



Electrochemical STEM Observations of Sn Lithiation Reactions

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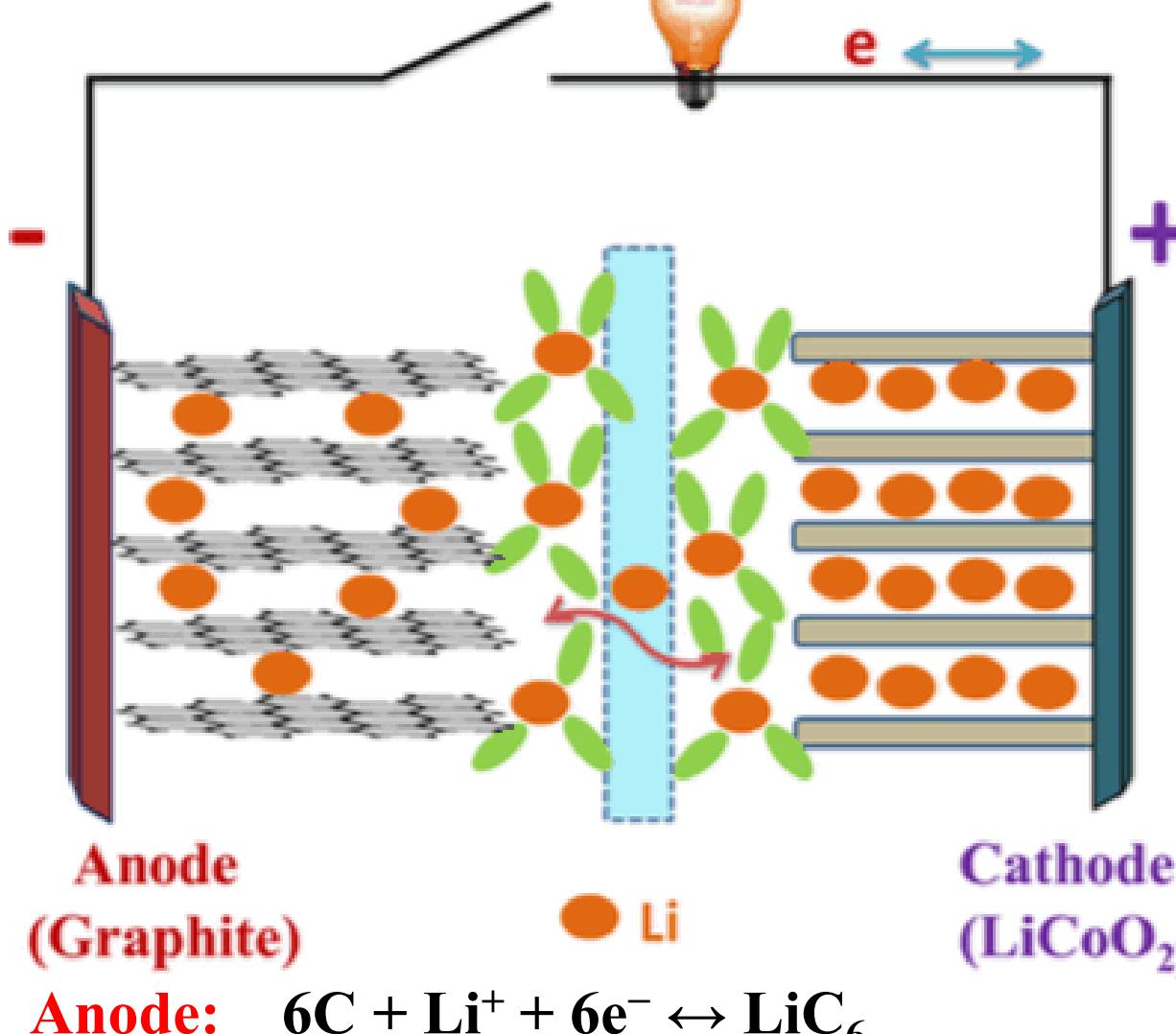
