Efficient and Stable Bi and Sb Anodes in Solid State Lithium Batteries

Itinerary

- **Background**

  - Motivation and Challenges of All Solid-State Batteries (ASSBs)

  - How a Solid Electrolyte Works

  - Mechanism and Benefits of Li Alloys (Review)

  - Conditions for Fracture in Li Alloys

- **Paper**

  - Presentation of Results

- **Questions as a Referee**

  - Questions regarding the paper

 - Questions about the theory and some underlying physics

All Solid-State Batteries (ASSBs)

- **Motivation**

  - Liquid electrolytes are highly flammable, a significant safety concern in electric vehicles (EVs)

  - SEs have potential for higher energy densities

- **Challenges**

  - Ionic conductivity lower than those of LEs

  - High interfacial resistance

  - Narrow operating window

Y. –K. Sun. *ACS Energy Lett.* (2020) 3221-3223
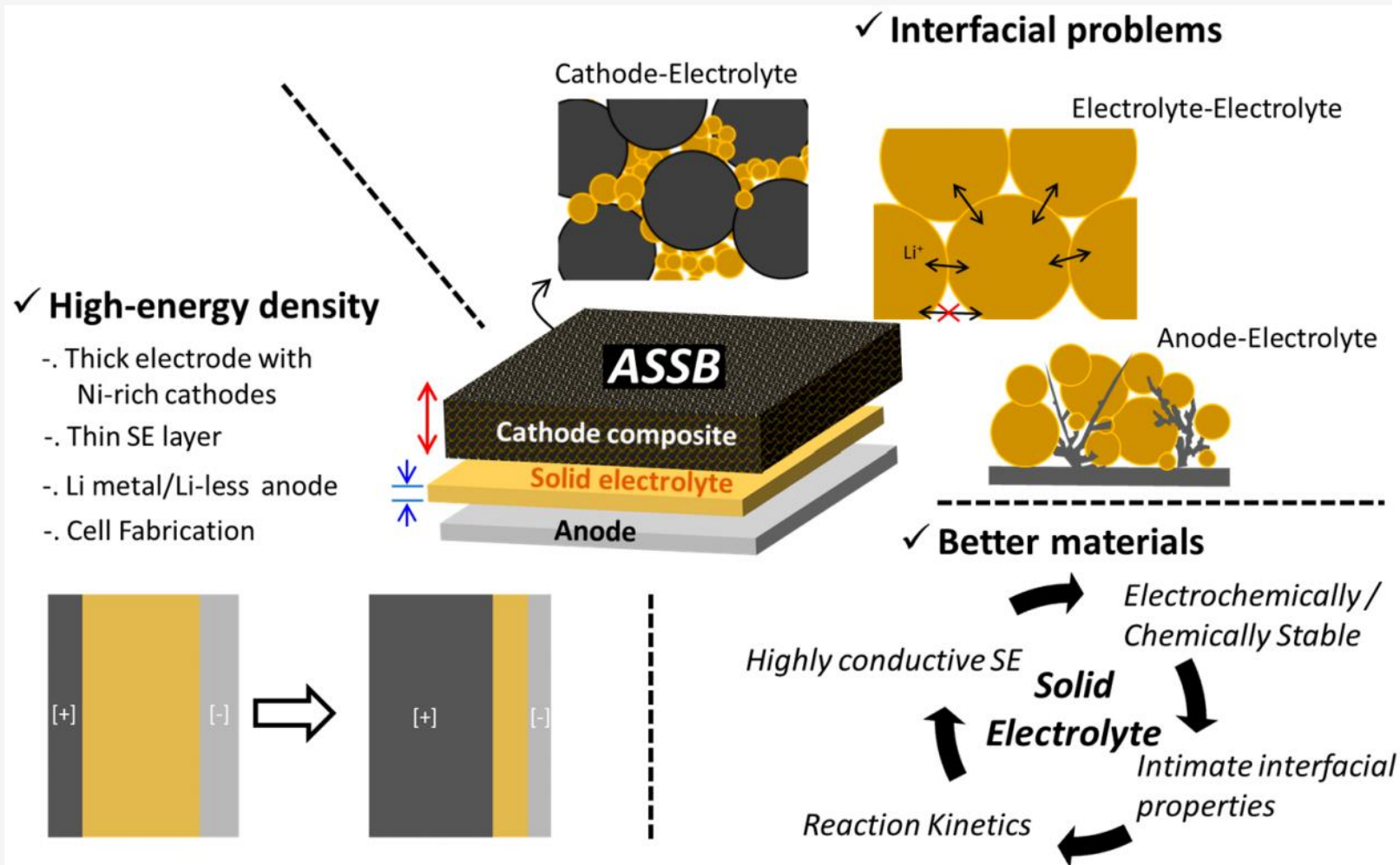
How a Solid Electrolyte Works

- Liquid electrolytes (LEs) are a Li salt dissolved in an organic solvent, relying on **diffusion of solvated ions**

