Probing the Structure and Evolution of Anode Materials in Thermal Batteries

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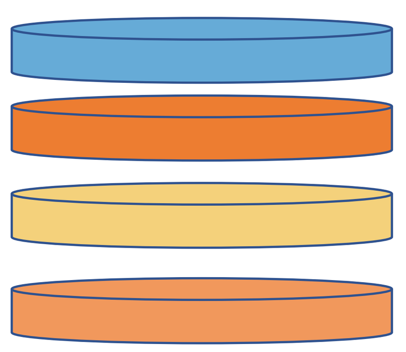
Thermal Batteries



Pyrotechnic source : $Fe/KClO_4$

Cathode: FeS_2

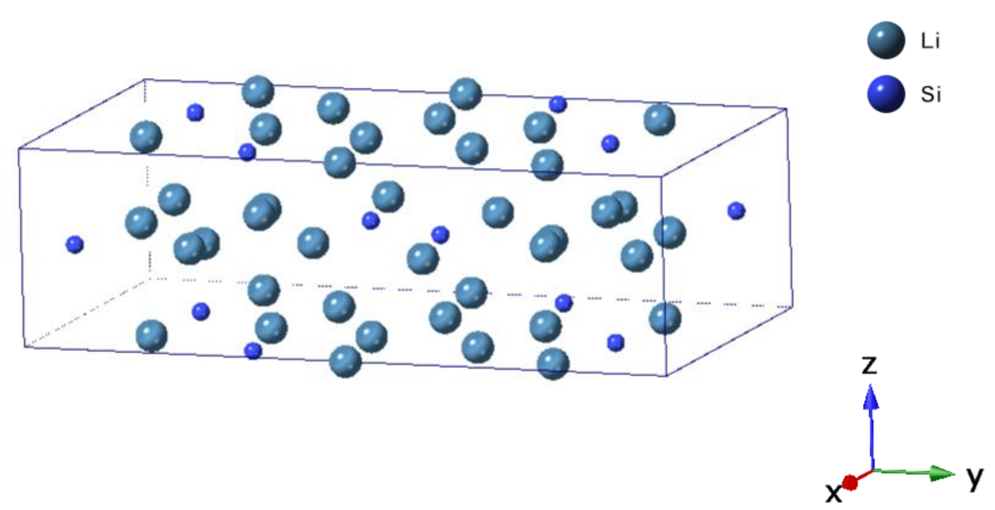
Electrolyte: LiCl-KCl eutectic (melting point = 352°C)

Anode: $Li_{13}Si_4$

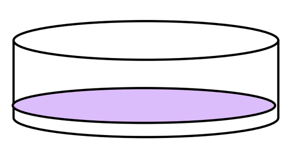
- Thermal batteries are used in aircraft emergency power supplies, space exploration, borehole drilling and military applications.
- This is because they are robust, reliable and have a long shelf life.
- Thermal batteries are primary (non-rechargeable) batteries.
- To activate the battery, a pyrotechnic heat source melts the solid electrolyte to a molten salt at high temperature (typically around 500°C).

Anode Material

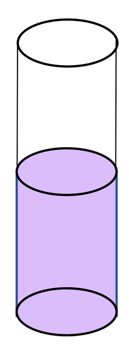
- $Li_{13}Si_4$ (the unit cell shown on the figure) is the preferred anode material for thermal batteries.
- $Li_{13}Si_4$ and other lithium-silicon phases are of interest because the high temperature structures and phase transitions have not been studied systemically yet.



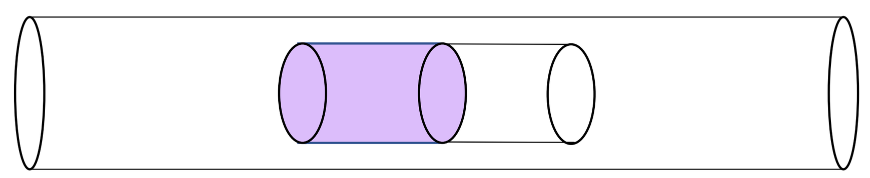
Synthesis of Phases



1. Stoichiometric ratio of lithium metal and silicon powder were mixed for 30 minutes in an argon-filled glovebox.



2. The mixture was placed into a quartz tube which was evacuated (10^{-5}mbar) and sealed by a torch outside of the glovebox.

