

## Towards Beyond-Lithium Batteries: New Insights from In Situ TEM Combined with Theoretical Modeling

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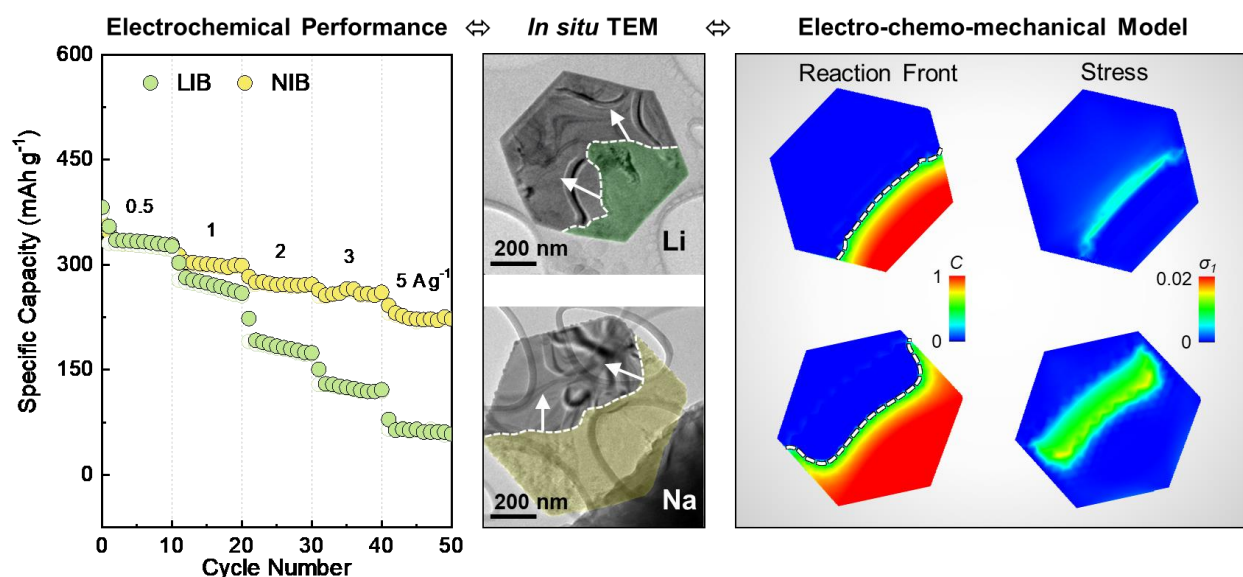
In situ transmission electron microscopy (TEM) has gained fast progress in the past decade and attracted tremendous attention in diverse scientific research because it can acquire information related to the dynamic material behavior along with the simultaneous property measurement of the target material system undergoing various controlled physical and chemical processes [1]. Rechargeable batteries are crucial for energy storage that underpins the advancement of consumer electronics and automobile propulsion technologies and further become an essential enabling technology for climate neutrality due to its capability to integrate renewable energy resources into viable power-grid applications. Despite the great success in commercial market, Li-ion batteries are still insufficient to meet the ever-growing energy demand for improved energy density, lifetime, and safety in large-scale and power-intensive devices, calling for alternative beyond-Li technologies. Therefore, fundamental understanding of the structure-property relationship of new battery materials with novel structures is critically needed. Specifically, in situ TEM has been widely used to carry out spatiotemporal characterization of materials transformation during electrochemical reactions [2], which can be further combined with theoretical modeling to offer insightful information as guiding principles for the design and development of beyond-Li batteries.

Here, we report the systematic applications of in situ TEM for comparative studies of anode materials used for Li-ion batteries (LIBs) and sodium-ion batteries (NIBs). The exemplar in situ TEM case studies focus on electrode materials with three different reaction mechanisms, i.e., intercalation, alloying, and conversion, as well as their combinations, particularly focusing on NiO [3, 4], black phosphorus [5], and bismuth telluride [6]. In a typical in situ TEM operation, we build nanoscale battery cells to include active electrode materials and alkali metals using in situ dry-cell setup and perform cyclic discharge and charge processes in potentiostatic mode. By comparison between electrochemical reactions with Li and Na, we found that reaction mechanism, reaction pathway, and reaction kinetics may be largely different between the corresponding lithiation and sodiation processes. These distinct behaviors may stem from various factors, such as ionic diffusion barrier, electrochemically-induced stress, and geometric constraint, which can be simulated by theoretical modeling and calculation. For example, in the scenario of electrochemical reactions of two-dimensional bismuth telluride with Li and Na (Figure 1), we found that both lithiation and sodiation were carried out through two-step conversion and alloying reactions, missing the expected intercalation step at the beginning. It is also worth noting that sodiation exhibited unexpected high reaction kinetics than lithiation, in accordance with its superior high-rate performance in coin-cell tests. This phenomenon was further explained by first-principles calculations and electrochemo-mechanical modeling, which suggested the critical interfacial stress effect induced by the geometric dependence of reaction front propagation, as shown in Figure 1. The comparative investigation of electrode material behaviors in LIBs and NIBs provides valuable insights into

understanding the alkali-ion electrochemistry and kinetics that can be further leveraged as design principles for continued development of Li-ion and beyond-Li battery technologies.

#### References:

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**Figure 1.** Comparative study of electrochemical lithiation and sodiation of bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) nanoflake anode materials using the combination of in situ TEM and electro-chemo-mechanical modeling, providing insights into mechanistic understanding of high Na-ion kinetics induced by the geometry-dependent reaction front and interfacial stress.