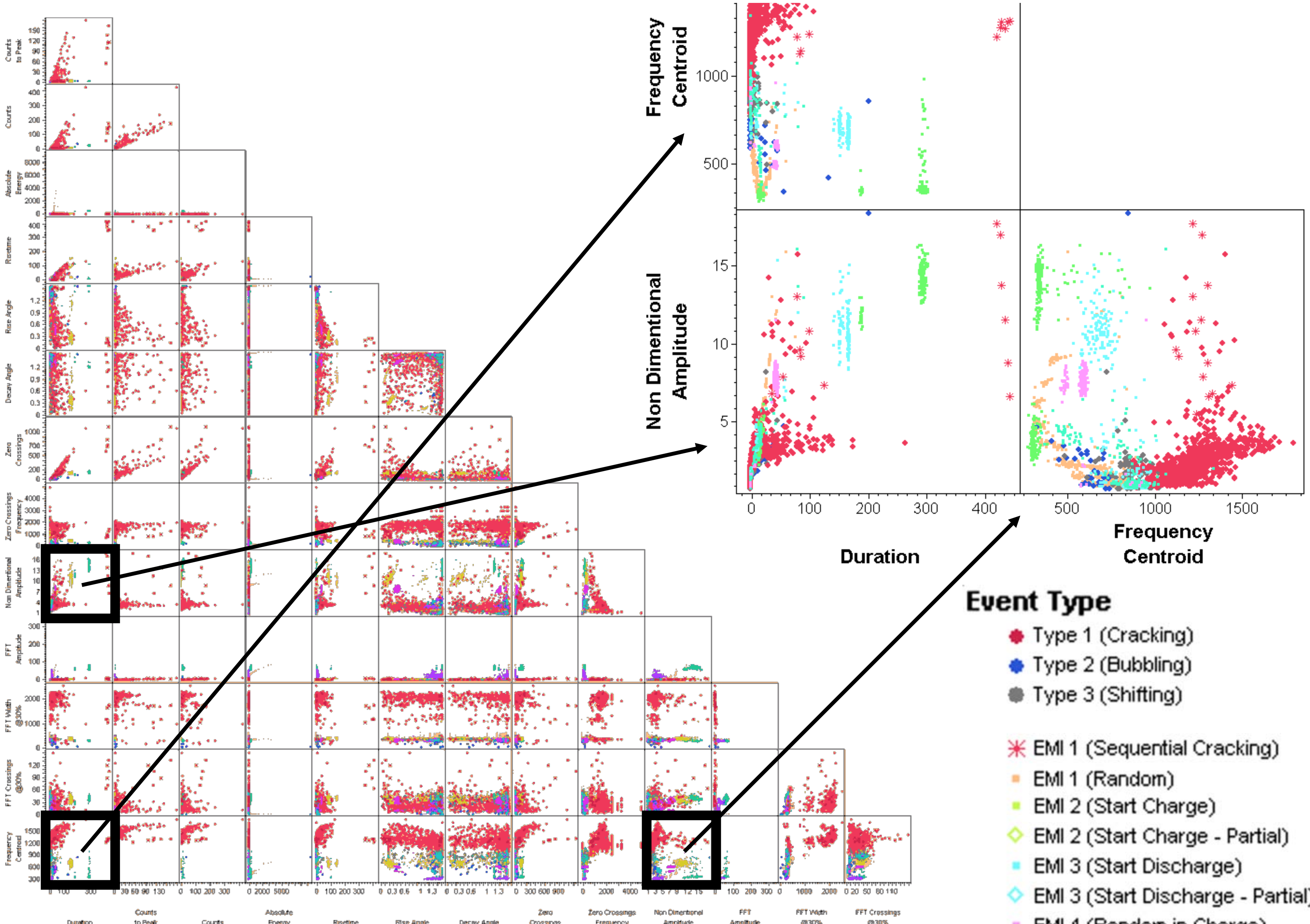
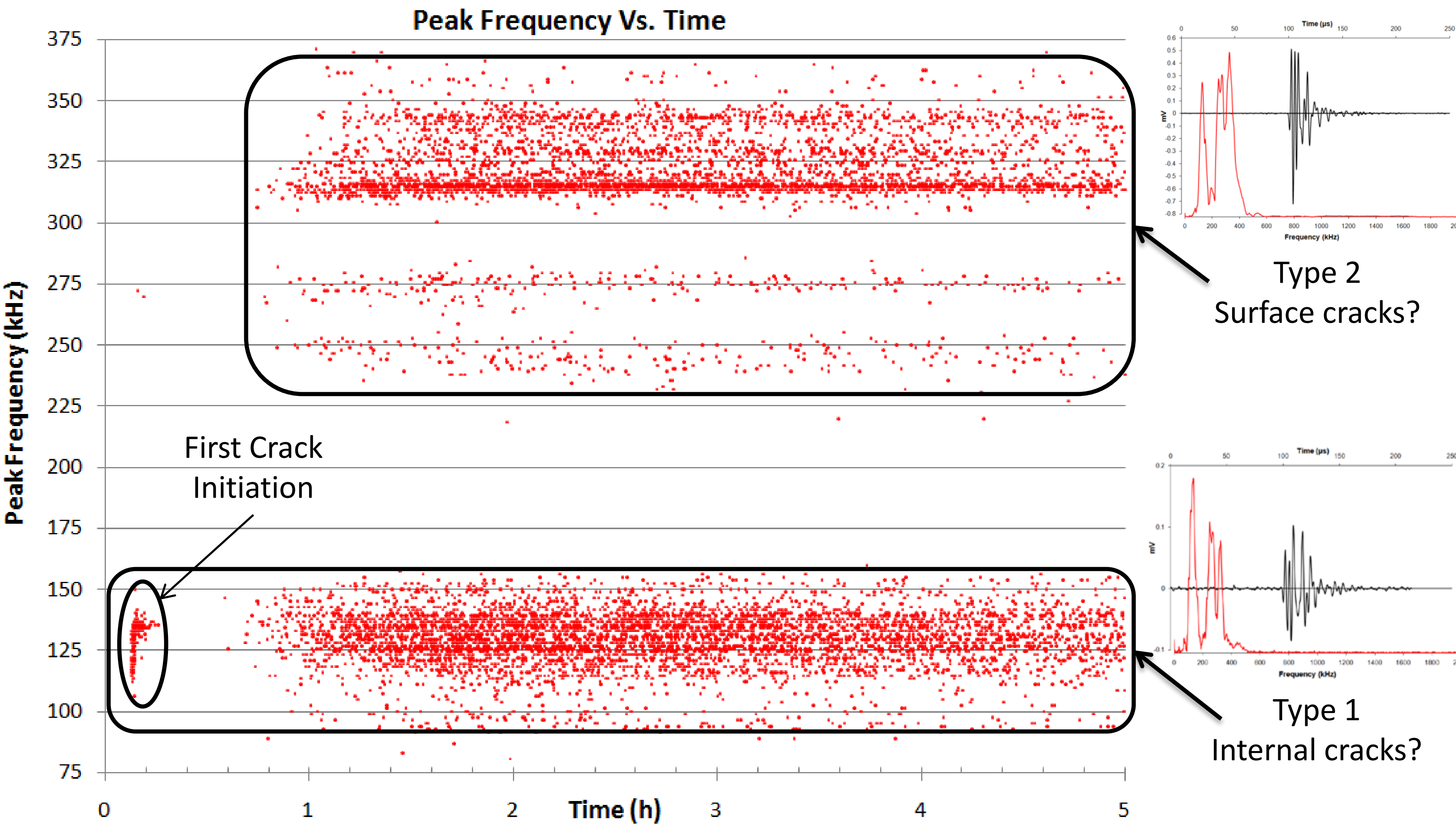
Data is prepared in training sets to train software for automatic event classification, background and noise are classified and removed



