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In Situ S/TEM Observations of Electrochemical Lithiation and De-lithiation of TiO_2@Sn Nanostructures in A Sealed Liquid-cell

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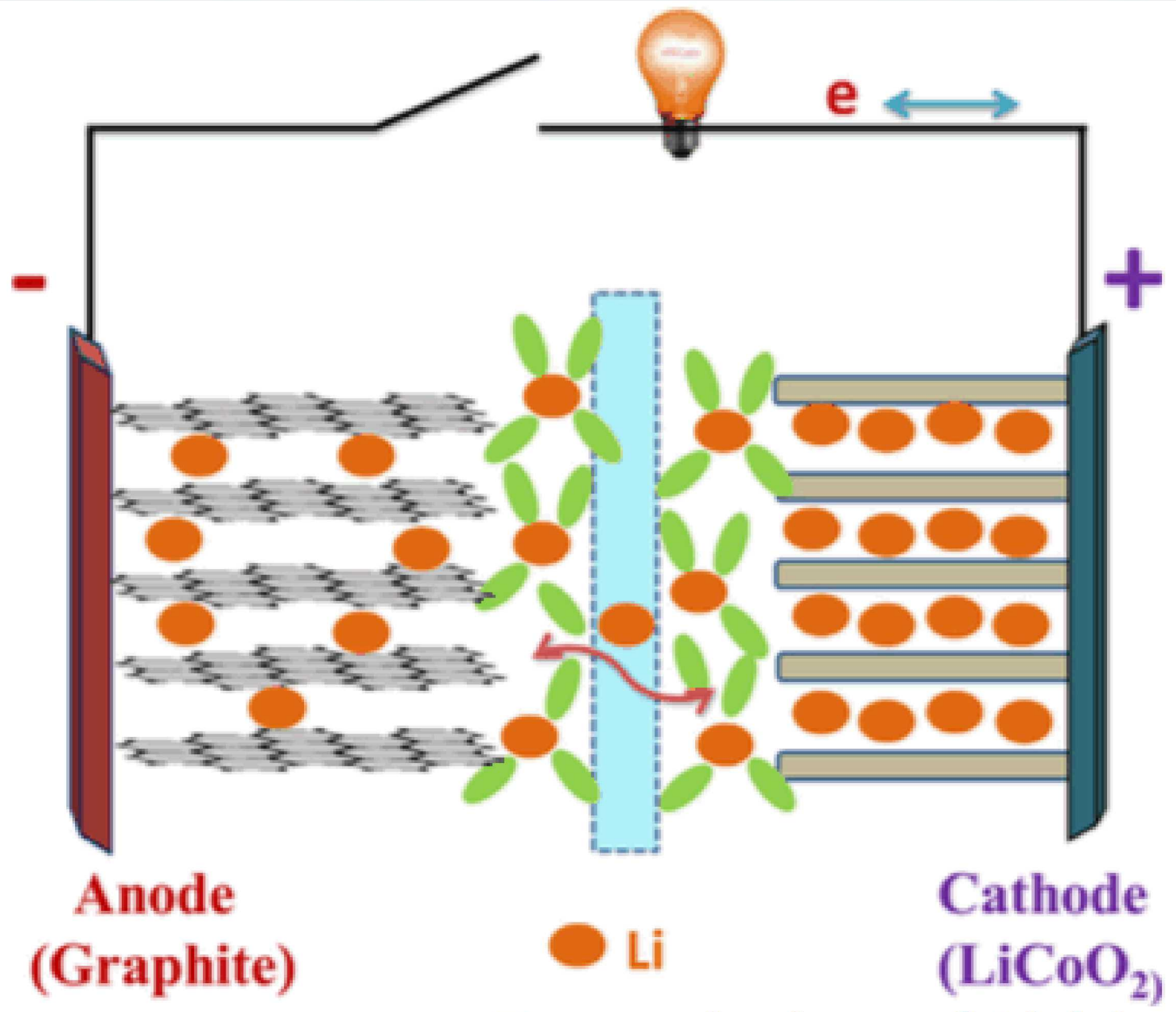
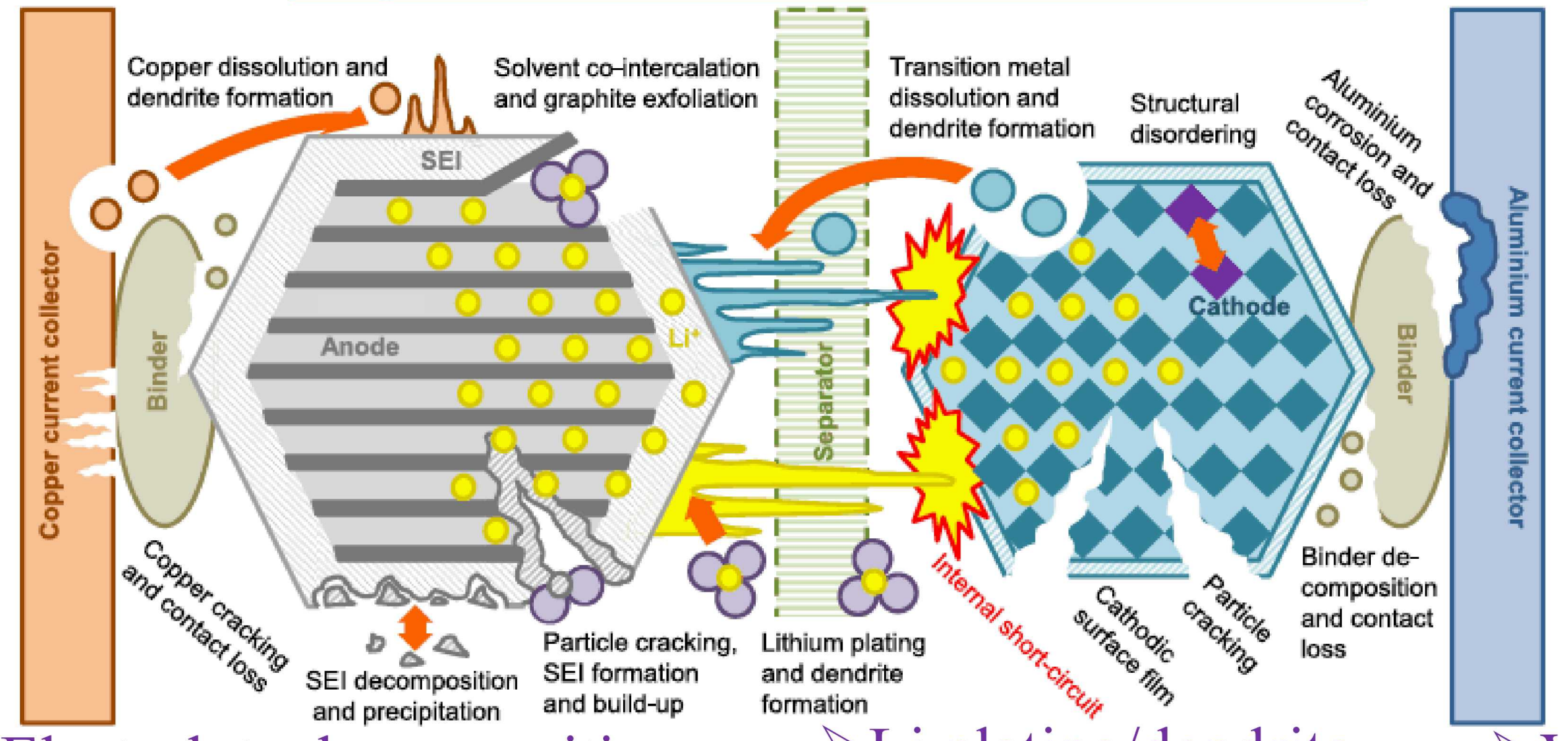
Lithium Ion Batteries



