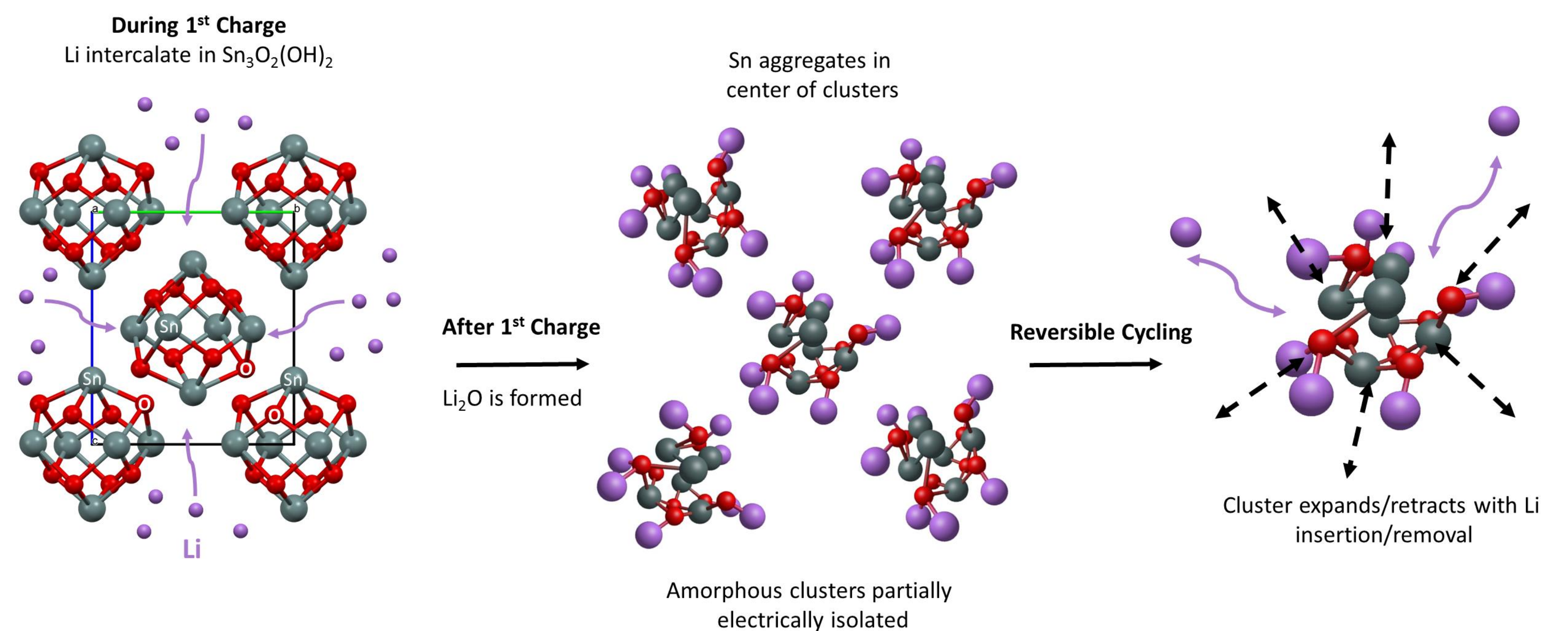


Motivation

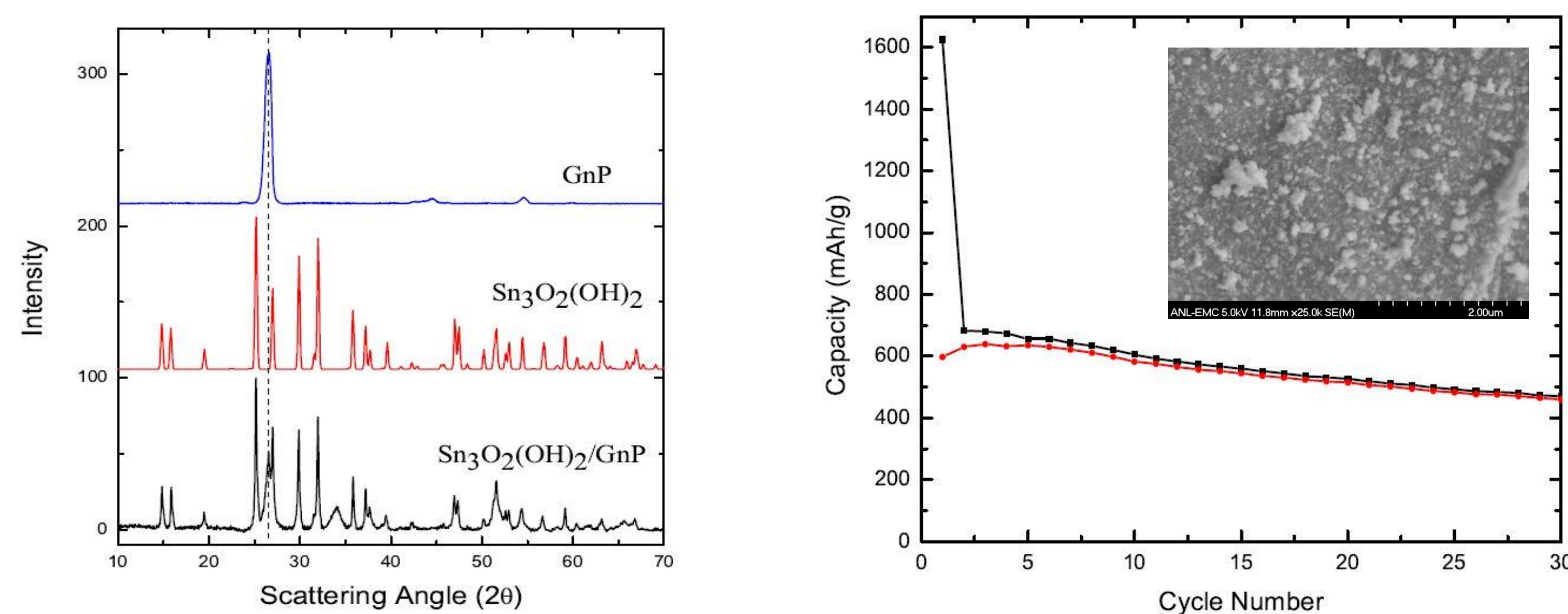
Integration of lithium-ion batteries (LIB) in large scale applications is contingent on the improvements in electrode materials. Tin (Sn) and tin oxide anodes could three-fold increase the capacity of currently utilized in LIBs carbon anodes (from 372 mAh/g for carbon to 994 mAh/g for Sn). However, structural stresses (up to 260% volumetric changes) during lithium intercalation/deintercalation create irreversible destruction of the anode and loss of connectivity which quickly reduces the overall capacity and efficiency. The approaches to mitigating this effect are reduction of particle sizes or addition of lithium-inactive elements to act as a conductor and buffer during volumetric changes. In our research we designed unique hybrid nanomaterials that incorporate both approaches: high energy density tin oxide nanoparticles are grown directly on nano-graphite sheets. With the modified particle morphology we were able to achieve good electrical conductivity to an ensemble of individual $\text{Sn}_3\text{O}_2(\text{OH})_2$ nanoparticles. We used in-situ x-ray absorption spectroscopy (XAS) to track the local Sn environment in $\text{Sn}_3\text{O}_2(\text{OH})_2/\text{graphene}$ nanoplatelets (GnP) as a function of charge/discharge to determine quantitatively observe these volumetric changes.



Schematic diagram of changes around Sn derived from in situ EXAFS modeling $\text{Sn}_3\text{O}_2(\text{OH})_2$. On first charge material segregates into Sn clusters with Li_2O layers around it. Individual atomic clusters expand/contract when charged/discharged. Isolation of atomic clusters results in loss of electrical connectivity and capacity degradation.

