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Phase Transition Behavior of a Processed Thermal Battery

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Abstract

In order to fully understand the transition mechanism of a processed thermal battery, Micro X-ray Diffraction (μ -XRD) and Micro X-ray Fluorescence (μ -XRF) were employed to characterize various quench states. The transition of interest in this report is the formation of Li_7Si_3 from $\text{Li}_{13}\text{Si}_4$ (initial anode material). The unit cell conditions during $\text{Li}_{13}\text{Si}_4$ transition to Li_7Si_3 show a contraction of 0.04 and 0.02 Å (a and b-axis respectively), an expansion in the c-axis of 0.02 Å, and an overall reduction in the cell volume from 541.13 Å³ to 539.21 Å³ for the $\text{Li}_{13}\text{Si}_4$ Orthorhombic (Pbam) component. The contraction in the a-b plane results from the loss of lithium atoms; the expansion in the c-axis direction is due to reorganization of the lithium and silicon within the unit cell. Transition processing also requires that an excess of $3\frac{2}{3}$ moles lithium (within anode region) react with sulfur (within cathode region) to form Li_2S . Micro-XRF confirms a definite migration of sulfur through the separator region during the transition. These results both explain peak shifts (in anode regions) and the formation of Li_2S during transition states.

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Nomenclature

Deg	degree
°	degree
μ	micro
μm	micrometer
min	minute
s	second
θ	theta
K_{α}	K alpha radiation
K_{β}	K beta radiation
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
μ-XRD	Micro X-ray Diffraction
μ-XRF	Micro X-ray Fluorescence
Pbam	orthorhombic space group
R-3m	rhombohedral space group

Introduction

Molten salt batteries (thermal batteries) are devices that utilize electrolyte materials that are solid at ambient temperatures and liquefy at elevated temperatures. This is very useful due to the fact that at ambient temperatures the device is inactive but upon heating or ignition the device becomes operable, allowing electrochemical reactions to proceed. This characteristic gives the device the ability to have a long shelf life (assuming hermetic conditions) with the ability to remain inert until energy is required.[1] Thermal batteries have primary applications in missile delivery systems that require long shelf lives and energy at an instant to power trajectory guidance systems. A thermal battery is composed of a cathode, a separator, and an anode. Typical materials that make up the cathode region are composed of iron sulfide (FeS_2) and halide salts (KCl , LiCl , KBr , and various solid solutions).[2,3] The separator region typically contains salts (salt material mentioned above along with LiBr) and magnesium oxide (MgO).[2] The anode region, which is of particular interest in this study, starts as lithium silicide ($\text{Li}_{13}\text{Si}_4$) with some salt type materials (KCl , LiCl , and KBr).[4] The FeS_2 from the cathode and Li from the anode react to form Li_2S as the sulfur migrates across the cell cross-section. As Li migrates from the anode toward the cathode it results in various reaction products.

The interest of this study is to determine the process by which $\text{Li}_{13}\text{Si}_4$ reacts to form Li_7Si_3 . This is particularly important due to unknown intermediate processes that occur during discharge. Typically when these thermal batteries are analyzed linearly through the cross-sectional area of the sample, there is a spatial dependence of phases detected via Micro X-ray Diffraction ($\mu\text{-XRD}$). As the reaction is initiated, component identity varies spatially across the anode. The transition usually starts near the separator/anode interface and proceeds out toward the edge of the anode region until the reaction is complete. So the transition from one phase to another does not occur in an instant, but it is dictated by spatial location. There is interest in determining transition states or phases that occur during the process. In most cases there are diffraction peak shifts that occur with gain or loss of lithium atoms; these correspond to either cell expansion or contraction.[5] These specifics will be used to determine how the unit cell changes as a function of thermal battery quench condition. The goal of this study is to resolve what these shifts correspond to and attempt to formulate the mechanism by which this transformation occurs within the anode.

The cross-sectioned samples analyzed were taken from quenched batteries that were stopped at various stages of the battery's chemical reaction. Micro X-ray Fluorescence ($\mu\text{-XRF}$) and $\mu\text{-XRD}$ have been used to determine the phase identification and elemental locations for each quench condition of the thermal battery. The unit cell data resolved via $\mu\text{-XRD}$ is critical in determining how the unit cell changes as a function of quench condition. This information will aid in determining the process that elapses as the thermal battery reacts.