- Solid electrolytes (SEs) rely on **hopping through Li vacancies**

M. R. Busche, et al. *Nature Chemistry.* 8 (2016) 426-434
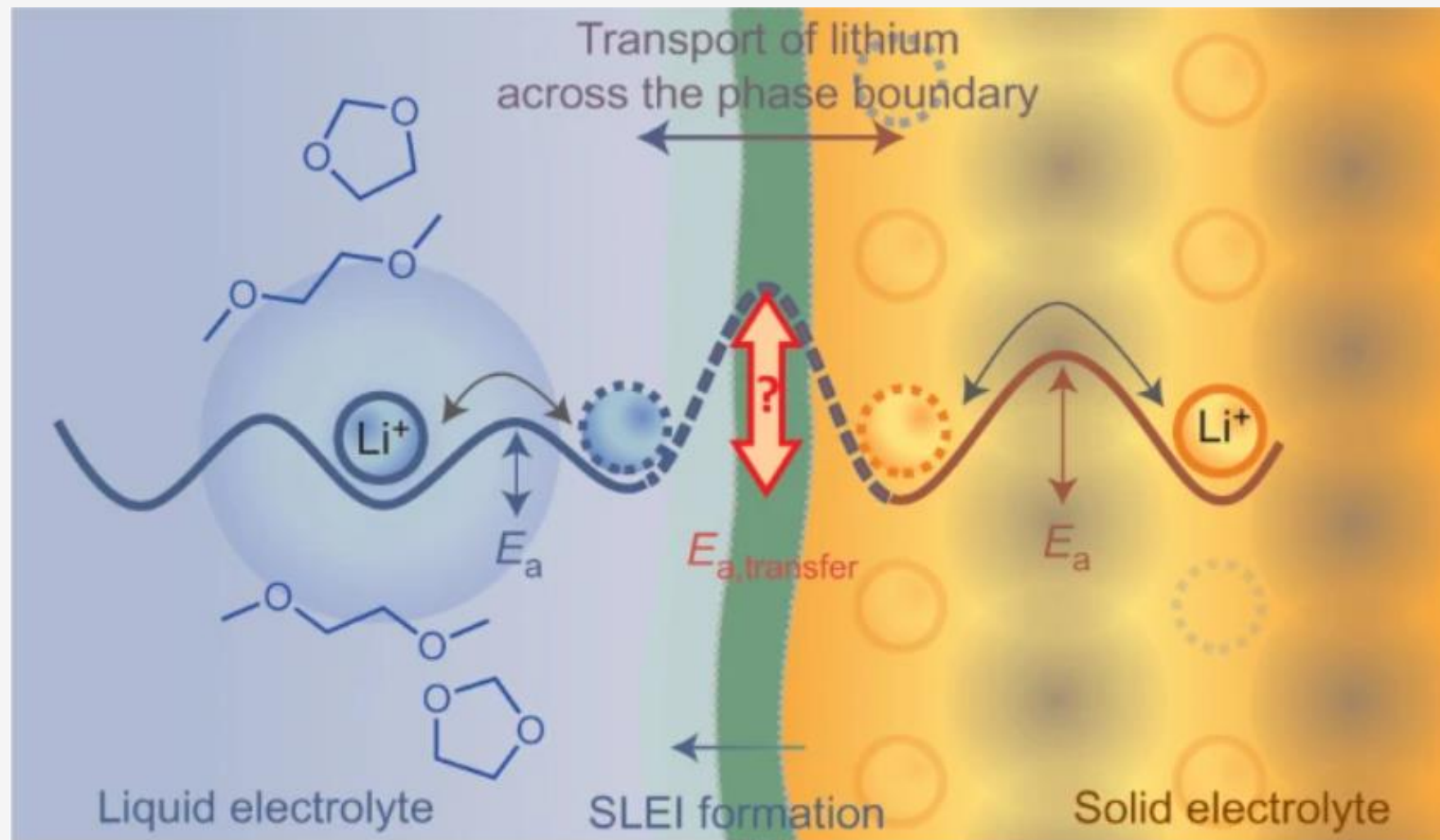
Li Alloys (Review)

- Alloy materials **allow more lithium per amount of metal than intercalation** ($\leq$ 1)

