

The Study of Performance of a High Entropy Material for Anodes in Lithium Batteries

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MOTIVATION

High entropy materials have been studied as longer lasting and higher performing anodes for Lithium-Ion batteries. The high entropy oxides offer increased charge capacity and longer cycling times. This research objective is to create a single phase of Magnesium Oxide, Nickel Oxide, Manganese Oxide, Iron (III) Oxide, and Cobalt Oxide using a ball milling and annealing process. This anode material was examined in multiple ways. X-ray diffraction and scanning electron microscope measurements were taken in the laboratory at Illinois Tech to ensure that the sample was a single phase high entropy oxide and to determine morphology and overall composition of the sample. Ex situ EXAFS measurements were performed at 10-BM to study the valence states and local structures of each of the five metal ions in the pristine sample and in anodes which are in the lithiated and delithiated states after 1 and 100 cycles. These measurements will help to determine structural changes and failure mechanisms during charge and discharge cycling.

MAJOR ACCOMPLISHMENTS

X-ray diffraction confirmed that the anode material was a single phase rock salt structure composed of Magnesium Oxide, Nickel Oxide, Manganese Oxide, Iron (III) Oxide, and Cobalt Oxide (MgCoNiFeZnO) (Figures 1,2)

One hundred cycles were completed comparing Specific capacity and charge efficiency (Figure 3) which indicate minimal performance change over the cycle time.

The five cycles of cyclic voltammetry plotted in Figure 4 indicate that there is a large, irreversible reduction (lithiation) capacity in the first cycle corresponding to the destruction of the rock salt structure, followed by stable reduction and oxidation reactions at 0.9 V and 1.9 V respectively. It is notable that the flat reduction and oxidation trace behavior.

