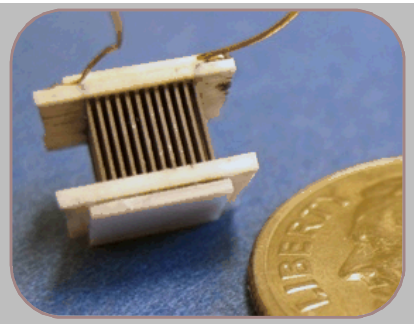
SAND2016-4781C

Exceptional service in the national interest

Sandia National Laboratories



Accelerated Aging of Li(Si)/FeS_2 Thermal Batteries

Daniel E. Wesolowski*, Ashley Allen, Chad Staiger, Andrea Ambrosini, Nancy Missert, Henry Peebles, Travis Anderson

Sandia National Laboratories
PO Box 5800, MS-0614
Albuquerque, NM 87185

June 15, 2016

*Corresponding author: dewesol@sandia.gov

U.S. DEPARTMENT OF ENERGY

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Aging in Thermal Batteries

Sandia National Laboratories

- Li(Si)/FeS_2 thermal batteries have been fielded for three decades
- Many analytical techniques can be used to examine materials from old batteries

Techniques Sandia Applies to Examining Field Return Batteries

Battery Characteristic	Analytical Tech.	Purpose
Leak check	He bomb	Recheck; possible weld fractures
Structure	X-ray	Measure stack relaxation
Gas composition	Case puncture and HR-MS	Rate of O_2 absorption, H_2 generation
Anode oxidation	Neutron activation analysis	Rate of oxidation
Calorific output	Bomb calorimeter	Rate of heat pellet degradation
Burn rate	High speed camera	Rate of heat pellet degradation
Ignition sensitivity	Laser flash	Rate of heat pellet degradation
Cell capacity	Single-cell test	Capacity change vs. gas composition
Microanalysis	SEM/EDS	Anode and cathode phase changes
Spectroscopy	FTIR	Cathode sulfate formation

Test unit and piece parts

Problems:

Unknown relationship between analytical results and performance

No baseline information- no equivalent tests on identical materials at time of production

New Baseline Aging Study

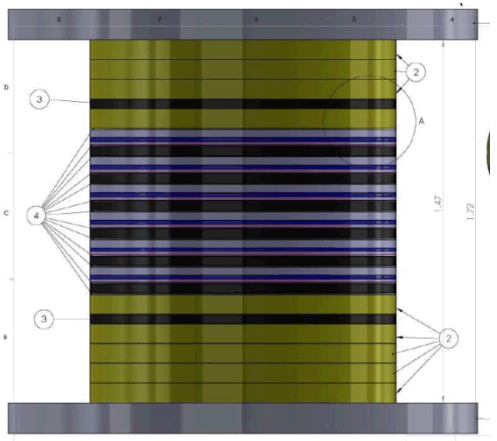
Aging study design

Variable	Levels
Temperature	75°C, 130°C, 180°C
Time	3m, 6m, 12m, 24m (75°C only)
Water content	Dry to best efforts, insulation exposed to moist air

- Battery-like units built with modern production process, material of known pedigree
- Temperatures selected without presumption of activation energy
- Water used as an additional accelerator
  - Only confirmed aging mechanism for thermal batteries is water/oxygen reaction with lithium
    - Forms basis for leak rate measurement (see 45th PSC paper 35.4)
  - Leak rate can't be easily controlled, so water was added to the battery instead
- Times selected for convenience and comparison to legacy work

Battery-like unit

- All battery materials except ignitor or heat paper
- Fiberfrax insulation
- Stack shimmed to 250 PSI
- Welded stainless steel can



Activation Energies req. for 30x acceleration

Aging T (°C)	E_a (kJ/mol)
75	86
130	32
180	24

Results: What changed (or not)?

Sandia National Laboratories

Quantitative measurements WITH statistically significant changes from start

Both dry and wet units

- Total pressure
- Overall gas composition
- Heat pellet calorific output
- H_2, O_2 content