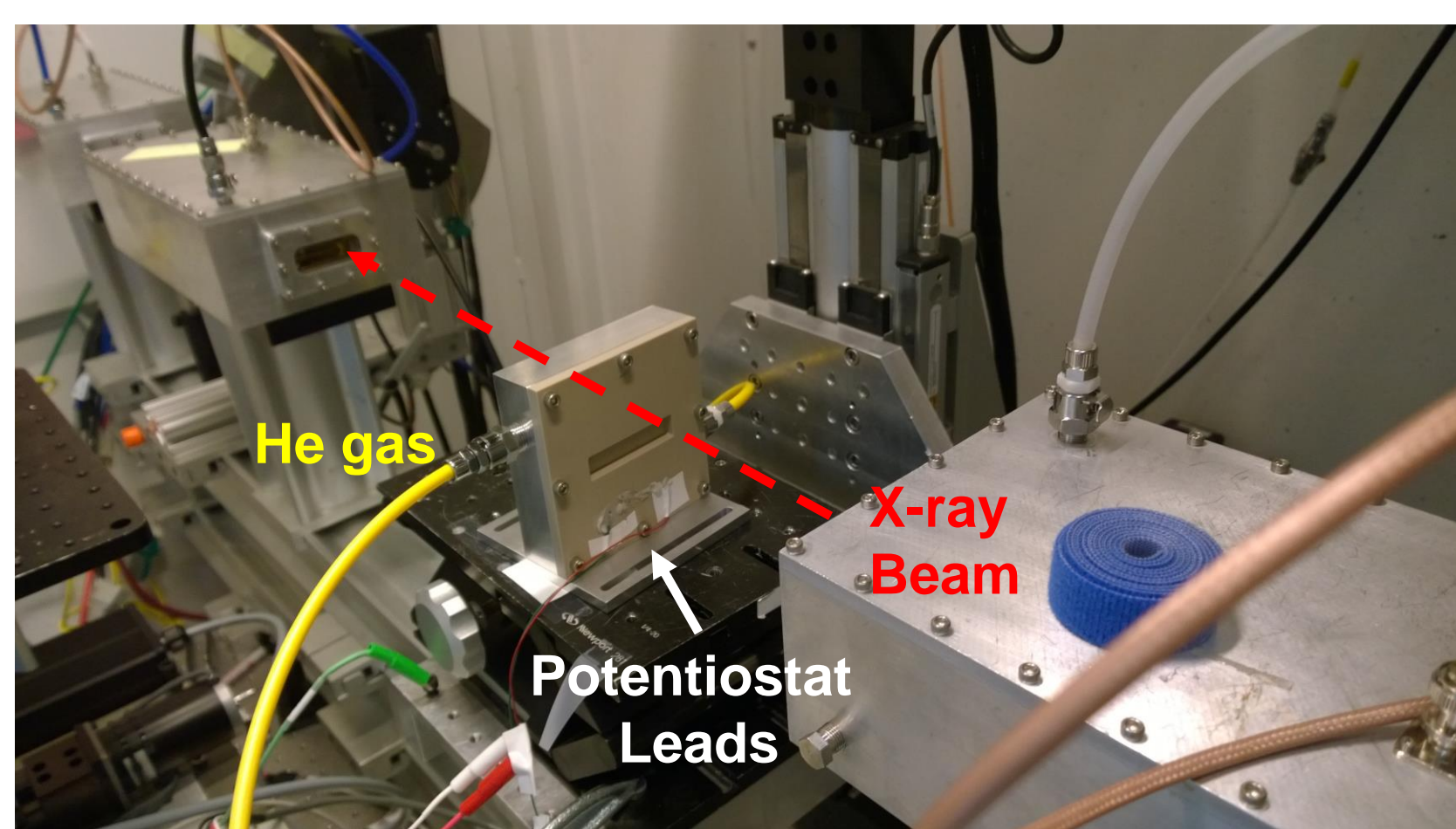
$\text{Sn}_3\text{O}_2(\text{OH})_2/\text{GnP}$ Synthesis

$\text{Sn}_3\text{O}_2(\text{OH})_2$ nanoparticles were synthesized on the surface of GnP through a one-pot solvothermal synthesis technique. The nanocomposites were characterized through x-ray diffraction (XRD) and scanning electron microscopy (SEM) images as shown below.