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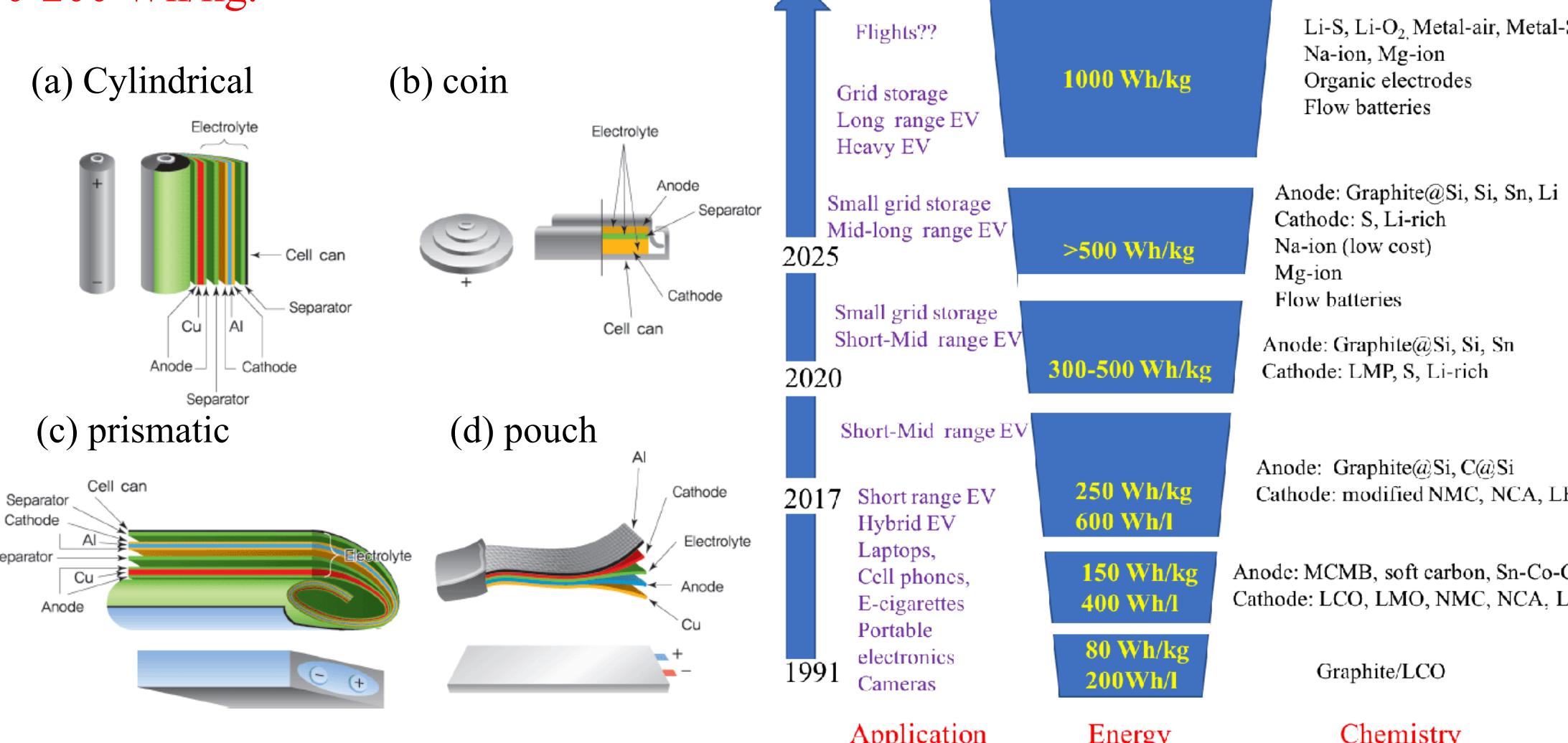
Lithium Ion Batteries