Wet units only

- Capacity
- Impedance
- Peak Voltage
- Anode oxidation

Quantitative measurements WITHOUT statistically significant changes

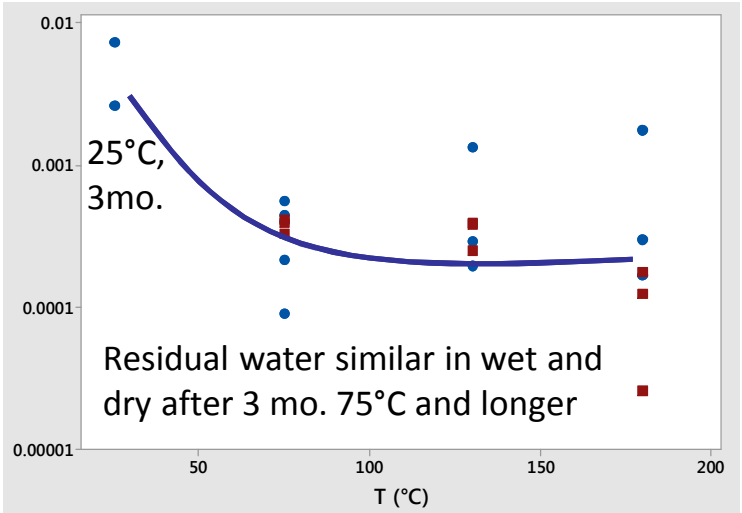
Dry units only

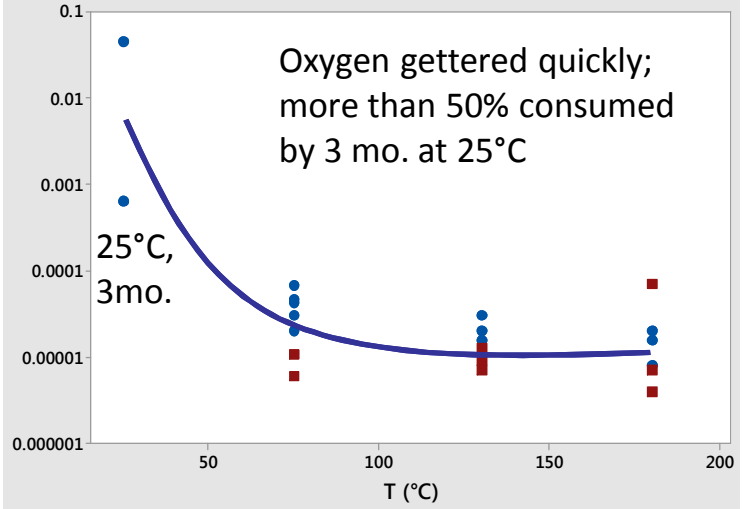
- Capacity
- Impedance
- Peak Voltage
- Anode oxidation

Both dry and wet units

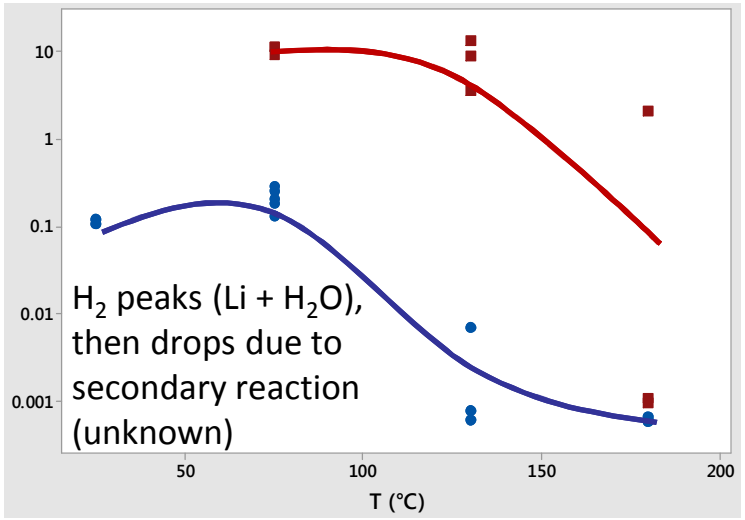
- Heat capacity (anode, cathode and separator)
- Electrolyte melting point
- Heat of fusion
- N_2 and Ar content

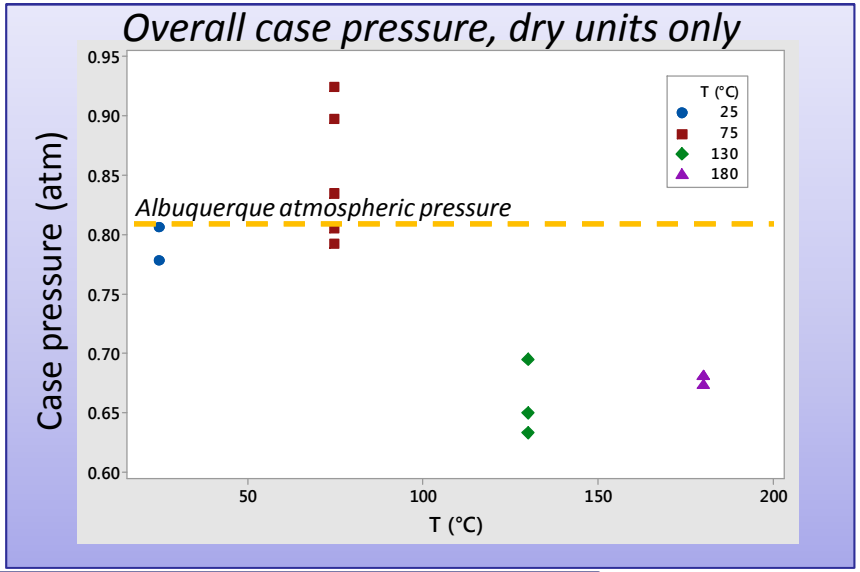
Common change: O_2 consumed, H_2 forms and is then consumed





