

The Effects of Vanadium Substitution on One-dimensional Tunnel Structures of Cryptomelane: Combined TEM and DFT Study

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Lithium-ion batteries play a critical role as portable energy storage systems in modern society. The major components of lithium-ion batteries are the cathode, anode, separator, electrolyte and binder. The central scientific problem of these systems that needs to be addressed is how to scientifically advance the different components to improve the rate capability, reduce cost, increase cycle life and achieve safe operation.

Among the candidates, manganese oxides have the special advantage of low-cost.[1,2] Further, the rich structural polymorphs of manganese oxide provide vast opportunities for exploring the effect of material structure on electrochemistry. Tunnel-type (or hollandite) manganese oxide with one-dimensional Li diffusion channels is a very interesting material for studying the fundamental electrochemistry of manganese oxides. Hollandite structures have attracted special attention due to the homogenous tunnel structure and moderate space within the tunnel.

Structural features including particle size, surface defects and volume (bulk) defects can impact the electrochemistry of battery materials. Nanomaterials are beneficial for lithium-ion batteries as they provide a short Li diffusion path length. Both surface structure and the stability of electrode materials are critical to the electrochemistry, as the surface is the interface with the electrolyte and structural stability facilitates the diffusion of Li ions from electrode to electrolyte. Surface coating and doping have been generally adopted to stabilize the surface structure for high voltage battery electrode materials. In addition, surface defects are beneficial for Li diffusion across tunnels. Finally, volume (bulk) defects can be important, as demonstrated by the improved cycling performance in Ni-rich layered cathodes caused by tailoring grain boundaries within the material.

State-of-the-art scanning transmission electron microscopy (STEM) and in-situ TEM techniques are carried in the present study.[3] We substitute Mn atoms with V to tune the electrochemistry of cryptomelane (K_xMnO_2) from the perspective of its atomic structure. In the pristine nanorod, irregular 2×1 and 2×3 boundary tunnels are identified along with the dominant 2×2 tunnel framework. Upon V substitution, these irregular tunnel sizes are no longer observed while tunnel lengths are reduced. Atomic level electron energy loss spectroscopy (EELS) mapping shows that V dopants occupy the tunnel wall positions, directly substituting Mn atoms as shown in Figure 1a with agrees with the DFT simulation results in Figure 1b-1d very well.[4]

We carried out in-situ and ex-situ EELS measurements using a nanofactory holder using Li metal with partial oxidation layers to probe the cryptomelane samples. Both in-situ and ex-situ results show that valence change of Mn is much larger than that of V upon reduction by lithium metal. Consistent with the experimental observations, DFT simulations also reveal the substituted V ions to be in a slightly oxidized state and that upon lithiation V is reduced only slightly as compared to Mn. In a former theoretical paper,[5] it is predicted that there might be two possible structural evolution mechanism upon lithiation. In our ex-situ study on lithiated samples, we observed the evidence for both evolution mechanisms. Our future work will further clarify the parameters affecting the different structural evolution pathways for the tunnel structures.

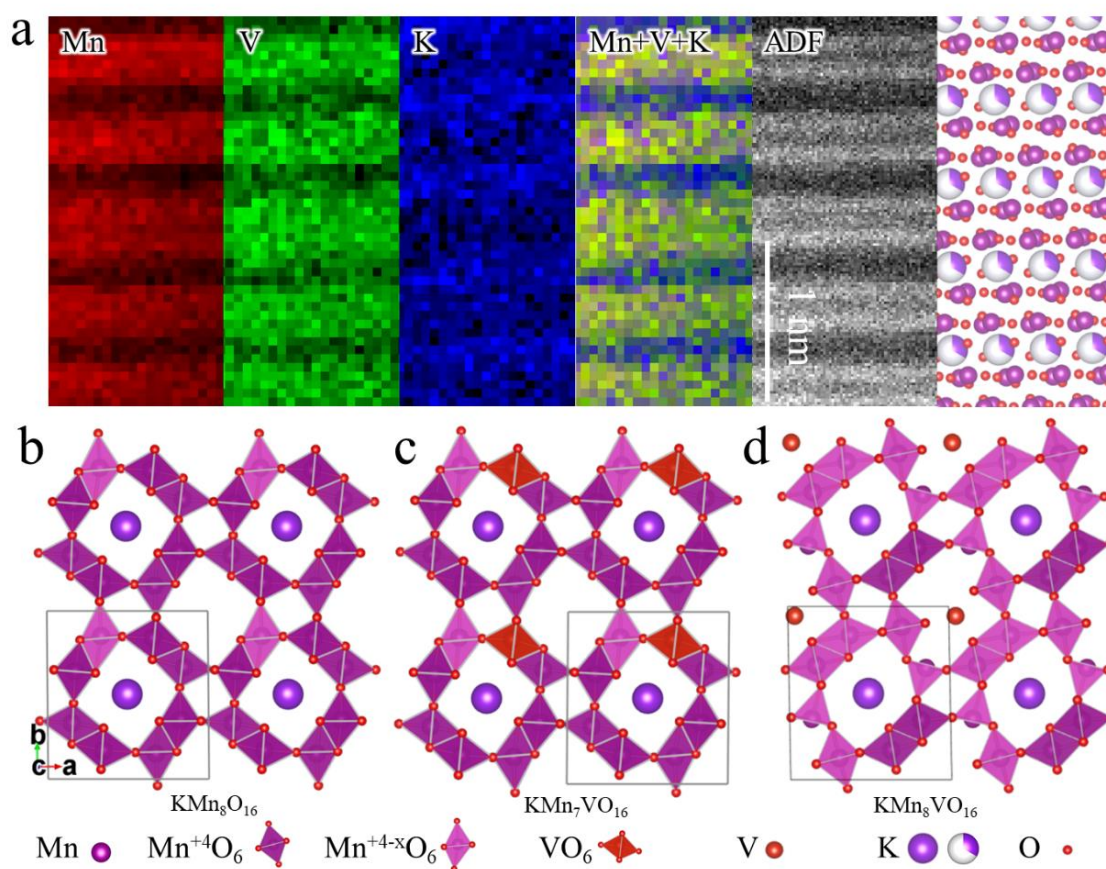


Figure 1. (a) STEM EELS mapping results for the 5% V- substituted sample (K_{1.02}Mn_{7.63}V_{0.37}O₁₆) showing Mn (red), V (green) and K (blue) with composite (Mn-V-K), and related ADF image and structural models shown to the right; (b) Structural model for pristine cryptomelane (KMn₈O₁₆), with K⁺ in the tunnel highlighted as a large ball and the reduced Mn shown in semi-transparent polyhedra; (c) Structural model for V-substituted cryptomelane (KMn₇VO₁₆), with dopant in the tunnel wall shown as red polyhedra; (d) Structural model for V-centered cryptomelane (KMn₈VO₁₆), with dopant in the tunnel shown as red ball.

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