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)

We need 2 to 5 times more energy density than the present Li-ion batteries ~ 150-200 Wh kg^{-1}

Degradation of Lithium Ion Batteries



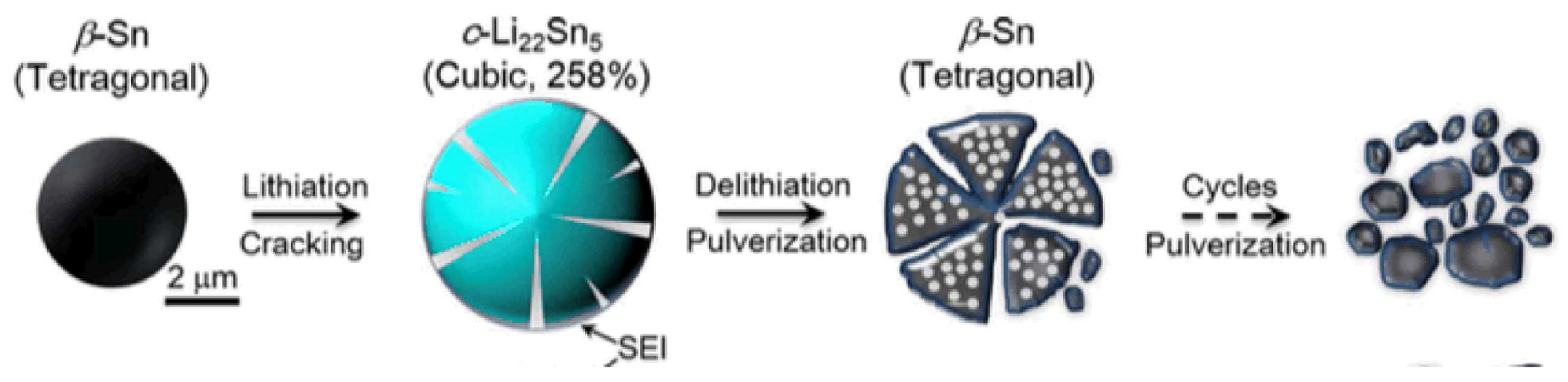
Causes

- ❖Temperature
- ❖Voltage (Low/high)
- ❖Current density
- ❖Electrode composition
- ❖Stoichiometry
- ❖Mechanical stress
- ❖Engineering

- ➢Electrolyte decomposition
- ➢SEI growth and decomposition
- ➢Structural disordering
- ➢Li plating/dendrite
- ➢Loss of contact
- ➢Loss of active material
- ➢Volume expansion
- ➢Electrode cracking
- ➢Corrosion of Cu/Al

S. Goriparti et al, *J.Power Sources*, 257 (**2014**) 421; Birkl et al., *J.Power Sources,* 341 (**2017**) 373

Sn as Anode for Lithium Ion Batteries



Advantages

- ➢ High Theoretical Capacity ~994 mAh g^{-1}
- ➢ $5Sn + 22Li^+ + 22e^- \longleftrightarrow Sn_5Li_{22}$
- ➢ High electrical conductivity