Dry units
Wet units





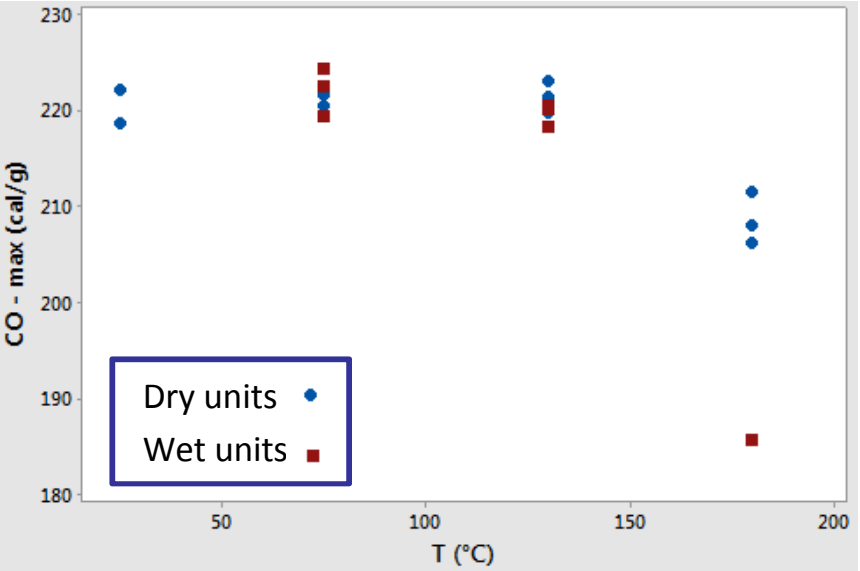
Fast O_2 gettering AND Fast H_2 production, followed by slow H_2 decline

Common Change: Heat Pellet Calorific Output

- Heat pellets deteriorate with temperature
  - Too much scatter to calculate activation energy
- Water was not proven to reduce calorific output, but…
  - 2/3 of 180° C wet samples failed to light and were excluded (implies reduced ignition sensitivity)

Follow up work required:

- Ignition sensitivity measurement
- IC to establish degradation mechanism
- More data at wet, high T to determine if water contributes to CO reduction



What was different between units?

- Used general linear model to look for significant changes

$$\hat{y} = \beta_0 + \beta_1 T(°C) + \beta_2 t(days) + \beta_3 (Wet?) + \epsilon$$

  - Looking for significant changes with temperature or moisture ($p<0.05$ for β_1 and β_3)

	Analytically Measured Value	Change with temperature $p\ \beta_1$, dry samples	Change with temperature $p\ \beta_1$, wet samples	Change with moisture, $p\ \beta_3$
	Calorific Output (cal/g)	0.00	0.00	0.71
Single cell electrical	**Anode Oxidation (%)**	0.17	0.13	0.00
Single cell electrical	**Cell capacity .3V (Ah/g)**	0.14	0.00	0.00
Single cell electrical	**Mid-discharge impedance (Ohm)**	0.71	0.01	0.05
Gas sampling	**Case Pressure (atm)**	0.00	0.01	0.01
Gas sampling	**H_2 partial pressure (atm)**	0.00	0.01	0.02
Gas sampling	**Gas Quantity (µmol)**	0.00	0.02	0.01
		Gray = not a significant change	Blue = significant change	

- Only gas composition / quantity changed with T for dry units
- Water much more effective accelerator for battery deterioration

Electrochemical performance

Sandia National Laboratories

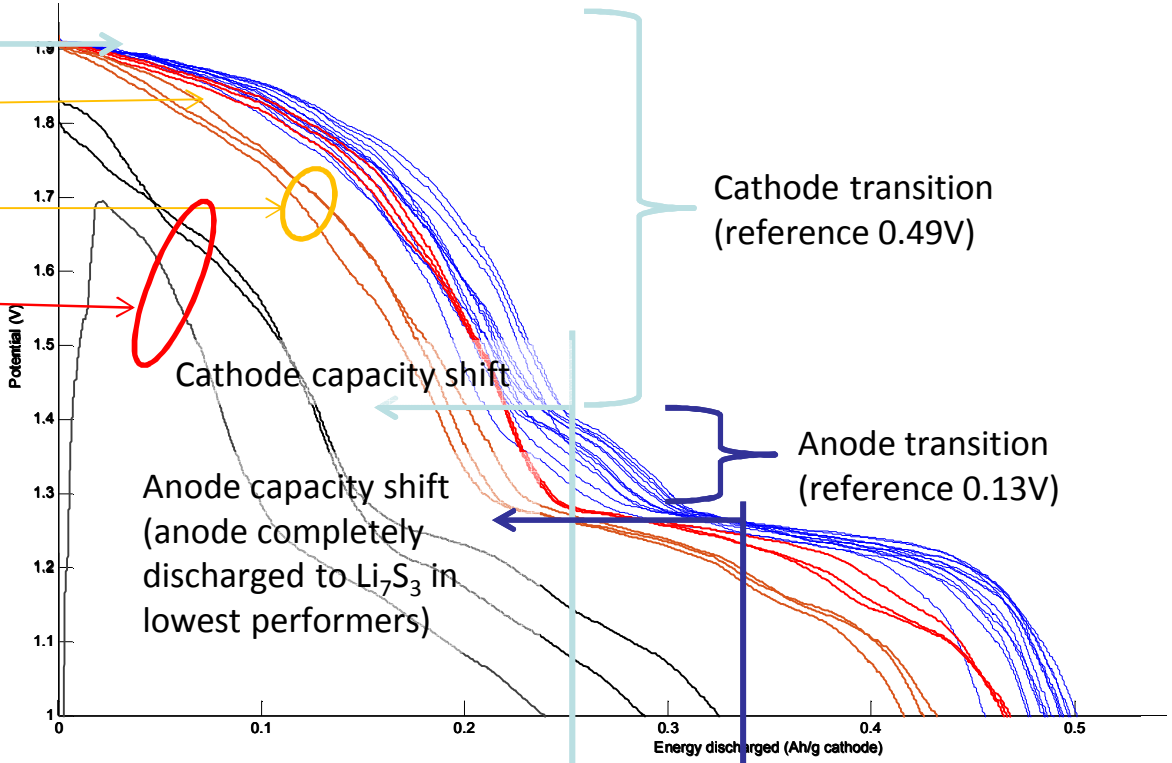
β_3:Wet insulation causes clear decline in capacity (up to 75% loss)

