

Dynamic Study of Sodiation Process in Single Crystalline α -MnO₂ Nanowires

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α -MnO₂ is widely applied as an energy storage electrode in rechargeable batteries due to its unique 2×2 tunneled structure that facilitates diffusion of charge carriers^[1]. By now, it is unclear how the intercalated charge carriers such as Li⁺, Na⁺ and Mg²⁺ interact with the tunnel-based host due to the lack of atomic scale understanding of the tunnel configuration and the complicated effect from generally existing tunnel stabilizers (like K⁺).

In this paper, using aberration-corrected scanning transmission electron microscopy (ACSTEM) to cross sectioned K⁺-stabilized α -MnO₂ nanowires, the 1×1 and 2×2 tunneled structures as well as defective 2×3 and 2×4 tunnels are clearly demonstrated at atomic level. An open cell design in TEM for dynamic study of α -MnO₂'s sodiation process confirms that an intermediate phase Na_xMnO₂ will first appear upon sodiation and finally the tunneled structure will totally collapse, generating Mn₂O₃ polycrystals embedded in Na₂O matrix. The originally existing tunnel stabilizer K⁺ will be partially removed upon sodiation, as shown in Figure 1. It also shows that defective 2×3 and 2×4 tunnels function as the fast sodiation path during initial Na⁺ intercalation stage. This study provides fundamental understanding of the tunnel-charge carrier interaction and reveals the structural evolution mechanism of sodiation in α -MnO₂. The key role of 2×3 and 2×4 tunnels on increasing the discharge rate is also demonstrated, shedding light on potential tunnel-level modification for improving the overall performance of tunnel-based electrodes.

Reference:

[1] Yuliang Cao et al, *Advanced Materials* **23** (2011), p. 3155

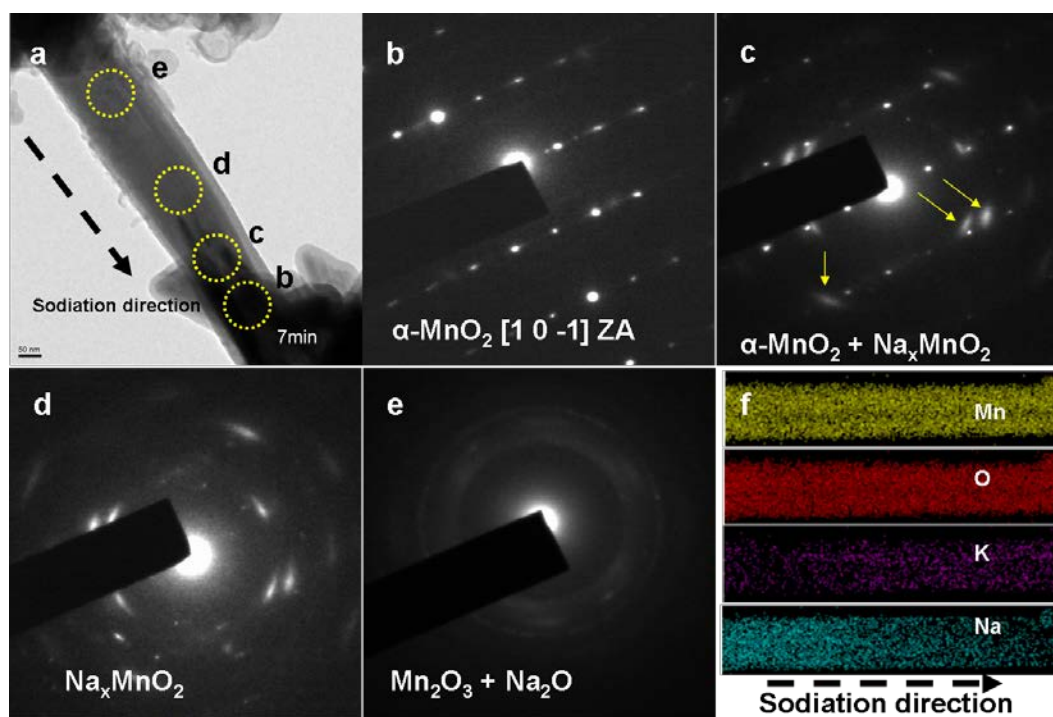


Figure 1 (a) in-situ TEM image of one α - MnO_2 nanowire being sodiated with four areas circled as b, c, d and e; (b-e) corresponding selected area diffraction patterns from areas b, c, d and e as indicated in (a); (f) EDS mappings of Mn, O, Na and K inside one partially sodiated K^+ -stabilized α - MnO_2 nanowire.