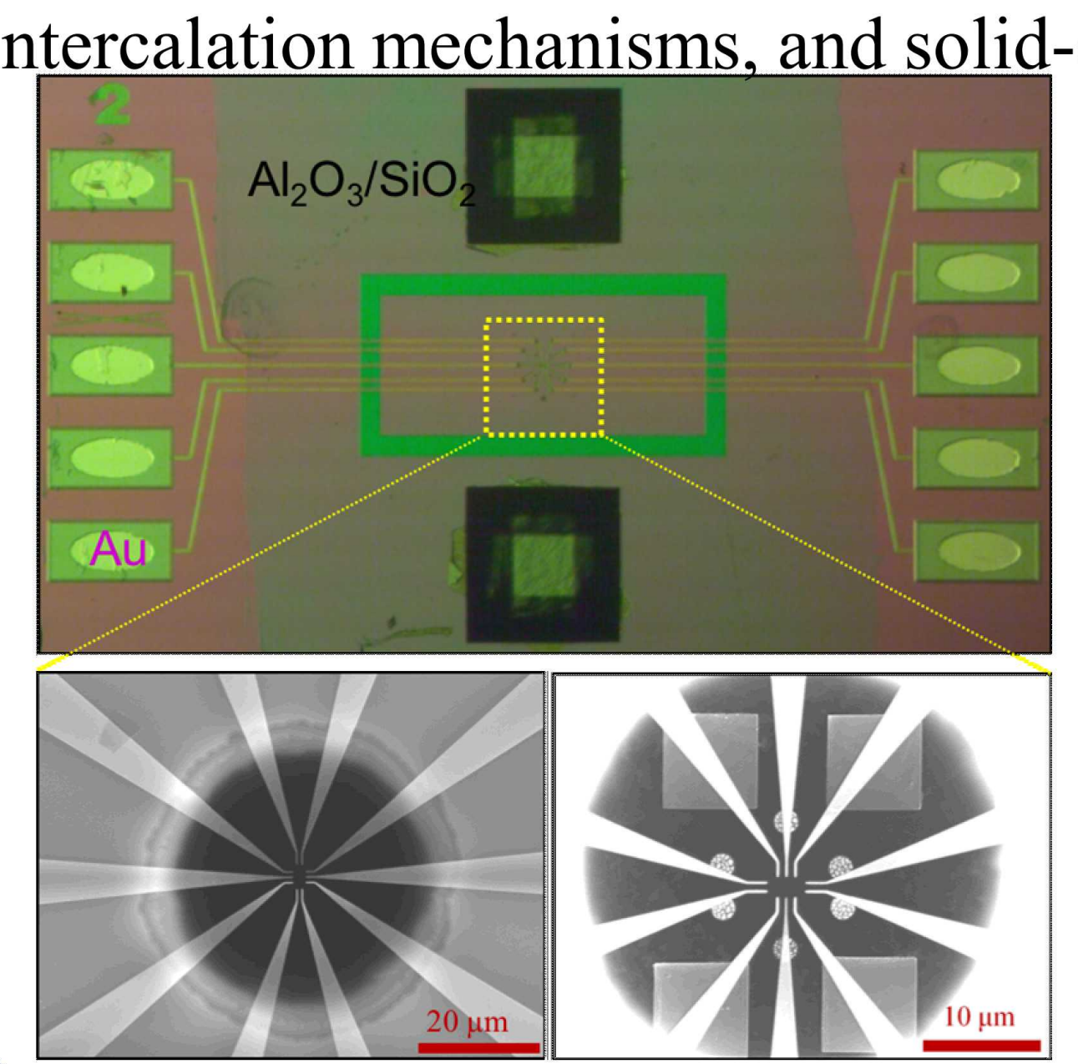
J. Wang et al, J. Electrochem. Soc, 161 (2014) F3019

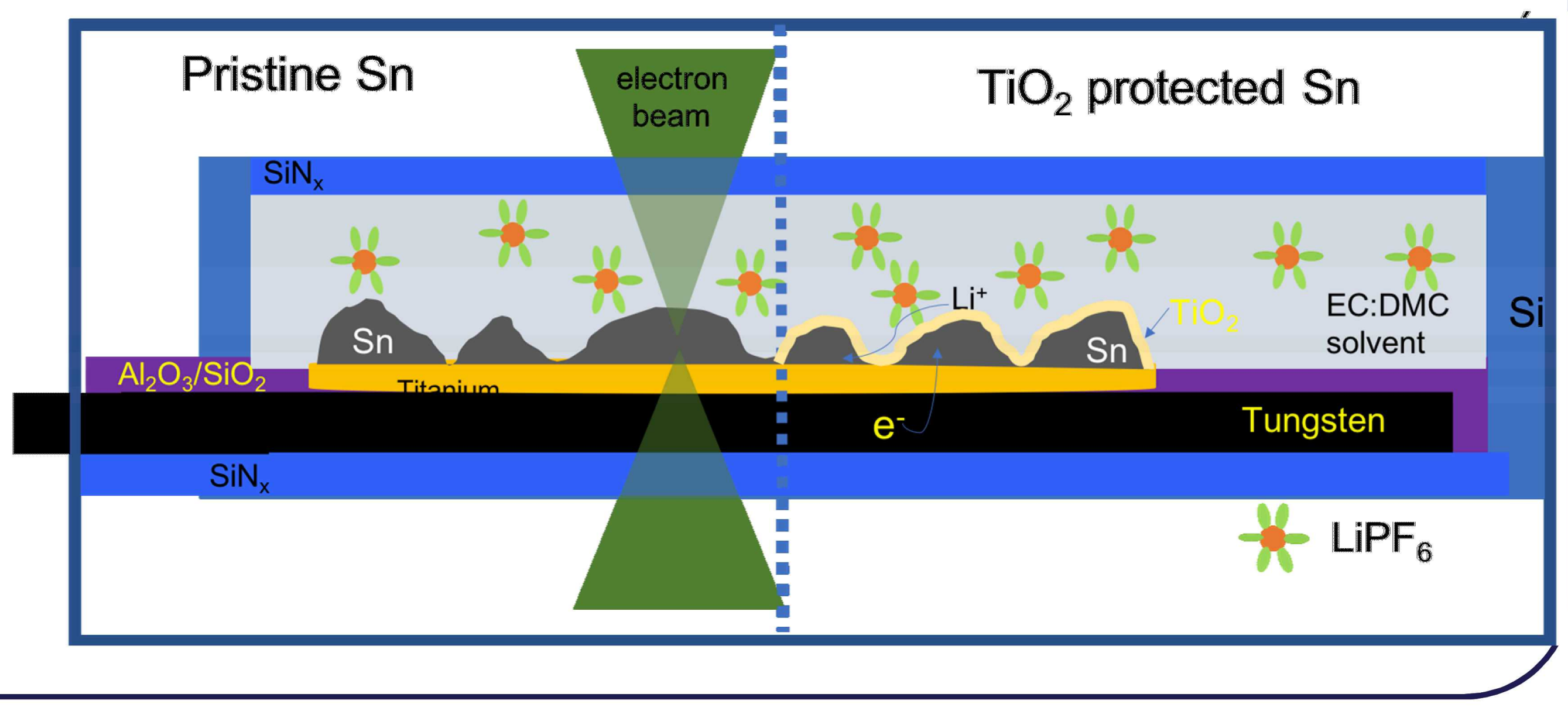
Challenges

- ❖ Huge volume expansion while lithiation and de-lithiation
- ❖ 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

Electrochemical S/TEM Platform

The Center for Integrated Nanotechnologies (CINT) at Sandia National laboratories 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 and 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.