Baseline (dry)

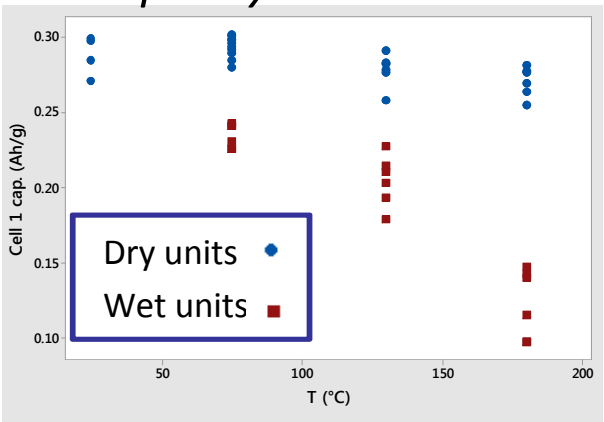
75°C, wet

130°C, wet

180°C, wet



Capacity to 1.3V vs T



All dry samples have capacities within dry cell capacity variability (75°C, dry, 6m best)

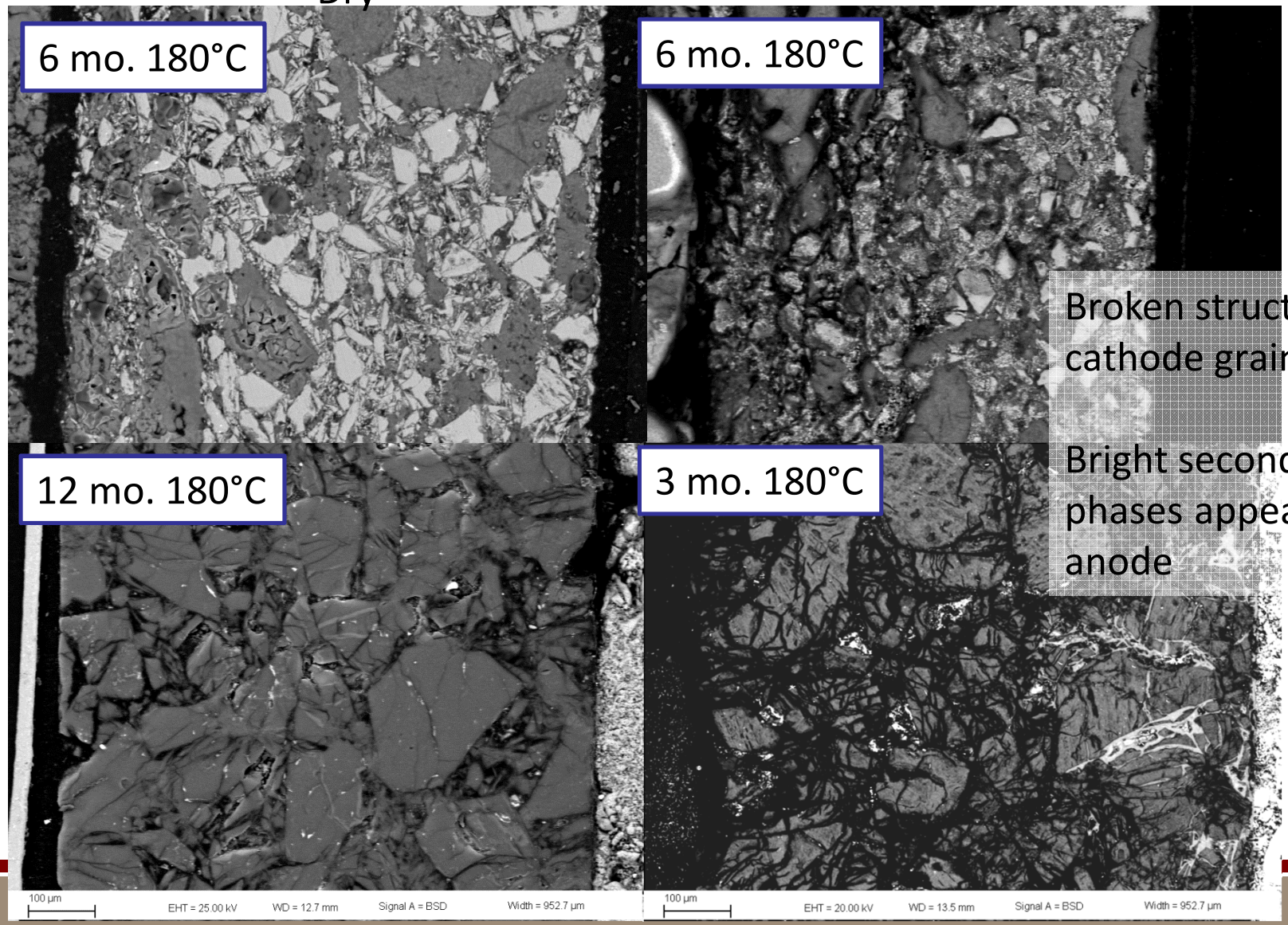
Anode does NOT protect cathode from water damage