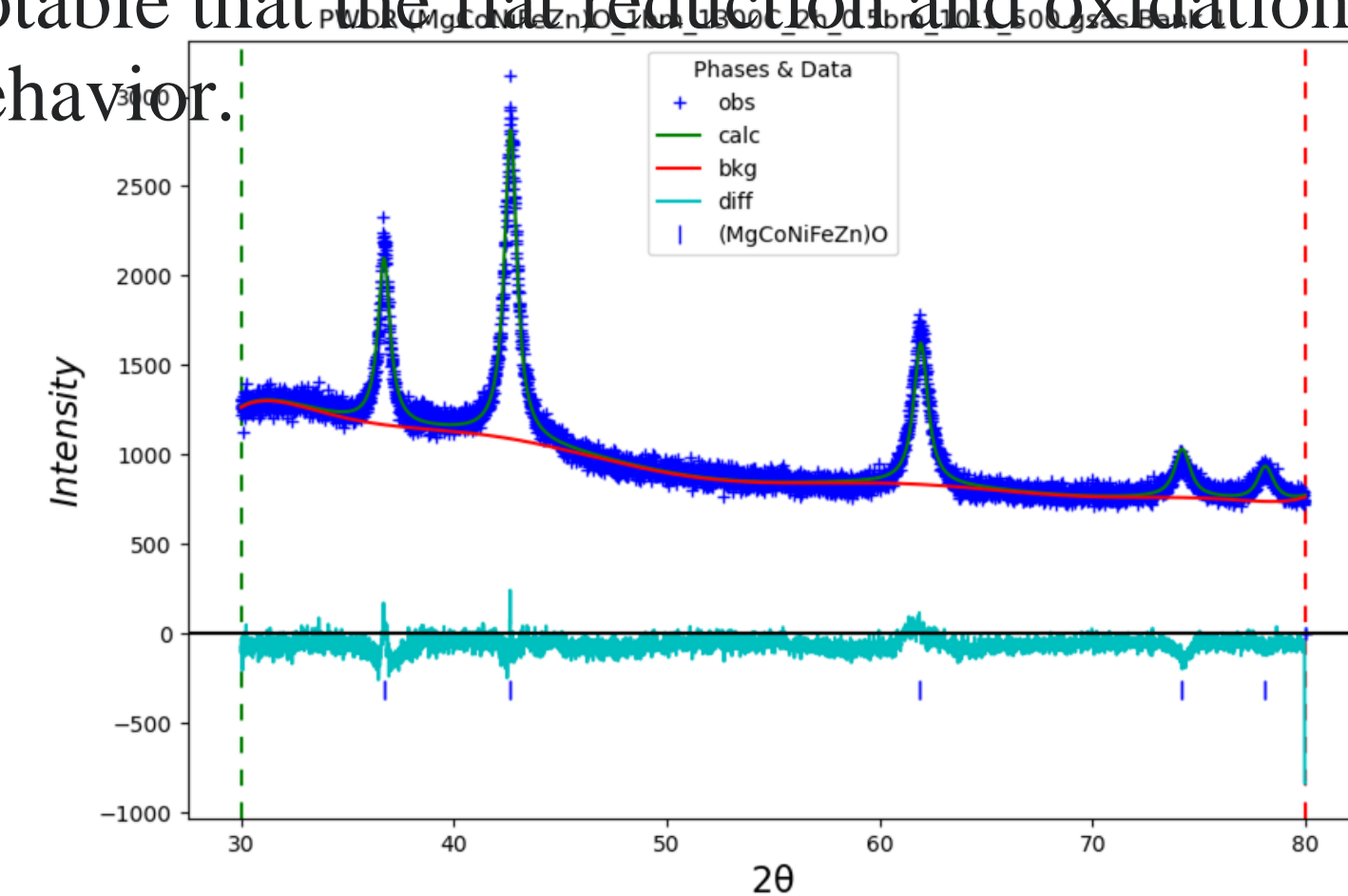


Figure 1

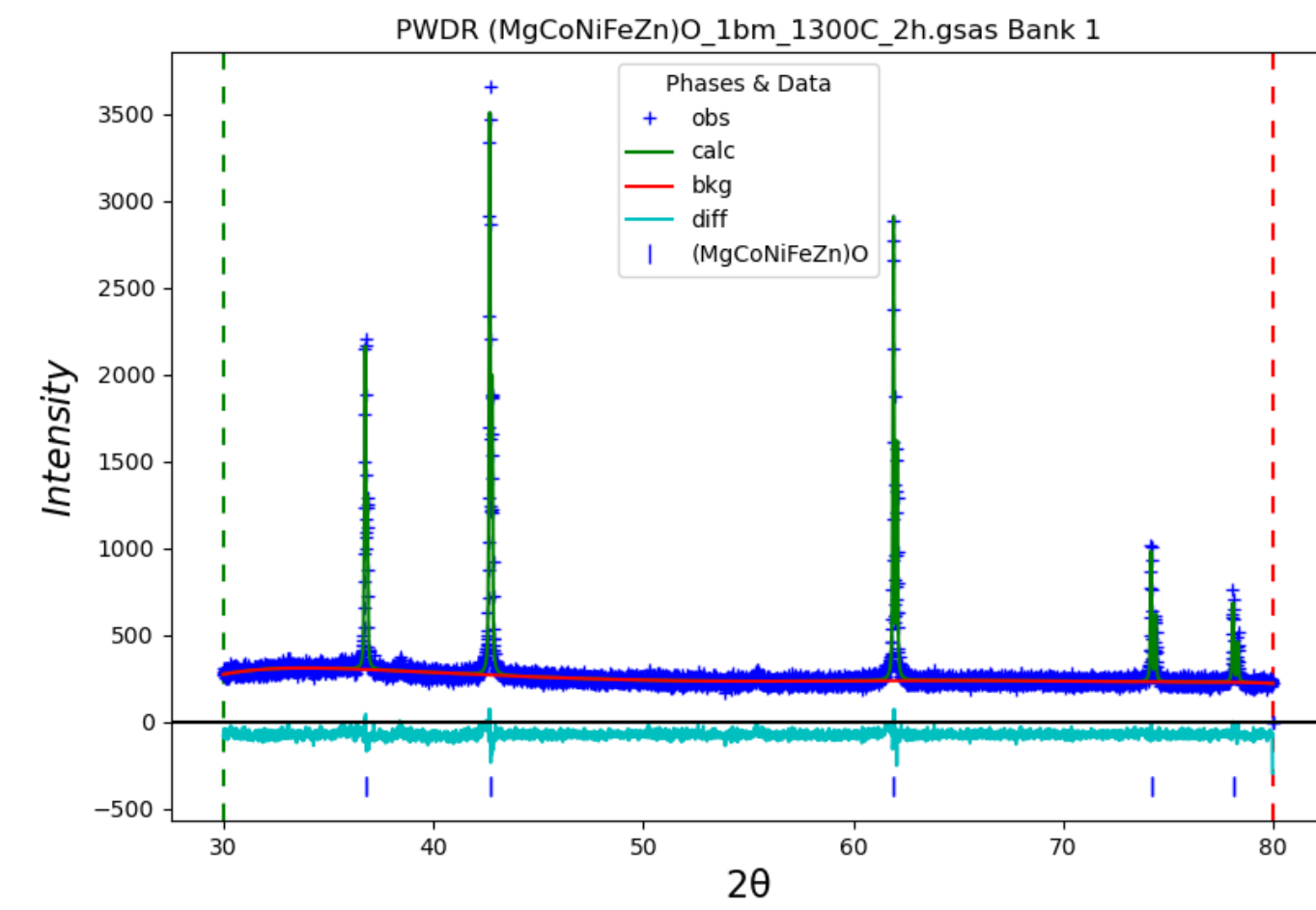


Figure 2

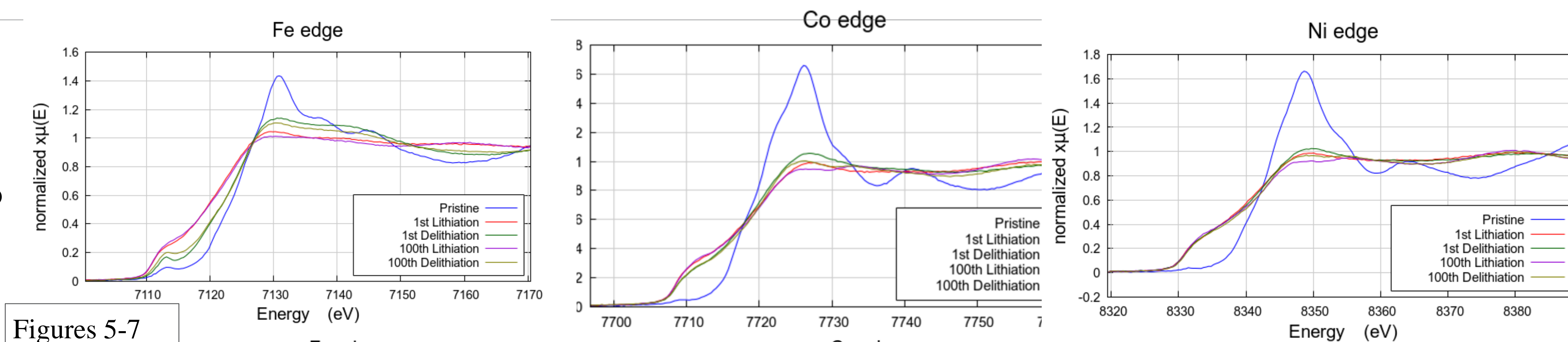
EXAFS Analysis (Figures 5-12) confirmed that long range order of the rock salt structure was destroyed after the first lithiation. Co and Ni appear to form metallic nanoparticles which remain even after delithiation, while Fe shows oscillation between metallic (lithiated) and partially oxidized (delithiated) states. Zn always appears in an oxidized state with a short Zn-O bond in the EXAFS Fourier Transform, however it is likely that the lithiated state has been compromised by exposure to oxygen from the time the sample was extracted from the coin cell and the glove box to when it was measured at the beamline.

The coin cell performance is stable and even improving at 100 cycles. This is consistent with results of MgCoNiCuZnO high entropy rocksalt structures and is likely due to both reduction/oxidation of Zn, Fe, and possibly Co ions and the isolated metal nanoparticles