Experimental Procedure

Specimens were prepared from discharged thermal batteries quenched at different operation intervals. The preparation was conducted in an industrial dry room where battery components were sectioned using a low-speed, thin kerf diamond saw. The component pieces were then mounted in an epoxy resin and oblique angle mounts were used to increase the interlamellar distance of each sample to allow for a larger sampling area.[6] To ensure specimen protection from moisture in the atmosphere, a thin layer of mineral oil was added to each specimen along with a 25 μ m polypropylene X-ray transparent film. To further protect the specimen during transport between buildings, the specimen was placed inside a glass jar with desiccant.

Thermal battery specimens were analyzed using μ -XRD on a Bruker D8 Discover system. The system is equipped with a sealed tube Cu (K_α) X-ray source employing a 300 or 500 μ m collimator preceded by an incident beam mirror for removal of K_β radiation.[7] The diffracted beam was detected using a Hi-Star Area detector. In order to ensure that the thermal battery was not exposed to air, the thin polypropylene film was left on the specimen during data collection. A series of θ -2 θ scans over the range of 19-54° (2 θ) was run to spatially determine the composition of materials present throughout the cathode, separator, and anode regions of the thermal battery. To further verify the μ -XRD results, the sample was also analyzed using μ -XRF on a Bruker M4 Tornado system; this process determined the elemental composition of the materials present within each sample.[8] For μ -XRD the Bruker D8 system is capable of measuring down to a 300 μ m spot size, so the spatial distribution of sampling steps was held to 500 μ m increments with a scan time of 60s per frame. For μ -XRF the Bruker M4 Tornado parameters were specified to collect a region with individual spot sizes of 25 μ m for approximately 10min of total scan time. The μ -XRF results were generated as spatial maps of each element by employing the scaled intensity of a given emission energy (e.g. Si map used Si K_α energies).

Results and Discussion

Before moving forward, the result of interest within this paper is to be able to determine the mechanism by which $\text{Li}_{13}\text{Si}_4$ reacts to form Li_7Si_3 . The steps that typically occur during discharge are the following, $\text{Li}_{13}\text{Si}_4$ to Li_7Si_3 to $\text{Li}_{12}\text{Si}_7$. [9] Some patterns that have been encountered suggest that cell expansion or contraction must occur within the $\text{Li}_{13}\text{Si}_4$ unit cell prior to transition to Li_7Si_3 . This study seeks to understand the possible intermediate conditions that occur between the two phases during battery discharge. The transition between Li_7Si_3 to $\text{Li}_{12}\text{Si}_7$ will not be addressed in this report.

Micro-XRD data were analyzed using JADE software.[10] A series of plots were made in order to spatially determine the phases present as a function of step number; these plots will be referred to as contour plots. A series of merged patterns was also generated over the anode, separator, and cathode sections in order to improve sampling statistics for each distinct region of the cross-section; these plots will be referred to as merged patterns. Together, the plots enable determination of the phases present as well as tell some information about the unit cell dimensions of the material within the anode region. Combining the results from μ -XRD and μ -XRF, a mechanism for thermal battery transition shall be deduced.

Pre-transition $\text{Li}_{13}\text{Si}_4$

A quenched thermal battery taken early in the reaction was analyzed and the data to follow shows the conditions prior to the transition to Li_7Si_3 . Figure 1 shows the contour plot for pre-transition with $\text{Li}_{13}\text{Si}_4$ present in the anode. Focusing primarily on the anode region, it is shown that this specimen represents a pre-transition thermal battery due to the fact that the major Li-Silicide phase present is $\text{Li}_{13}\text{Si}_4$. A merged series of patterns from the cathode, separator, and anode region are shown in Figure 2, showing only $\text{Li}_{13}\text{Si}_4$ and salt-type materials (LiCl and KCl) for the anode material of this specimen. The phases labeled in Figure 1 were determined with aid of the standard 2θ plots in Figure 2. These data will be later utilized to determine the unit cell conditions of the particular $\text{Li}_{13}\text{Si}_4$ structure prior to transition. Micro-XRF analysis for this thermal battery coincides with the results seen from μ -XRD showing the respective phases within each region of the battery; see Figure 3. The anode region of the thermal battery shows a strong signal for Si which directly corresponds to the presence of a Li-Silicide material. The presence of the Li is assumed in these results due to the fact that the μ -XRF system is only sensitive to detect elements above atomic element Na; elements below Na go un-detected. The remainder of the thermal battery shows elemental signals that correspond to what is expected in each region of the battery.

Figure 1. Contour plot for pre-transition $\text{Li}_{13}\text{Si}_4$ thermal battery.