Present Li-ion batteries comprises mostly of graphite as anode while lithium transition metal oxides or phosphates as cathode, are separated by ionically conductive membrane and lithium electrolyte (LiPF_6 in organic carbonates) [1]. Graphite has a theoretical capacity of 372 mAh g⁻¹ and can cycle efficiently up to current rates at 1C (1-hour charge and discharge). The lithium ion battery reactions are as follows,

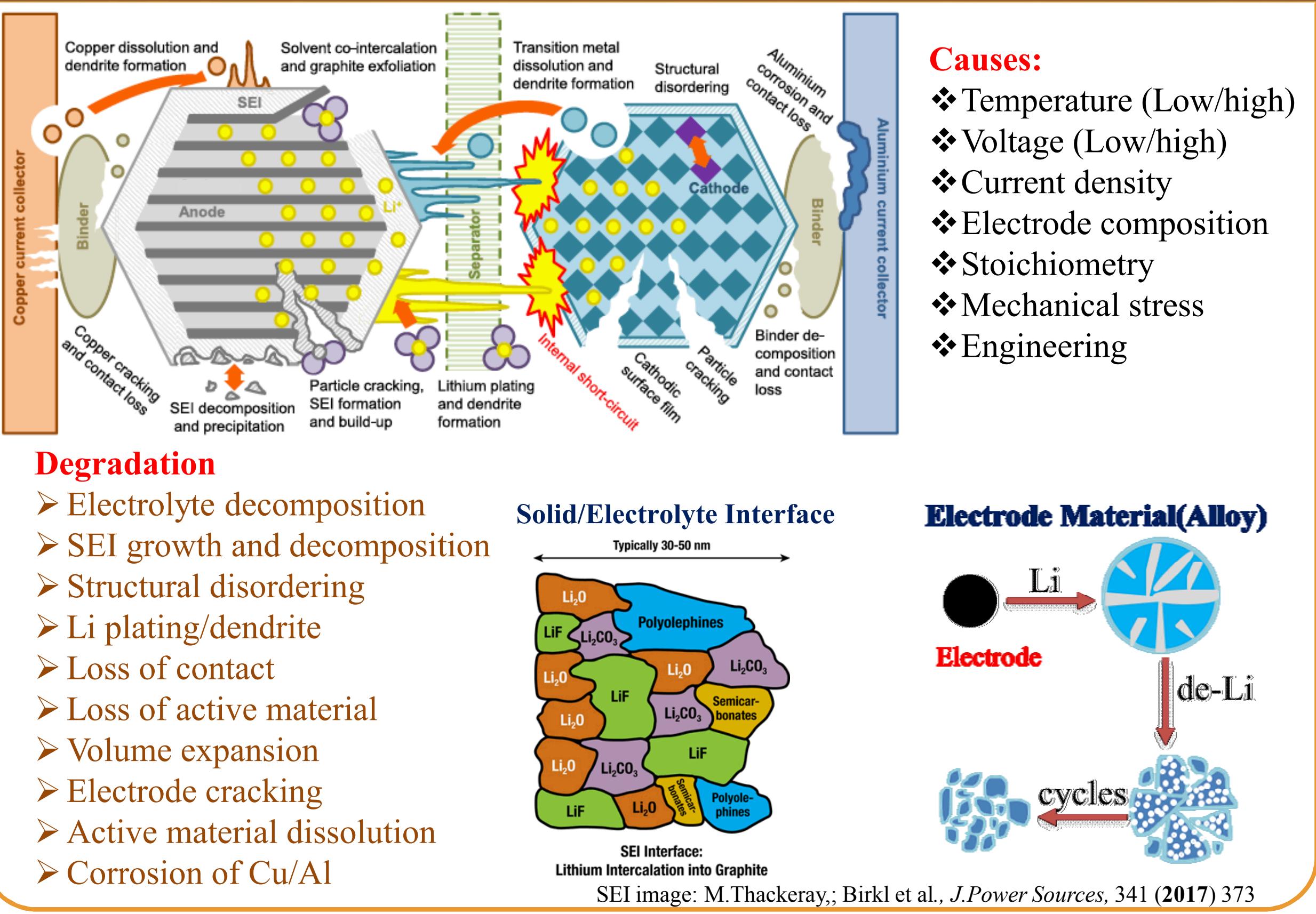


The efficient employment of present Li-ion batteries in electric vehicle or grid storage requires from two to five times more energy density than the present batteries can offer ~ 150-200 Wh/kg.