*Cathode is 75% FeS_2, Li(Si) is 70% cathode mass

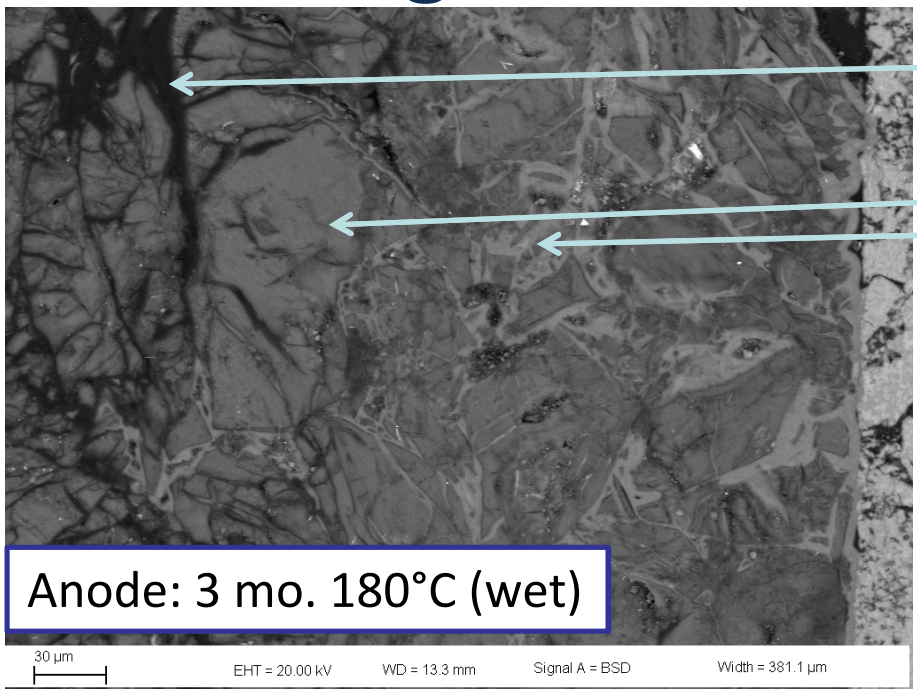
Microstructural evidence of reaction

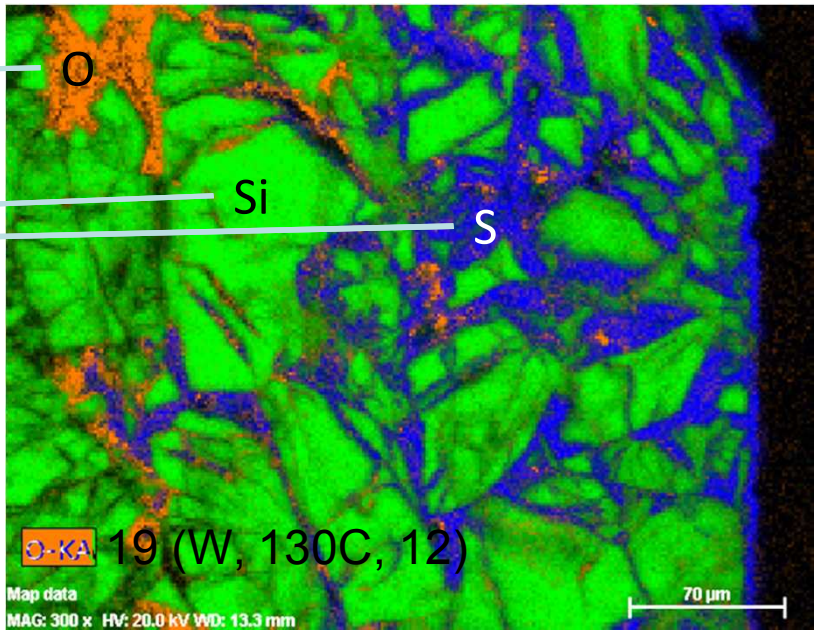
Sandia National Laboratories

Pitting and phase changes appear in both anode and cathode of wet samples



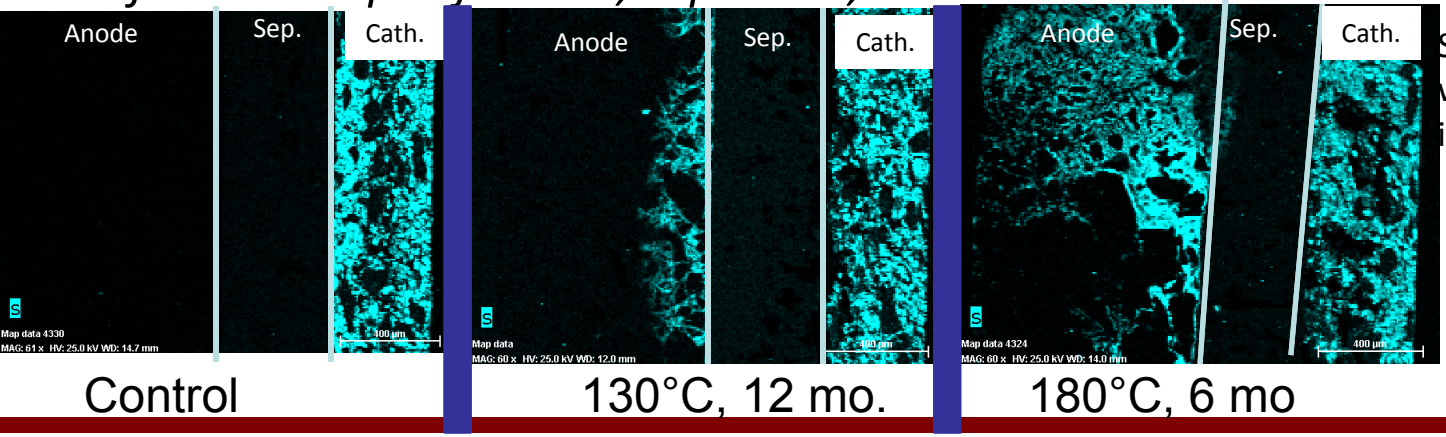