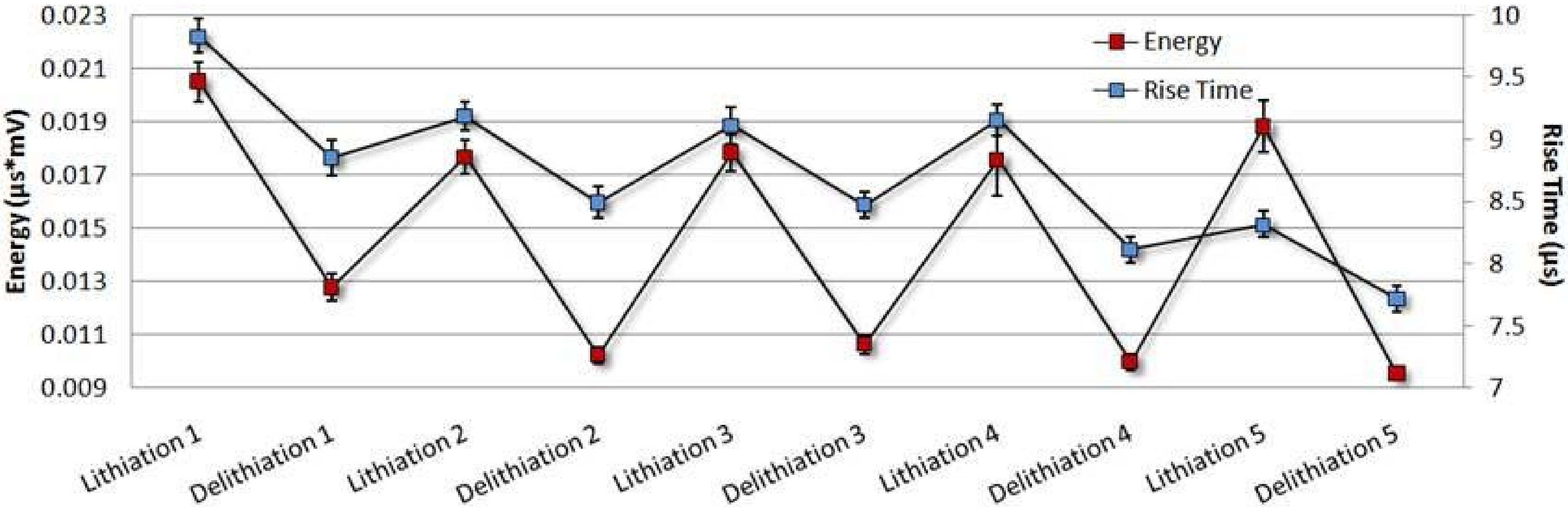
K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, J. Electrochem. Soc. (submitted).