Tarascon et al., *Nature* 414 (2001) 359; S. Goriparti et al., *J. Power Sources*, 257 (2014) 421; Blomgren et al., *J. electrochem. Soc.*, 164 (2017) A5019

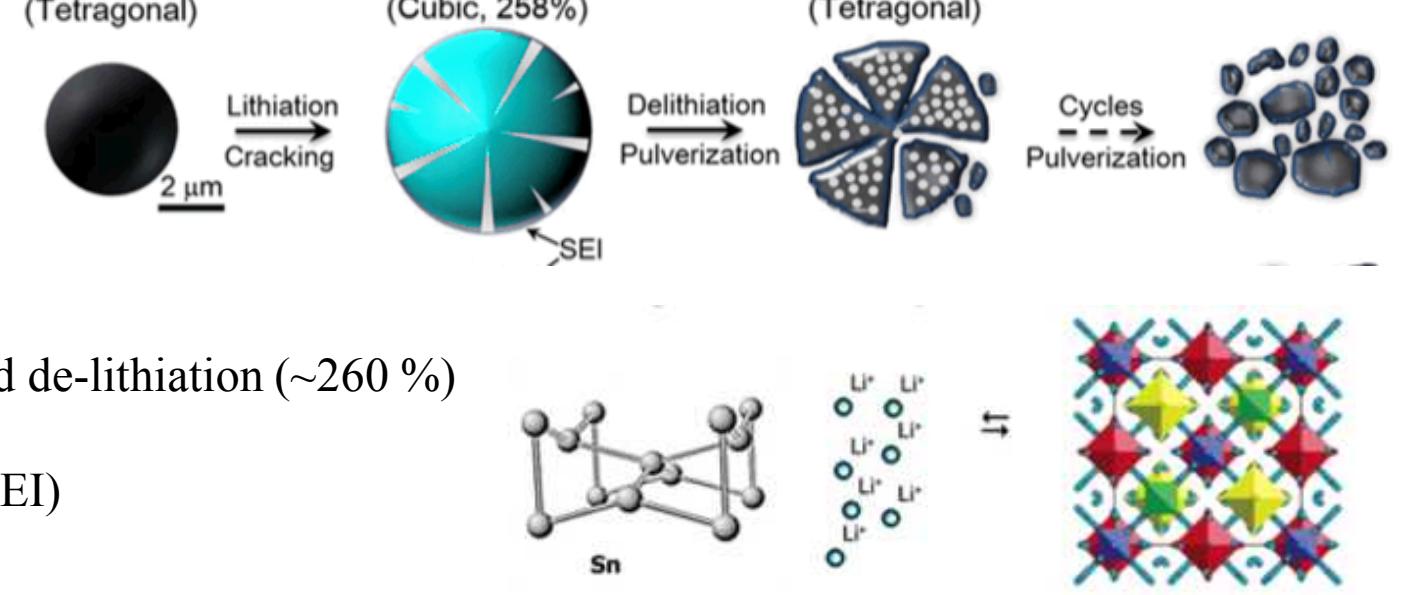
Degradation of Lithium Ion Batteries



Sn as Anode for Lithium Ion Batteries

Advantages:

- High Theoretical Capacity ~994 mAh g⁻¹
- $5\text{Sn} + 22\text{Li}^+ + 22\text{e}^- \leftrightarrow \text{Sn}_2\text{Li}_{12}$
- High electrical conductivity



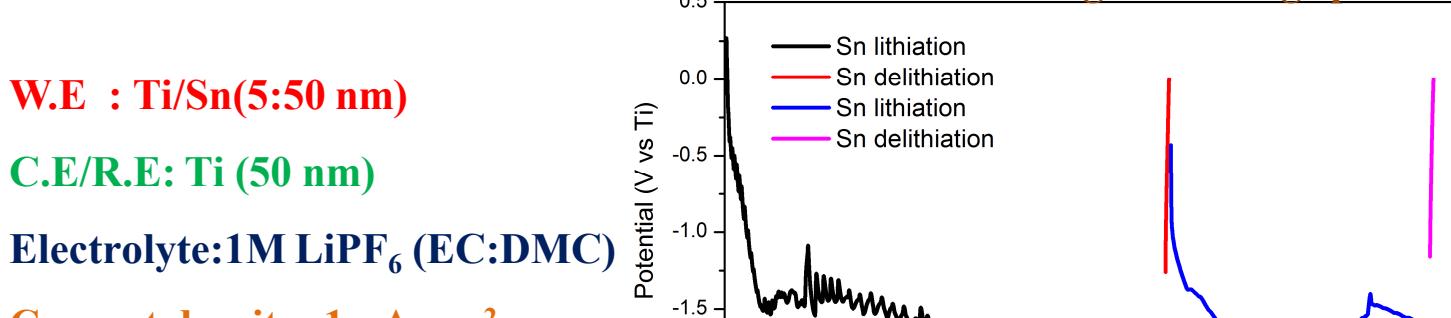
Challenges:

- Huge volume expansion while lithiation and de-lithiation (~260 %)
- Strain-induced pulverization
- Electrode/electrolyte interface reactions (SEI)
- Loses of contact from the current collector
- Aggregation of active particles while cycling
- Capacity fading with cycling

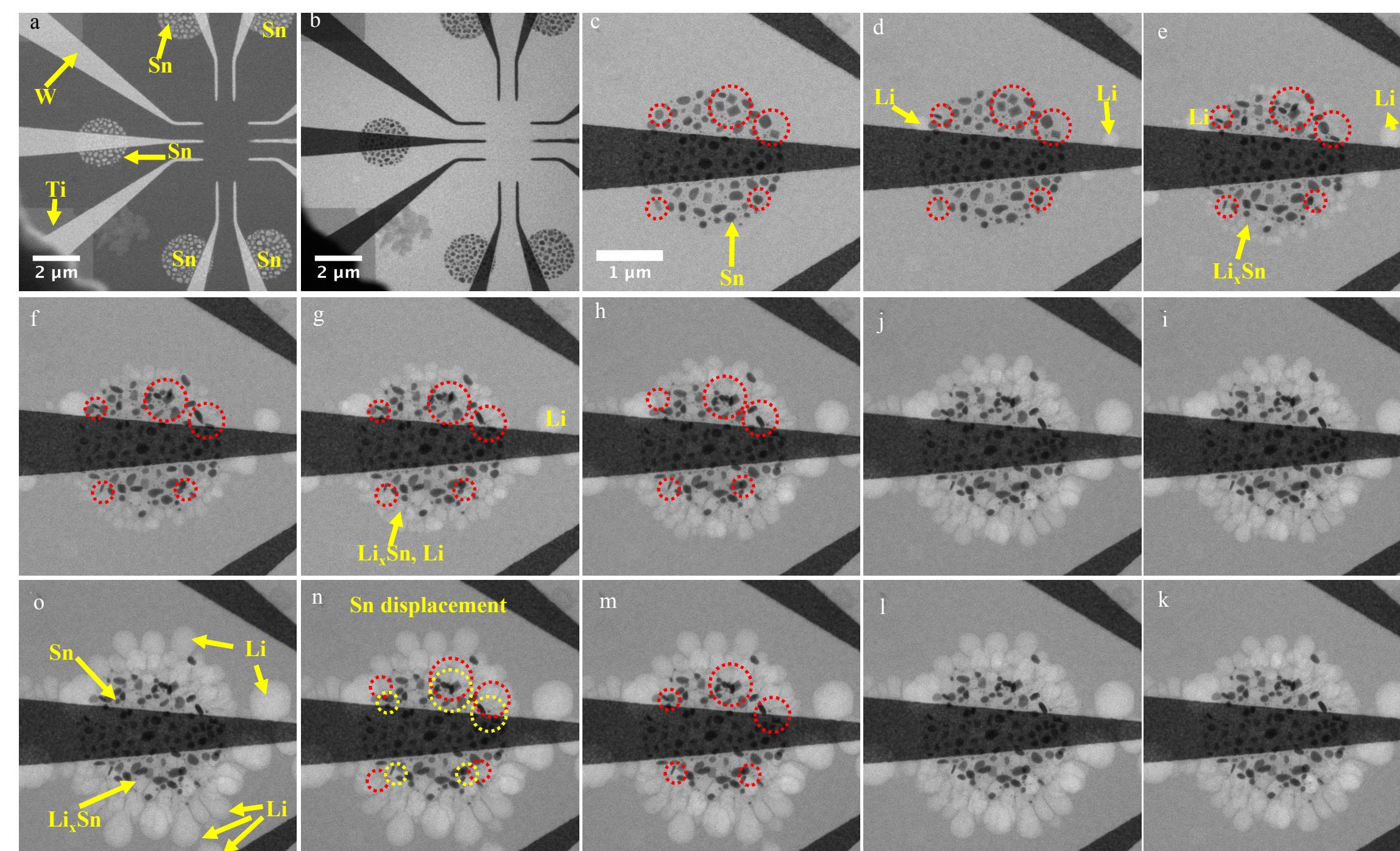
J. Wang et al., *J. Electrochem. Soc.*, 161 (2014) F3019