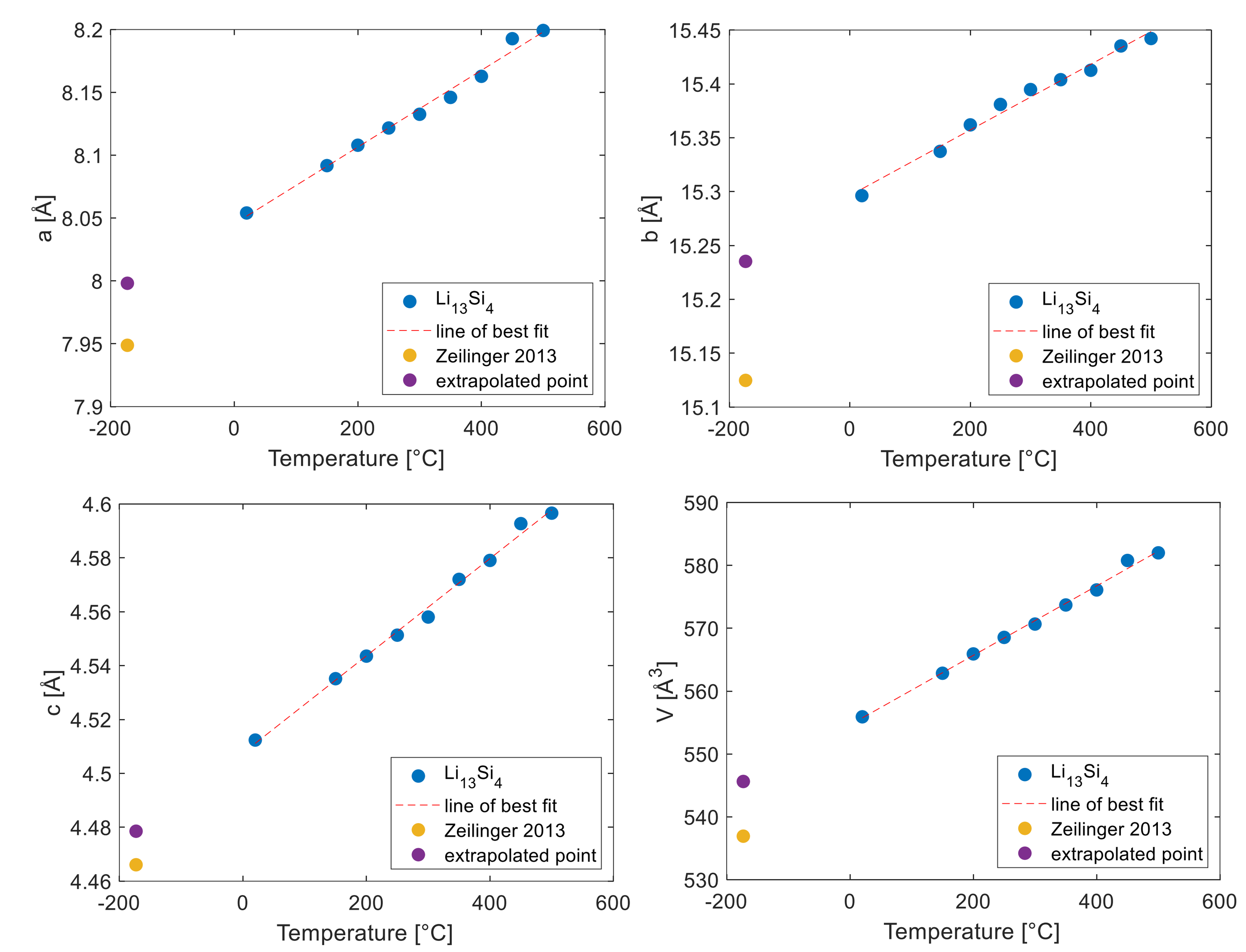


3. The lithium metal in the mixture melted at 180.5°C for 2 hours in a tube furnace.
The mixture was heated to 500°C, and remained at 500°C for 12 hours [1]. The reaction was quenched after the temperature cooled to less than 180.5°C. The lithium-silicon product was collected after breaking the quartz.