Sulfur migrates to anode interface





Extensive oxidation in anode away from separator interface- sulfur stay near interface

Sulfur EDS maps of anode, separator, and cathode

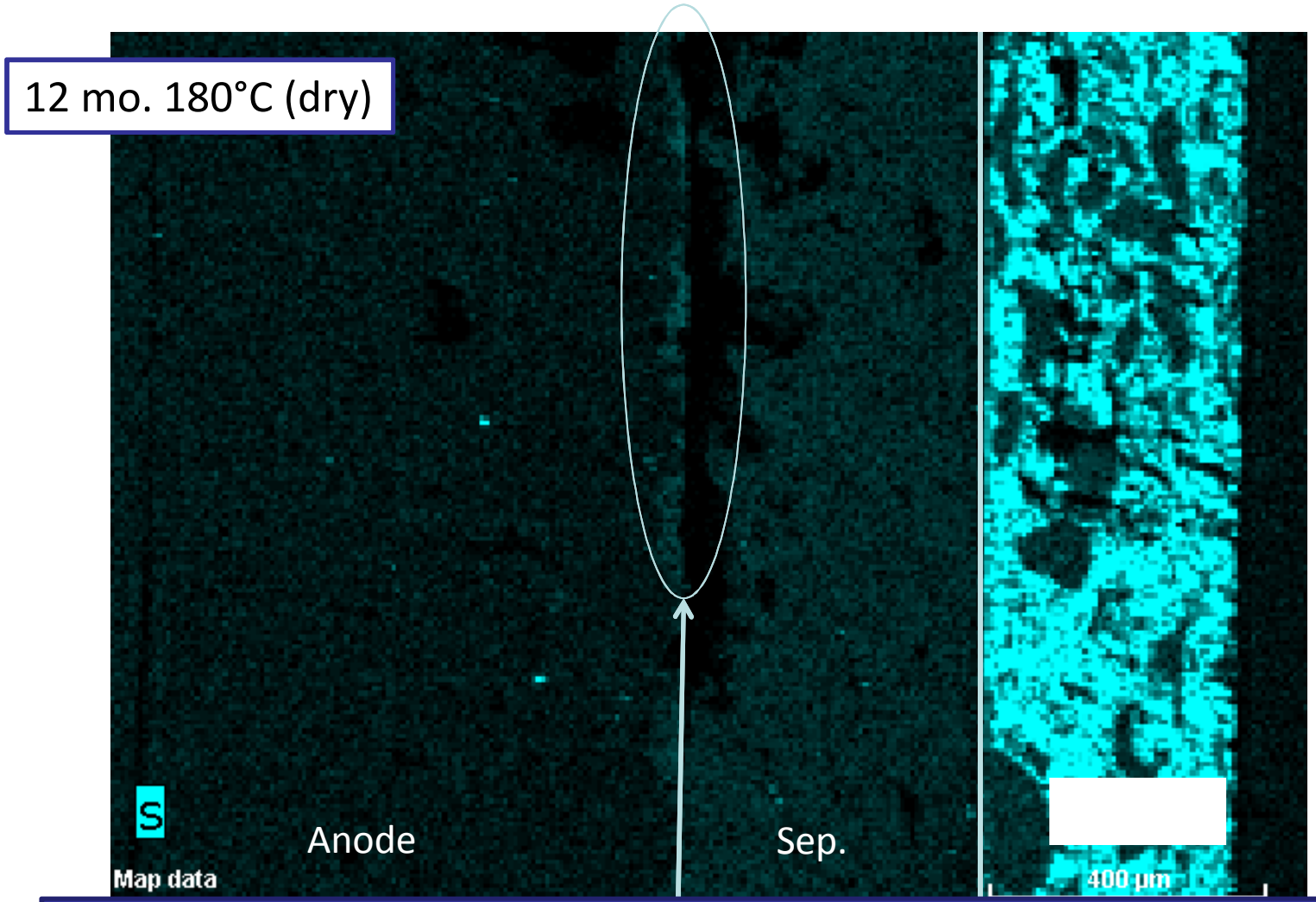


Sulfur migrates across separator with time and temperature, but is not present in separator

