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Dynamic Study of Sodiation Process in Single Crystalline α-MnO_2 Nanowires

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α-MnO_2 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 Mg^{2+} 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-MnO_2 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-MnO_2's sodiation process confirms that an intermediate phase Na_xMnO_2 will first appear upon sodiation and finally the tunneled structure will totally collapse, generating Mn_2O_3 polycrystals embedded in Na_2O 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-MnO_2. 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

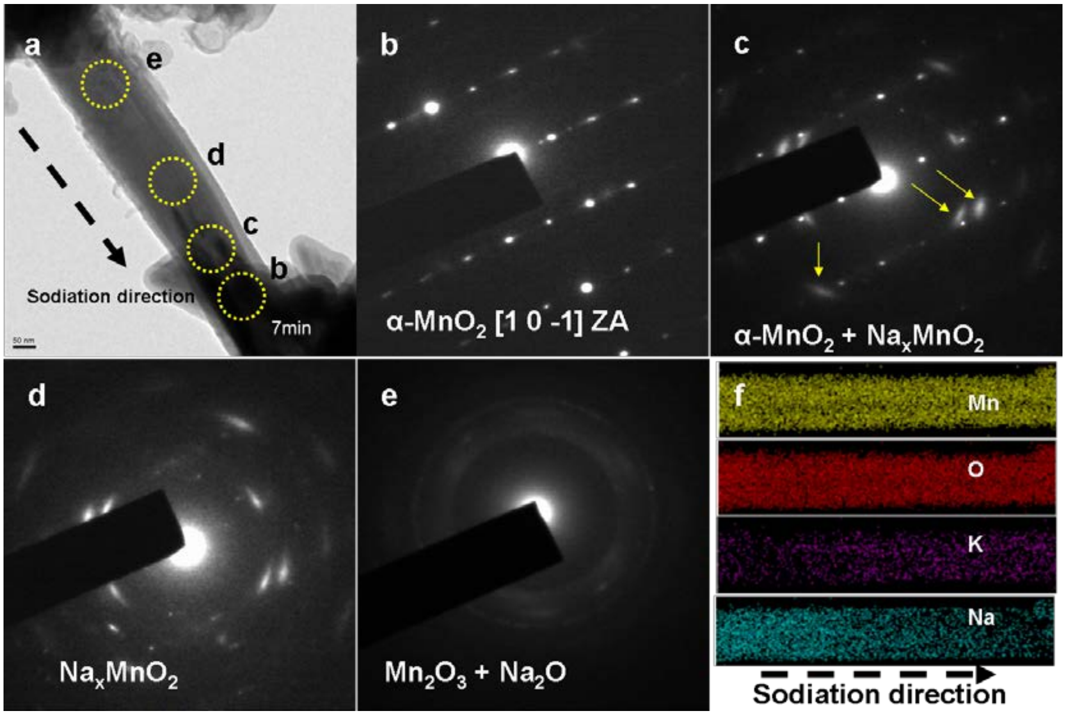

Figure 1 (a) in-situ TEM image of one α-MnO_2 nanowire being sodiated with four areas circled as b, c, d and e; (b-e) corresponding selected area diffraction patterns from areas b, c, d and e as indicated in (a); (f) EDS mappings of Mn, O, Na and K inside one partially sodiated K^+-stabilized α-MnO_2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