Frequency may be able to distinguish source of cracks



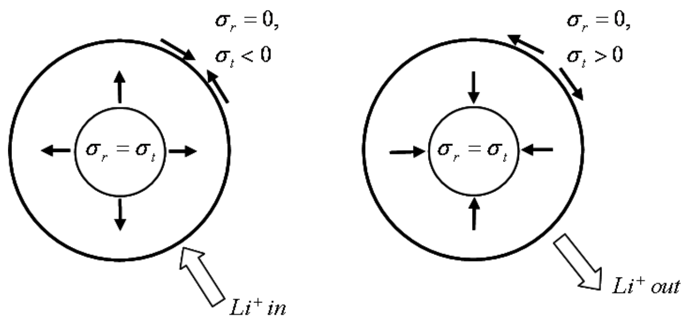
AE from Cycling silicon – CCCV – 50mV-1.3V @ C/20

High energy acoustic emissions are generated during lithiation Hence, mud crack theory for cracking in electrode particles may not be correct



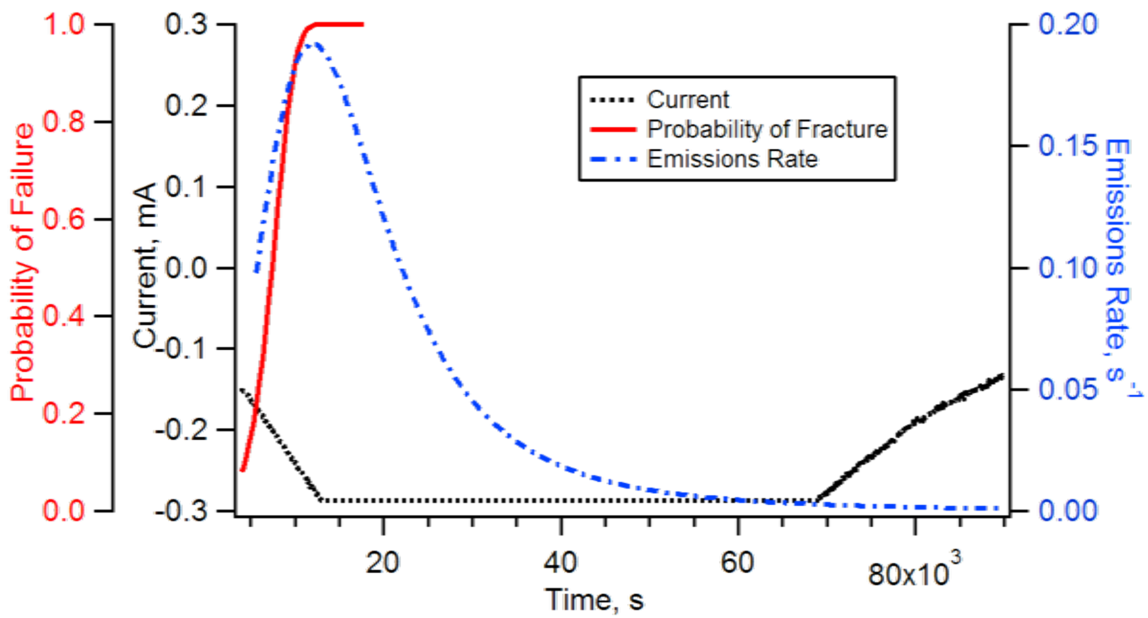
silicon

Theory of probability of failure can be applied to lithiation phenomena



$$P_f(t) = 1 - \exp\left(-\int_V \left(\left(\frac{\sigma_r(r,t)}{\sigma_o}\right)^m + \left(\frac{\sigma_\theta(r,t)}{\sigma_o}\right)^m\right) dV\right)$$

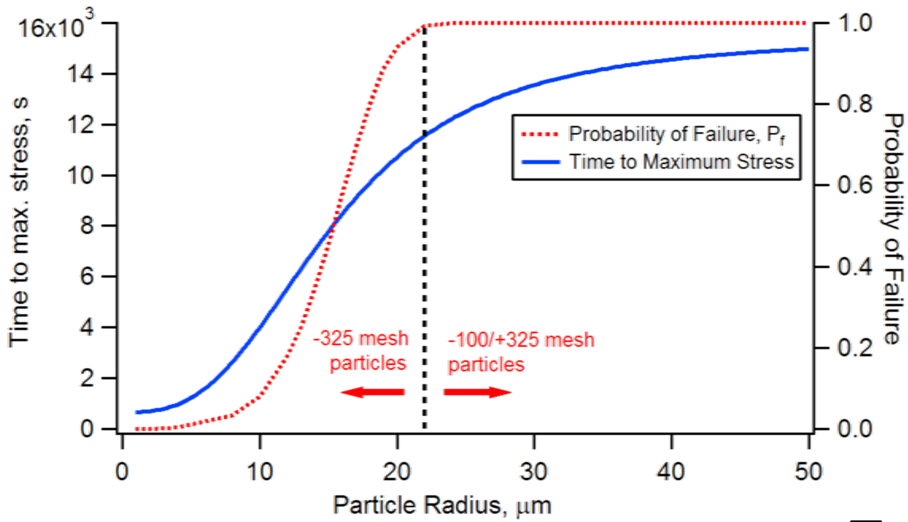
The work is under way for formulation of physically sound damage parameter which will account for change in material elasticity upon cycling. At this time the mechanism(s) responsible for the growth of defects and damage accumulation in silicon particles is unknown but it is the subject of investigation.



