

Revealing the Working and Degradation Mechanisms in Lithium-Ion Batteries via In-situ Transmission Electron Microscopy

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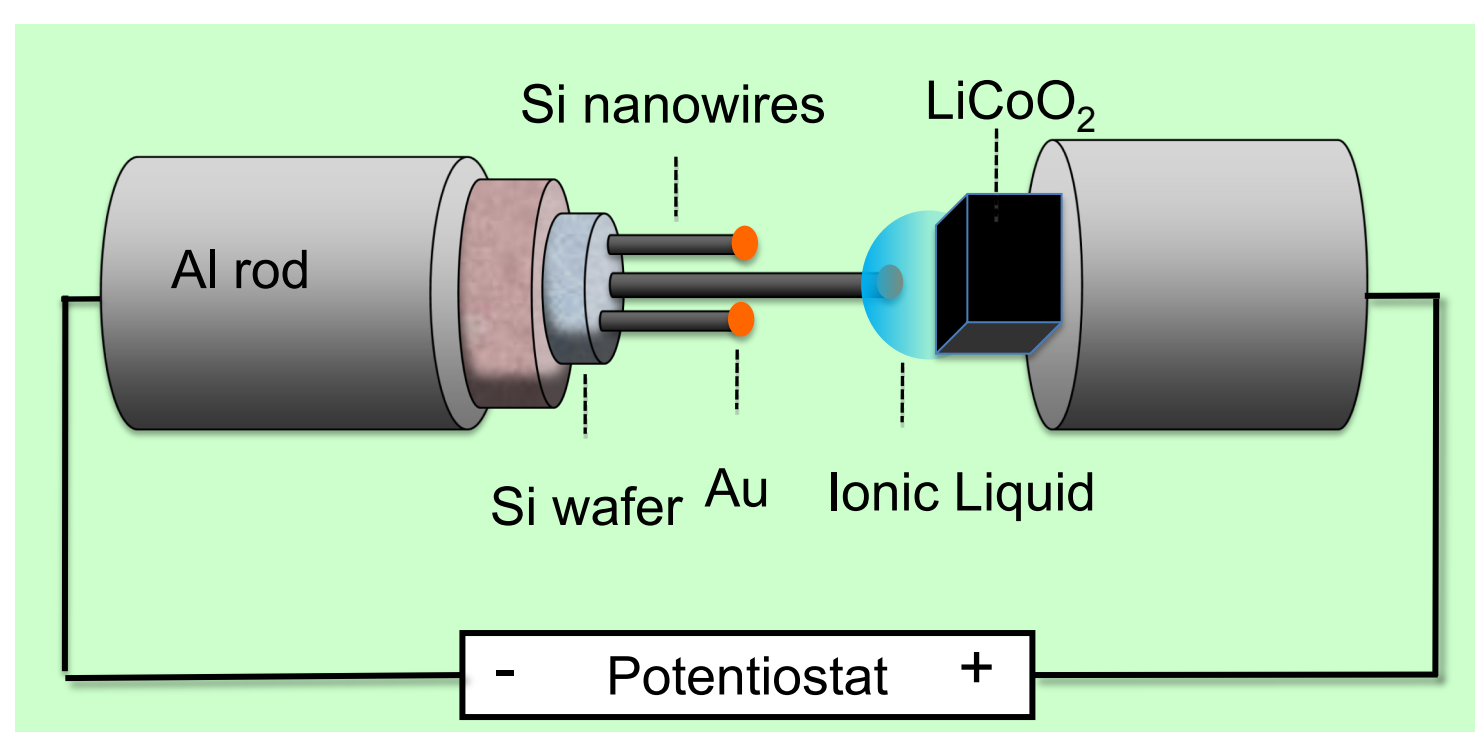
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Motivation

Lithium ion batteries (LIBs) have received extensive attention as a top performing energy storage system. However, due to the intrinsic complexity of LIBs, for instance, the concurrent events of electrochemical, physical and mechanical processes during cycling, little progress has been achieved in making advanced batteries with enhanced performance. Therefore, understanding the mechanisms of the electrochemical reactions and electrode degradation from a microscopic view is highly important for guiding the design of high performance LIBs.

