

## Dynamic Observation of Tunnel-driven Lithiation Process in Single Crystalline $\alpha$ -MnO<sub>2</sub> Nanowires

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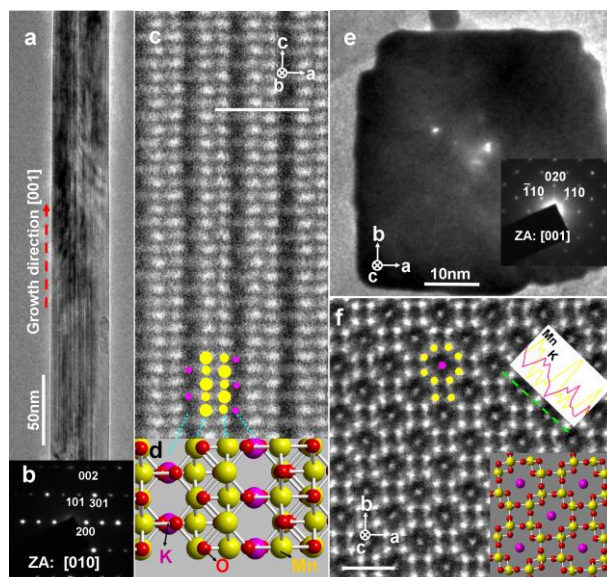
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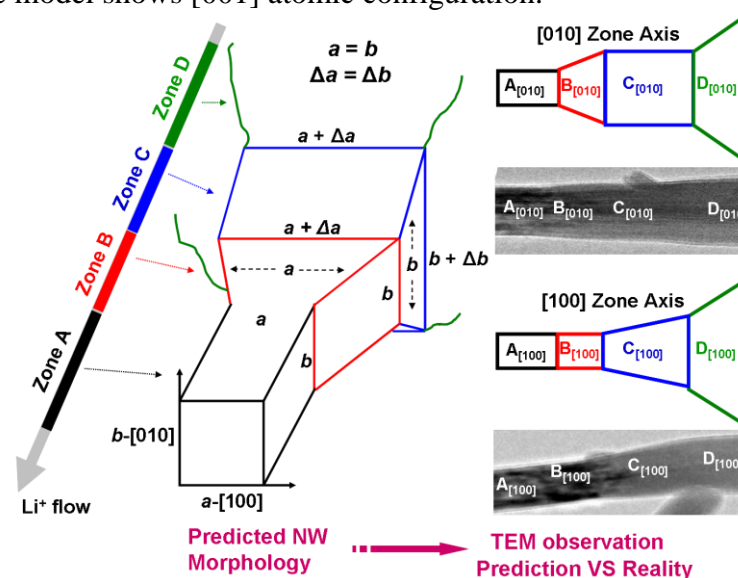
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Manganese dioxide (MnO<sub>2</sub>) possess various allotropic forms such as  $\alpha$ -,  $\beta$ - and  $\gamma$ -phases, which are constructed by combination of octahedral [MnO<sub>6</sub>] building blocks to exhibit various tunneled structures. These unique structures are believed to account for the various characteristics of MnO<sub>2</sub> when it is employed as electrode material in lithium (ion) batteries [1-2]. There is, however, lack of direct proof demonstrating the role of tunneled structure during electrochemical lithiation/delithiation of MnO<sub>2</sub>.

In this work, by applying aberration-corrected scanning transmission electron microscopy (ACSTEM) to single  $\alpha$ -MnO<sub>2</sub> nanowire along both axial and radial directions, the tunneled structure is clearly shown and characterized in Figure 1. The  $\alpha$ -MnO<sub>2</sub> nanowire is single crystalline and grows along [001] direction. Cross-sectional ACSTEM shows that the nanowire has a squared cross section and 2×2 tunnels align parallelly along its growth direction [001], matching very well with simulated crystal structure. An open cell design inside TEM for dynamic observation of MnO<sub>2</sub>'s lithiation/delithiation process is also demonstrated. It is found that upon lithiation, the  $\alpha$ -MnO<sub>2</sub> nanowire shows different orientation-sensitive morphologies. That is,  $\alpha$ -MnO<sub>2</sub> unit cell expands asynchronously along [100] and [010] directions, resulting in macroscopic difference under [010] and [100] zone axes observations. Electron Energy Loss Spectroscopy further confirms such an asynchronous expansion property via quantification of Mn valence during lithiation. DFT simulation demonstrates that the asynchronous essential originates from the specific Li-occupancy sequence at Wyckoff 8h sites inside  $\alpha$ -MnO<sub>2</sub>'s 2×2 tunnels. Following the theory, the predicted morphology of one partially lithiated nanowire and the experimental observation are shown in Figure 2, where both match very well. These findings provide fundamental understanding for stepwise potential variation during the discharge of Li/ $\alpha$ -MnO<sub>2</sub> batteries as well as the origin for low practical capacity and fast capacity fading of  $\alpha$ -MnO<sub>2</sub> as an intercalated electrode.



**Figure 1** (a,b) TEM image of a single  $\alpha$ -MnO<sub>2</sub> nanowire and its SAED along  $\langle 010 \rangle$ ; (c,d) HAADF image of the same  $\alpha$ -MnO<sub>2</sub> nanowire and the atomic model structure along  $\langle 010 \rangle$  direction; yellow spots indicate Mn atoms, while pink represents K and red indicates O atoms. (e) TEM image of an  $\alpha$ -MnO<sub>2</sub> nanowire cross section and the corresponding SAED along  $[001]$  direction; (f)  $[001]$  atomic resolution HAADF showing K (pink) atomic columns and Mn (yellow) columns forming  $1 \times 1$  and  $2 \times 2$  tunnels; scale bars in c and f are both 1 nm; two inserts: the green line indicates EDS scan to distinguish Mn and K columns; the model shows  $[001]$  atomic configuration.



**Figure 2** Left: 3D model showing the asynchronous expansion of a partially lithiated K<sup>+</sup>-stabilized  $\alpha$ -MnO<sub>2</sub> nanowire; Right: Schematic  $[010]$  and  $[100]$  zone axes observation under TEM and the experimental TEM results. The color code (black, red, blue and green) indicates the corresponding zones observed in-situ.

#### References:

- [1] Chen K. et al, The Journal of Physical Chemistry C **117** (2013), p.10770.
- [2] Xun Wang, Y. L., Journal of the American Chemical Society **124** (2002), p.2.