silicon

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

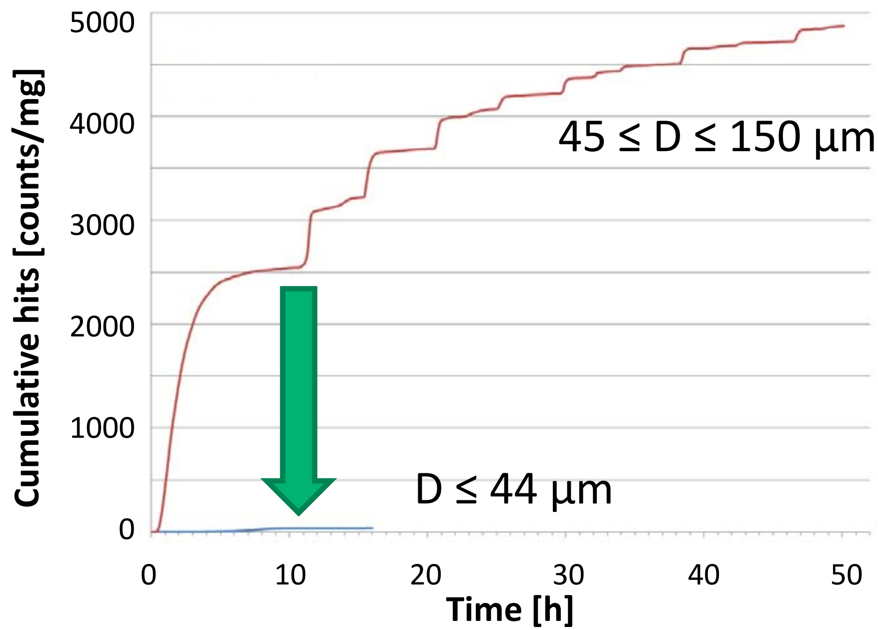
Brittle intercalation compounds may not need to be nano-sized to significantly reduce damage



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

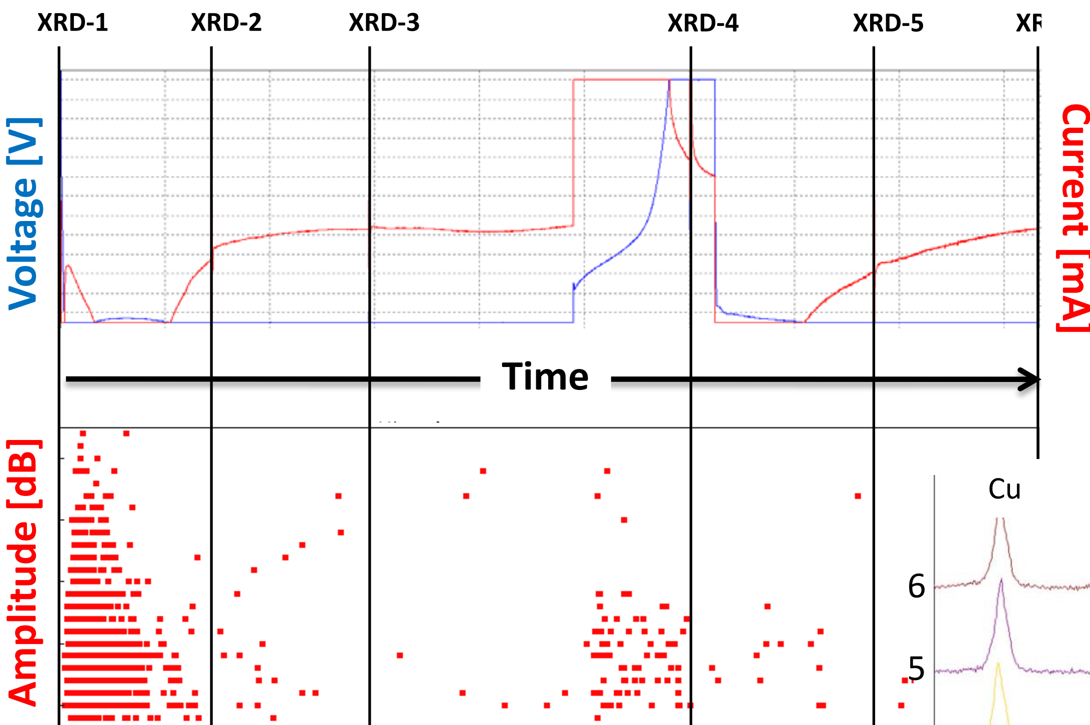
Theory:
Particle sized below **44μm** should have no or little cracking