- **Alloying materials (-)** alloy with lithium, causing massive volume expansions

- Alloy materials **expand our electrochemical tool kit:** we expand from solely transition metal oxides (Ti, Mn, Fe, Co. Ni) and C to Mg, Al, Si, Zn, Ga, Sn, Sb, Pb, and Bi

- **Lithiation/Delithiation**: Insertion/removal of Li from your host structure
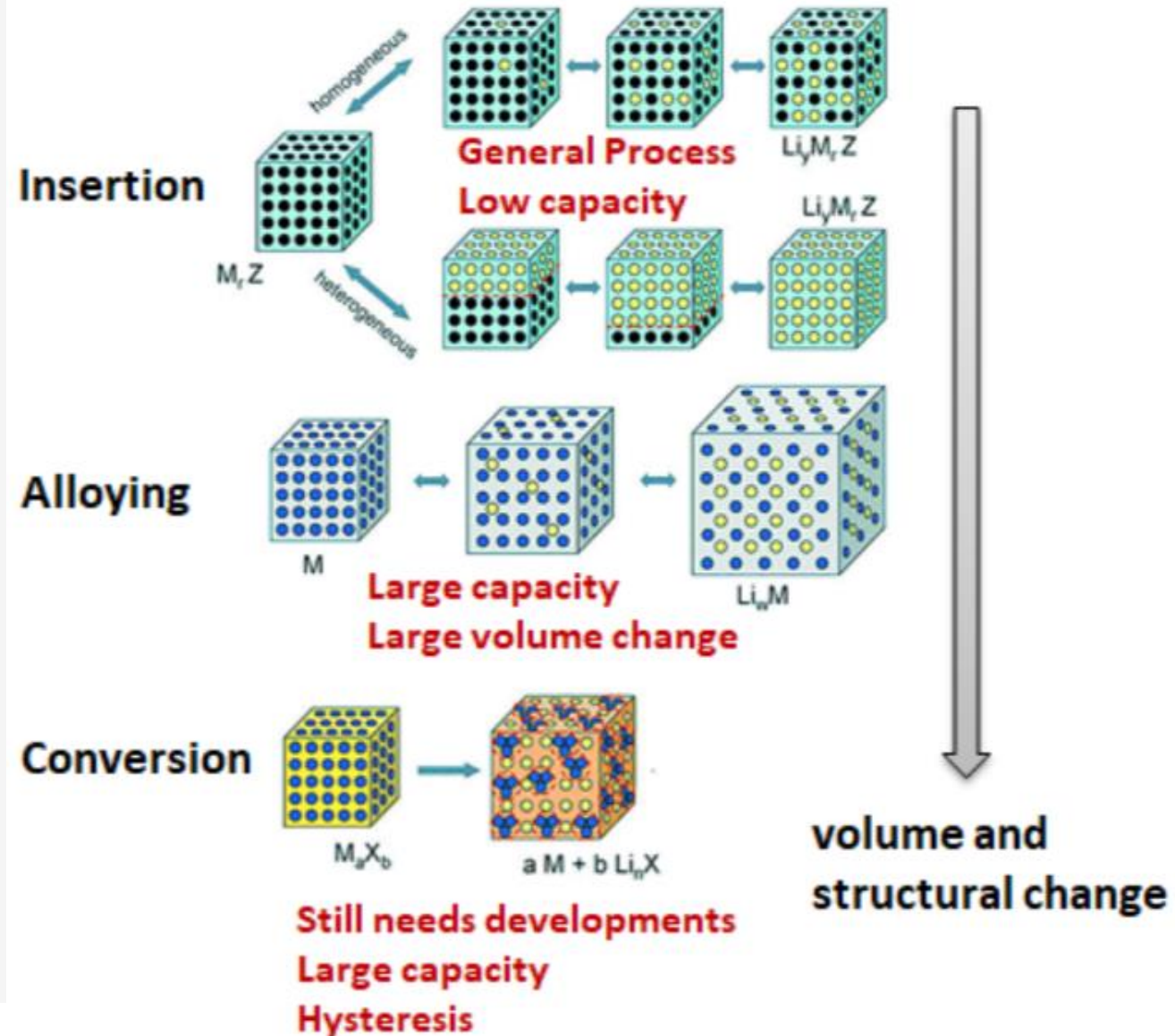
Li Alloys, Gravimetric (Specific) Capacity

- ***Gravimetric Capacity quantifies how much charge can theoretically be obtained per gram of material***