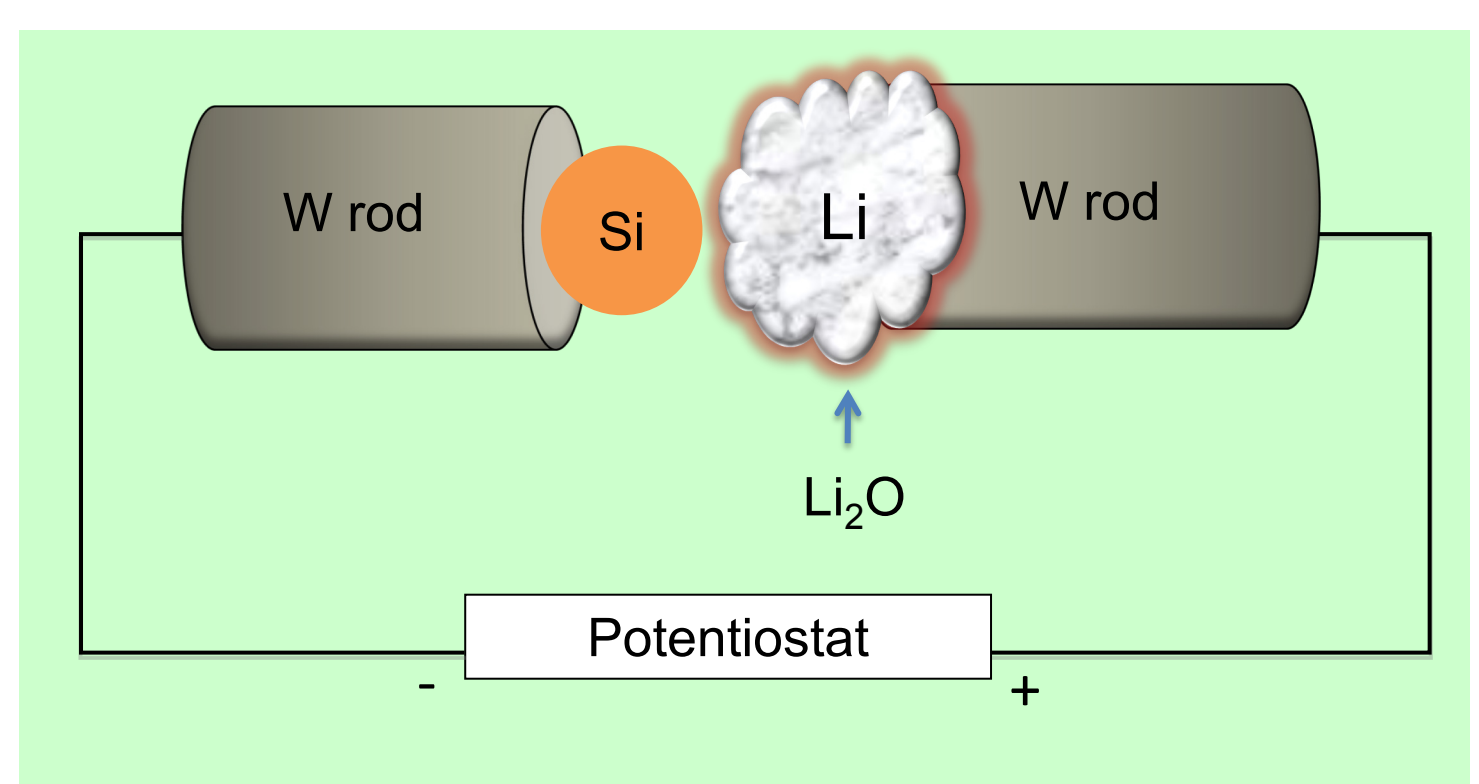
Methods

Liquid cell



- Introduce the ionic liquid into the transmission electron microscope (TEM), which can survive the high vacuum.¹
- The first working in-situ Li-ion cell inside a TEM, enabling real time observations of electrochemistry process at atomistic length scales.²⁻³