Electrochemical Lithiation and De-lithiation of Sn and TiO_2@Sn

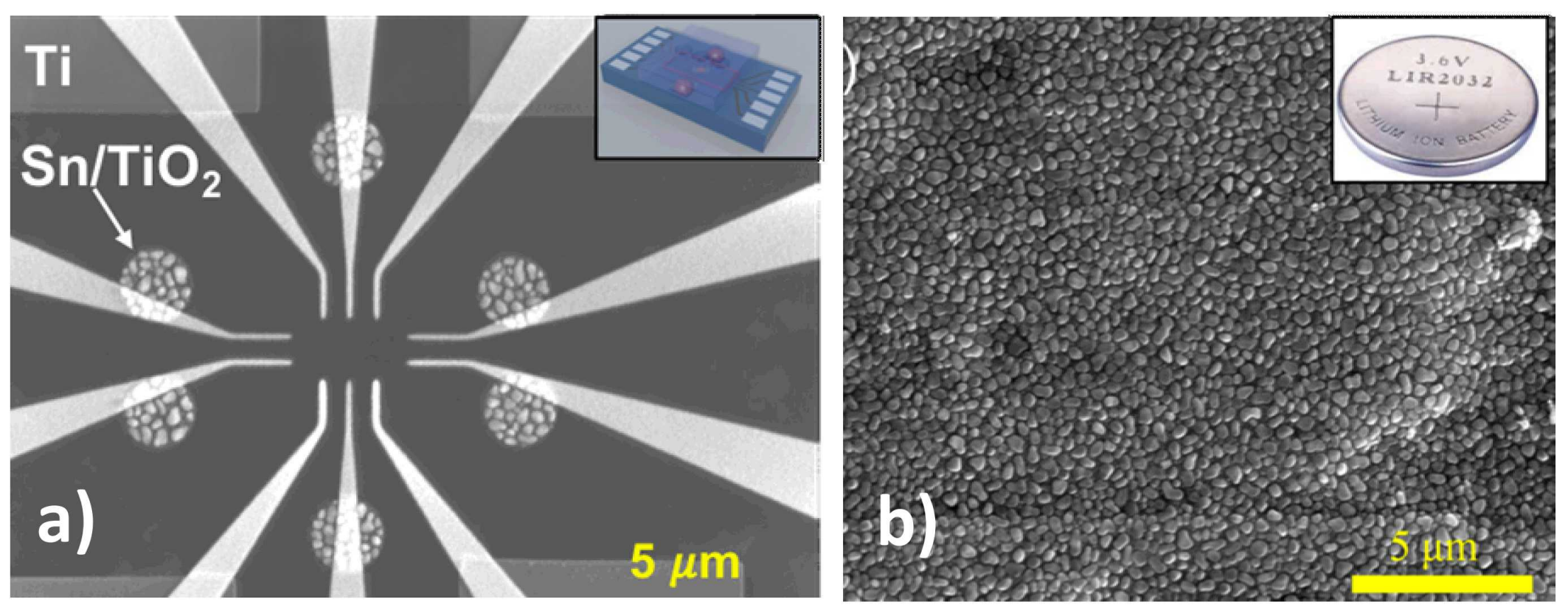


Figure. SEM images of (a) Titanium and TiO_2 coated Sn electrodes fabricated in CINT custom designed Electrochemical STEM Liquid Cell platform (b) TiO2 coated Sn electrodes nanostructures on Copper foil for coin cell studies