- $Q_{theoretical}$ *= (nF) / (3.6*M$_W$)   mAh g^{-1}*

- For Bi: Q_{Bi} = ((3 mol * 96485 A s mol^{-1}) / (208.98 g)) * (1000 mA/A) / (3600 s/h)

    Q_{Bi} = 385 mAh g^{-1}

- For Bi: Q_{Sb} = ((3 mol * 96485 A s mol^{-1}) / (121.76 g)) * (1000 mA/A) / (3600 s/h)

    Q_{Sb} = 660 mAh g^{-1}

- Values listed below do not account for the Li present and changes in density

Materials	Li	C	$Li_4Ti_5O_{12}$	Si	Sn	Sb	Al	Mg	Bi
Density (g cm^{-3})	0.53	2.25	3.5	2.33	7.29	6.7	2.7	1.3	9.78
Lithiated phase	Li	LiC_6	$Li_7Ti_5O_{12}$	$Li_{4.4}Si$	$Li_{4.4}Sn$	Li_3Sb	LiAl	Li_3Mg	Li_3Bi
Theoretical specific capacity (mAh g^{-1})	3862	372	175	4200	994	660	993	3350	385
Theoretical charge density (mAh cm^{-3})	2047	837	613	9786	7246	4422	2681	4355	3765
Volume change (%)	100	12	1	320	260	200	96	100	215
Potential vs. Li (~V)	0	0.05	1.6	0.4	0.6	0.9	0.3	0.1	0.8

Fracture in Li Alloys

- Lithiation causes **compression on the larger-specific-volume phase and tension in the other layer**

- A simple 1D stress model predicts **the critical fracture size to be below 10nm** for Bi (consistent with literature)

- **Fracture of lithium alloys happens both during lithiation and delithiation** (seen later)

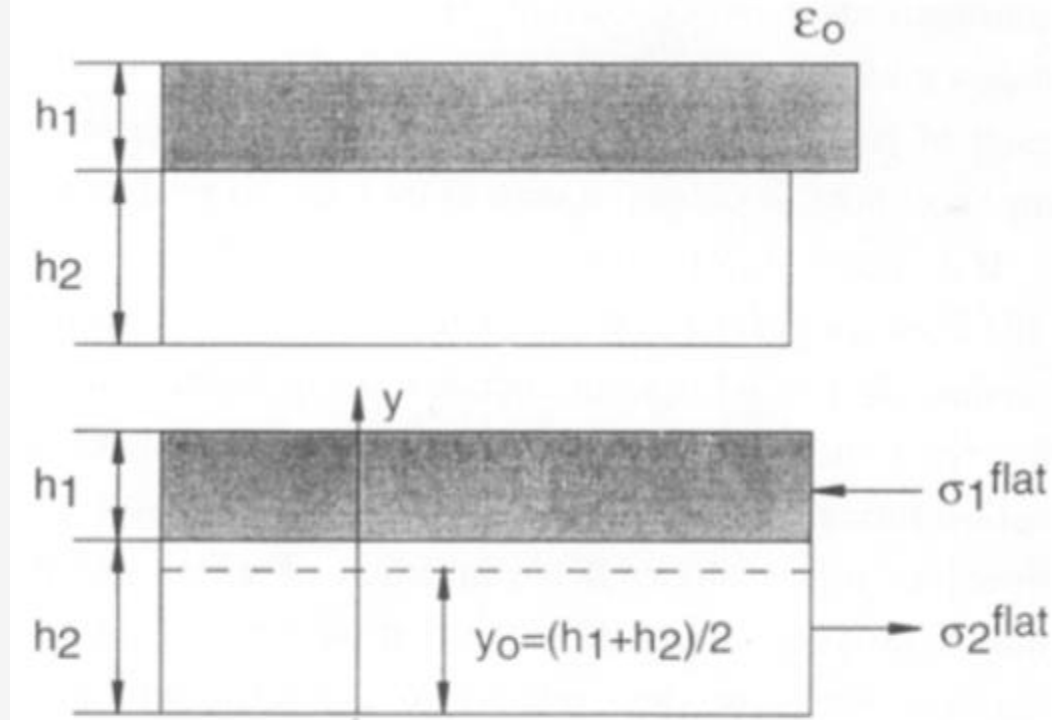- *Lithium alloying process forms two-phase reaction boundary*

Fig. 1. Geometric relations in the simple one-dimensional bilayer model.