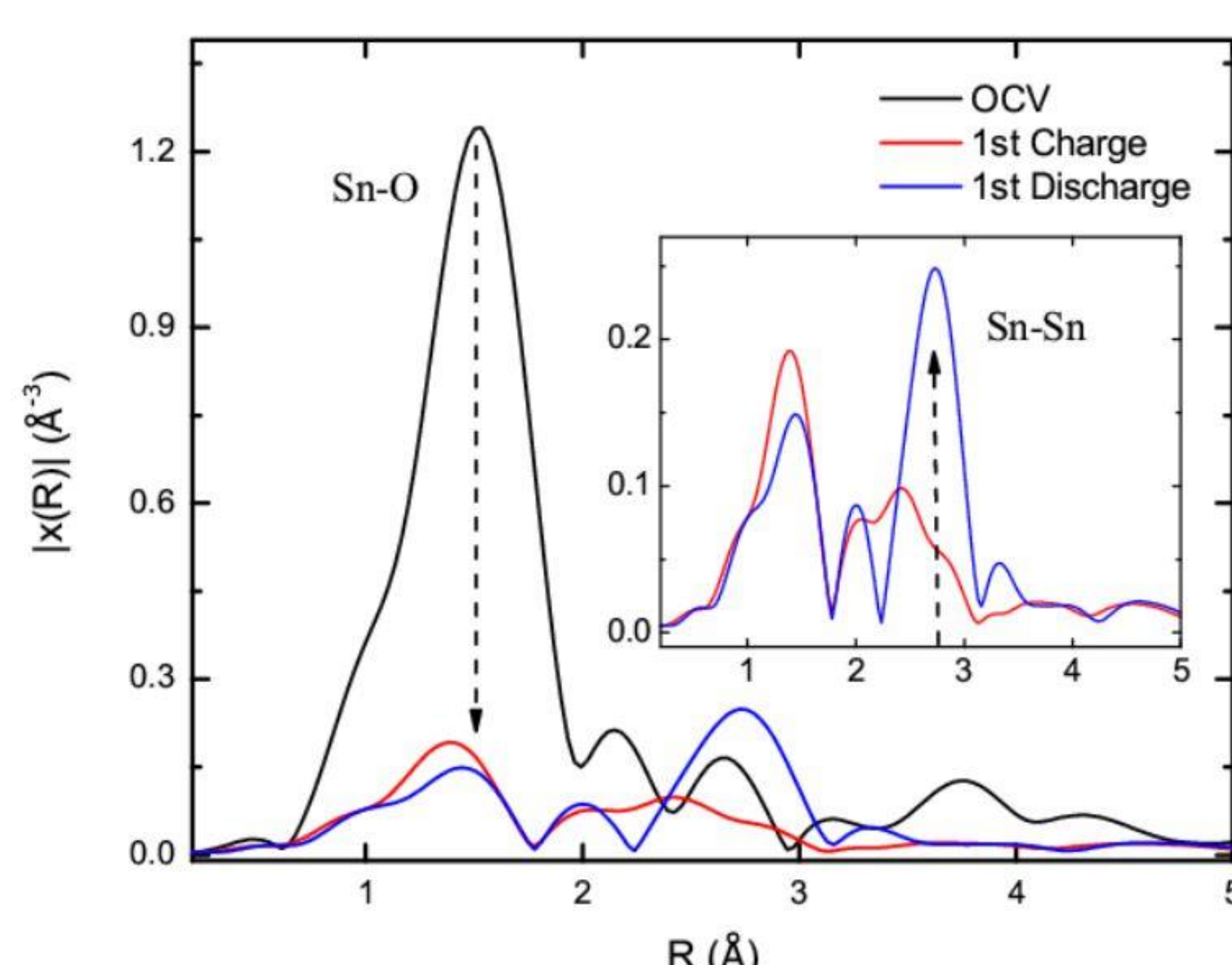
X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirm $\text{Sn}_3\text{O}_2(\text{OH})_2$ phase and 40-50 nm particle size of $\text{Sn}_3\text{O}_2(\text{OH})_2$ on the surface of the larger GnP through both XRD peak broadening and visual inspection of SEM images. First charge shows irreversible capacity of 1400 mAh/g and the reversible capacity of this hybrid anode materials starts at ~500 mAh/g and gradually fades with cycling.

XAS experimental set up. Electrochemical half cell placed inside in-situ box to ensure inert atmosphere with He flow. $\text{Sn}_3\text{O}_2(\text{OH})_2/\text{GnP}$ charged/discharged between 0.01 V and 1.5 V vs Li^+/Li galvanostatically. XAS spectra measured at 0.01 V (charged) and 1.5 V (discharged) potentials.

