

# Cycling Effects on Battery Anode Structure for a High Entropy Oxide

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## ABSTRACT

While reversible energy storage technology has improved over the past few decades, the need for batteries that can store greater amounts of energy and last longer has grown as well. This research focuses on high entropy oxides (HEO) as a promising battery material. This experiment involved the creation of an anode half-cell composed of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{NiO}$ . Five anodes were made by mixing, ball milling, and annealing these powders to create  $(\text{Al}_{0.2}\text{Fe}_{0.2}\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ . Based on the thesis work of Christina Rost, the team was confident that the anodes material took on the desired spinel structure. After forming the HEO slurry, a thin layer of the compound was 'painted' onto aluminum foil and then hand-punch it into coin cell-sized anodes. An automatic cycler was used to charge and discharge the half-cells through a specified number of cycles. The anodes were then removed from the batteries and EXAFS data were collected. It was determined that this HEO is indeed a candidate for battery anode material.



Figure 1. Image on the left shows GBS student weighing the compound needed for the mixture. Photo on the right shows the entire Glenbrook South High School ESRP team.

## MOTIVATION

Although traditional rechargeable lithium-ion batteries have advanced to modest efficiencies, the exploration of HEO anodes could lead to further developments in rechargeable battery technology. In particular, understanding the detailed role of each element making up the HEO anode and its contribution to the cycling stability and eventual failure can provide insight into designing improved battery electrodes. The results of such research may be used to evaluate the potential of HEO anodes in developing superior non-lithium batteries. Electric vehicles, for example, can surely benefit from the next generation of batteries that could withstand thousands of charging cycles and that can store a greater amount of energy when compared to that of current batteries. In addition, this experiment offered a wide range of learning opportunities for the students involved as they played an active role in the research, design, and testing of battery cells.



Figure 2. Left image depicts students performing stoichiometry calculations to determine the amount of each compound needed for formation of the desired HEO electrode. Center image shows students making a pellet of the desired compound prior to the annealing process. The right picture illustrates the x-ray diffraction analysis used to determine whether or not the desired structure was created through the ball milling and annealing process.

## DATA COLLECTION & EXPERIMENTS

After initial research was conducted to decide on the compound that would be used for the experiment, a set of metal oxides were weighed then mixed through the ball milling process. This mixture was then compressed into a pellet and annealed in an oven multiple times at different temperatures until the compound's spinel structure was formed. After the spinel structure achieved, the pellet was ball milled again into a nano-sized particles and combined with an active material (70%), carbon black (20%), PVDF binder (10%), and NMP solvent (amount depends on viscosity) to create a slurry that was deposited onto a piece of aluminum foil. A quarter-sized piece was cut from the foil and slurry sheet and then assembled into a battery cell in an argon-filled glovebox. The half cell was made with lithium sheet as the counter electrode, electrolyte, a polymeric membrane separator, the cell (electrode), and the spacer and spring components for structural stability. After assembly, the crimping machine was used to seal (to avoid contact with air) the half cell. A total of five half cells were created and tested—one pristine (the control), one that was lithiated once, one that was lithiated and delithiated once, one that was charged/discharged 100 hundred times ending in the lithiated state, and another cycled 100 times ending in the delithiated state. After cycling, the electrode was taken out of the cell for EXAFS where it was placed into the APS beamline for x-ray fluorescence experiments to see how the structure changed through the cycling process.

