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Preparation of electron and X-Ray Transparent Inorganic Particles for Analytical Microscopy Using the Ultramicrotome

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Introduction

Many advanced materials characterization techniques that perform at the highest spatial and energy resolutions have strict dimensional requirements on acceptable samples. For example, the transmission electron microscope (TEM) generally requires samples to be electron transparent (3 mm-diameter discs <100 nm thick). Electron energy loss spectroscopy (EELS) in the TEM places further restrictions on sample thickness (typically < 50 nm). Likewise, scanning transmission x-ray microscopy (STXM) requires samples be x-ray transparent for x-ray absorption spectroscopy (XAS) and typically < 500 nm thick. Common sample preparation techniques include dimpling and Ar-ion milling or focused Ga-ion beam (FIB) thinning. However, this can be challenging for samples that are made up of a collection of 100 nm – 5 µm diameter particles. For example, preserving the arrangement of particles in an electrochemical experiment for ex situ microscopy is difficult. Artifacts caused by redeposition and beam damage from ion beam removal techniques can be difficult to prevent. Here, we demonstrate the successful use of the ultramicrotome [1], usually used for soft and biological materials, for the preparation of thin inorganic particle samples.

[1] D. Studer and H. Gnaegi, Journal of Microscopy-Oxford 197 (2000)

Process Development

Sample Preparation

There are **2 methods** for sample preparation each is defined by the type of material.

Fig. 1 illustrates the before and after of a microtome sample starting from a powder dispersed in an epoxy resin 16.5mm x 7.75mm

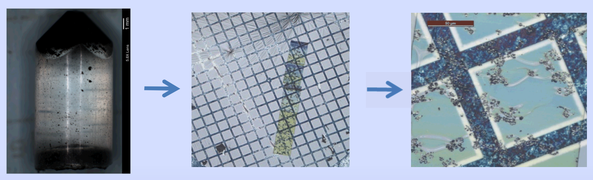

Fig. 1

Fig. 2 illustrates how to prepare a sample from a composite thin film of particles held together with a polymer binder. 5mm x 4mm Plastic supports are glued to the sample, and then the sample is microtomed.

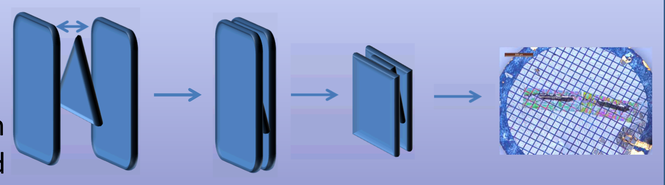

Fig.2

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Example 1: Surface Modified Powders for Hydrogen Storage

Our first example shows how the ultramicrotome can be used to prepare thin sections of metallic Pd-alloy based powders for hydrogen storage. Surface modification of these powders can have a large impact on their thermal stability, hydrogen storage properties, and kinetics of hydrogen uptake and release [5].

The ultramicrotome provides a way to make samples that can then be imaged showing surface modifications that range from tens of nanometers to sub-nanometer dimensions. In this case, a <1 nm-thick layer of Rh deposited using electroless atomic layer deposition provides a benefit to the hydrogen storage properties. An FEI probe-corrected G2 Titan with ChemiSTEM is used to image this thin layer.

References

[5] P.J. Cappillino, *et al.*, *Langmuir* **30** (2014)

