

Investigating the Electrochemical Reversibility of Transition Metal Oxide Conversion Materials Through STEM-EELS

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Current lithium ion battery technologies require improvements to their energy storage capacity and reversibility for wider deployment. One strategy for dramatically increasing energy storage capacity is by using electrode materials that undergo a conversion reaction with Li, such as nanoscale transition metal oxides. This conversion reaction describes a two-electron redox process that fully reduces the oxide to its metallic state along with concurrent formation of Li_2O , as seen in Figure 1A. Thus, it is possible to achieve twice the theoretical energy storage capacity over current batteries that operate through a single-electron Li-intercalation process. Unfortunately, conversion systems suffer from poor cycling issues due to irreversible phase transformations and the formation of electrically insulating reaction products (i.e. Li_2O), among other technical challenges. [1]

The conversion reaction mechanisms of several nanoscale transition metal oxides have been analyzed [2,3], but these studies largely focus on phase transformations during reaction and lack close analysis of the reaction products and their role in affecting reversibility. XANES studies have highlighted the importance of understanding interfacial structure and composition of reaction products in order to solve issues with irreversible cycling, due to their effects on electron and ion transport and electrochemical activity. [4]

In this presentation, we report deeper investigation into transition metal oxides as a conversion reaction material, focusing on the effects of reaction products on their electrochemical activity and reversibility. Utilizing the atomic-resolution capabilities of STEM, it is possible to correlate the electrochemistry with the (sub-)nanoscale interfacial structure and composition of the reaction products. Particle size, surface structure, and distribution can be directly imaged (Figure 1B,C) and compared across a series of transition metal oxides (e.g. Fe_2O_3 , Co_3O_4 , NiO) after conversion. Furthermore, inhomogeneities in composition and bonding chemistry of reaction product species are revealed by considering characteristic EELS edge features across the entire energy loss spectrum. For example, the full signature of NiO conversion to Ni and Li_2O can be seen in Figure 1D, where lithiation leads to a strong Li K signature (55 eV) and notable shift in the maximum of the O K edge (538 eV to 535 eV), but also noticeable shifts in the main plasmon peak (25 eV to 20 eV) and changes to the fine structure of the Ni L_3 edge (855 eV). EELS maps based on the strong changes to many edge features also reveal composition distribution from length scales of <1nm to ~100nm.

This close structure/composition analysis of conversion reaction products provides insight into the nanoscale issues hindering improved electrochemical performance of transition metal oxides. Moreover, the work covered in this presentation should lead to developing new strategies for improving on the electrochemical reversibility issues preventing conversion materials from becoming a larger player in the battery field [5].

References:

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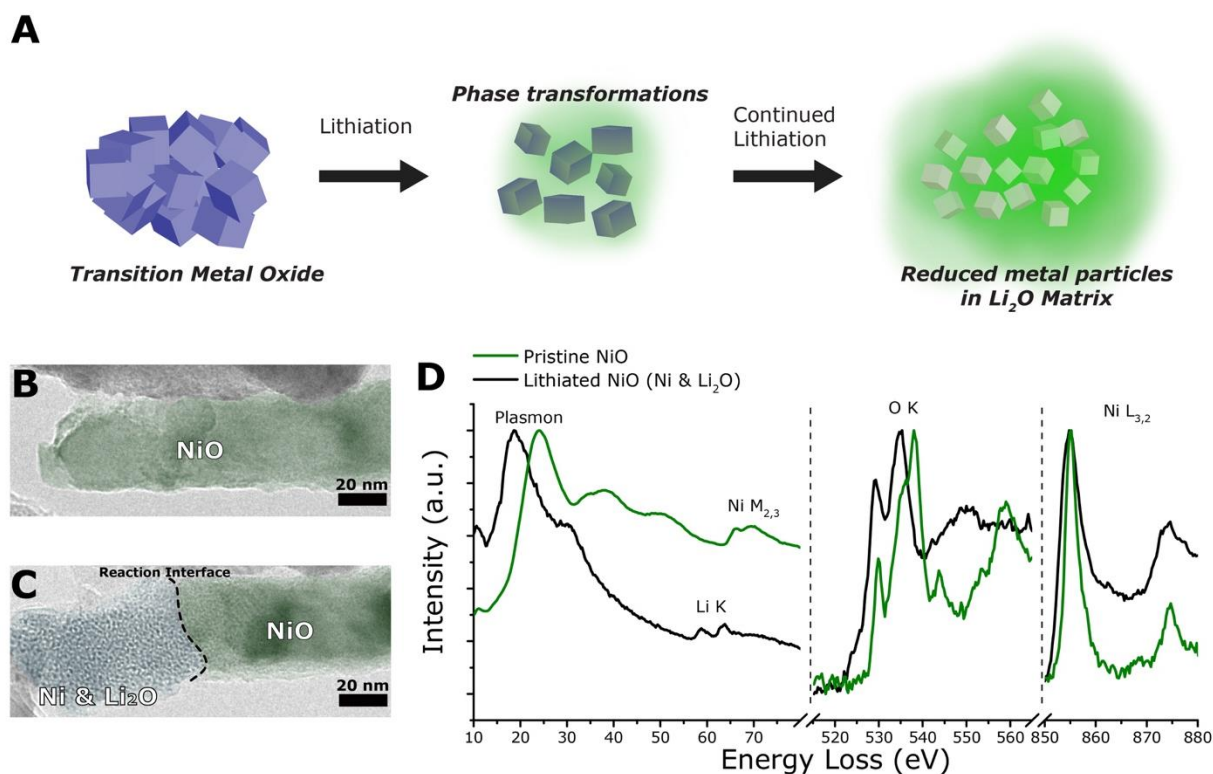


Figure 1. Chemical and structural evolution of NiO during conversion. (A) Schematic illustration of the conversion reaction in transition metal oxides. (B) Pristine NiO in a nanowire morphology (green) and (C) the same nanowire where part of its structure has undergone conversion (light blue). The speckled contrast seen in the reacted segment is a result of the phase transformations that occur during the conversion process; Ni particles approximately 3 nm in size form in a matrix of Li_2O . (D) EELS spectra of the pristine NiO wire (green) and the lithiated and reacted segment (black). Analysis of features across the entire energy loss spectrum show notable shifts in the plasmon peak maxima upon lithiation along with changes in the fine structure of O K and Ni L edges.