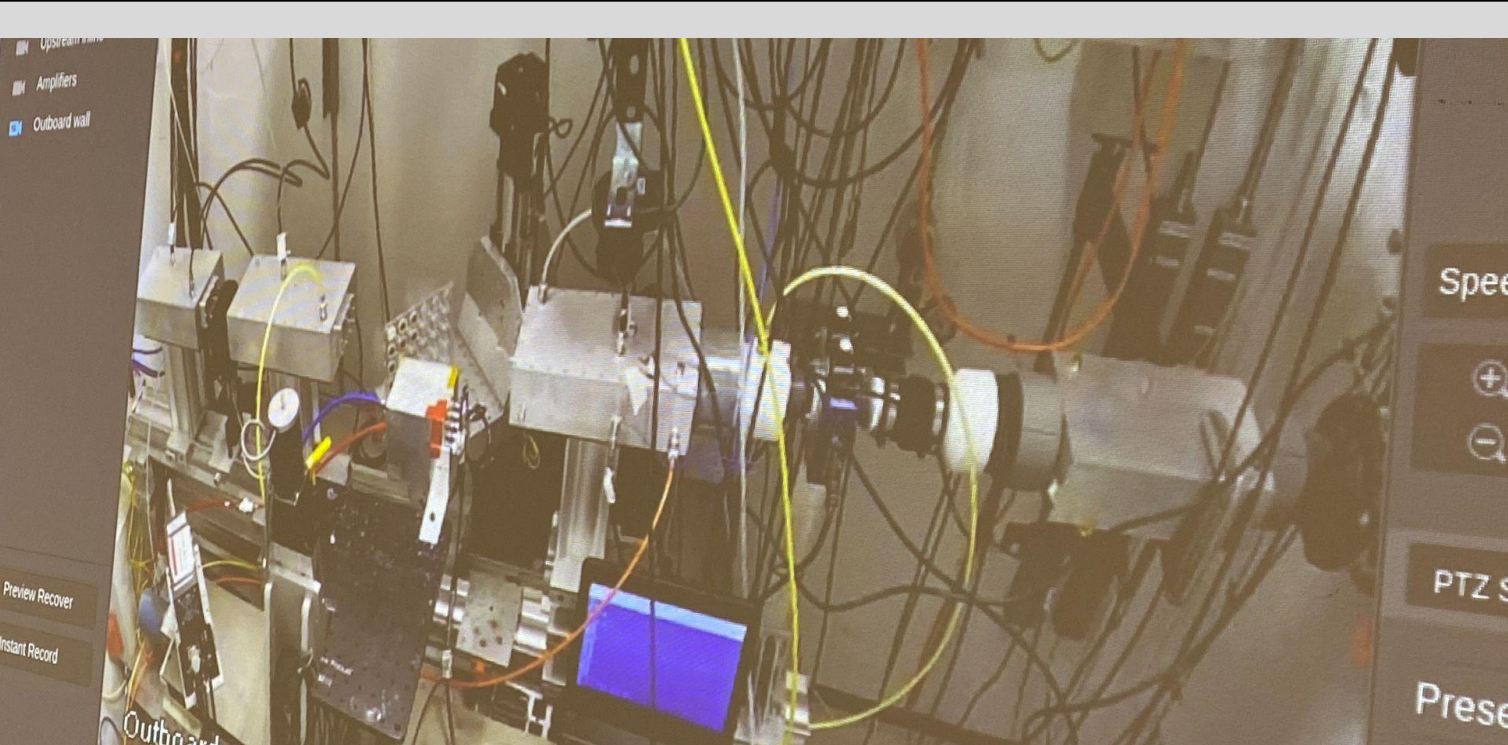