XRD (not shown) confirms FeS in FeS_2; cathode is sulfur source

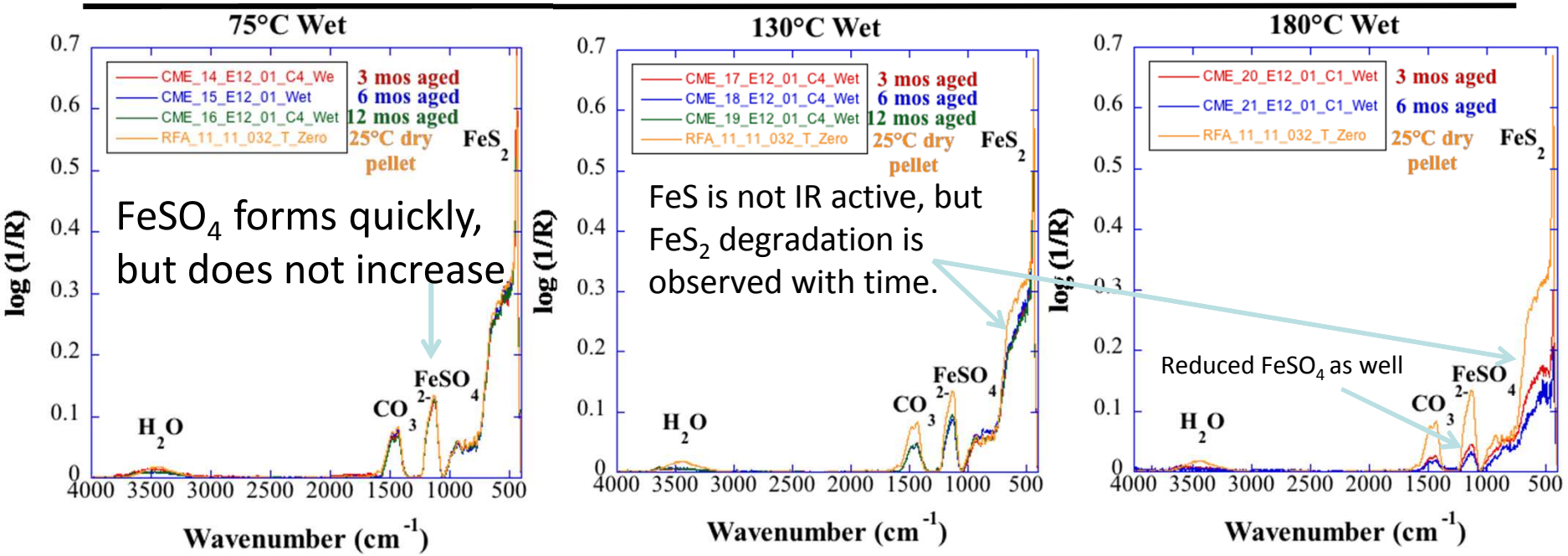
Behavior occurs in dry samples

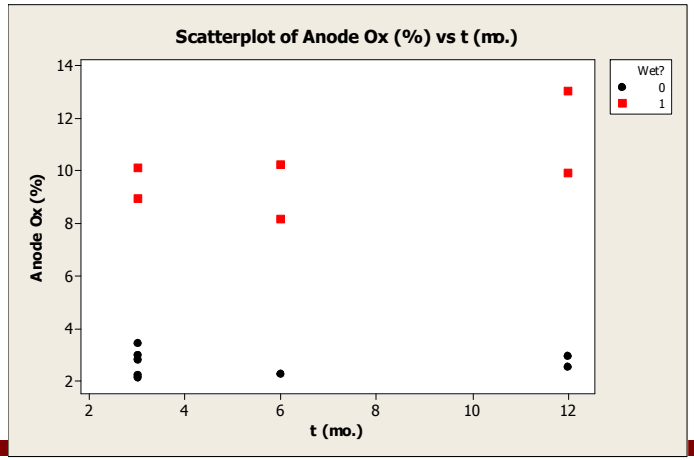
Reaction at 12m, 180°C, dry demonstrates sulfur migration in standard batteries
Suggests this mechanism is slowed by limited reactant in typical batteries



Need reaction, rate constants, and activation energy to determine significance

Chemical analysis shows reaction products (FTIR, FNAA)





Anodes oxidize much more extensively with additional water, but oxidation is time independent

Time dependent capacity loss is related to water causing a slower reaction that reduces FeS_2