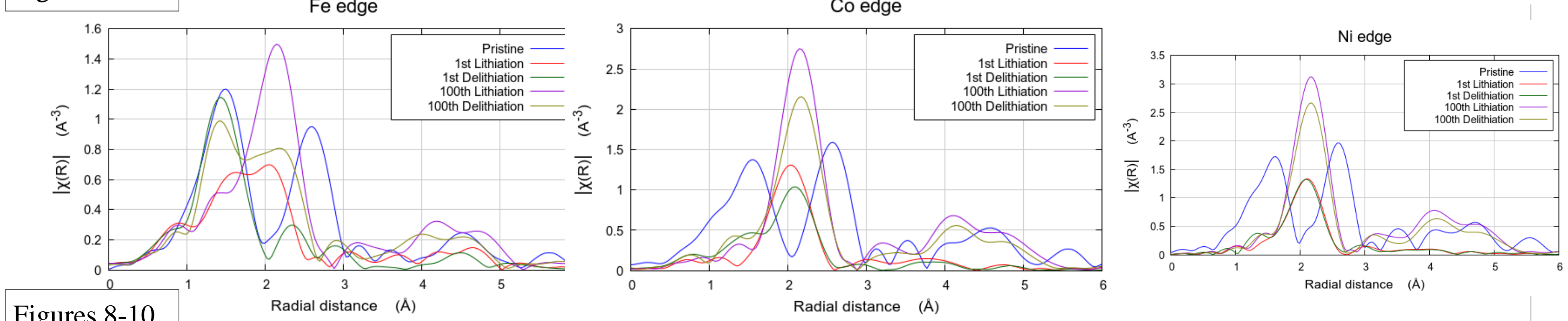
as capacitive sinks for charge.

IMPACT

- High entropy oxides are an interesting conversion anode material because of their high, stable capacity which outperforms their pure metal oxide components.
- The initial randomly distributed ions of varying species contributes to the formation of isolated metal nanoparticles which grow only slowly upon cycling and enhance the capacity.
- The presence of ions which oscillate between the metal nanoparticles and an amorphous oxide matrix prevents nanoparticle agglomeration and maintains Li-ion and electrical conductivity.
- Understanding the differing roles of the individual metal ions and longer term cycling until failure can lead to designing improved high entropy oxide anodes which could have some technological impact.