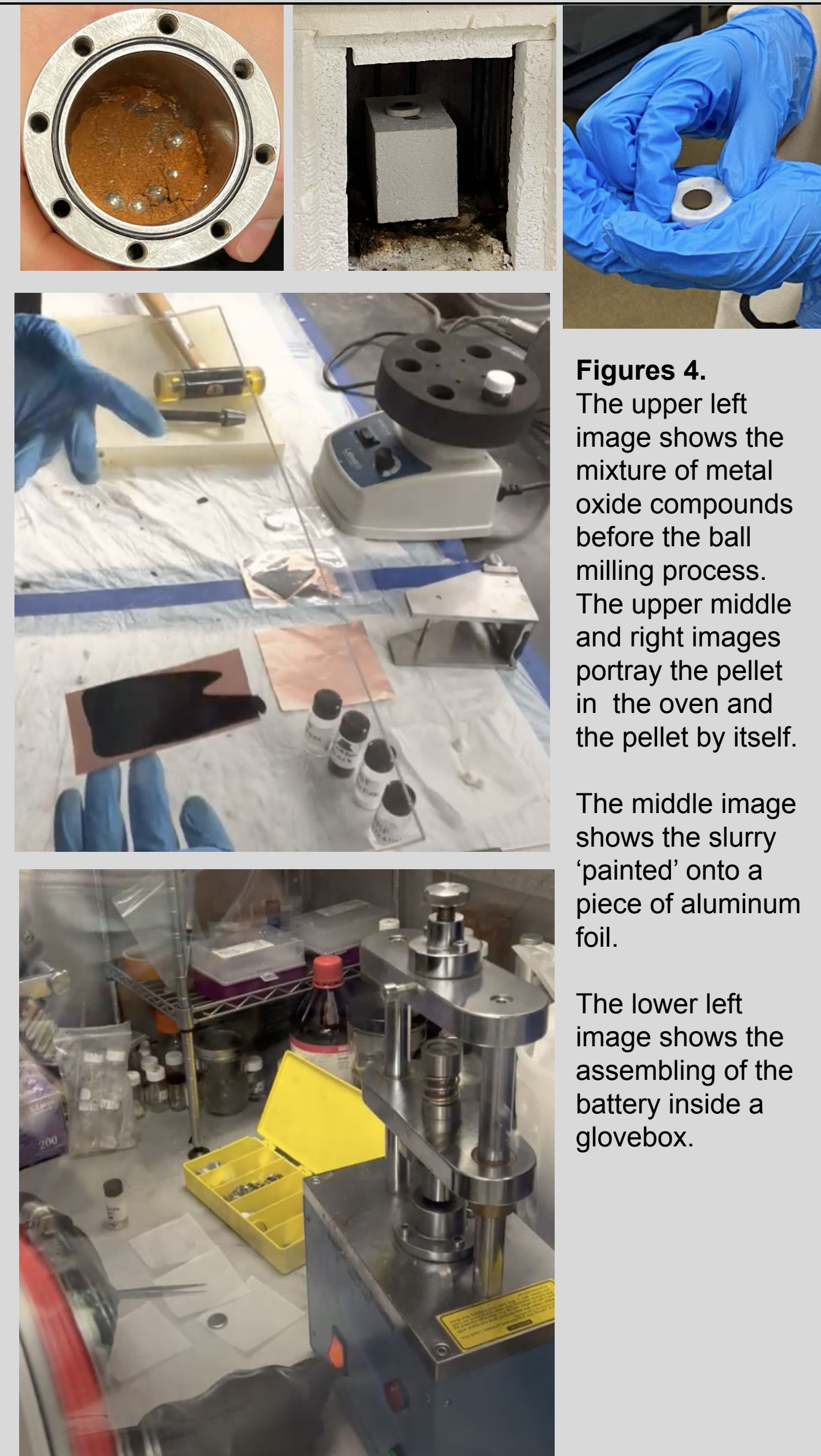