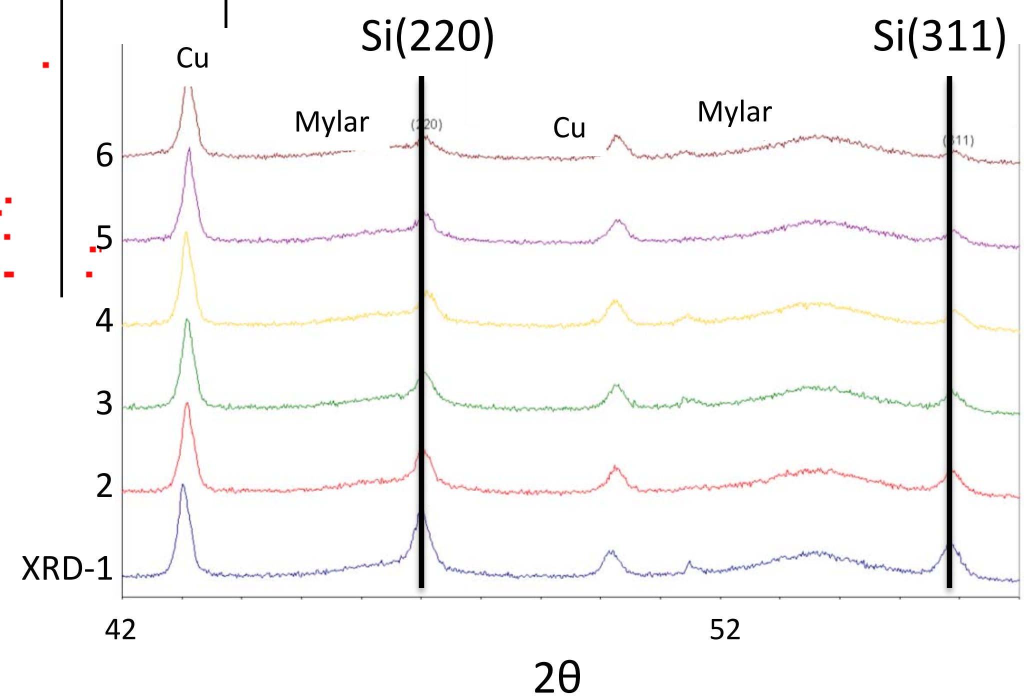
Experiment:
Confirms that those particles show more than 2 orders of magnitude less emissions



silicon

Combined acoustic emissions and X-ray diffraction has been demonstrated





Future work

- Validation of scientific indications/ hypotheses
- Development of in-situ combination characterization
- Full understanding of relationship between particle size and mechanical degradation
- Widening of included material beyond carbon and silicon materials (anodes and cathodes)
- Life time understanding, predication, and “fatigue” theory development

Summary

- Work has been limited to carbon and silicon anode materials. Work will soon be expanded to other materials (anodes and cathodes).
- Monitoring of active material degradation in cycling batteries has been demonstrated.
- AES techniques using coin cells have been developed and offer excellent signal transmission and cycling reproducibility.
- Combined AES and XRD has been demonstrated
- Complimentary characterization methods (in-situ and ex-situ) are added in order to understand physical evidence of emission
- Importance of mechanical degradation to capacity fade will be investigated
- New quantitative "fatigue" theory models will be developed in order to understand degradation accumulation and failure

Scientific indications obtained – to be verified in future work

- Emission frequency may allow for distinguishing the source of cracks.
- Mud crack theory is not applicable to non-thin film electrodes. Most cracking occurs during lithiation. Cracks may initiate in the core of the particles.
- Brittle intercalation compounds may not need to be nano-sized to significantly reduce cracking.

Acknowledgements

- Contributors
  - Kevin Rhodes, Nancy Dudney, Edgar Lara-Curzio, Sergiy Kalnaus
- Collaborators
  - Rosa Trejo, Jim Kiggans, Larry Walker

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