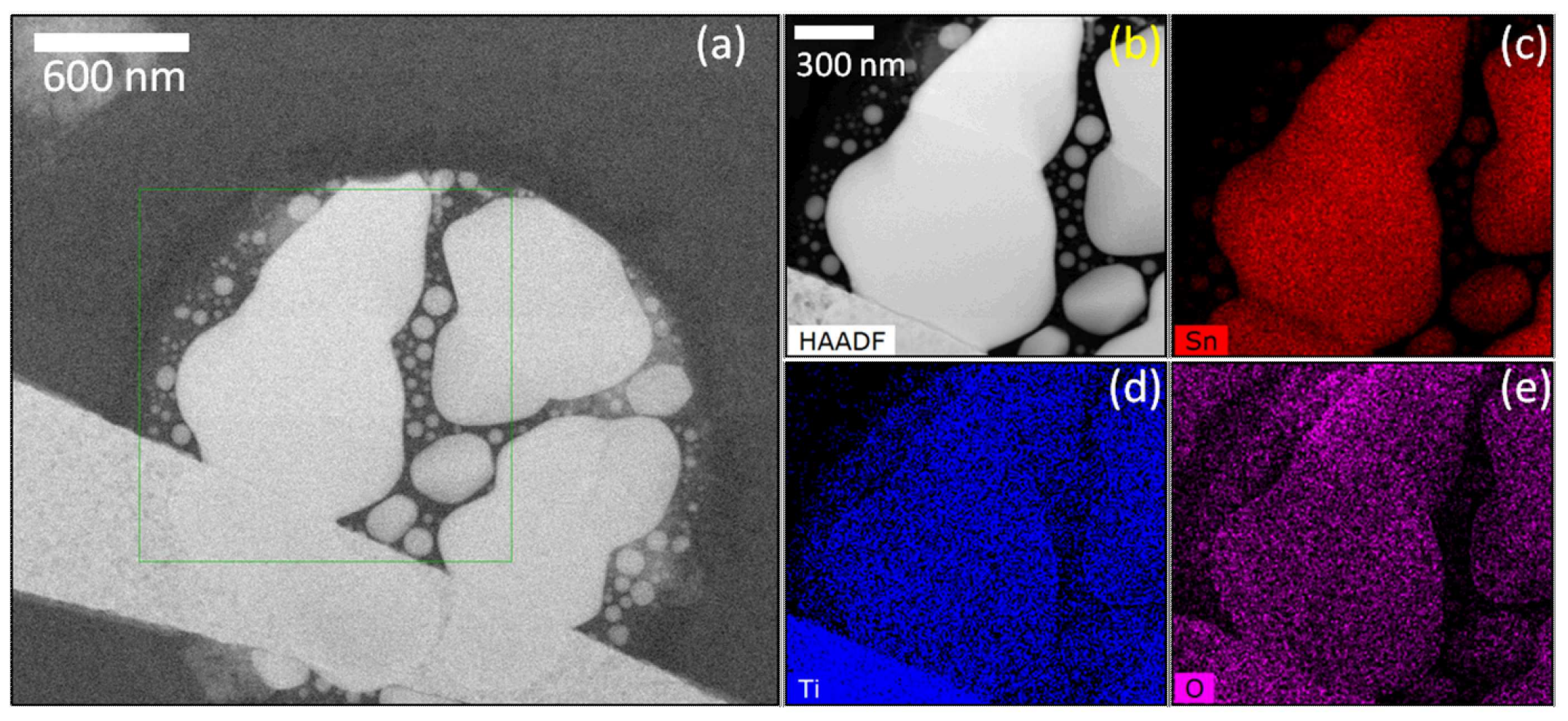


Figure . Energy Dispersive Spectroscopy mapping of TiO_2 coated Sn nanostructures. (a) HAADF image TiO_2 coated Sn nanostructures patterned in TEM platform, (b) the zoomed area of from “a “ and their corresponding elemental mappings, (c) Sn, (d) Ti and (e) O

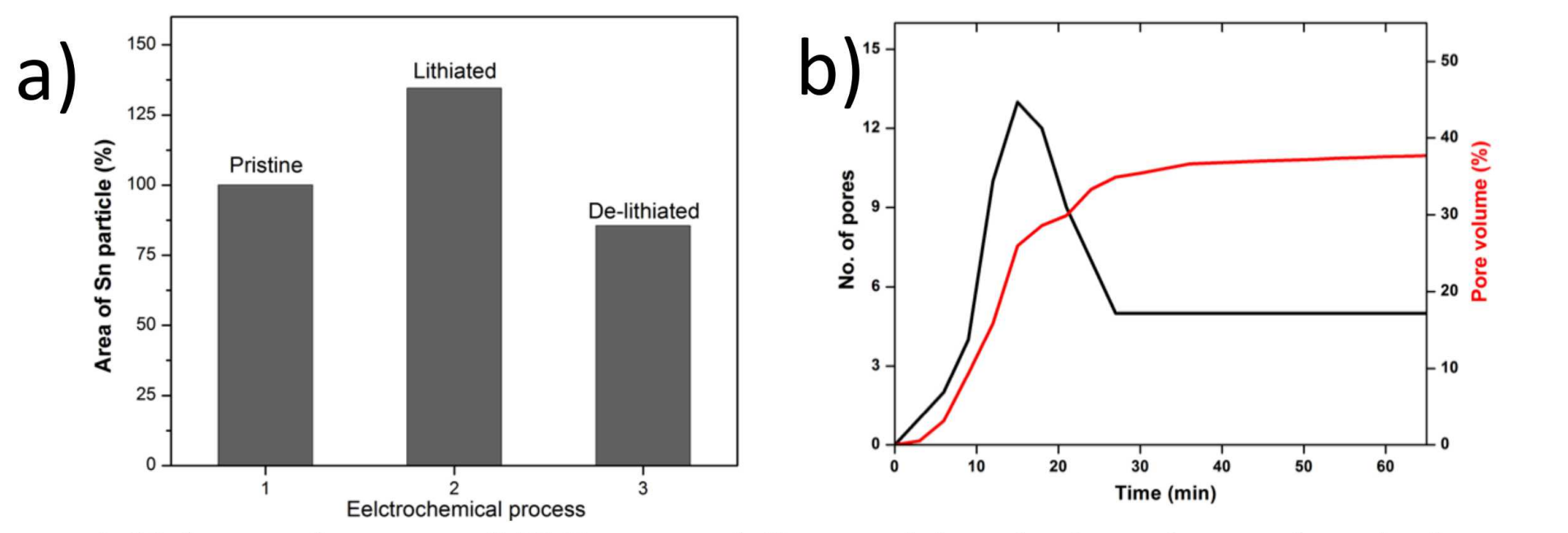


Figure. a) Volume changes of TiO_2 coated Sn particles during electrochemical process and b) the plot between number pores and total pore volume *vs* electrochemical reaction process time in minutes

Electrochemical STEM of Sn

Electrochemical STEM of TiO_2@Sn

W.E : Sn or TiO_2@Sn (50 or 53 nm)
C.E/R.E: Ti (50 nm)
Electrolyte:1M $LiPF_6$ (EC:DMC)
Current density: 1mA cm^{-2}