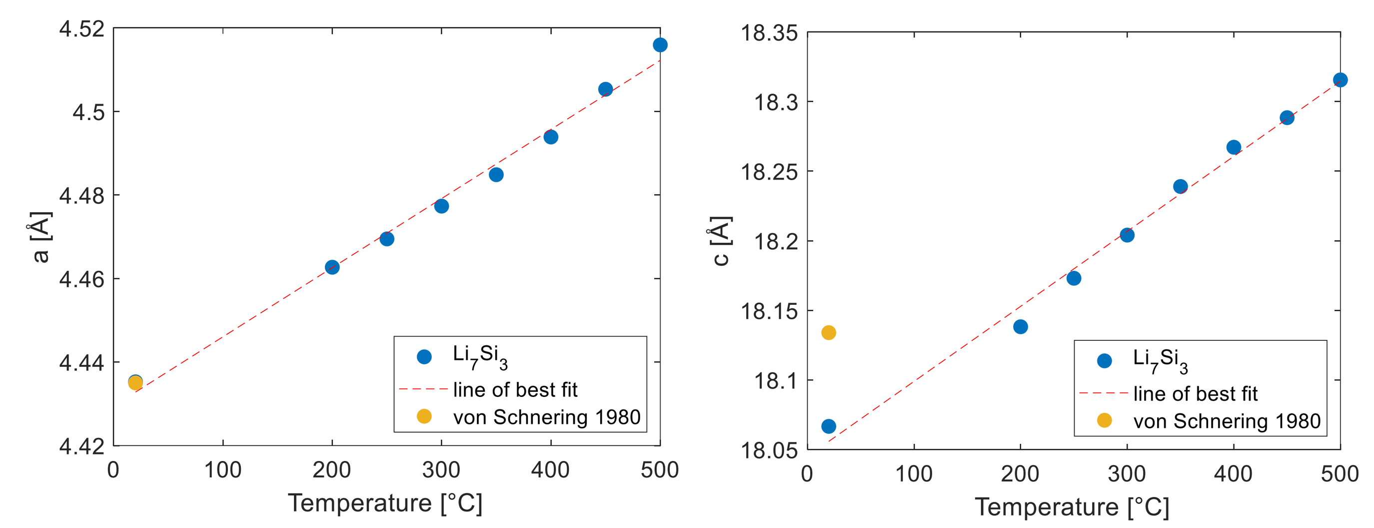
In Situ Neutron Diffraction

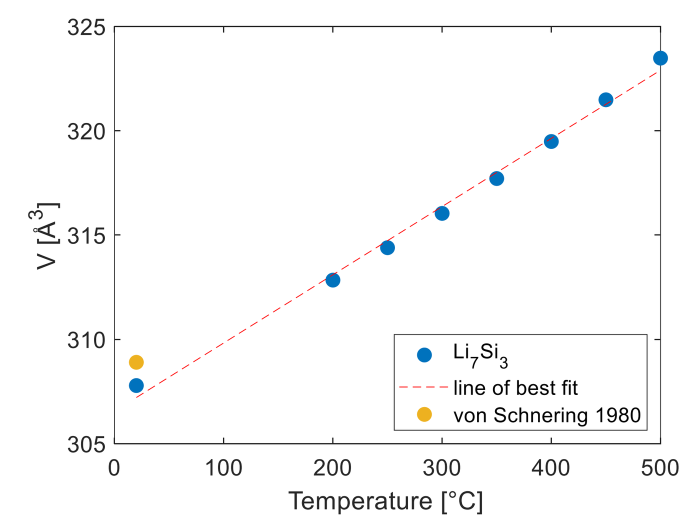
- Neutron diffraction was performed at the ISIS facility, Rutherford Appleton Laboratory, UK.
- The neutron beam goes into the sample and scatters off of the atoms.
- The scattered neutrons leave the sample towards different detectors.
- The angles at which the neutrons scatter gives a diffraction pattern that shows the sample's structure and location of the atoms.
- Neutrons interact with the nuclei whereas X-rays interact with the electron clouds of atoms. Neutrons detect light atoms with a low number of electrons better than X-rays.