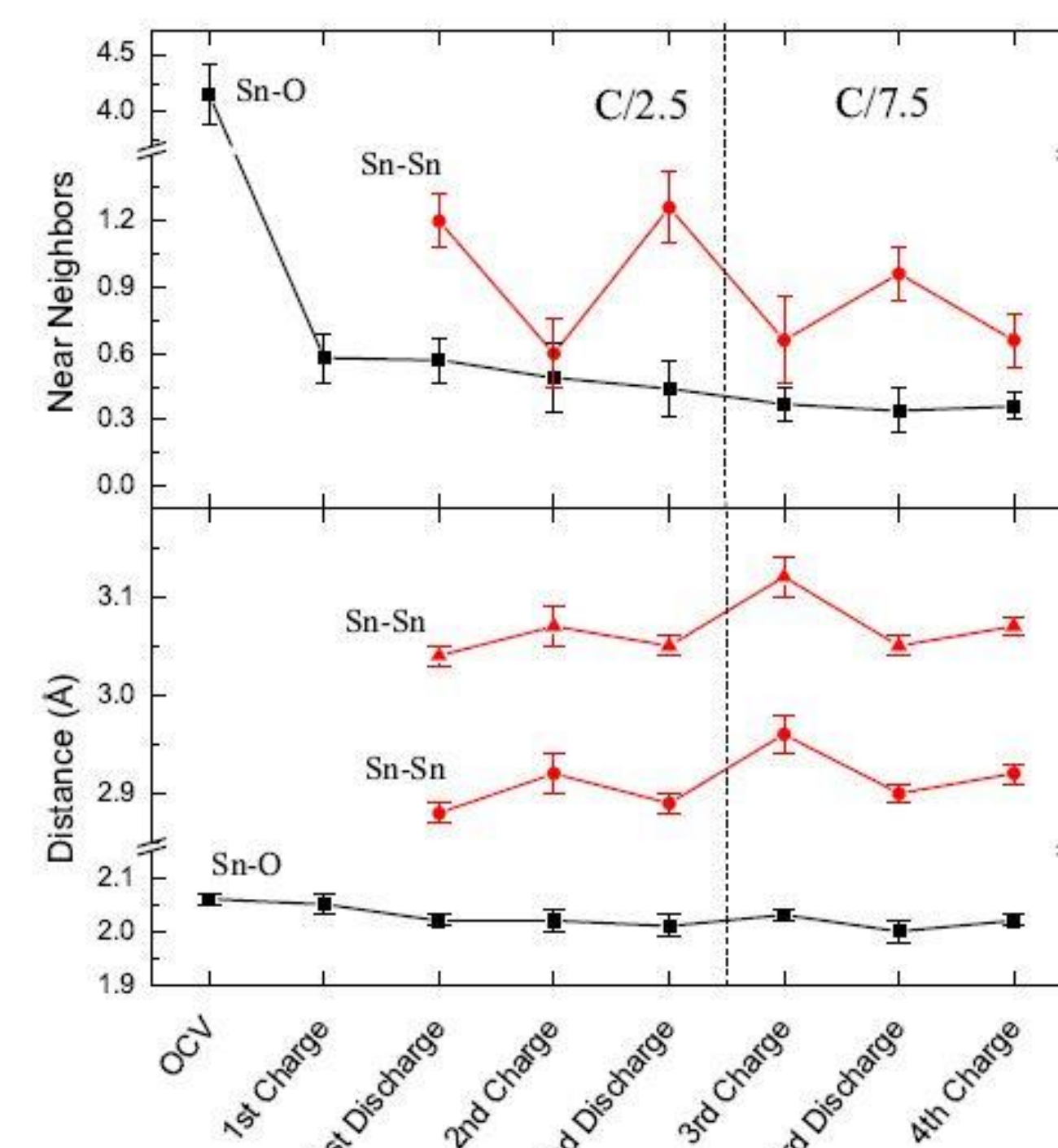


XAS Results

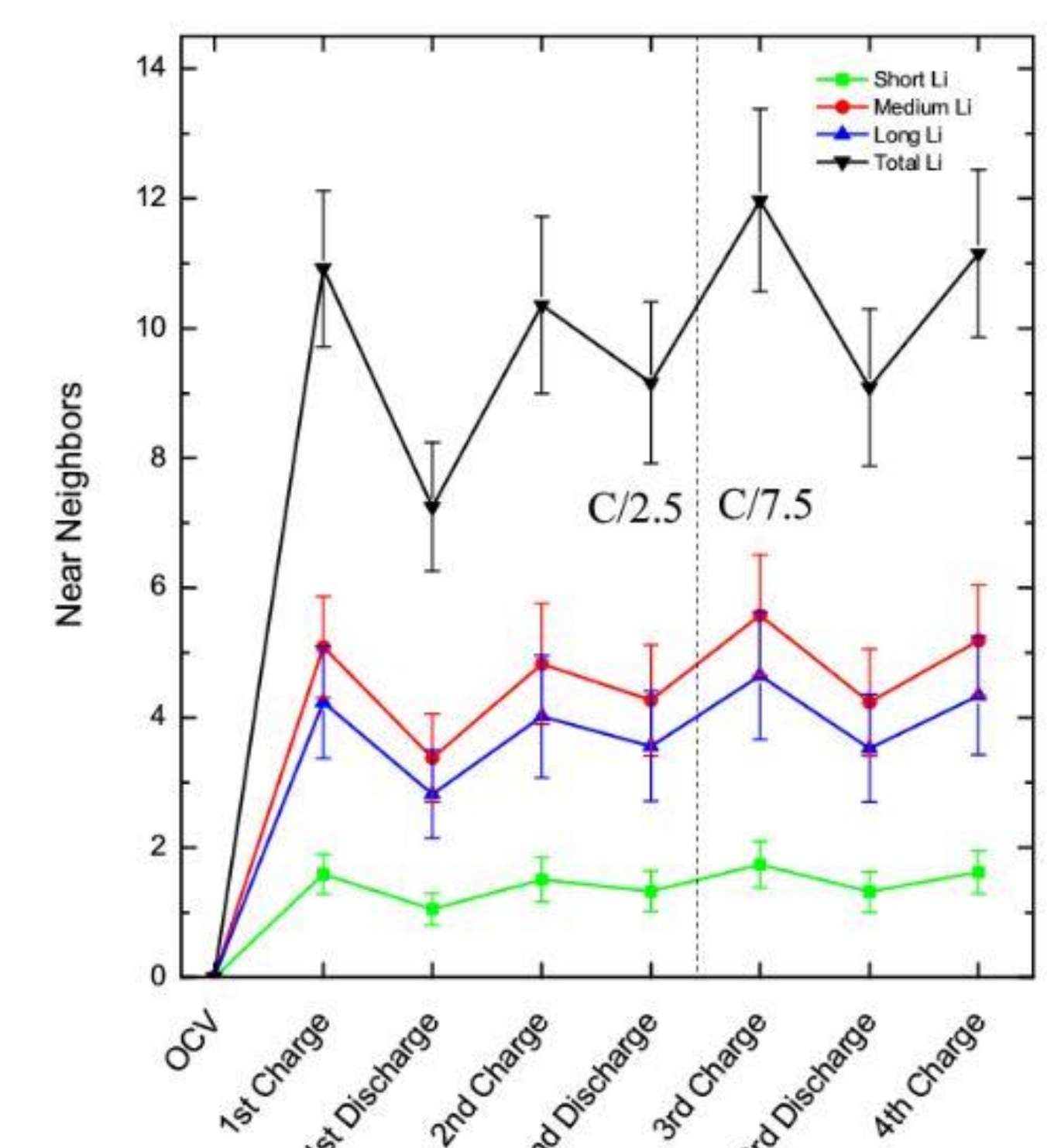
Analysis of extended x-ray absorption fine structure spectroscopy (EXAFS) measured at Sn-K edge allowed observation of detailed local atomic structural changes around Sn atoms in a charged or discharged state for four cycles.



R-space plot of starting material at open-circuit voltage (OCV), after 1st charge, and 1st discharge show drastic changes in Sn local environment. On first charging peak related to oxygen near neighbors decreases, and an Sn-Li phase evolves upon full charge. An amorphous Sn-Sn environment is created upon discharge. Subsequent cycles show similar behavior.



EXAFS fitting results for Sn-O and Sn-Sn paths. After the first charge, the Sn-Sn distances expand and contract with Li addition/removal. Similarly, the number of Sn-Sn near neighbors decreases/increases in a charged/discharged state.



EXAFS fitting results for the number of Sn-Li near neighbors. Li intercalation/deintercalation is clearly seen in a charged/discharged state. However, since Li is still present even in discharged states, it suggests that significant amounts of Sn clusters have lost electrical contact, therefore no longer participate in the lithiation process.

Summary

Through in-situ XAS measurements, the local structure around Sn atoms in $\text{Sn}_3\text{O}_2(\text{OH})_2/\text{GnP}$ nanocomposite anode for LIBs was observed during charge and discharge cycles. The expansion/contraction of Sn-Sn bonds during charge/discharge was quantified in both the atomic distances between Sn-Sn atoms along with the number of Sn near neighbors. The presence of Sn-Li neighbors in discharged states suggests a significant amount of Sn lost electrical contact, thus no longer participating in the electrochemical reaction which is reflected in the experimental loss of capacity in these materials.

Although our composite nanomaterials showed good conductivity to nanoparticles at macroscopic level, the crystalline structure of $\text{Sn}_3\text{O}_2(\text{OH})_2$ and formation of Li_2O layers around Sn-Li clusters is proposed as a mechanism for electrode passivation and capacity loss.

Acknowledgments

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