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Phase Transition Behavior of a Processed Thermal Battery

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Motivation

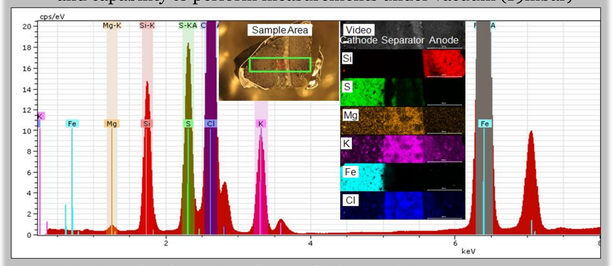
- Thermal battery transition behavior is of interest to determine how the anode's chemical structure changes as the thermal battery discharges
  - this poster will address peak shifts observed in XRD patterns and also allow for a transition model to be determined

Approach

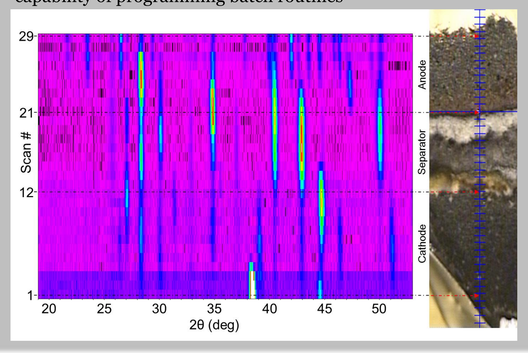
- Both micro X-ray Fluorescence (μ-XRF) and micro X-ray Diffraction (μ-XRD) were employed to determine the chemical species present as well as the respective phases associated to each chemical species
- Fluorescence analysis (μ-XRF) was performed on a Bruker M4 Tornado system and μ-XRD was performed on a Bruker D8 Discover system
- Each is capable of performing micro analysis
- Lattice parameter refinements were performed using JADE 9.4.1
- Lattice parameter refinements were analyzed to look for expansion or contraction in unit cell parameters

μ-XRF and μ-XRD Capabilities

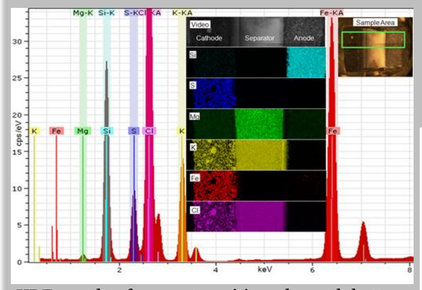
- XRF Results for a Discharged Thermal Battery
  - Spot size ~25μm, Rh source with polycap optics, SDD detector setup, and capability to perform measurements under vacuum (19mbar)



- XRD Results from Discharged Thermal Battery
  - Spot size ~300μm, equipped with a High-Star area detector, and the capability of programming batch routines

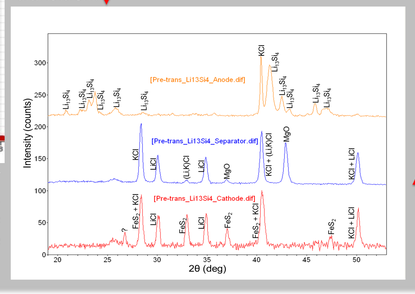


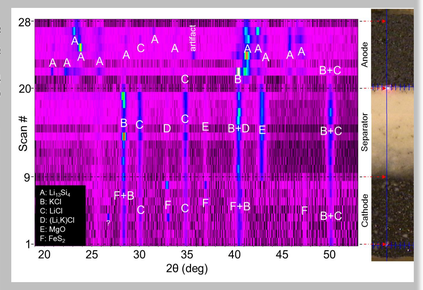
Thermal Battery Pre-Transition



XRF results for pre-transition thermal battery showing Fe, S, and salt type electrolyte material in the cathode, Mg and salt type electrolyte material in the separator, and primarily Si in the anode.

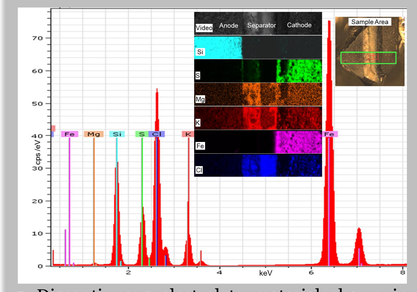
Standard XRD 2θ plots for each region of the thermal battery are shown. We focus on the anode region where the primary phase is $Li_{13}Si_4$ and represents a thermal battery prior to transition.





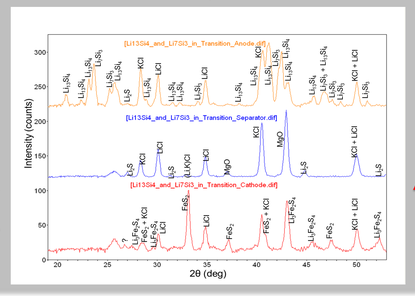
Standard XRD plots compiled are into a contour image to show the respective phases present as the thermal battery region is linearly spanned. Focusing on the anode region the primary phase observed is $Li_{13}Si_4$ (label A).