R.A. Huggins and W. D. Nix, *Ionics* 6 (2000) 57

Fracture in Li Alloys

- Analysis grows increasingly complex when accounting for:

  - changes in surface energies with lithiated phases

  - plastic flow (inelastic strain)

  - preferred lithiation orientation

  - anisotropy

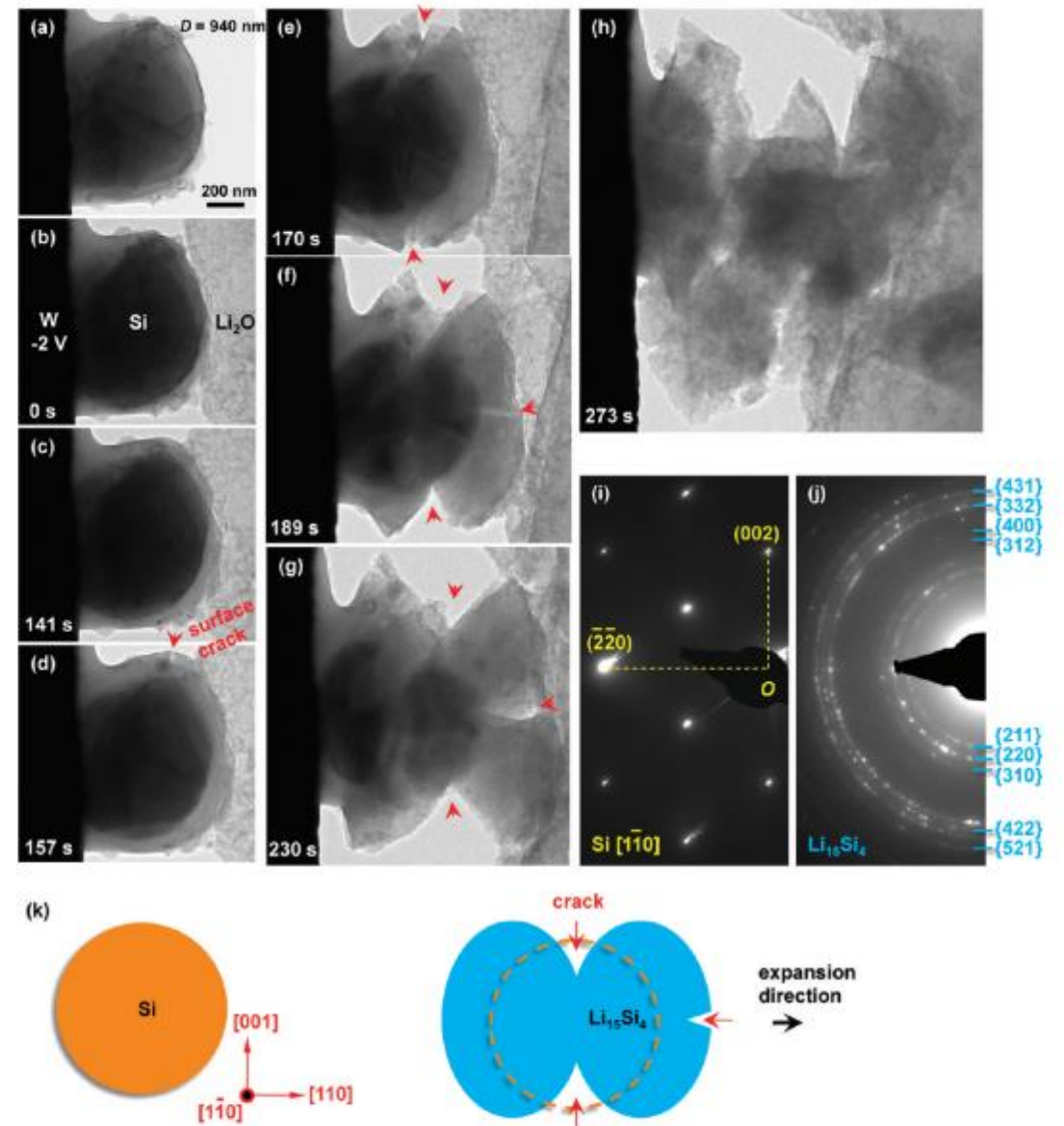 - spherical geometries and small dimensions comparable to lattice units