Figure 3. Optical hutch (beamline) setup.



Figures 4. The upper left image shows the mixture of metal oxide compounds before the ball milling process. The upper middle and right images portray the pellet in the oven and the pellet by itself. The middle image shows the slurry 'painted' onto a piece of aluminum foil. The lower left image shows the assembly of the battery inside a glovebox.

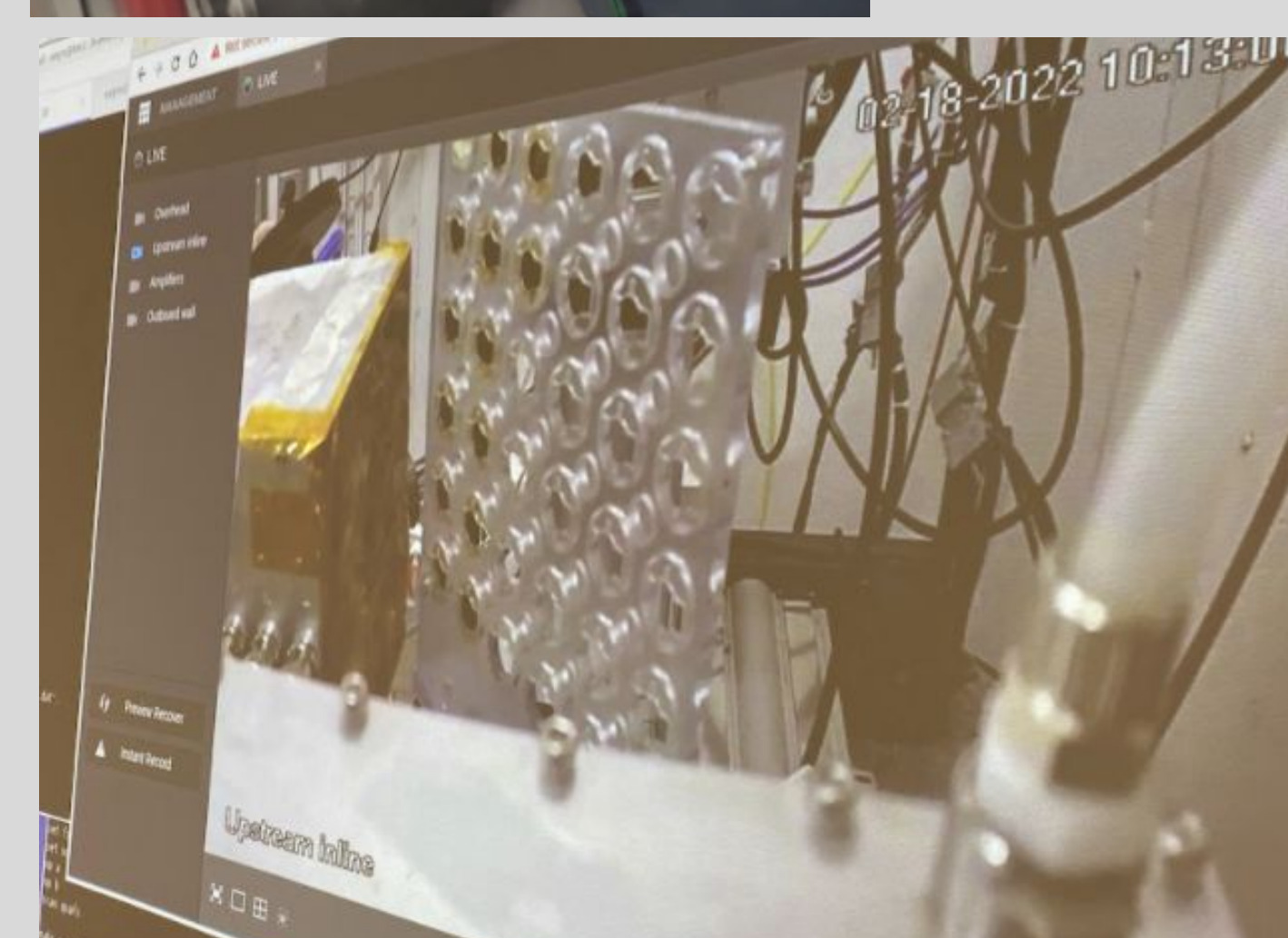


Figure 5. Photo of the samples in the beamline for testing.