$Li_{13}Si_4$



Li_7Si_3

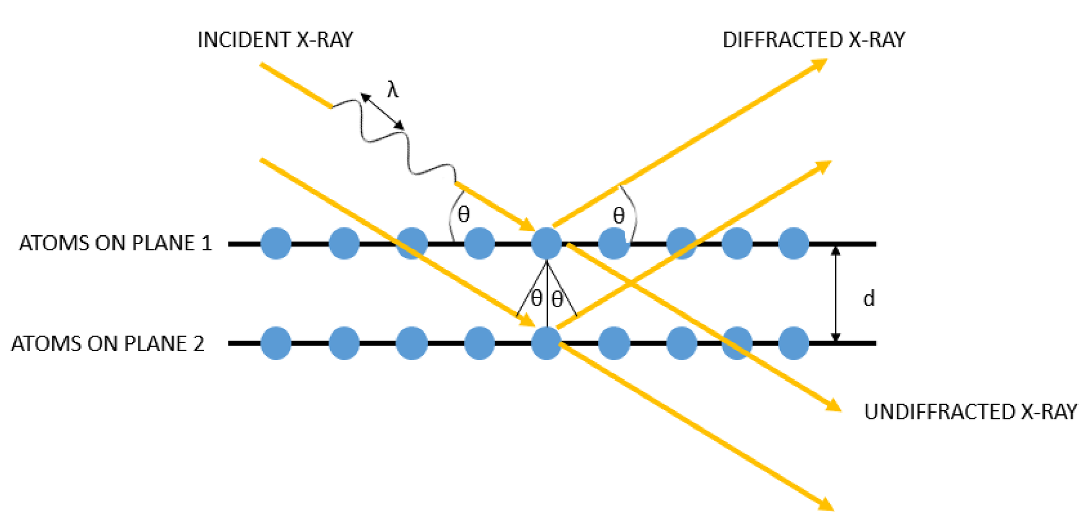




The figures show the a, b, c axes and unit cell volume of $Li_{13}Si_4$ and Li_7Si_3 as a function of the temperature.

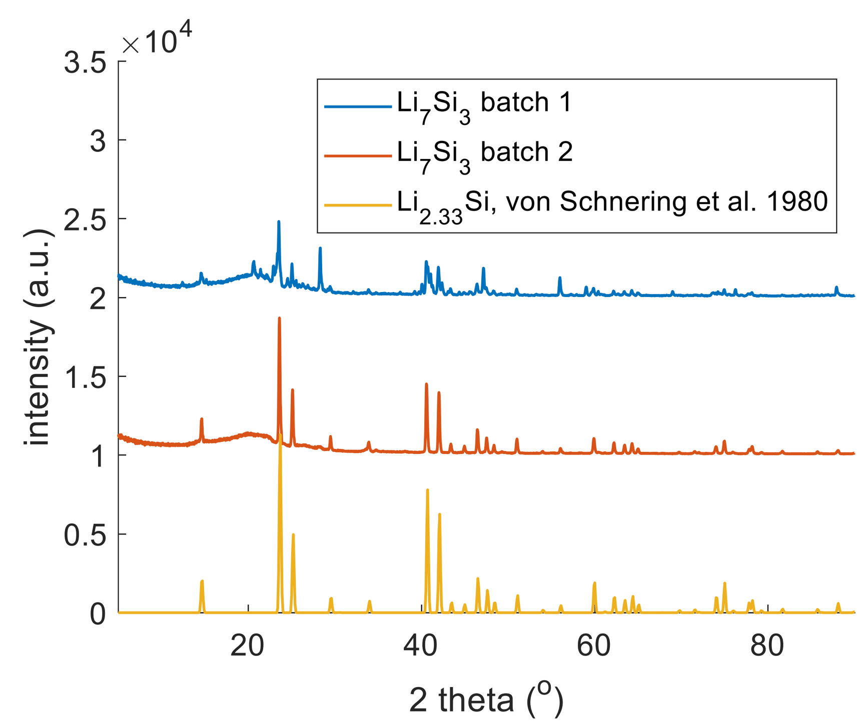
- The cell parameters for $Li_{13}Si_4$ in the literature by Zeilinger et al. are smaller than that observed in this work [4].
- On the other hand, the cell parameters for Li_7Si_3 by von Schnering et al. are larger than that observed in this work, although the cell parameter a at room temperature matches very well with that measured by von Schnering et al [3].
- As can be seen from the figures, the trend of the cell parameters is linear.
- The neutron data indicates that there are no phase transitions between room temperature and 500°C.
- Both phases did not become amorphous at 500°C and the unit cells for both phases expand as the temperature increases.

