

Strain Coupling During Lithiation of a Fe₃O₄/SrTiO₃ Epitaxial Thin Film

Sooyeon Hwang¹, Qingping Meng¹, Dong Su¹, Kim Kisslinger¹, Yimei Zhu¹, Eric A. Stach¹, Ping-Fan Chen² and Ying-Hao Chu^{2,3}

¹ Brookhaven National Laboratory, Upton, New York, USA

² Institute of Physics, Academia Sinica, Taipei, Taiwan.

³ National Chiao Tung University, Hsinchu, Taiwan.

Strain-related issues are of the extraordinary importance for the performance of lithium ion batteries. For the conversion- and alloy-types electrode compounds, the cracks originated from the electrochemically-induced-strains are considered as the primary reason for their capacity fading and short cycle life[1]. Further, the transport of lithium ions themselves is affected by the strain during insertion/extraction into/from active materials. Besides electrochemically-induced-strain instigated inside single particles, the external strain also exist due to solid-to-solid interfaces in the electrode. For example, during operation, each particle undergoes volumetric changes, which generates external strain to neighboring particles. In all-solid-state-batteries, external strain is a more important issue due to the solid nature of electrolyte. Even though the electrode in lithium ion batteries can be influenced by various external and internal sources of strains, it is still not clear that how they affect the kinetics of lithiation. Especially, the coupling effect of electrochemically induced strain and external strain on electrode materials have not been investigated yet.

In this work, we performed in-depth TEM analysis to investigate the coupling between electrochemically induced strain and interfacial strain in an epitaxial Fe₃O₄ thin film grown on a SrTiO₃ single crystal (Fig. 1). The *in situ* measurements and tomography were performed on a JEOL 2100F TEM operated at 200 kV. The high-resolution imaging and analytical EELS were conducted on a Hitachi HD2700C STEM operated at 200 kV and equipped with a probe aberration corrector. Combined *in situ* TEM and analytical TEM methods (Fig. 2), we observe that the compressive strain around the interface of thin film and substrate plays a critical role in decelerating the conversion reaction of Fe₃O₄; thus, intermediate phase of Li_xFe₃O₄ is found in the vicinity of interfaces. We observed that further lithiation, facilitating the conversion reaction of remaining intermediate phase, leads to the delamination of thin film. Electrochemical test in real Li-half cell confirms that the mechanical failure is a result of deep discharge of compressed thin film. Further, we used phase-field simulation to demonstrate the effect of strain coupling to kinetics of lithiation process, showing that preexisting external strain indeed controls the speed of lithium insertion [2]. Our work here not only clarifies the effect of compressive strain on reaction kinetics but also suggests that pre-existing epitaxial strain can be used to effectively tune and control the electrochemical reaction [3].

References:

[1] H. Tavassol *et al*, Nat. Mater. **15** (2016), p. 1182.

[2] Sooyeon Hwang *et al*, Submitted

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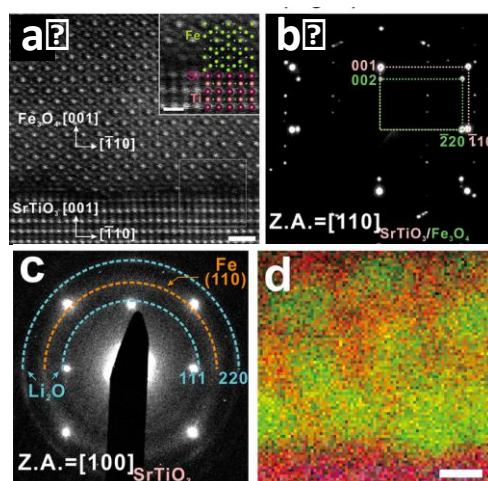


Figure 1. (a) Atomic resolution HAADF-STEM image and (b) SAED pattern of pristine Fe₃O₄/STO. (c) SAED pattern and (d) STEM-EELS mapping of reacted specimen. Scale bars in (b) and (d) denote 1 nm and 2 nm, respectively.

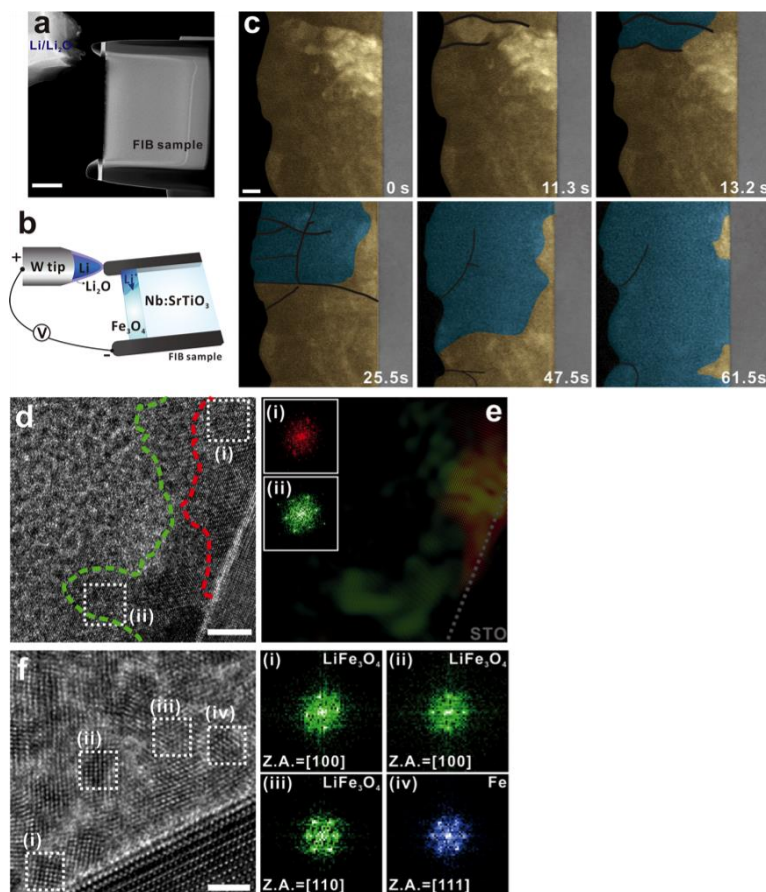


Figure 2. Phase evolution during *in situ* lithiation. (a) Low mag HAADF image of FIB sample (b) Schematic illustration of *in situ* setup. (c) ADF-STEM image series captured in real time. False color of yellow and blue represents the pristine and lithiated areas, respectively. (d) HREM image and (e) corresponding phase map during the lithiation process. (f) HREM image after the conversion reaction. (i)-(iv) FFT results obtained from designated areas.