## RESULTS

### Annealing Temperature Analysis

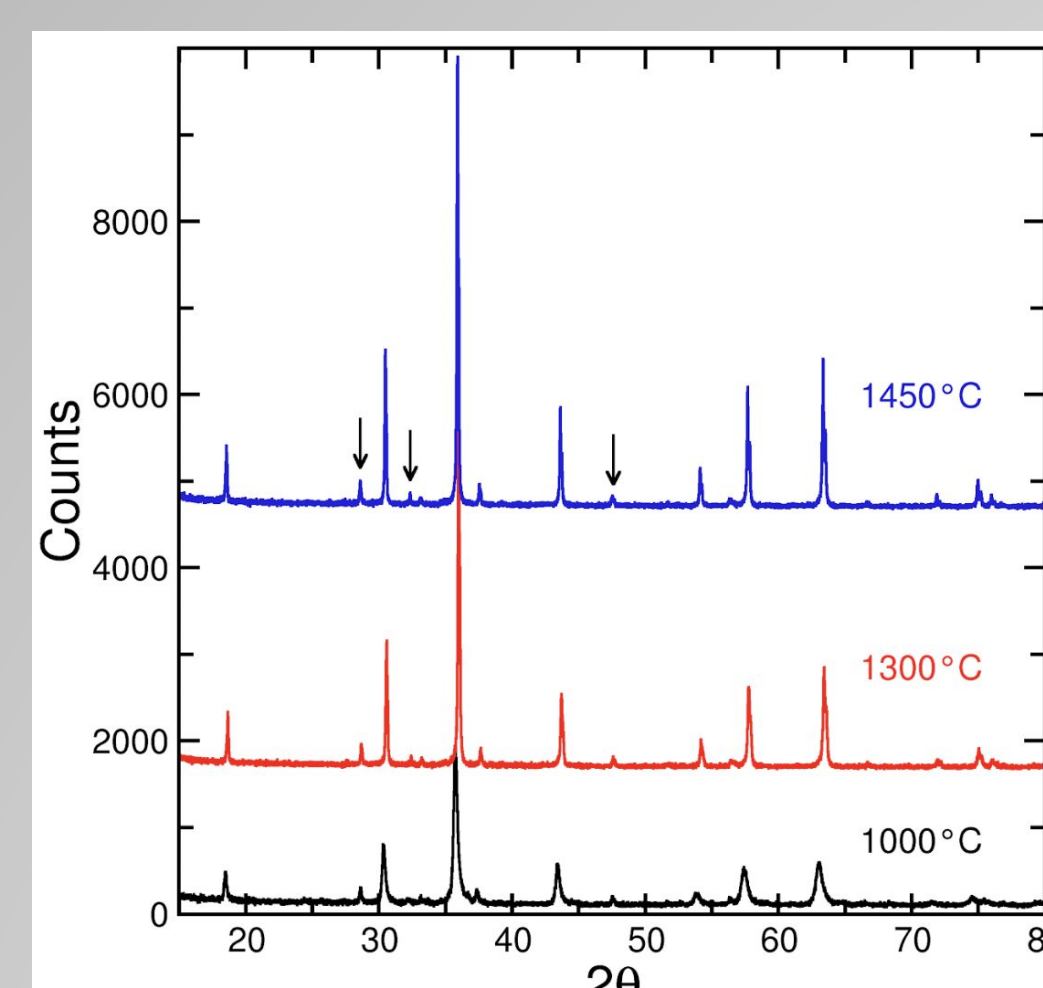


Figure 6. X-ray diffraction graph comparing structural differences of the sample after successive firing with increasing temperatures. Chromium impurities are shown as small peaks denoted by black arrows. Higher peaks formed as the temperature increases indicate the formation of the desired spinel structure.