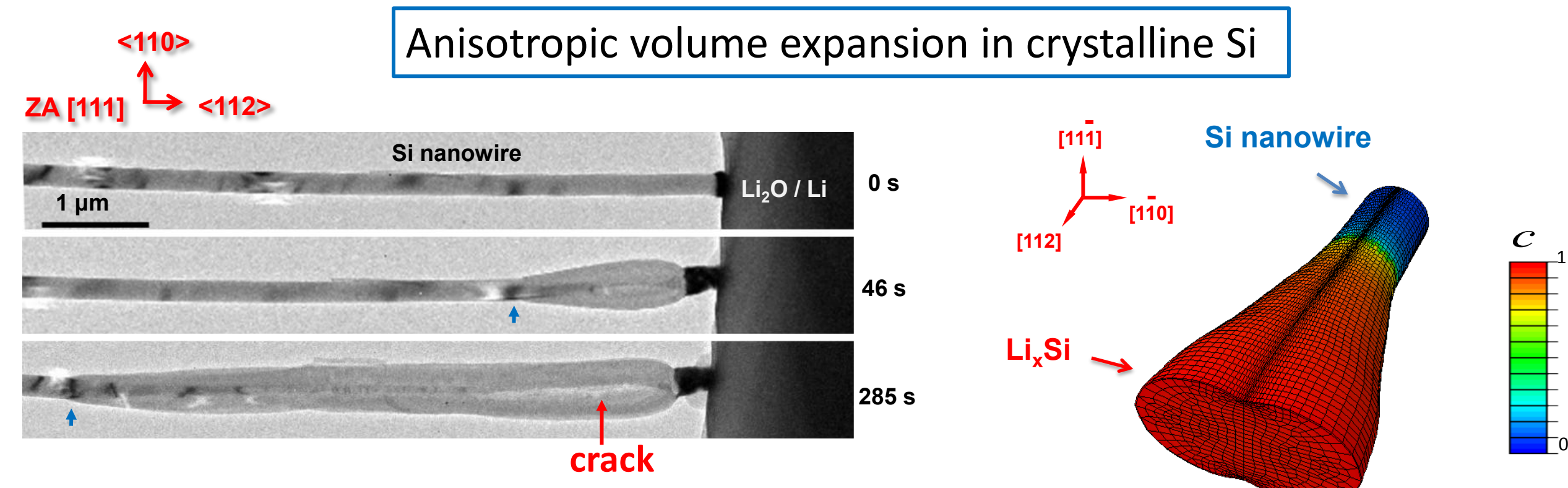
Solid cell



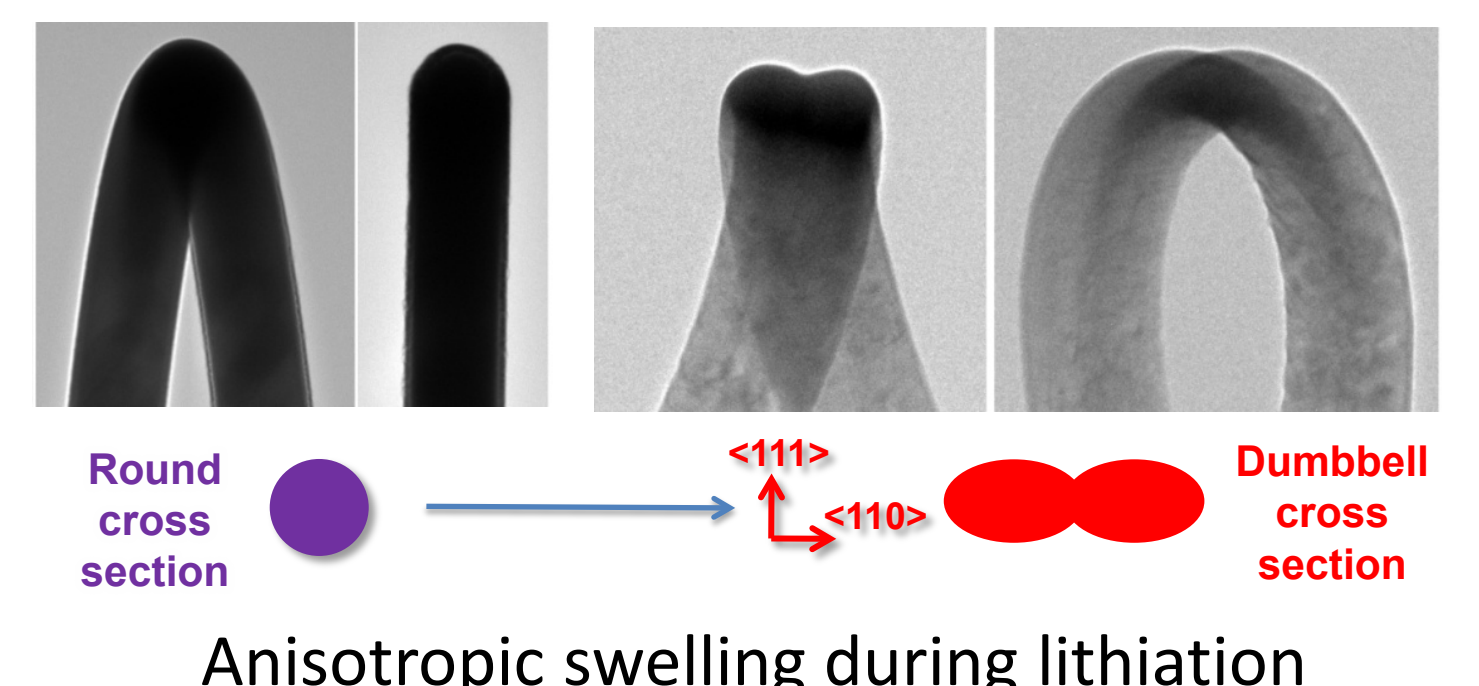
- Very clean system, no binder.
- Allowing in-situ TEM studies of electrochemical processes down to single nanoparticle with size less than 10 nm level!
- The Li₂O here can be replaced by other kinds of more stable solid electrolytes, such as LiPON and LiAlSiO.

