

Discrete Hopping Lithiation of ZnO Nanowires

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Lithium ion batteries (LIBs) are attracting attention for energy storage device for electric vehicles where high power, energy density, and cyclability are required. Nanowire (NW) electrode [1] has advantage over conventional electrodes due to its unique geometry that enhances the electron and Li^+ transport. In addition, NWs can accommodate large volume change during charge/discharge cycles [2], leading to the improved cyclability and stability. In this study, the lithiation processes of individual ZnO NW electrodes in a LIB configuration were observed by *in-situ* transmission electron microscopy (TEM) using a unique nano-battery setup inside the TEM [3] developed recently for observing the electrochemistry processes in real time.

The nano-battery consisted of a single ZnO NW as an anode, an ionic-liquid electrolyte (ILE), and LiCoO_2 particles as cathode. Figure 1 shows the lithiation process of the ZnO NW. The initial NW was straight and had smooth surface (Fig. 1A). After contact with ILE, a potential of -4.0 V with respect to the LiCoO_2 counter electrode was applied to the ZnO NW (Fig.1B). The solid-state reaction front propagated along the longitudinal direction of the NW away from the ILE (Fig. 1B-K). As the reaction front propagated, the diameter and the length of the NW increased, causing the NW to bend. Figure 1L-O shows detailed view of the reaction front propagation. Interestingly, the reaction front did not move progressively along the NW. Instead, it advanced by initiating discrete cracks about 80 nm before the reaction front (Fig. 1M, red arrowheads). The lithiation then propagated laterally along its two side (Fig. 1 N-O). The cracks divided the NW into smaller segments. The new crack grew in a similar fashion to the old crack, and this process repeated until the entire nanowire was lithiated. From the above observations, the lithiation of the ZnO NW consists of three steps. 1) The Li^+ adsorbs on the NW surface initiating the lithiation. 2) The reaction leads to crack formation in the NW making path from the surface inward the bulk. 3) Li^+ penetrates into the NW from the crack and reacts with the NW. The lithiation process is schematically illustrated in Fig. 2A. The crack formation during the lithiation process caused the ZnO NW to break into multiple segments (Fig. 2B).

The fracture of the NW is considered to cause poor cyclability of the battery when ZnO is used as the LIB electrode. Our observations provide important insight for developing battery with higher performance and longer lifetime by providing the failure mechanism of the electrode material [4].

References

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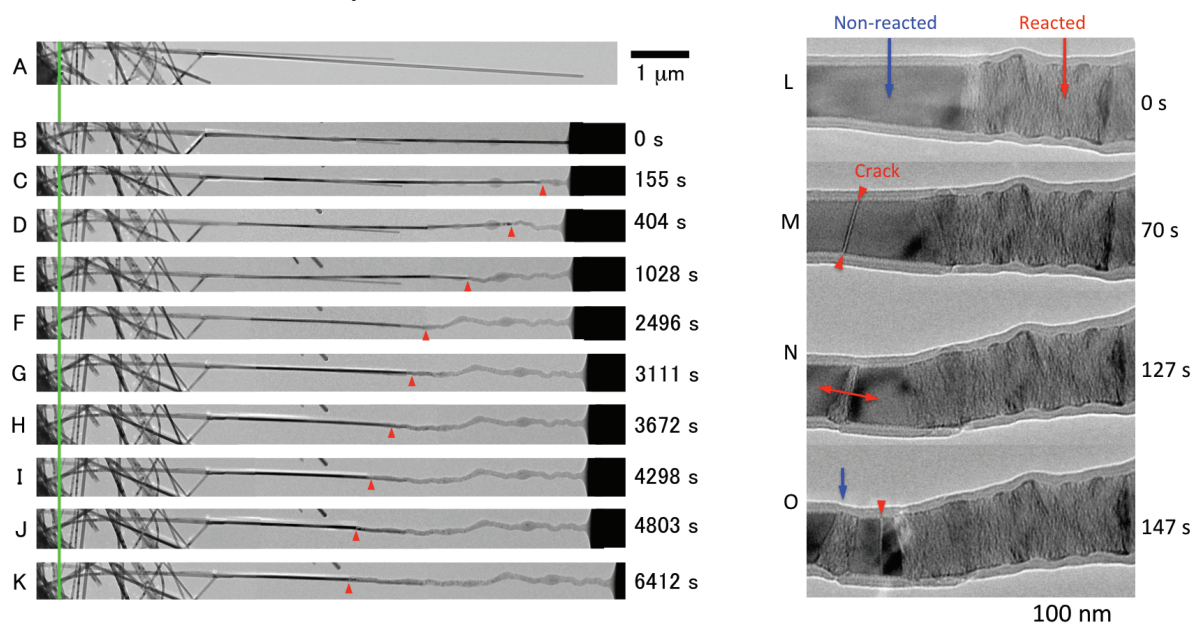


FIG. 1. (A-K) Typical lithiation process of the ZnO nanowire. Triangles in the figure indicate the propagation of the reaction front during the lithiation. (L-O) Discrete crack nucleation ahead of the reaction front. Cracks formed near the reaction front in the non-reacted part of the ZnO NW as indicated by the triangles in the figure separating the NW into multiple segments.

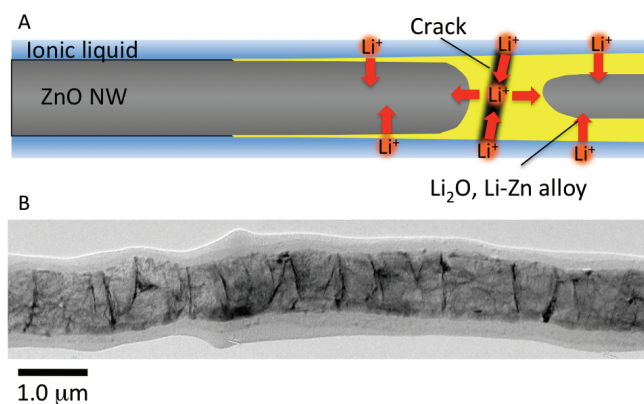


FIG. 2. (A) Schematic illustration explaining the lithiation mechanism of ZnO NW. The lithiation first takes place at the surface of the NW forming a crack from the surface inward the core. Then, the Li⁺ penetrates inside the NW from the crack. As a result, the NW was separated into multiple segments after the lithiation (B).