### Annealing Process Before and After Ball Milling

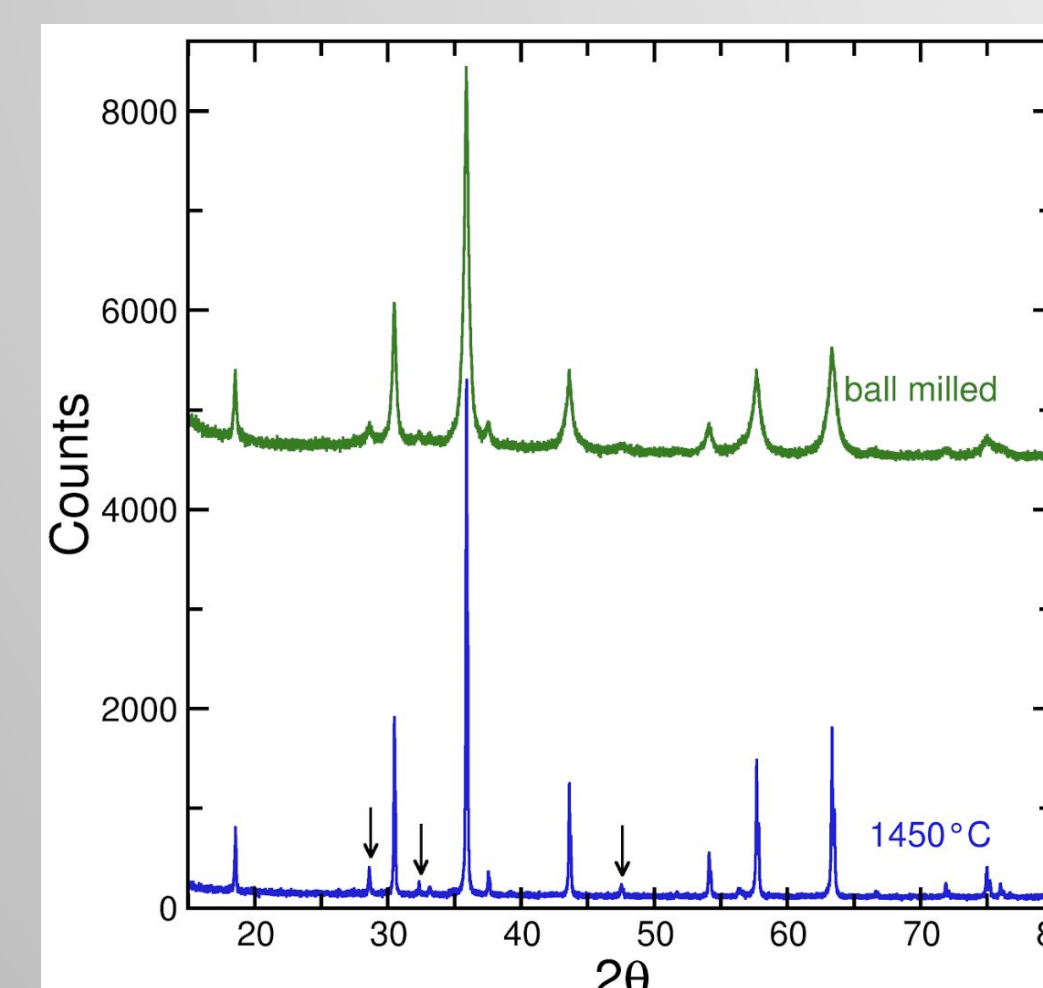


Figure 7. X-ray diffraction plot comparing the structural differences of the sample before (blue) and after (green) the final ball-milling step. Chromium impurities are indicated with black arrows. Broader peaks present after ball-milling indicate a smaller particle size (~80 nm) compared to sample after the 1450 °C annealing process alone.

### Discharge Capacity & Efficiency Measurements

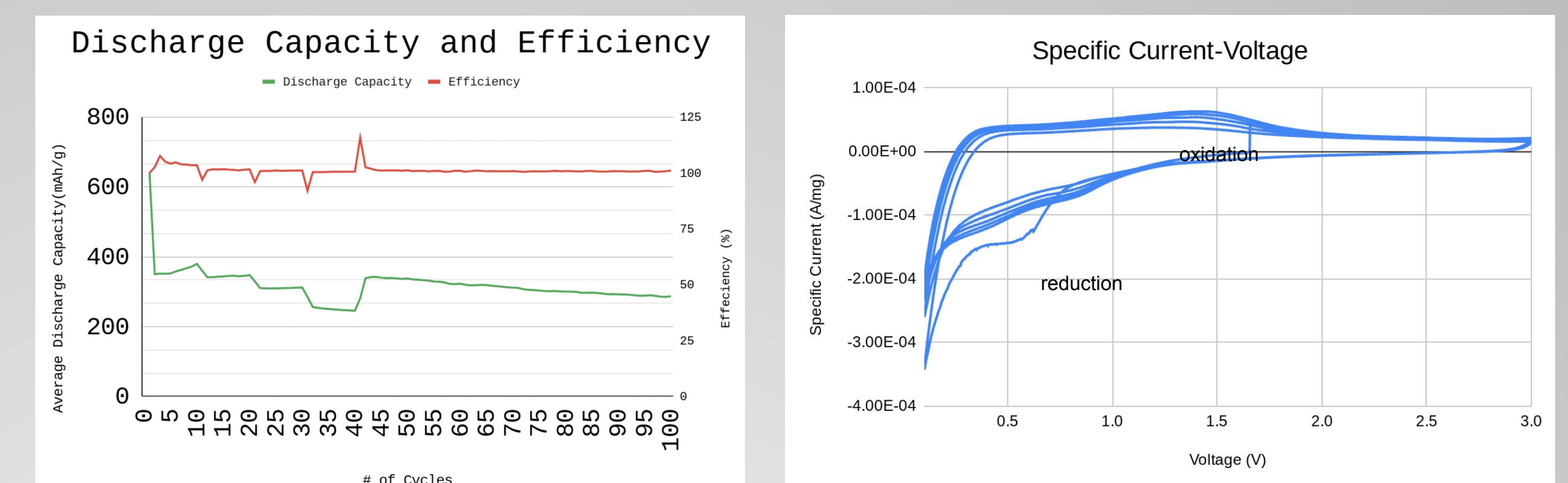


Figure 8. The left graph shows discharge capacity decreases quickly after the original spinel structure is lost, but then continues to decrease at a modest rate as the batteries are cycled. The discharge efficiency is generally around 100% for the entire charge and discharge cycle. The right graph shows specific current vs. voltage illustrating that there are some losses in capacity through cycling.