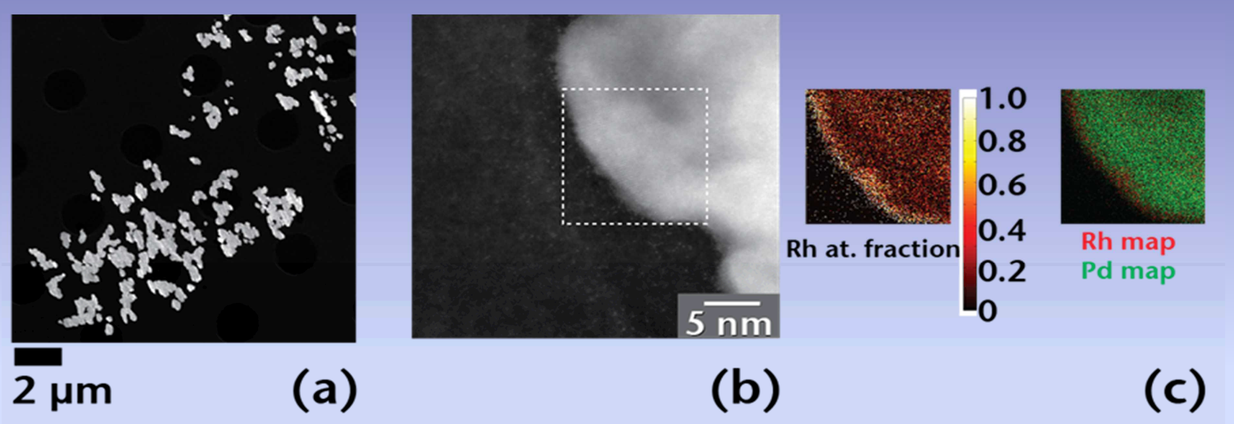


Figure 3: (a) Lower magnification HAADF STEM image of Pd-alloy particles used for hydrogen storage. A higher magnification image near a particle surface is shown in (b) where lattice fringes are visible, demonstrating the high quality of this thin sample. Compositional analysis from EDS is shown in (c) where a <1 nm-thick surface modification layer enriched in Rh (by atomic layer electroless deposition) is visible.

Example 2: Li-ion Battery Electrode Particles

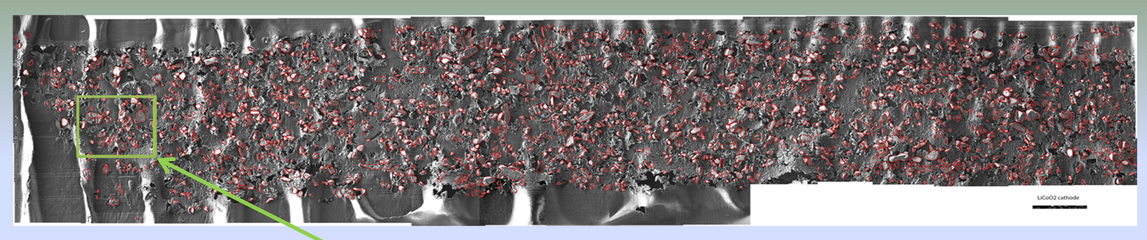
Li-ion battery electrodes generally consist of inorganic oxide particles mixed with an organic binder. By mapping the spatial distribution of ion state of charge in the electrodes particle-by-particle, it is possible to understand the mechanisms of the charge/discharge reaction and degradation in these materials [2-4]. In our first example, the ultramicrotome provides a way to make thin samples from battery electrodes in which the electrode particle arrangement is preserved and particles can be imaged with nanometer spatial resolution.

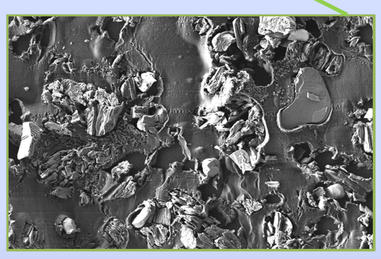
References

[2] J.D. Sugar, *et al.*, *Journal of Power Sources* **246** (2014)

[3] Y. Li, *et al.*, *Nat Mater* **13** (2014)