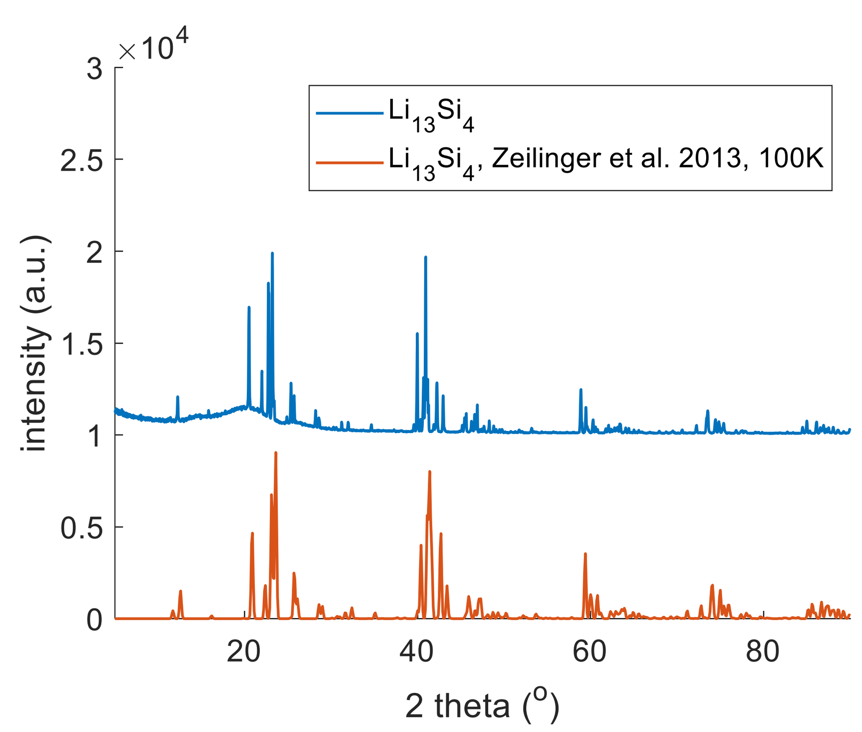
X-ray Diffraction



- X-rays have a wavelength, λ, similar to inter-atomic distances that exist in crystals (1 to 3Å).
- The atoms in the crystal lattice are like points in a set of reflection planes.
- The reflection planes are parallel to each other. The crystals are rotated in the diffractometer which changes the angle between the X-rays and reflection planes.
- The angle is the called the angle of incidence, Θ. The distance , d, between adjacent reflection planes changes also. The order of diffraction is n [2].
- This gives the Bragg's law: 2dsinΘ = nλ [2].

From the figures, the synthesis gave a pure phase of Li_7Si_3 as it matches the reference pattern by von Schnering et al [3]. $Li_{13}Si_4$ (purchased from Albemarle) was also phase pure as it matches the reference pattern by Zeilinger et al [4].





References

[1] Key, B., Bhattacharyya, R., Morcrette, M., Seznéc, V., Tarascon, J. and Grey, C., 2009. Real-Time NMR Investigations of Structural Changes in Silicon Electrodes for Lithium-Ion Batteries. *Journal of the American Chemical Society*, 131(26), pp.9239-9249.

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Acknowledgement

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