

## Using Energy-Filtered TEM to Solve Practical Materials Problems with Inspirations from Gareth Thomas

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Gareth Thomas' legacy, scientific accomplishments, and inspirational reach extended beyond his own students to his students' students, as evidenced by the work discussed here. One topic researched by Gareth Thomas during his extensive career was the spinodal decomposition of Cu-Ni-Fe alloys [1-3]. Diffraction-contrast imaging was used to study the effects of composition and coarsening on the modulated structure that naturally develops in Cu-Ni-Fe alloys. An example from this work is shown in **Figure 1 a**). In subsequent work, graduate students under the direction of a former student of Thomas (R. Gronsky) studied the effects of volumetric encapsulation on the coarsening and compositional modulation of Cu-Ni-Fe alloys [4]. The utilization of a post-column energy filter to the TEM supplemented the original diffraction-based measurements performed by Thomas et al., enabling direct imaging of the compositional modulation, as shown in the corresponding zero-loss image in **Figure 1 b**) and overlaid elemental maps in **Figure 1 c**). In this way, it was possible to show that the decomposition reaction could be geometrically directed, as shown by the single domain of modulation in **Figure 1 c**). This work in the Cu-Ni-Fe system initiated the discovery of the importance of TEM to solving materials problems to the present authors, and the microscopy skills developed became essential to the follow-on work that the authors encountered.

One example of later work where energy-filtered TEM (EFTEM) was used to understand materials microstructure and properties is demonstrated in **Figure 2** with battery electrode research. In this case, the analytical microscopy techniques developed for Cu-Ni-Fe alloys were further perfected to determine and map the valence of the Fe ion in LiFePO<sub>4</sub> battery electrodes. This information was needed to determine that the charge/discharge reaction occurs particle-by-particle in LiFePO<sub>4</sub> [5, 6]. **Figure 2** is one example showing that the individual LiFePO<sub>4</sub> particles in the electrode are either fully charged or fully discharged. It is rare to find a single particle with an interphase boundary. This suggests that nucleation is the limiting factor in controlling the charge/discharge rate in LiFePO<sub>4</sub> cathodes. Without Gareth Thomas' influence on the direction of materials science and electron microscopy at the University of CA, Berkeley, and the original Cu-Ni-Fe work, the inspiration and capabilities needed to perform the battery electrode characterization shown here would not have existed.

### References:

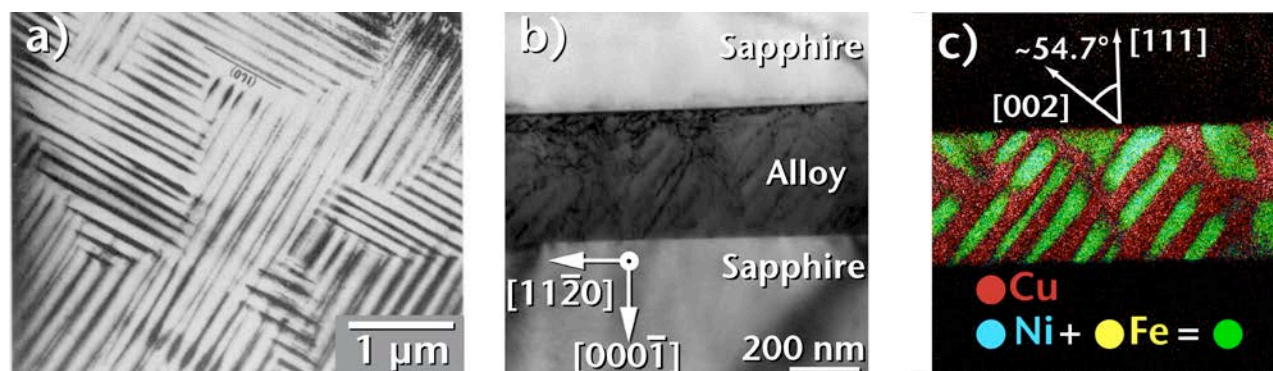
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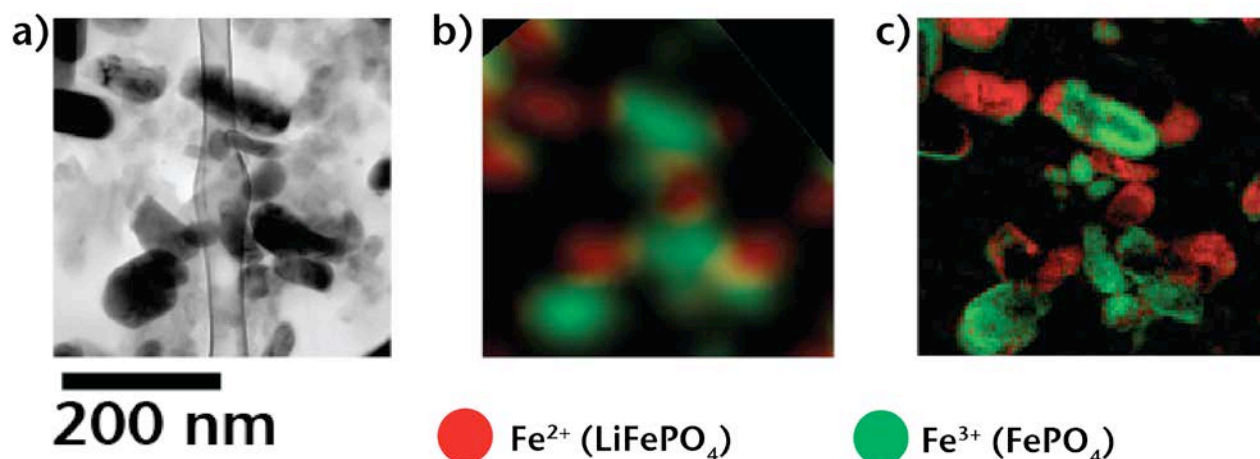
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[7] Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



**Figure 1.** (a) Bright-field TEM image of Cu-Ni-Fe alloy aged 100 hr at 800°C, clearly showing the modulated compositional structure (from [3]). In (b), a zero-loss image of the Cu-Ni-Fe alloy encapsulated in sapphire and annealed for 188 hr at 700°C is shown. The corresponding compositional modulation is shown in the overlaid energy-filtered maps shown in (c).



**Figure 2.** (a) Bright-field TEM image of particles in a partially charged  $\text{LiFePO}_4$  battery electrode. The Fe valence is mapped using scanning transmission x-ray microscopy (STXM) in (b) and energy-filtered TEM (EFTEM) in (c). Both techniques are in good agreement.