Reaction mechanism I: Alloying

Anisotropic volume expansion in crystalline Si

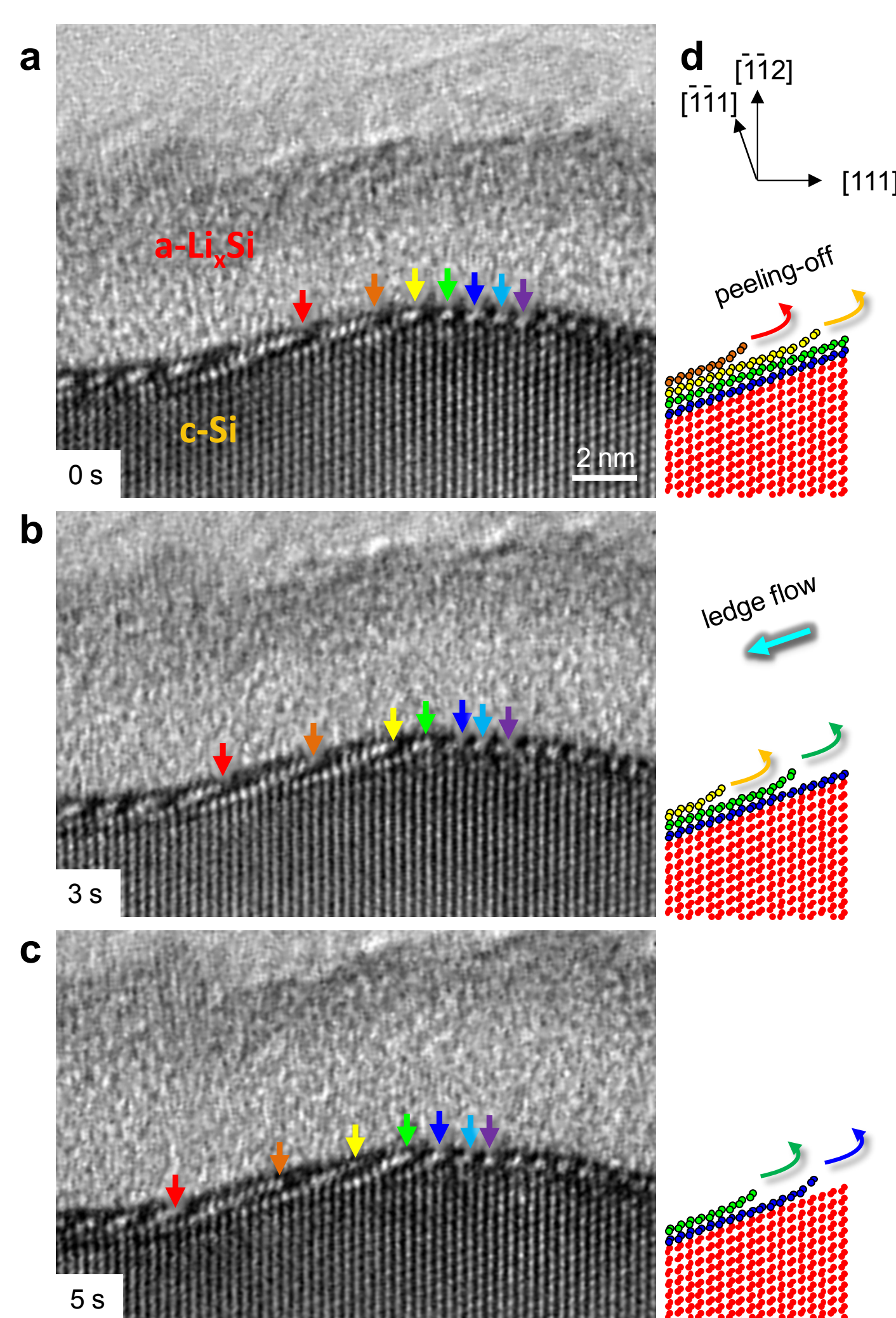


- The lithiation of crystalline Si was found to be highly anisotropic, with the largest volume expansion along the <110> direction and the smallest volume expansion along the <111> direction.⁴
- Crack was observed, due to the buildup of the high stress during lithiation.