The vertical scale shows scan number and the horizontal is scaled as a function of 2θ angle. The image at the right of the figure was taken at the time of measurement to show the respective spatial location of each scan. The intensity for each peak is shown as a function of color where magenta is background counts, blue is low counts, and green is medium counts, red to white is max counts.

Figure 2. Standard 2θ plot of pre-transition thermal battery.

A series of merged scans over the cathode (red), separator (blue), and anode (orange) regions was taken as a function of peak intensity and 2θ angle.

Figure 3. μ -XRF analysis results for the pre-transition $\text{Li}_{13}\text{Si}_4$ thermal battery.

An image was taken to show the sample area, outlined in green (image at the top right). The spectrum shows intensity on the vertical axis and energy on the horizontal axis. The series of images in the middle of the figure are elemental maps corresponding to each element detected, along with a video image taken during collection.

Li₁₃Si₄ and Li₇Si₃ in transition

Figure 4 shows the contour plot for a thermal battery quenched during transition. Discoloration seen in the separator region is segregated to areas closest to the anode. This discoloration corresponds to Li₂S which is typically seen when the thermal battery is undergoing reaction to form Li₇Si₃. Figure 5 summarizes the standard 2θ μ-XRD data obtained for the cathode, separator, and anode regions which were used to characterize the phases present within each region. The results confirm the presence of Li₂S which is expected for a battery under discharge.[3,6,11,12] The formation of Li₂S appears to occur during the transition from Li₁₃Si₄ to Li₇Si₃. The anode shows a mixture of Li₁₃Si₄ and Li₇Si₃ which is expected for a thermal battery going through transition. These data were used to determine the unit cell conditions of Li₁₃Si₄ and Li₇Si₃ during transition. Figure 6 shows the μ-XRF mapping that indicates sulfur migration within the separator region which coincides with the Li₂S identification in the contour map of Figure 4. The additional μ-XRF results obtained complement the results obtained from standard μ-XRD data showing the respective region where each element should be found within the thermal battery.

Figure 4. Contour plot for thermal battery with Li₁₃Si₄ and Li₇Si₃ in transition.

The vertical scale shows scan number and the horizontal is scaled as a function of 2θ angle. The image at the right of the figure was taken at the time of measurement to show the respective point of each scan. The intensity for each peak is shown as a function of color where magenta is background counts, blue is low counts, green is medium counts, yellow is high counts, and red to white is max counts.

Figure 5. Standard 2θ plot of $\text{Li}_{13}\text{Si}_4$ and Li_7Si_3 in transition.

A series of merged scans over the cathode (red), separator (blue), and anode (orange) regions was taken as a function of peak intensity and 2θ angle.

Figure 6. μ -XRF analysis results for $\text{Li}_{13}\text{Si}_4$ and Li_7Si_3 in transition.

An image was taken to show the sample area, outlined in green (image at the top right). The spectrum shows intensity on the vertical axis and energy on the horizontal axis. The series of images in the middle of the figure are elemental maps corresponding to each element detected, along with a video image taken during data collection.

Post transition Li_7Si_3

Figure 7 shows the contour plot for a thermal battery quenched after $\text{Li}_{13}\text{Si}_4$ was fully converted to Li_7Si_3 . The phase present in the anode region is primarily Li_7Si_3 . This shows that the thermal battery transitioned from $\text{Li}_{13}\text{Si}_4$ to Li_7Si_3 . Figure 8 shows the standard 2 θ plots for the cathode, separator, and anode regions which were used to determine the specified phases within each region of the thermal battery. The labeling in Figure 7 was determined via the standard 2 θ plots in Figure 8. These data were used to determine the unit cell condition of Li_7Si_3 after transition. The μ -XRF results obtained for the thermal battery after transition are shown in Figure 9; they are consistent with the results obtained from standard 2 θ data. The μ -XRF results also show a reduced concentration of sulfur within the separator region and a concentration that is restricted primarily to the anode-separator interface. These concentrations can be explained by a small presence of Li_2S shown in the standard 2 θ plot for the separator in Figure 8. It is also very important to note that there are additional maps shown in Figure 9 due to the fact that there are salt type materials composed of Br in addition to Cl materials. The salt variation should not affect the results regarding the Li-Silicide structural parameters due to the fact that the result of interest is to characterize the anode region of the discharged thermal battery.

Figure 7. Contour plot for post transition thermal battery.

The vertical scale shows scan number and the horizontal is scaled as a function of 2 θ angle. The image at the right of the figure was taken at the time of measurement to show the respective spatial location of each scan. The intensity for each peak is shown as a function of color where magenta is background counts, blue is low counts, green is medium counts, and red to white is max counts.