### EXAFS Analysis of Metals After a Variety of Cycling States

#### Manganese

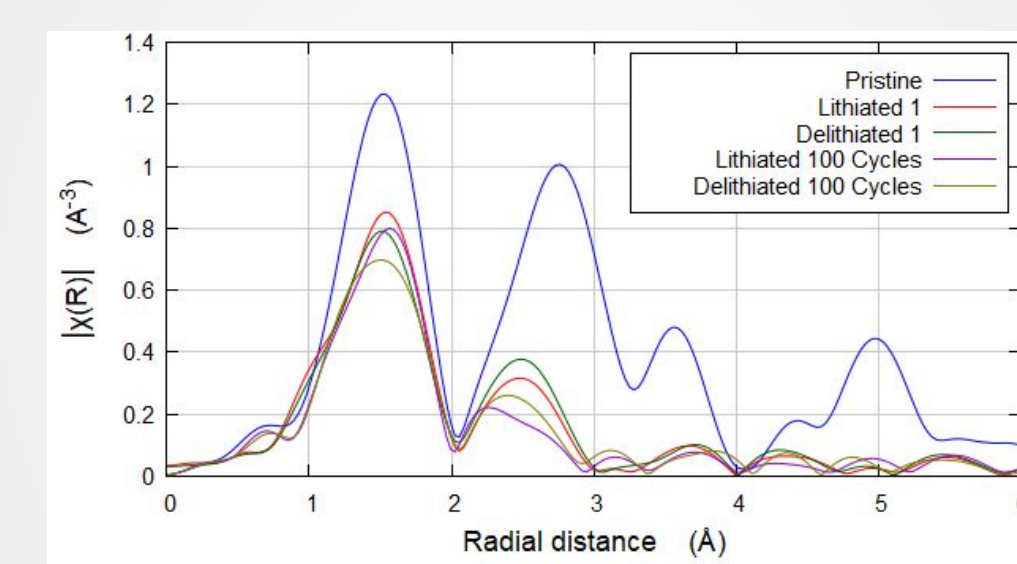


Figure 9. Manganese remains as an oxide - or at least returns to an oxidized state - after delithiation.

#### Nickel

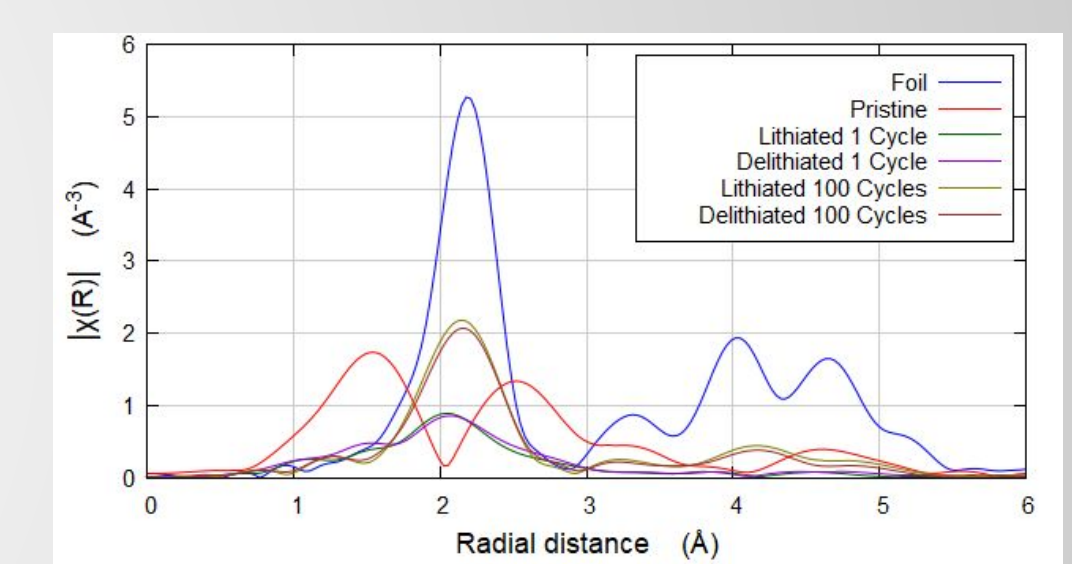


Figure 10. Nickel is partially converted to metallic nanoparticles on the first cycle (since there is little difference between the lithiated and delithiated states after one cycle.) Nickel is fully converted to metallic nanoparticles by the 100th cycle.