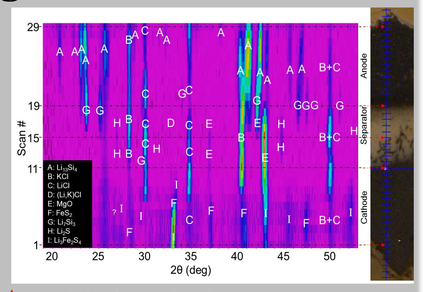
Thermal Battery Quenched During Transition



- Discontinuous electrolyte material shown in separator
- Sulfur migration observed (attributed to Li_2S observed via XRD)

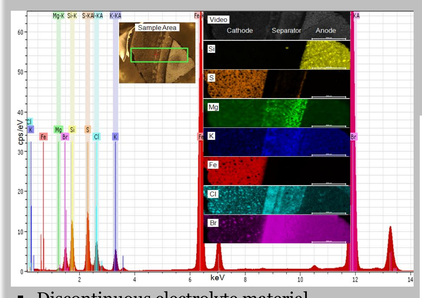
- 2nd phase of Li_7Si_3 observed in anode
- Li_7Si_3 formation starts near separator interface
- Formation of $Li_3Fe_2S_4$ shown in cathode





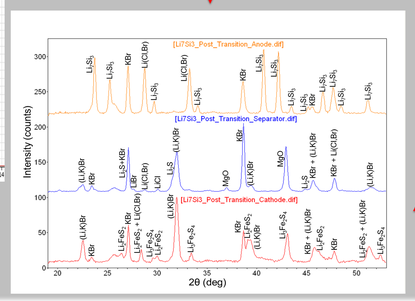
- Li_2S (H) observed in the separator
- Li_7Si_3 (G) starts at separator/anode interface and proceeds out to battery edge
- Reaction proceeds as $Li_{13}Si_4$ diminishes from anode (see below)

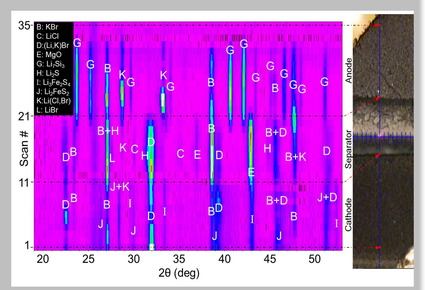
Thermal Battery Post-Transition



- Discontinuous electrolyte material
- Line of sulfur observed at the anode/separator interface
- Bromine signal from electrolyte material

- Loss of $Li_{13}Si_4$ as expected for post transition
- Minimal Li_2S observed
- $Li_3Fe_2S_4$ and Li_2FeS_2 observed in the cathode





- Primary phase of Li_7Si_3 observed in the anode
- No $Li_{13}Si_4$ contained in the anode
- Weak presence of Li_2S shown

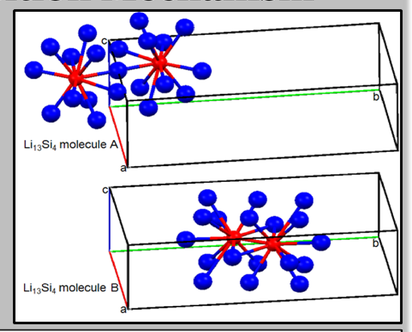
Lattice Parameter Refinements

$Li_{13}Si_4$ Cell Data	Cell Type	Cell dimensions (Å)	Cell Volume (Å^3)
Published $Li_{13}Si_4$	orthorhombic (Pbam)	7.99 , 15.21 , 4.43	538.37
Pre-transition $Li_{13}Si_4$	orthorhombic (Pbam)	7.99 , 15.18 , 4.46	541.13
$Li_{13}Si_4$ in transition	orthorhombic (Pbam)	7.95 , 15.16 , 4.48	539.21
Li_7Si_3 Cell Data	**Cell Type**	**Cell dimensions (Å)**	**Cell Volume (Å^3)**
Published Li_7Si_3	rhombohedral (R-3m)	4.44 , 18.13	308.90
Li_7Si_3 in transition	rhombohedral (R-3m)	4.44 , 18.08	308.27
Post transition Li_7Si_3	rhombohedral (R-3m)	4.43 , 18.08	307.16

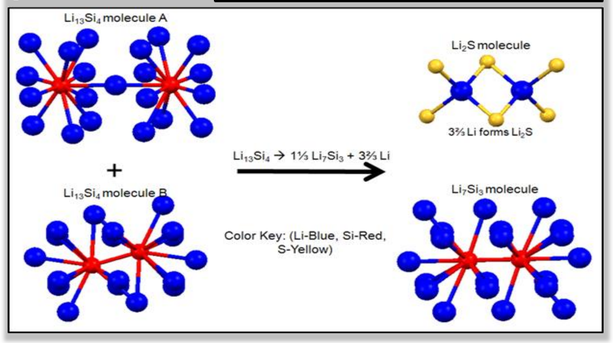
- $Li_{13}Si_4$ contracts in the a and b-axes with an expansion in the c-axis during transition
- Post transition a, b contraction is likely due to Li loss

Transition Mechanism

Right:
Molecules contained in $Li_{13}Si_4$ unit cell



Below:
Schematic model of transition taking place



Summary

- Intermediate Li_2S formed due to an excess of 3⅓ Li from the breakdown of $Li_{13}Si_4$; formation indicative of discharge
- Confirmed presence of Li_2S phase via XRD
- Sulfur migration observed in the separator via XRF
- During transition, $Li_{13}Si_4$ contracts in the a and b-axes due to loss of Li atoms
- Slight expansion in the $Li_{13}Si_4$ c-axis to accommodate for reorganization of cell

Acknowledgements

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U.S. DEPARTMENT OF ENERGY

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