In Situ Synchrotron XRD Studies of Microstructure Evolution During the Salt-Mediated Coarsening of Nanoporous Metals

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Nanoporous metals (NPMs) are highly desirable for applications as catalysts or electrodes due to their high surface areas and large (> µm) secondary particle size. Prior synthetic techniques for preparing NPMs (dealloying, templating) suffered from a lack of scalability and limited metals accessible via these routes. Newly developed conversion reaction syntheses (CRS) are a facile and generalizable route for synthesizing NPMs of both noble (Ag, Au) and non-noble (Fe, Co) metals, but it is more challenging to control particle size when prepared in this manner. 1 Ex and in situ synchrotron x-ray diffraction studies have been conducted in order to gain a mechanistic understanding of coarsening processes for NPMs and NPM-salt nanocomposites (NCs), with the ultimate goal of achieving precise morphological control for applications. Within GENESIS, we are working to understand the coarsening mechanism of CRS-derived NPMs, especially a rapid salt-mediated acceleration in reaction rate that occurs at low temperatures when NPM-salt nanocomposites are heated.

Ex situ annealing studies of Fe, Co and Cu NPMs and metal/salt NCs

Microstructure analysis on XRD data from NPMs and NCs as-synthesized and after 3h annealing at 300 or 600 °C.
- Crystallite sizes trend with self-diffusion coefficients (Fe < Co < Cu)
- Lower salt strain in Cu/LiCl from similar ionic radii of Li⁺ (0.76 Å) and Cu²⁺ (0.73 Å) vs. Co²⁺ (0.65 Å) and Fe²⁺ (0.55 Å)
- Following LiCl removal, Fe and Co grow minimally while Cu grows significantly
- For Fe and Co, drastic metal and salt changes after 600 °C annealing suggest a different high-T growth mechanism

In situ variable temperature annealing of metal/salt nanocomposites

Iron
- Exceptionally small primary particle sizes, typically 0.5 – 2 nm
- Drastic peak sharpening for metal phase occurs at about 510 °C
- LiCl peaks begin to sharpen at same T, indicating a coupled mechanism

Cobalt
- Similar coupled change in metal and salt
- Reaction occurs at a much lower temperature of about 200 °C
- Both HCP and FCC polymorphs are present, preferential FCC growth

Copper
- Cu and LiCl peaks sharp at room temp
- Gradual rather than rapid sharpening

General trends
- Rapid coarsening is mediated by solid, not molten salt (rxn T < salt T_m 605 °C)
- Likely chemical substitution of metal in the salt helps drive rapid coarsening

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