Physical Limitations for Electron Microscopy of Lithium and Sulfur Battery Materials

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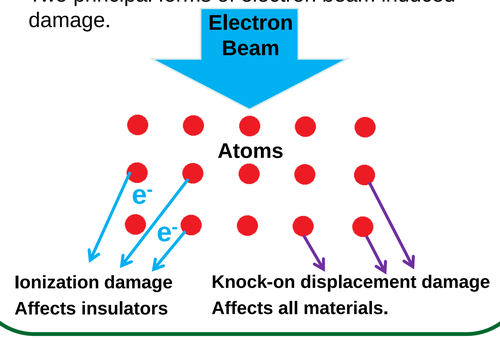
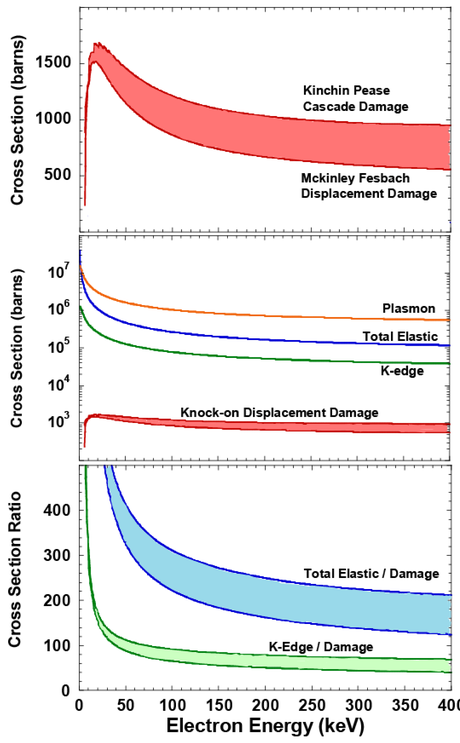
Why are Lithium and Sulfur difficult to image in TEM? How can these difficulties be overcome?

The Electron Beam Will Damage Lithium

- **There is a cross section for radiation damage.**
- **There is also a cross section for imaging signal.**
- **These cross sections depend on electron beam energy**
- **Our goal is to maximize the number of imaging events per damage event.**

Two principal forms of electron beam induced damage.





Damage Cross Section (σ_D) for Li peaks at low beam energy. [3]
Lower bound (Mckinley-Fesbach) assumes no inter-atom interaction. Upper bound (Kinchin-Pease) assumes cascades induced.

Signal cross sections are larger at lower beam energy.[4]
Cross sections for K-edge (σ_K), Plasmon (σ_P) and elastic scattering (σ_E) plotted with σ_D.

Ratios imply imaging conditions for Li are superior at lower beam energy.
Ratios of σ_K and σ_E against σ_D are greater at lower voltages, yielding more imaging events per damage event.

Conclusions

- **Imaging with Low Voltage TEM can reduce knock-on damage to Li.**
- **Voltage also subject to other factors e.g. sample thickness, beam spreading.**

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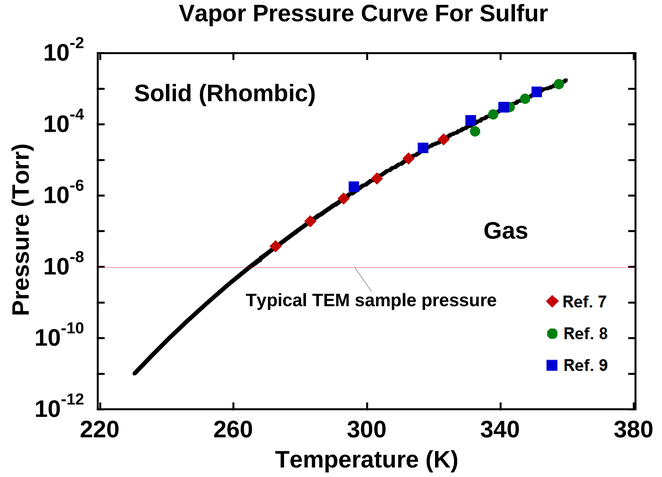
Bulk Sulfur Will Sublimate in the Vacuum of a TEM

Sulfur vapor pressure is ~ 10^{-6} Torr at room temperature.[5] Typical TEM pressures are ~10^{-8} Torr.

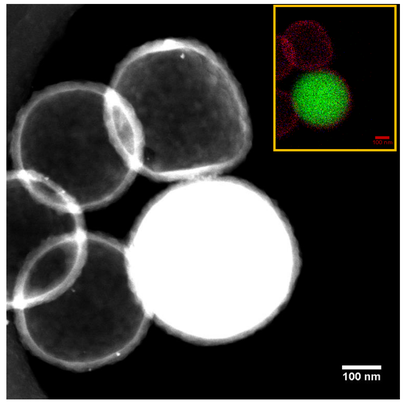


Vapor pressure curve for Sulfur, Kelvin/Antoine formula[6] extrapolation from experimental data. Typical TEM sample pressures ~10^{-8} Torr, (red line).

There are 3 ways to avoid Sulfur sublimation:

1. Encapsulate in material with < a few nm sized pores.[10]
2. Use environmental or air electron microscope.
3. Use a Cryo-electron microscope.

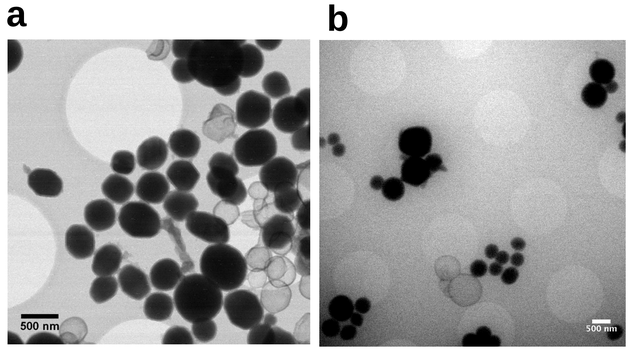
Solution 1: Encapsulation



HAADF STEM **image of** Sulfur encapsulated in a PAN shell.
Inset: EDX map. Red = Carbon, Green = Sulfur.
Sample provided by: Yingchao Yu, Weidong Zhou, Cornell Chemistry

Solution 2: Image in Air

Going from low-mag 200keV TEM to 30keV Air STEM , there is no significant loss of resolution.



a ABF STEM image of Sulfur particles in PAN shell.
b The sample was transferred to Air-SEM and imaged again with a STEM detector. Resolution sufficient to resolve empty shells clearly ~10nm.
Air SEM Imaging assistance from Kayla Nguyen, Muller Group, Cornell.

Conclusions

- **At low magnification, Air-STEM can be used to image Sulfur particles without sublimation. Further improvements possible.**
- **For high magnification imaging, Cryo-electron microscopy is an option.**

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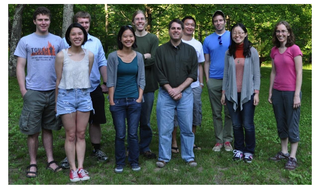

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