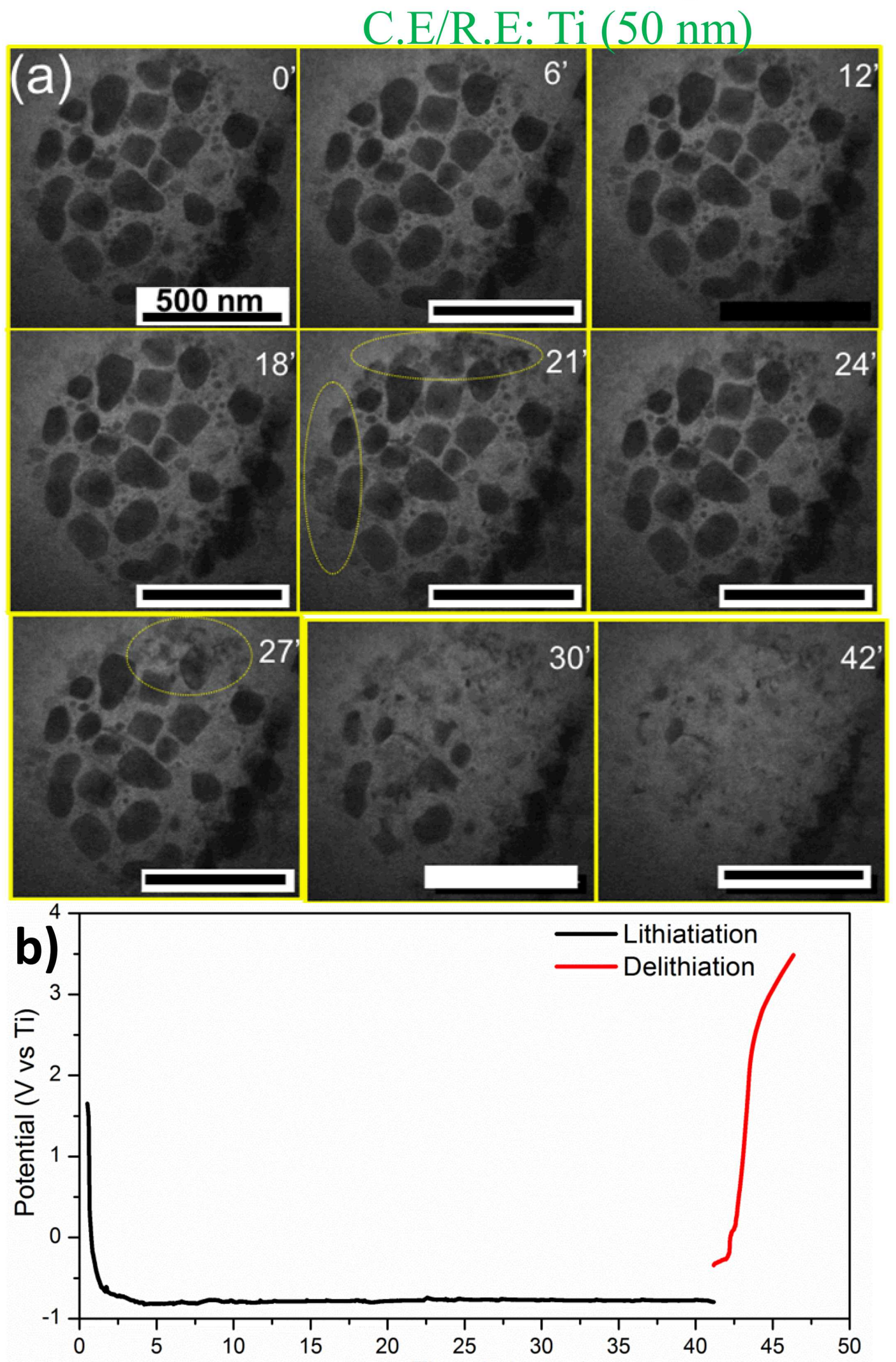


Figure . STEM bright field images of (a) electrochemical lithiation of Sn nanostructures. (b) corresponding galvanostaic lithiation and delithiation profile