STEM of Lithium electrochemical Insertions Reactions of Sn and Sn/TiO₂

Electrochemical STEM of Sn

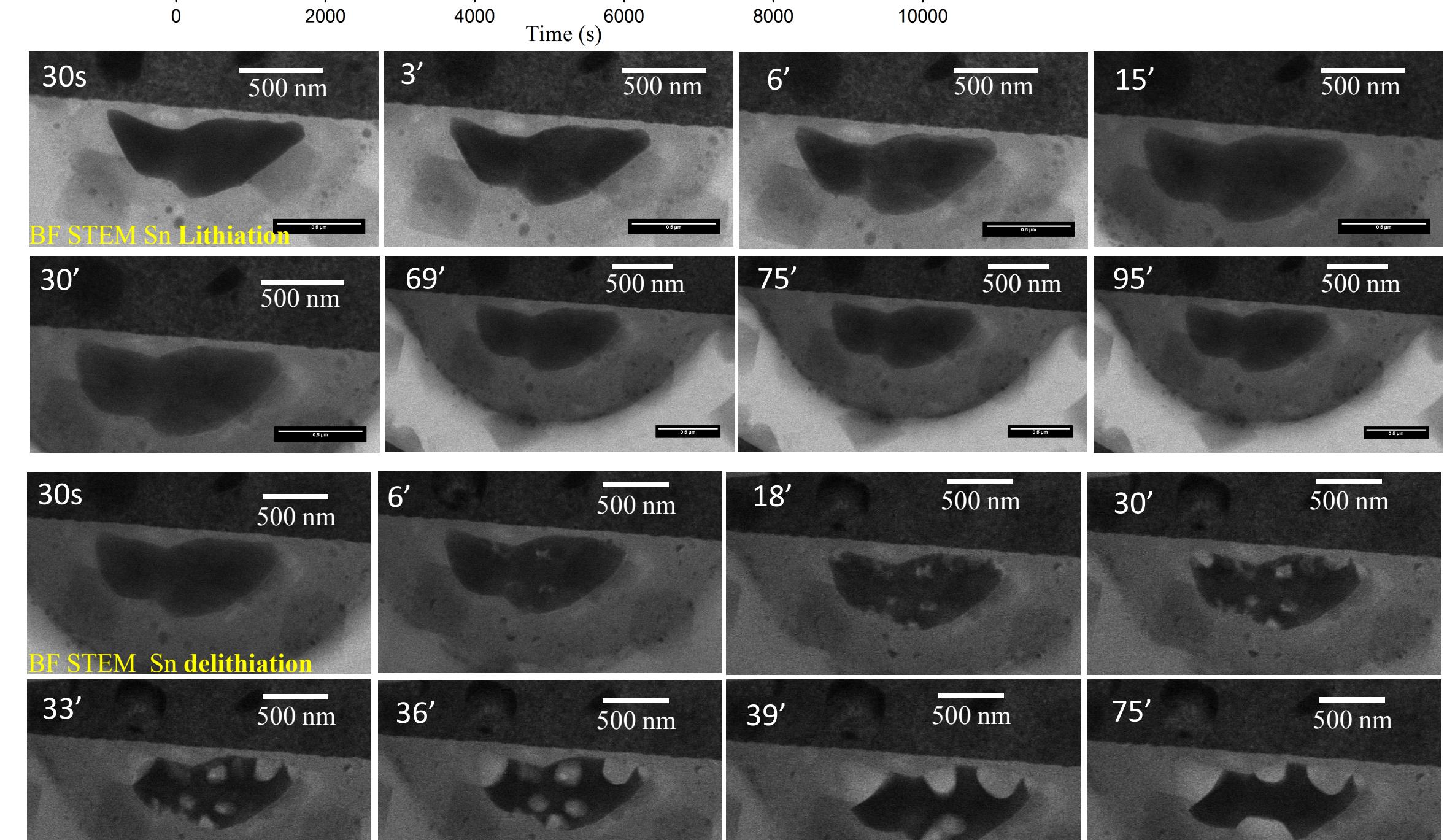
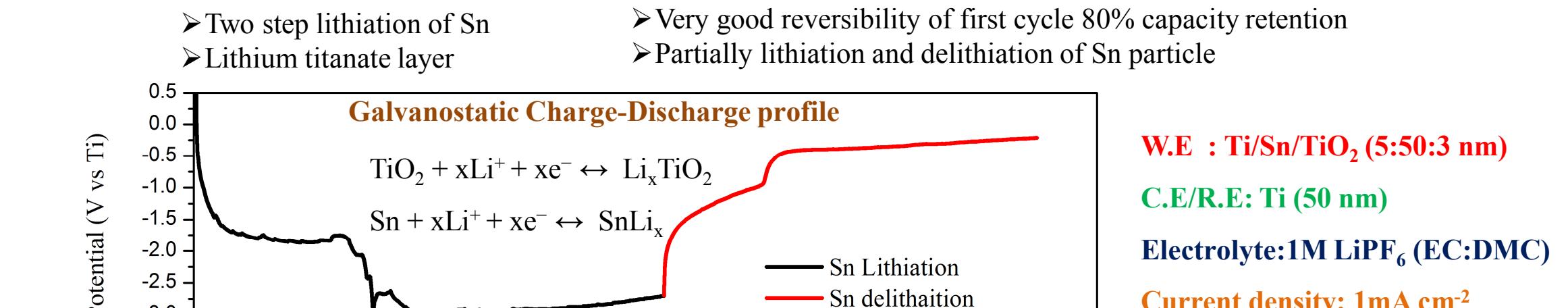