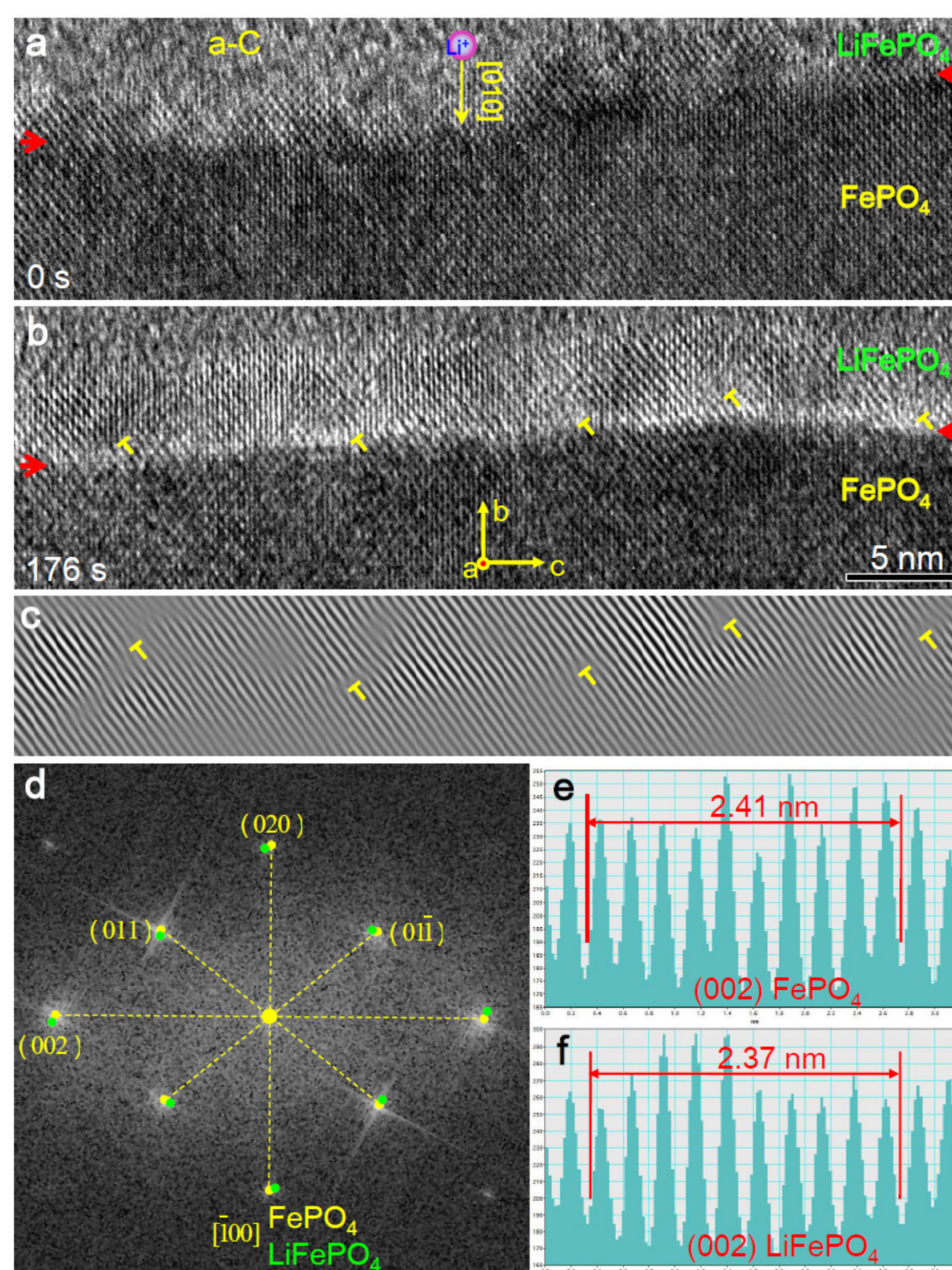
Anisotropic swelling during lithiation

Atomic-scale imaging of electrochemical lithiation in crystalline Si



- A sharp interface of about 1 nm thick was observed between the crystalline Si and an amorphous Li_xSi alloy.
- The lithiation kinetics are controlled by the migration of the interface, which occurs through a ledge mechanism.
- The ledge flow processes produce the amorphous Li_xSi alloy through layer-by-layer peeling off the close-packed {111} atomic planes.
- This observation of lithiation mechanism from the microscopic view can provide the root cause for the anisotropic expansion in Si upon first lithiation.⁵