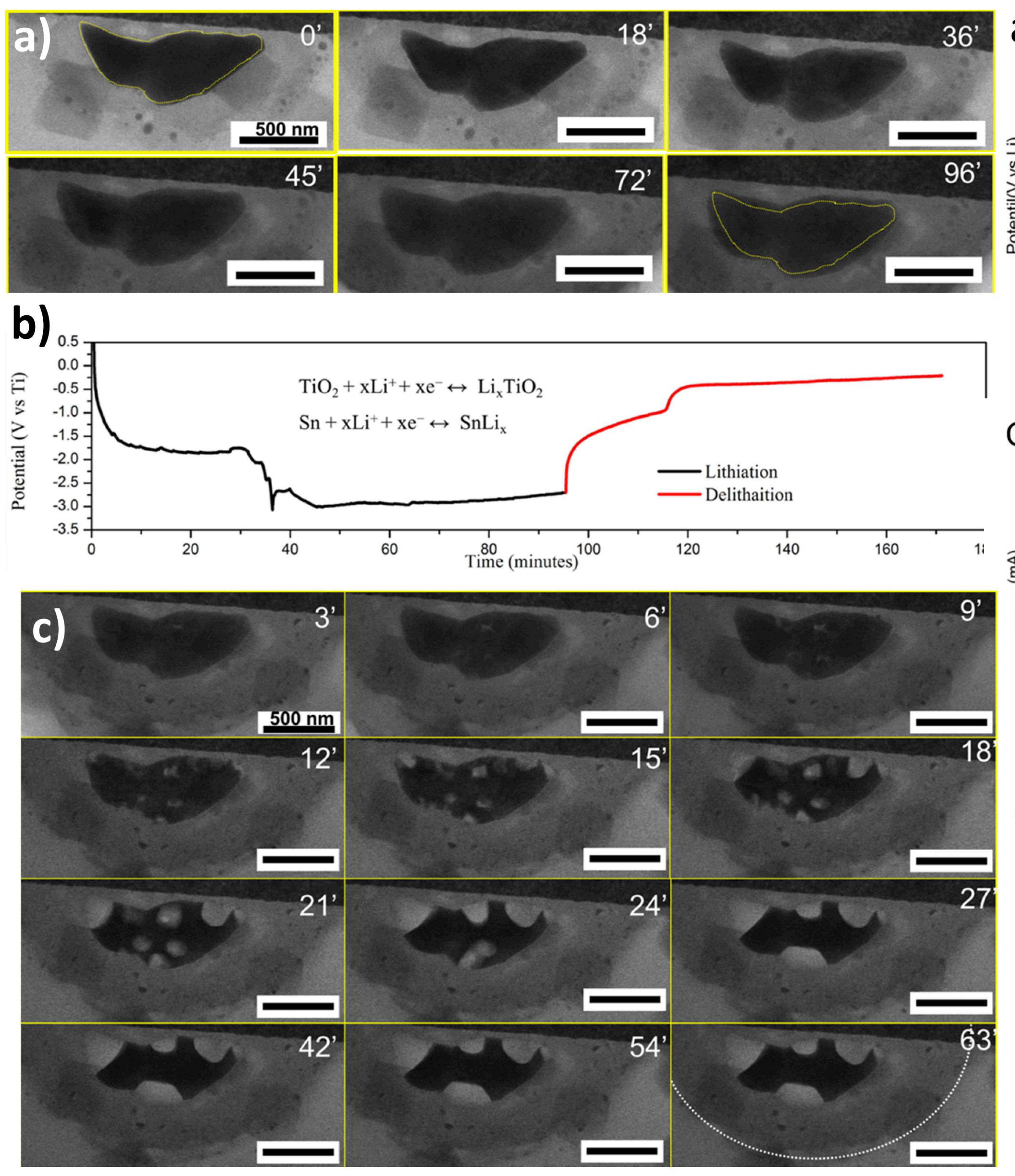


Figure. STEM bright field images of (a) electrochemical lithiation of TiO2 coated Sn; (b) corresponding galvanostaic lithiation and delithiation profile. (c) electrochemical delithiation of TiO2 coated Sn.

The top right of each STEM image represents the time (in minutes) of image has taken during electrochemical process. Each images were acquired with 3 minutes intervals.

Coin cell Studies of Sn and TiO_2@Sn

W.E : Sn or TiO_2@Sn
C.E/R.E: Li foil
Electrolyte:1M $LiPF_6$ (EC:DEC)
Current density: 5.7uA cm^{-2}

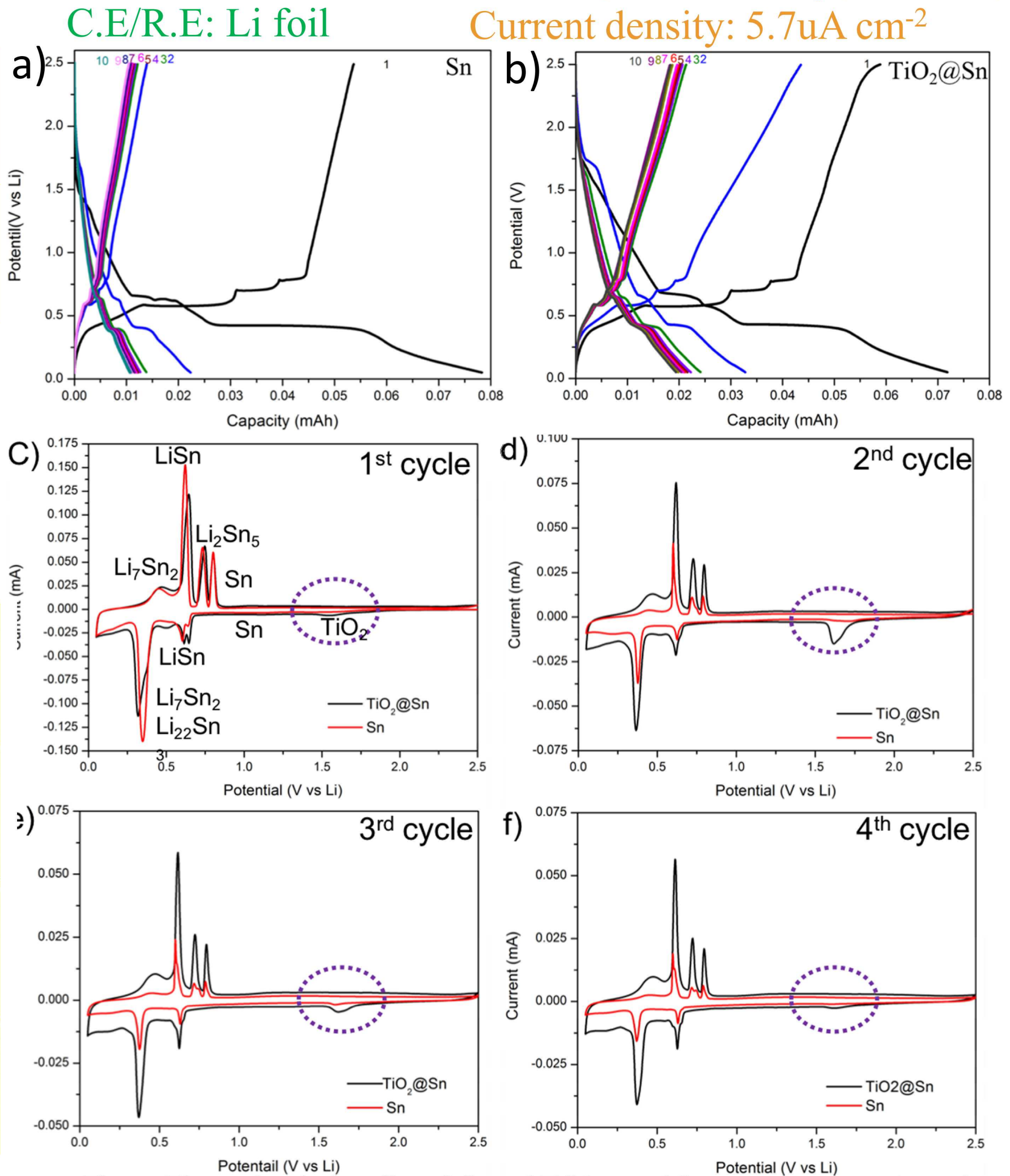
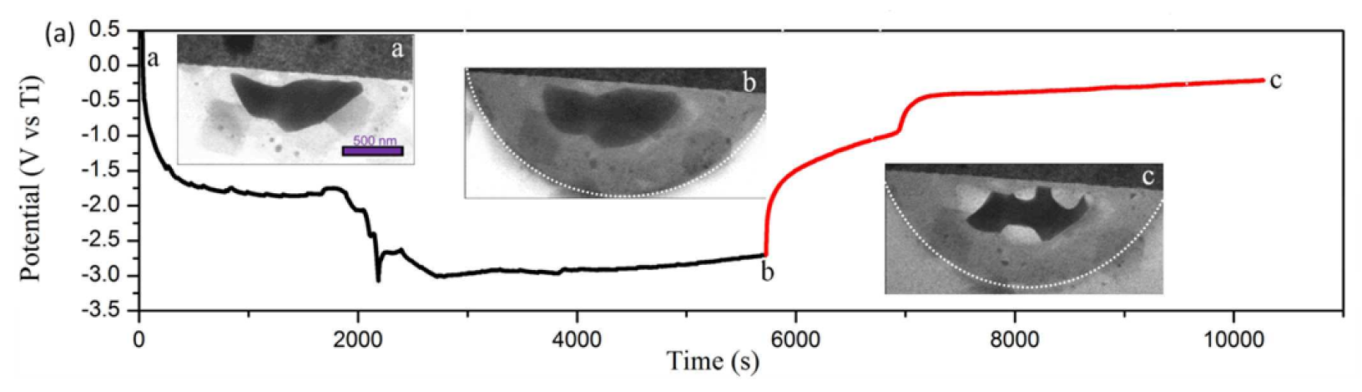