- Sn and Ti electrodes obtained by electron beam deposition
- Galvanostatic charge-discharge profile shown that there is no Sn-delithiation
- Lithiation of Sn observed initially and then lithium plating



STEM images (a) dark and (b) bright field images of Sn and Ti electrodes, (i-o) bright field images of Sn lithiation process at a current density of 1mA cm⁻². The presented images were taken every 15 minutes. Each image is no STEM exposure to electron beam during Li cycling and the total electron dose of < 10.14 e⁻ Å⁻² with image acquired every 3 minutes throughout lithiation.

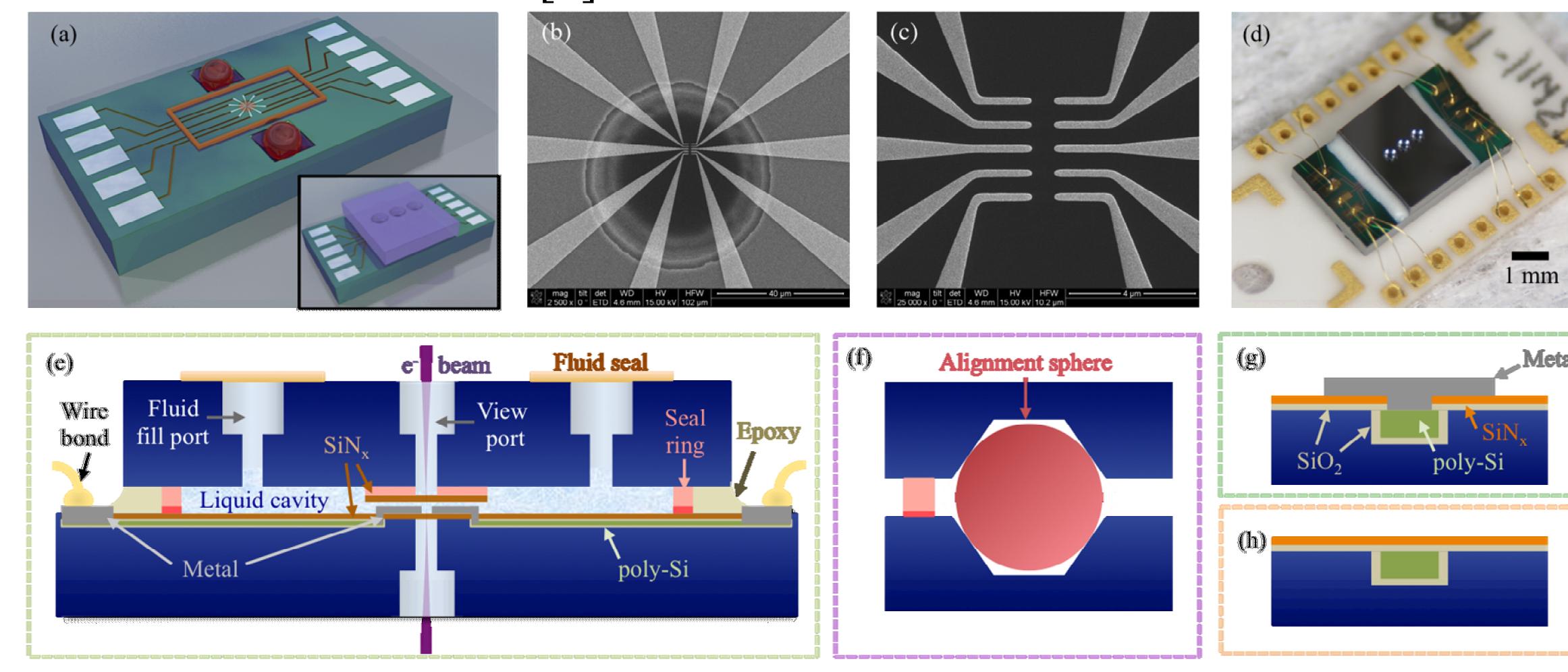
Electrochemical STEM of Sn/TiO₂



STEM bright field images of Sn/TiO₂ electrodes. Each image is no STEM exposure to electron beam during Li cycling and image acquired every 3 minutes throughout lithiation. The corresponding time of the image on the each image and the prime symbol (') represent minutes.

Electrochemical TEM Platform

The Center for Integrated Nanotechnologies (CINT) has successfully designed a microfabricated liquid cell [3] that can operate with quantitative femtoampere-level current control over 10 ultramicroelectrodes while imaging within a TEM [4]. The electrodes are patterned onto a 50 nm SiN_x membrane window, with a constant fluid gap around 150-200 nm. Microsphere lenses are used to align the individual top and base of the platform to overlap the 30 μm diameter membrane windows. Liquid is loaded post assembly of the two platform parts by pumping solution into a fluid fill port and allowing capillary forces to fill the cell, then the openings are capped and epoxy sealed. Battery materials are well suited for investigations in this platform for structural changes at electrode surfaces, deposition/stripping, intercalation mechanisms, and solid-electrolyte interphase (SEI) formation with 1 nm spatial resolution. This quantitative approach allows for coupled structural information with features observed in the electrochemical data [3].