Figures 5-7



Figures 8-10

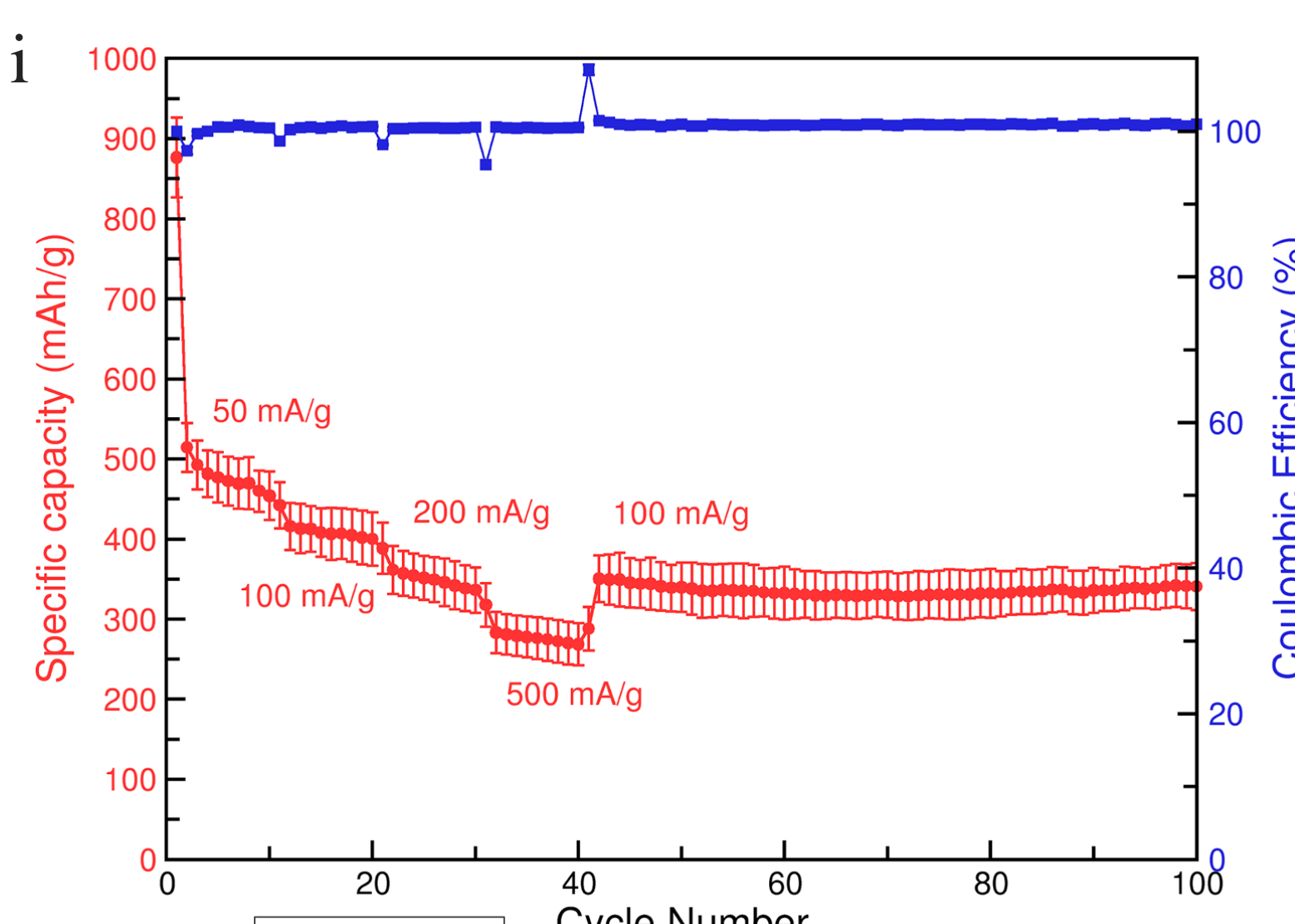


Figure 3

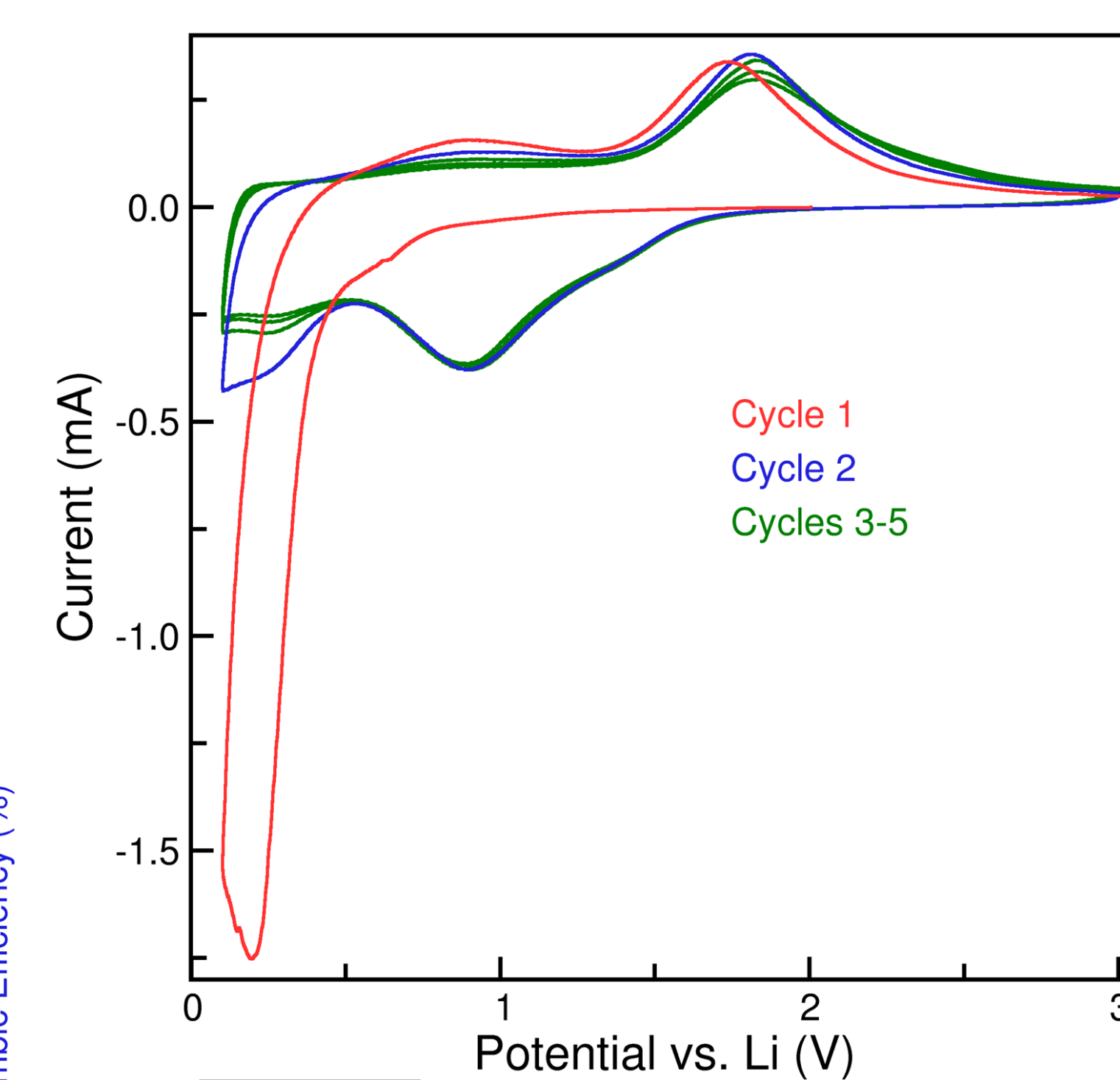
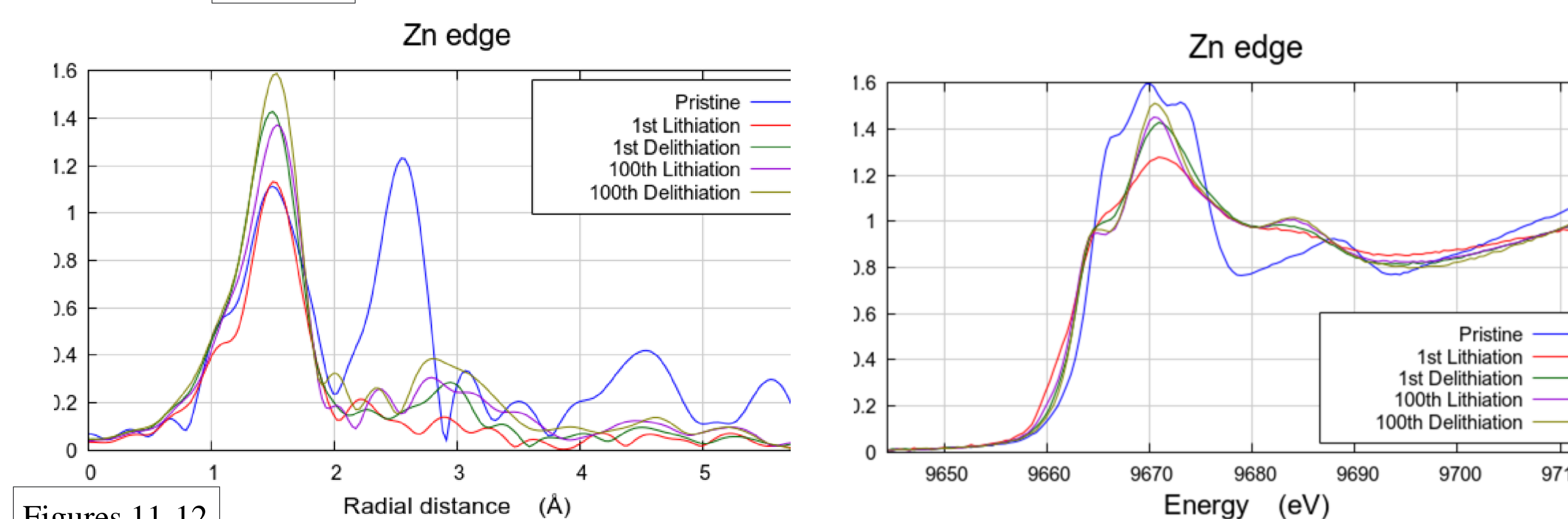


Figure 4



Figures 11-12

FUTURE DIRECTIONS

- Substitution of other metal ions with lower oxidation potentials have the potential to increase overall battery capacity by reducing the potential of the oxidation peak.
- Substitution of the presumably inactive Mg ion could lead to a higher capacity if high entropy structures can be prepared with the rock salt structure.
- In situ experiments could clarify the extent to which the Zn ions self-oxidize when removed from the coin cells in the lithiated state.

ACKNOWLEDGEMENTS

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