Rate of Reaction

- Dry sample capacity was pooled to give baseline performance

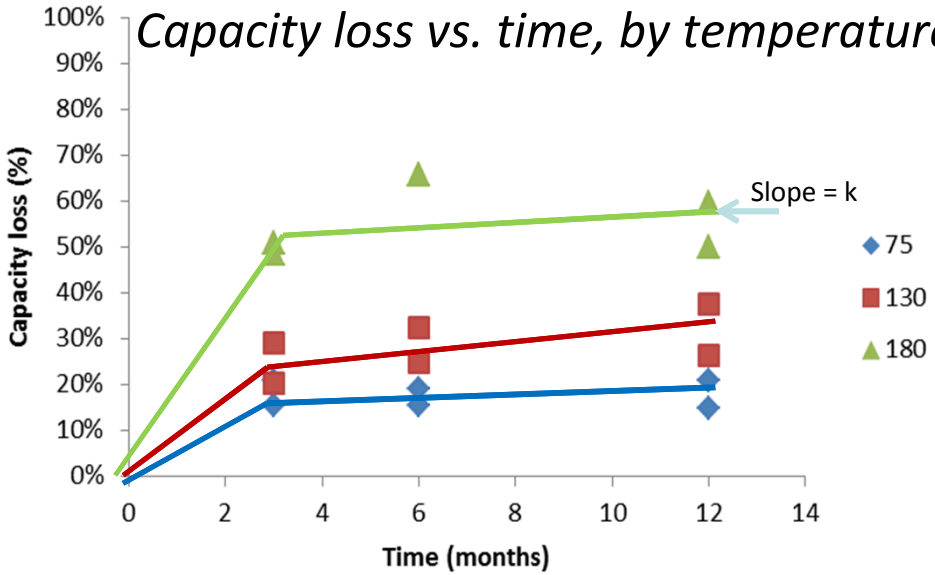
  Model of cap. loss C: $C = C_0 e^{-kt}$ Integrated reaction rate, 1st order reaction

- Insufficient data to calc. reaction constant *k*, but clear trend with temperature enables activation energy calculation (w/ assumptions)

$$\ln k = \ln k_0 - \frac{E_a}{RT}$$

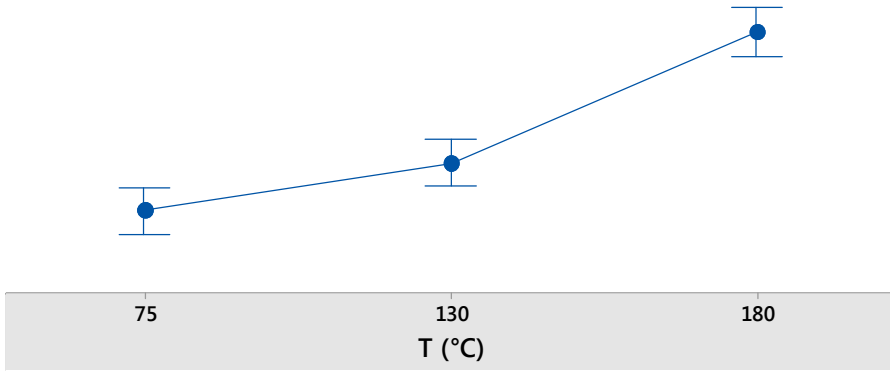
E_a = 14.1 kJ/mol

Capacity loss vs. time, by temperature



Possible indication of two-part reaction (fast to three months, slow beyond).

Cap. loss vs. temperature



Pooling time allows for E_a calculation (essentially for 1st part of the reaction)

Follow up: Need early data (k for 1st reaction), and more aging data (E_a for aging reaction)

Possible Reaction Pathway

Sandia National Laboratories

Overall reaction

$4Li + FeS_2 + H_2O = FeS + Li_2O + Li_2S + H_2(g)$ $\Delta G°(100°C)$ -693 kJ/mol FeS_2

Step 1: Lithium oxidation

$2Li + H_2O = Li_2O + H_2$ $\Delta G°(100°C)$ -163 kJ/mol Li

E_a (23-100°C) = 17 kJ/mol (Searcy)

Slowed by lithium passivation layer. Requires months at room temp.

Step 2: FeS_2 decomposition

$1.5O_2(g) + FeS_2 + H_2O = FeSO_4 + H_2S(g)$ $\Delta G°(100°C)$ -446kJ/mol FeS_2

$FeS_2 + O_2(g) = FeS + SO_2(g)$ $\Delta G°(100°C)$ -237 kJ/mol FeS_2

Reactions limited by H_2O and O_2

Step 3: Slow FeS_2 decomposition

$FeS_2 + H_2(g) = FeS + H_2S(g)$ $\Delta G°(100°C)$ +27 kJ/mol FeS_2

E_a (350°C) = 88 kJ/mol (Thomas)

This reaction is spontaneous when pH_2S is less than ~7 ppm (at 0.1 atm H_2 and 70°C), which it is because Li getters it:

$2Li + H_2S(g) = Li_2S + H_2(g)$ $\Delta G°(100°C)$ -394 kJ/mol Li_2S

$$\frac{a_{Li2S}\, p_{H2}}{a_{Li} p_{H2S}} = \exp\left(\frac{-\Delta G^{\circ}}{RT}\right)$$

$pH_2S = 6.7 \times 10^{-56}$ atm

H_2 catalyzes FeS_2 decomposition, creating continuous aging mechanism

Conclusion

- Hydrogen catalyzed FeS_2 decomposition may be a key aging mechanism for the electrochemistry in Li(Si)/FeS_2 batteries
  - Activated process (possibly 88 kJ/mol)
  - Occurs even with best-practices applied to drying pellets/insulation
- Heat pellet calorific output also deteriorates
  - Appears to be an activated process, but data is noisy
  - Moisture independent
  - Moisture may still influence ignition sensitivity- more work required

The authors would like to thank:
- Christine White for disassembly and inspection and calorimetry
- Jonathan Leonard for performing gas sampling
- Linda Johnson for single cell testing