Electrochemical TEM Liquid Platform [2]. (a) Representative schematic of the platform base, inset is the platform top set on the base. (b) SEM image of an electrode design over the SiN membrane window, scale bar represents 40 μm. (c) SEM image of the electrode tips on the SiN membrane, scale bar represents 4 μm. (d) Image of the sealed platform wire bonded to a chip carrier that connects to a 16 lead electrical feed through TEM holder. Cross-sectional schematic of the (e) platform operating within the TEM, (f) alignment sphere between the top and base units next to the seal ring, (g) metal electrodes exposed on the base unit, and (h) buried poly-Si traces on the base unit.

CINT User Proposal to Access the Platform

CINT is a Department of Energy/Office of Science Nanoscale Science Research Center (NSRC) operating as a national user facility devoted to establishing the scientific principles that govern the design, performance, and integration of nanoscale materials. Through its Core Facility in Albuquerque and Gateway to Los Alamos Facility, CINT provides open access to tools and expertise needed to explore the continuum from scientific discovery to the integration of nanostructures into the micro- and macro world. User proposals are accepted in the months of March and September, active user proposals last a duration of 18 months. Proposals entail a 2 page description of the proposed research project, impact of the research, experimental outline, details on user's contribution, and details on CINT's contribution. The user proposals are evaluated by a team of external reviewers on the merit of the proposal in relation to nanoscience and potential impact on the community.

References:

- S. Goriparti et al., *J. Power Sources*, 257 (2014) 421
- J. Wang et al., *J. Electrochem. Soc.*, 161 (2014) F3019
- M. J. Williamson et al., *Nat. Mater.* 2 (2003), p. 532.
- A. J. Leenheer et al., *J. Microelectromech.* 24 (2015) 1061
- A. J. Leenheer et al., *ACS Nano*, 10 (2016) 5670

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