Figure 8. Standard 2θ plot post transition.

A series of merged scans over the cathode (red), separator (blue), and anode (orange) regions was taken as a function of peak intensity and 2θ angle.

Figure 9. μ-XRF analysis results for post transition thermal battery.

An image was taken to show the sample area, outlined in green (image at top left). The spectral data shows intensity on the vertical axis and energy on the horizontal axis. The series of images in the middle of the figure are elemental maps corresponding to each element detected, along with a video image taken during data collection.

Formulation of transition mechanism

Using the data acquired from standard 2 θ measurements, lattice parameter refinements were performed using JADE software to determine how the unit cell parameters of $\text{Li}_{13}\text{Si}_4$ and Li_7Si_3 change as a function of the thermal battery state. Table 1 shows the lattice parameter data for the states discussed previously for both $\text{Li}_{13}\text{Si}_4$ and Li_7Si_3 ; each has different literature and refined lattice parameter values for each step during transition. The pre-transition $\text{Li}_{13}\text{Si}_4$ shows unit cell conditions that are fairly similar to those predicted from literature sources. When compared to the pre-transition conditions the $\text{Li}_{13}\text{Si}_4$ molecule in transition shows a contraction of the a and b-axes; this is due to the loss of bridging Li atoms of the $\text{Li}_{13}\text{Si}_4$ molecule A (see Figure 10). There is also a slight expansion in the c-axis, most likely due to the reorganization of the unit cell. In order for the transition to occur, an excess of $3\frac{2}{3}$ Li must be given off to form Li_2S , as shown in Figure 11.

The refined cell data for the post transition Li_7Si_3 shows a unit cell that has slight contraction in the a-axis compared to the literature values and those observed for and Li_7Si_3 in transition. This shows that during the Li_7Si_3 phase transition the unit cell has a slightly expanded a-axis and larger cell volume upon initial formation from $\text{Li}_{13}\text{Si}_4$.

The proposed mechanism in Figure 11 combines the information above into the likely sequence of events to form the transition from $\text{Li}_{13}\text{Si}_4$ to Li_7Si_3 . First, at least two Li atoms from $\text{Li}_{13}\text{Si}_4$ molecule A must be adjusted so as to coordinate to $\text{Li}_{13}\text{Si}_4$ molecule B to ultimately form the new Li_7Si_3 molecule. Through this process an excess of $3\frac{2}{3}$ Li is produced from the transition of $\text{Li}_{13}\text{Si}_4$ to Li_7Si_3 . This excess Li is then used to form Li_2S which confirmed through μ -XRD.

Table 1. Lattice parameter data.

Data from literature search compared to lattice parameter refinements of the respective thermal battery specimen.

$\text{Li}_{13}\text{Si}_4$ Cell Data	Cell Type	Cell dimensions (Å)	Cell Volume (Å³)
Published $\text{Li}_{13}\text{Si}_4$	orthorhombic (Pbam)	7.99 , 15.21 , 4.43	538.37
Pre-transition $\text{Li}_{13}\text{Si}_4$	orthorhombic (Pbam)	7.99 , 15.18 , 4.46	541.13
$\text{Li}_{13}\text{Si}_4$ in transition	orthorhombic (Pbam)	7.95 , 15.16 , 4.48	539.21
Li_7Si_3 Cell Data	Cell Type	Cell dimensions (Å)	Cell Volume (Å³)
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

Figure 10. Molecules of interest in Li₁₃Si₄ matrix. Two unique molecules are contained within each Li₁₃Si₄ compound where Si atoms are shown as red spheres and Li atoms are shown as blue spheres. a-axis (red), b-axis (green), c-axis (blue).

Figure 11. Proposed schematic model of Li₁₃Si₄ to Li₇Si₃ phase transition.

Conclusion

A mechanism was determined for the transition of $\text{Li}_{13}\text{Si}_4$ to Li_7Si_3 . Micro-XRD and μ -XRF results indicate that Li_2S forms as a reaction by-product due to excess $3\frac{2}{3}$ Li remaining after transition. Micro-XRD shows a definite phase of Li_2S and μ -XRF shows isolated regions of sulfur within the separator region of the thermal battery. This elemental presence of sulfur can be directly associated with Li_2S presence. Lattice parameter refinement data confirm slight contraction in the a-axis and b-axis along with slight expansion in the c-axis of $\text{Li}_{13}\text{Si}_4$. Contraction and expansion of the cell volume are necessary to accommodate the loss and gain of lithium atoms associated with thermal battery discharge.

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