

In Situ TEM Studies of Li and Na ion Transport and Li/Na-Induced Phase Transitions in Crystalline Materials

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Although batteries are inherently simple in concept, surprisingly their development has progressed much slower than other areas of electronics. This slow progress is due to the lack of suitable electrode materials and electrolytes, together with difficulties in mastering the interfaces between them. Working out the drastic impact of interfaces on ions transport and understanding the interrelationship between the electrode microstructure and battery performances is important for the design of high performance lithium ion batteries. For instance, it is still not well understood that how defect structures such as twin boundaries affect the transport of ions within crystalline materials. Also, triggered by the recent exploration of alternative technologies to Li-ion batteries, sodium has become a viable alternative to Li-ion batteries. Na-ion batteries hold the potential to become the technology of choice for large-scale electrochemical energy storage thanks to the high sodium abundance and low costs. However, the investigation of suitable electrode materials for sodium ion batteries is still in its infancy and few electrode materials meet the performance requirement for practical applications.

In-situ transmission electron microscopy (TEM) has been shown to be a very powerful technique in shedding light to some of the mysteries in electrochemical performance of new materials. Using this technique, here, we report our new findings on Zn-Sb intermetallic alloys, SnO₂ nanowires, and MnO₂ nanorods. Sb-based intermetallics, such as Zn-Sb system, which have been proved to be promising anode materials for Li-ion batteries, are also capable of storing of sodium ions. We investigated the microstructural changes and phase evolution of the Zn-Sb intermetallic nanowires using in-situ TEM¹. Our results indicate that the reaction between Zn-Sb and sodium proceeds through a different pathway during the first compared to the subsequent cycles. After first sodiation, the initial single crystal Zn₄Sb₃ nanowire change into the crystallized Na₃Sb and NaZn₁₃ nanoparticles; upon extraction of Na⁺ (desodiation), the Na₃Sb and NaZn₁₃ phases develop into the crystallized NaZnSb and Zn particles. Atomic resolution imaging shows that NaZnSb has a layered structure, which provides channels for fast Na⁺ diffusion.

We also explored the lithiation behavior of the individual SnO₂ nanowires containing twin boundary (TB). Our in-situ TEM results show that the Li transport pathways will totally change when the (101) TB exists inside the SnO₂ nanowires comparing with the single crystal SnO₂, in which the lithium ions preferred to diffusion along the [001] direction.¹ Direct atomic-scale imaging of partially lithiated TB-SnO₂ nanowire shows that the lithium ions prefer to intercalate in the vicinity of the (101) TB, which acts as a conduit for lithium ion diffusion inside the nanowires.

Furthermore, we utilized aberration-corrected scanning transmission electron microscopy (ACSTEM) to single α -MnO₂ nanowire to image the tunneled structures. Cross-sectional ACSTEM shows that the nanowire has a squared cross section and 2×2 tunnels align parallel to its growth direction [001]. An open cell design inside TEM for dynamic observation of MnO₂'s lithiation/delithiation process is also demonstrated. It is found that upon lithiation, the α -MnO₂ nanowire shows different orientation-sensitive morphologies. That is, α -MnO₂ 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.

These findings provide fundamental understanding for how Li and Na can be transported within crystalline materials. We also have shown that the induced phase transformation can be different in the presence of defects.

References:

- [1] A. Nie, R. Shahbazian-Yassar, et al. *Nano Lett.* **15** (2015), p. 610.
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