#### Chromium

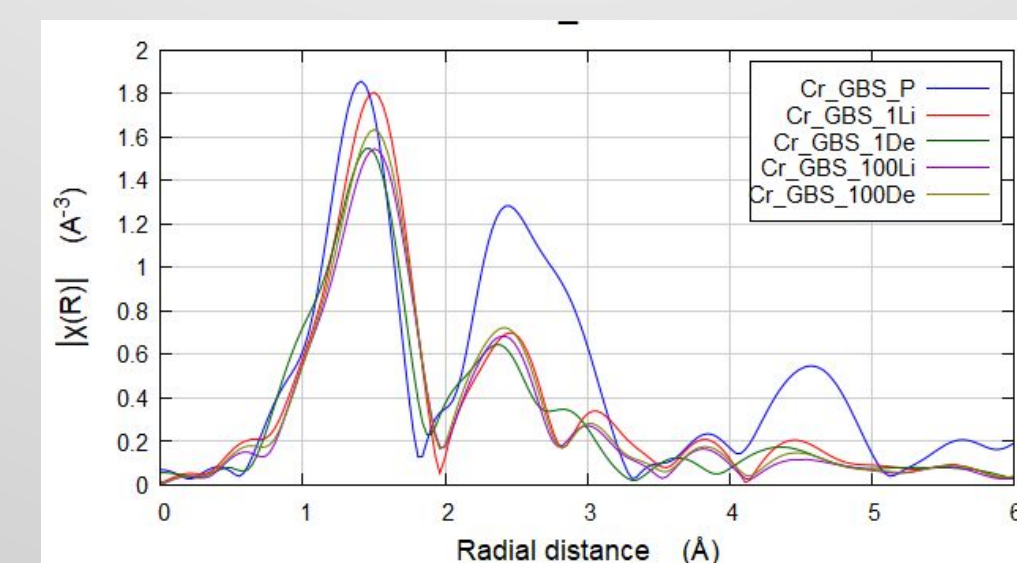


Figure 11. It does not appear that Chromium was even part of the spinel structure that was formed as it does not change significantly throughout the cycling process.

#### Iron

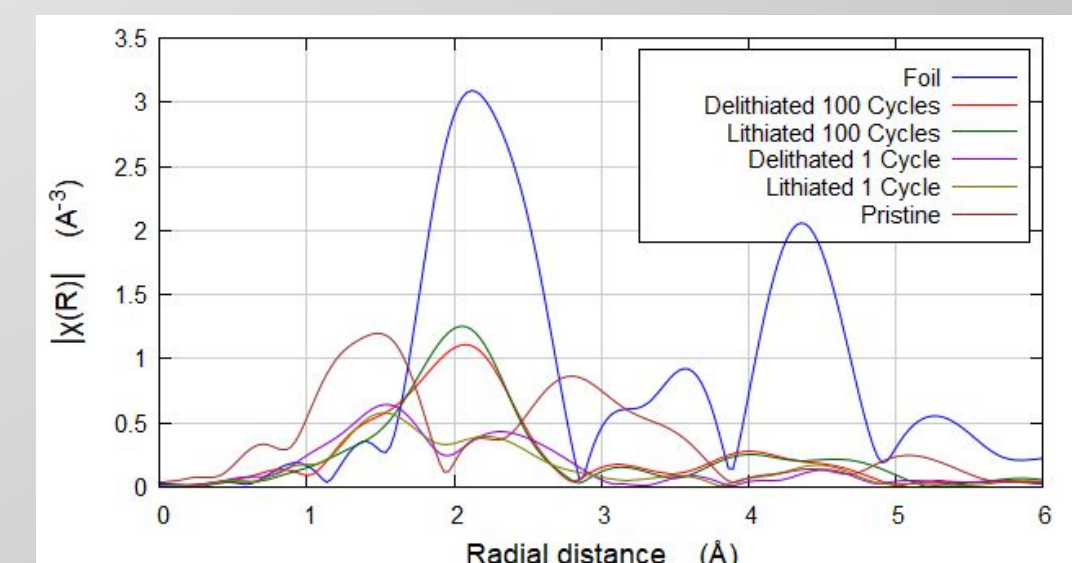


Figure 12. Like Nickel, Iron is partially converted to metallic nanoparticles on the first cycle (since there is little difference between the lithiated and delithiated states after one cycle.) Nickel is fully converted to metallic nanoparticles by the 100th cycle.

## CONCLUSION

The spinel structure of  $(\text{Al}_{0.2}\text{Fe}_{0.2}\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$  was achieved and five battery anodes were created using this material through an annealing process at 1450 °C. Mn, Ni, and Fe were involved in the cycling process, with Cr remaining in its oxidized state for the duration of the experiment. Outside the first delithiation, the batteries demonstrated only a modest drop in discharge capacity as a function of cycle. This result is indicative of a successful battery, and was obtained due to the Ni's constant metallic nanoparticle structure. Mn was oxidized during the half-cell's delithiation, whereas Fe was continually oxidized (to a nanoparticle structure) and reduced over time.

## ACKNOWLEDGEMENT

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