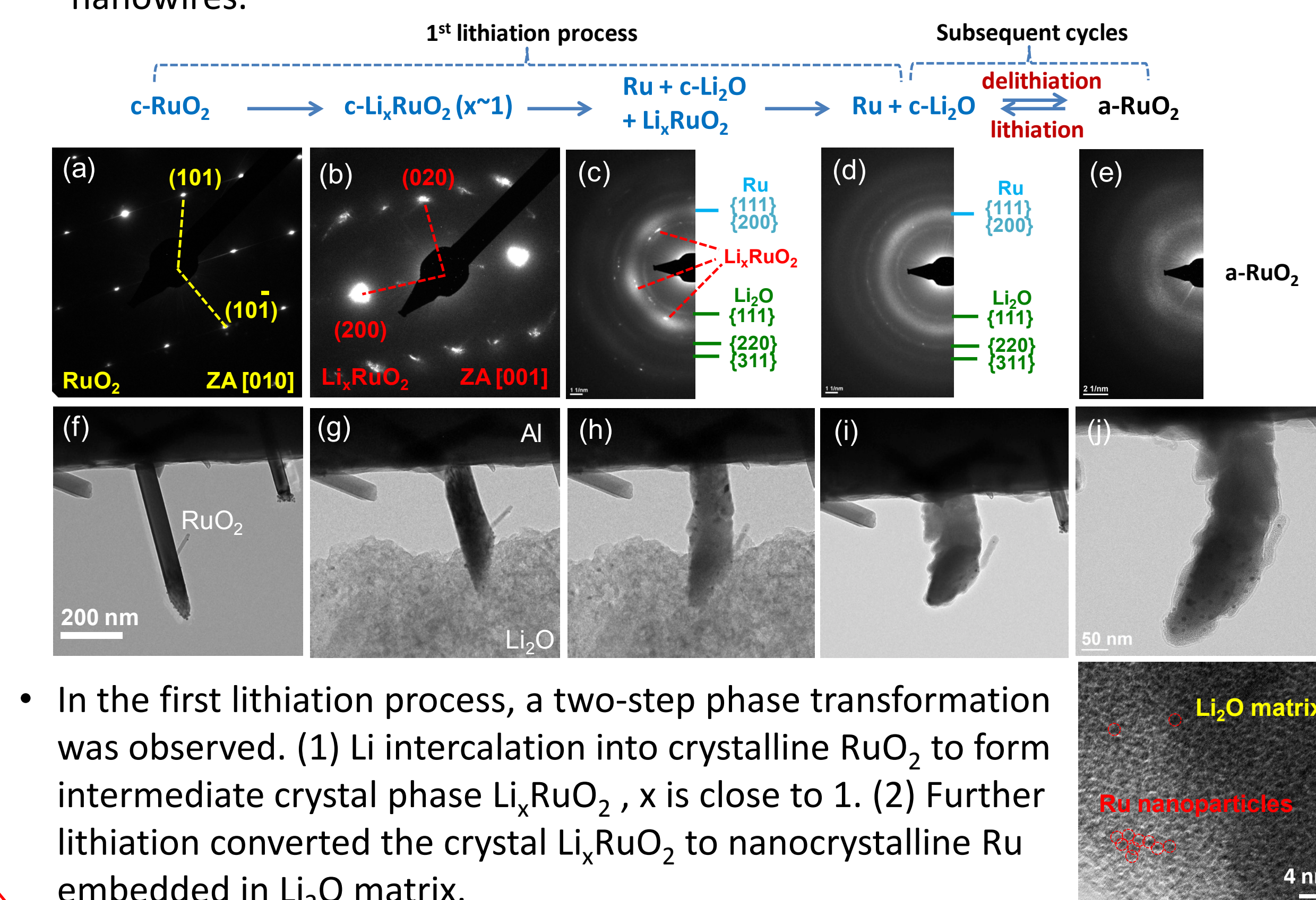
Reaction mechanism II: Insertion



- Anisotropic lithiation mechanism in FePO₄ was investigated in real-time with atomic-scale observation for the first time.
- A sharp (010) phase boundary between LiFePO₄ and FePO₄ was observed on ac-plane, which migrated along the [010] direction (b-axis) during lithiation.
- Dislocations were observed at/near the (010) phase boundary, due to the release of the stress generated by the lattice misfit at the phase boundary.⁶