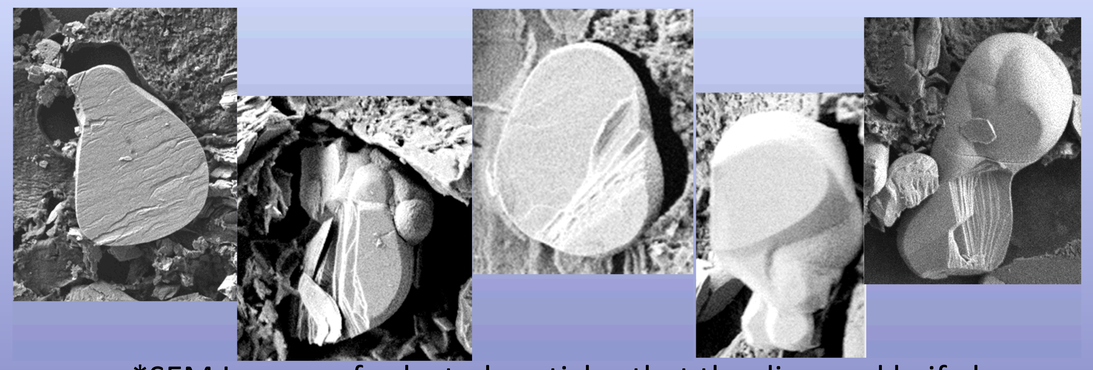
[4] W.C. Chueh, *et al.*, *Nano Lett* **13** (2013)





- 482 x 100 µm
- 1704 particles identified (red outlines above)

The UC7 microtome was used to create the sample in the SEM montage above.



*SEM Images of selected particles that the diamond knife has effectively sectioned.

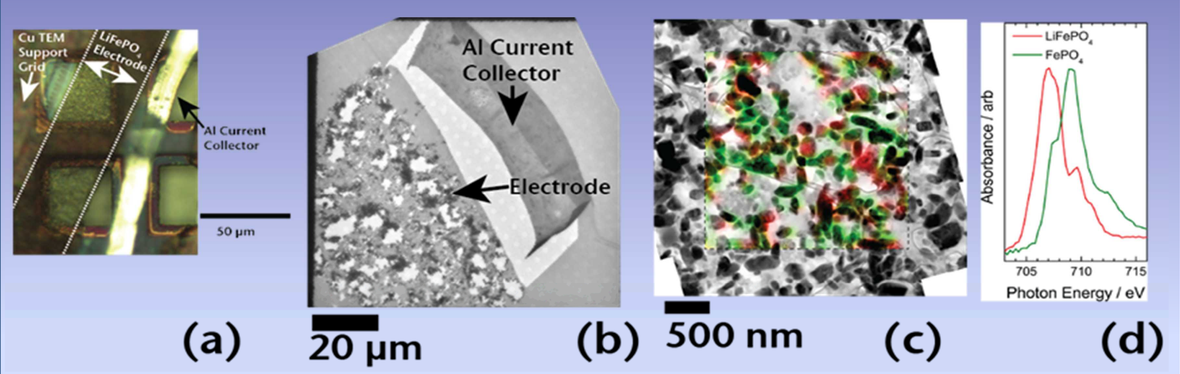


Figure 4: (a) Optical micrograph of LiFePO4 battery electrode sectioned with the ultramicrotome and attached to a TEM grid. The full section of the electrode is intact and the particle arrangement is preserved relative to the current collector. A lower magnification bright-field TEM image (b) shows that the cross section is electron transparent and a fraction of the particles have fallen off of the section. A STXM Fe state of charge map is overlaid a bright-field TEM image in (c) where the state of charge of the Fe cations is determined from the reference spectra shown in (d). It is possible to map the state of charge particle-by-particle in these Li-ion battery electrodes.

Conclusions

- Ultramicrotome can create Electron, x-ray transparent and artifact-free inorganic particle samples that are virtually damage free making it an ideal process for most materials.
- Ultramicrotome samples are appropriately dimensioned for performing high-quality electron and x-ray spectroscopy.
- Large areas of Ultramicrotome samples can be sectioned that contain multiple particles for statistical analysis.

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