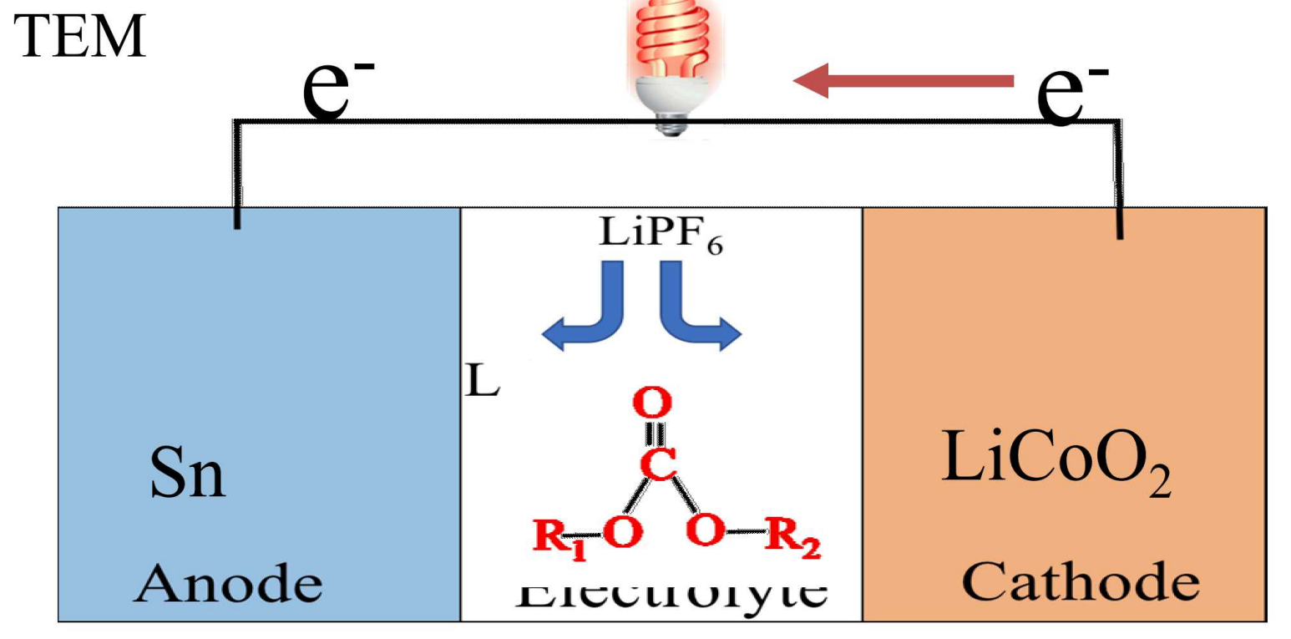
Figure. Electrochemical studies of Sn and TiO2 coated Sn nanostructures using coin-cells. The galvanostatic cycling performance of (a) Sn and (b) TiO2 coated Sn nanostructures at a current density of 5.7 uA/cm2; Cyclic voltommograms of Sn and TiO2 coated Sn nanostructures at a scan rate of 0.1 mV/s (a) first cycle (b) second cycle, (c) third cycle and(d) fourth cycle

Summary

- ➢ In situ electrochemical reversible lithiation and de-lithiation of Sn reactions has been observed via custom designed electrochemical platform, and S/TEM along with surface protection of Sn with TiO2 thin layer



- ➢ Currently working on employment of lithium based cathodes into STEM liquid cell platform towards a full cell liquid electrolyte Li-ion battery within the TEM



Publications(to be submitted)

1. Goriparti et al., In Situ S/TEM Observations of Electrochemical Lithiation and De-lithiation of TiO_2@Sn Nanostructures in A Sealed Liquid-cell

References:

[1] S. Goriparti et al, J.Power Sources, 257 (2014) 421; [2] J. Wang et al, J. Electrochem. Soc, 161 (2014) F3019
[3] M. J. Williamson *et al*, Nat. Mater. **2** (2003), p. 532; [4] A. J. Leenheer *et al*, J. Microelectromech. 24 (2015) 1061
[5] A. J. Leenheer *et al*, ACS Nano, 10 (2016) 5670

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