Reaction mechanism III: Conversion

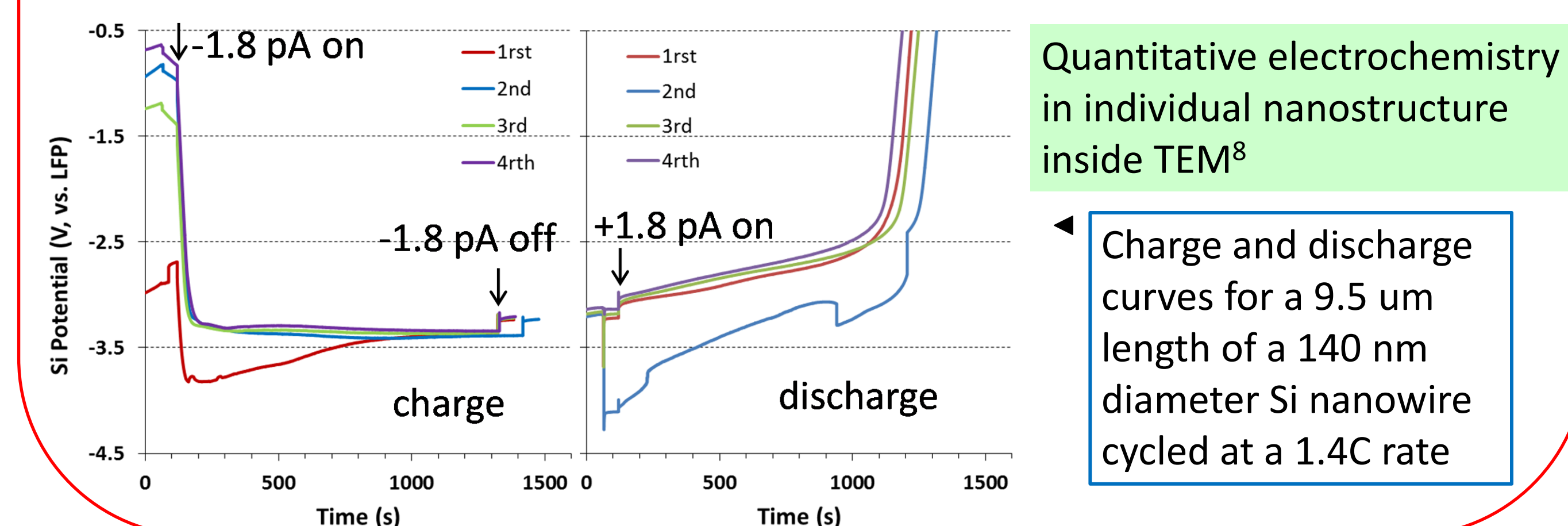
- The conversion reaction mechanism and reversibility of lithium storage in conversion reaction type electrodes were investigated using individual RuO₂ nanowires.⁷



- In the first lithiation process, a two-step phase transformation was observed. (1) Li intercalation into crystalline RuO₂ to form intermediate crystal phase Li_xRuO₂, x is close to 1. (2) Further lithiation converted the crystal Li_xRuO₂ to nanocrystalline Ru embedded in Li₂O matrix.

Conclusion and Perspective

- A novel technique of "in-situ TEM electrochemistry" has been developed to study the working and degradation mechanisms in LIBs.
- This allows for the dynamic observation with atomic-scale resolution of morphology evolution, phase transformation and chemical composition changes of battery materials.
- The future direction of this field is to introduce quantitative electrochemistry into the in-situ TEM, where structure and phase changes on individual nanostructure can be correlated with electrochemical signatures.



Quantitative electrochemistry in individual nanostructure inside TEM⁸

Charge and discharge curves for a 9.5 um length of a 140 nm diameter Si nanowire cycled at a 1.4C rate

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