X. H. Liu, et al., *ACS Nano*. 6 (2012) 1522-1531

Figure 1. Surface cracking and fracture of a large silicon nanoparticle (SiNP) during electrochemical lithiation. (a) Pristine SiNP with a diameter of ~940 nm. (b–h) Crack nucleation and fracture of the SiNP in the lithiation process. After the Li_2O/Li electrode contacted the SiNP sitting on the W electrode, a potential of −2 V was applied to the W electrode with respect to the Li metal (b). The lithiation occurred on the particle surface and proceeded inward as the gray-contrasted Li_xSi shell was thickened. When the shell thickness reached ~150 nm, the first crack emerged near the surface, as marked by the red arrowhead (d). More cracks nucleated and propagated along different directions upon further lithiation (e–g), and finally the particle exploded into many tiny pieces (h). (i,j) Electron diffraction patterns (EDPs) showing the phase transformation from single crystalline Si (i) to polycrystalline $Li_{15}Si_4$ after lithiation (j). (k) Schematic illustration showing the crystallography, expansion, and crack formation. The swelling was along Si ⟨110⟩ directions.

Fracture in Li Alloys
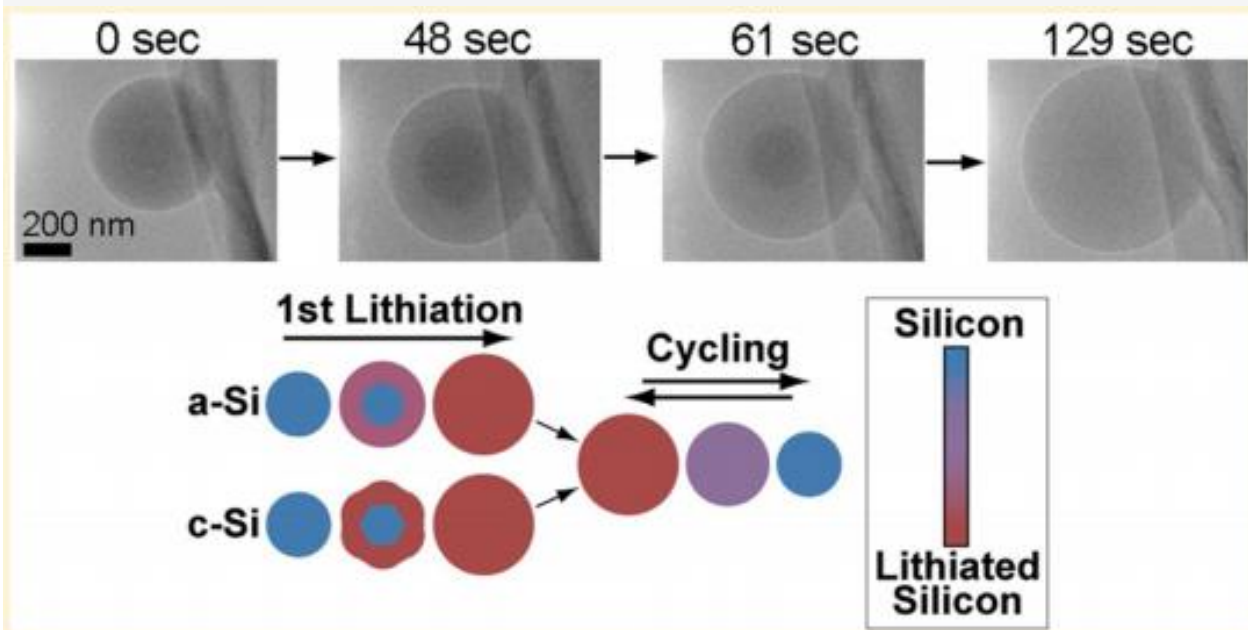
M. T. McDowell, et al., *Nano Lett*. 13 (2013) 758-764
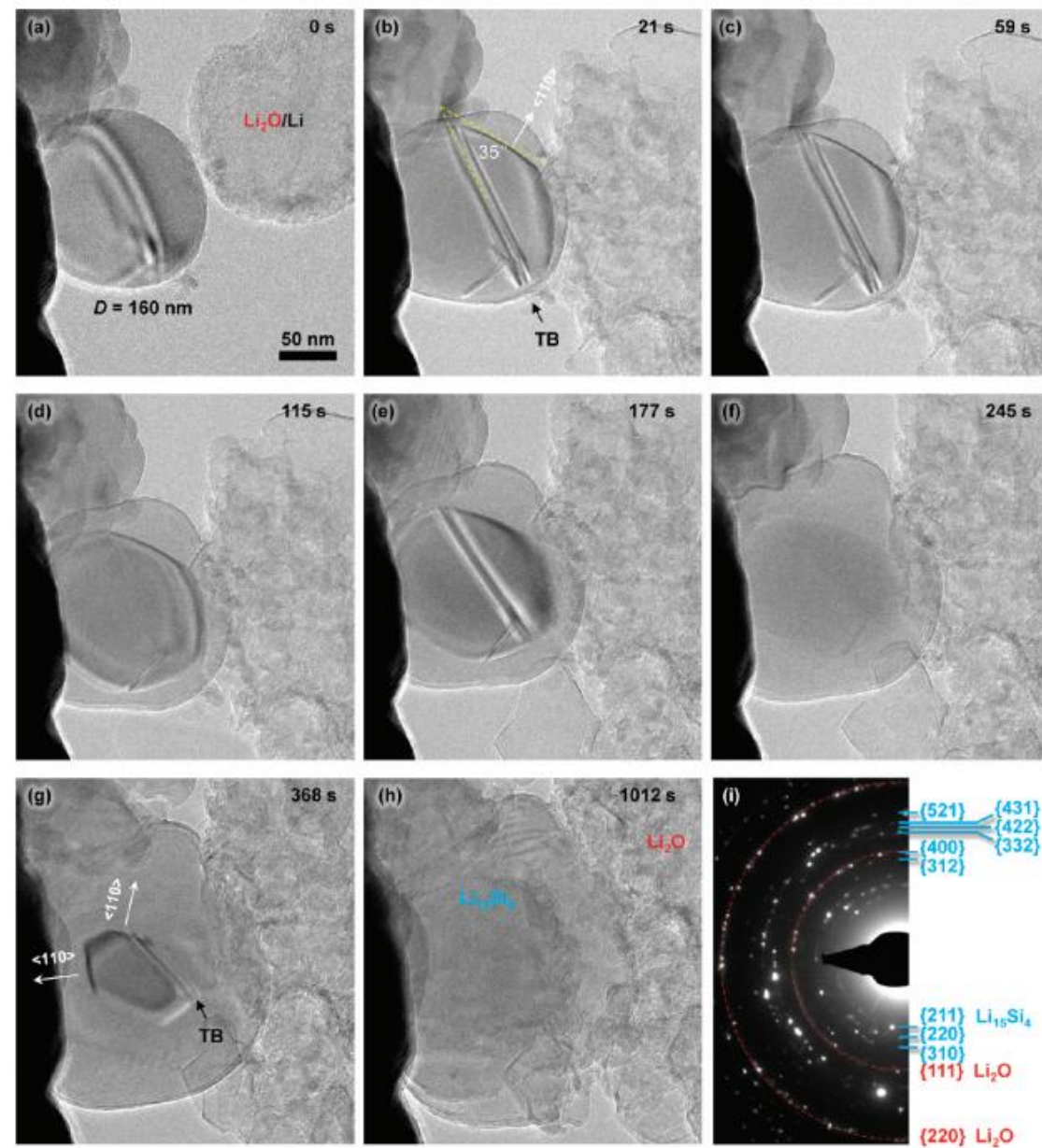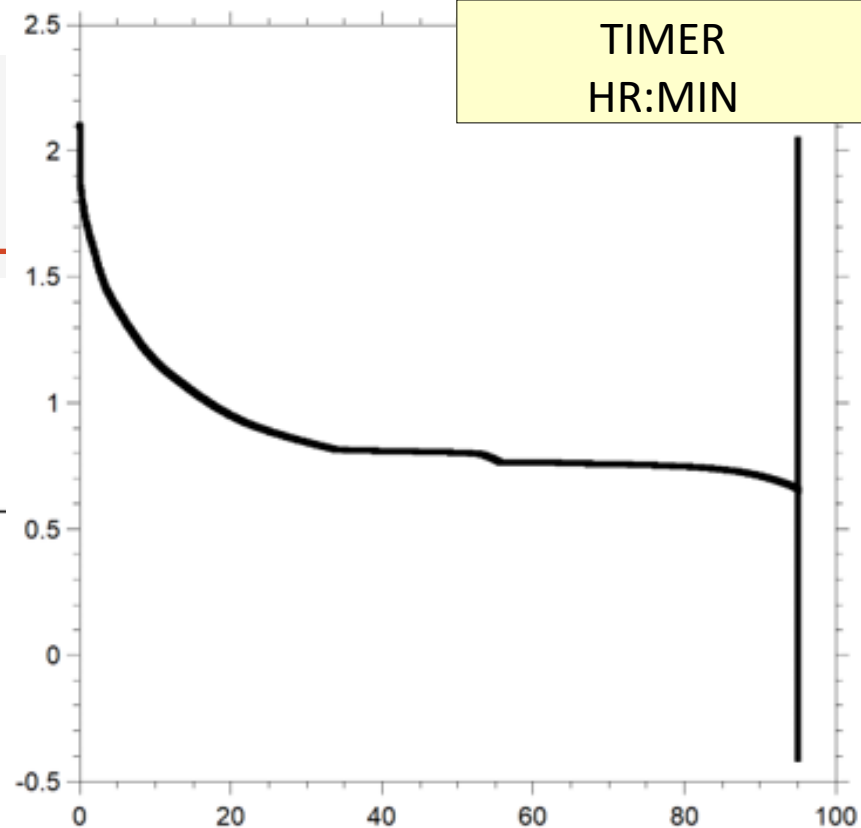
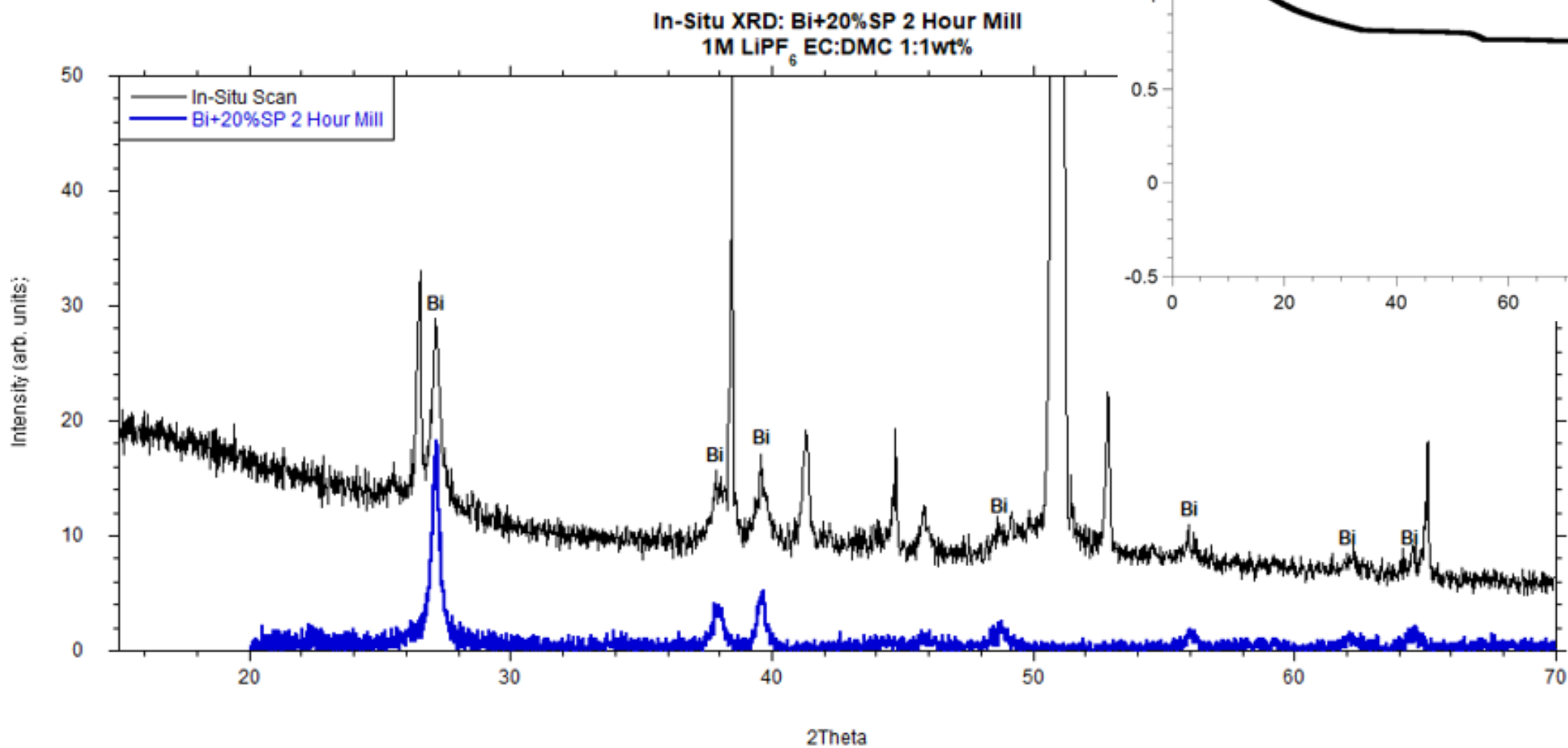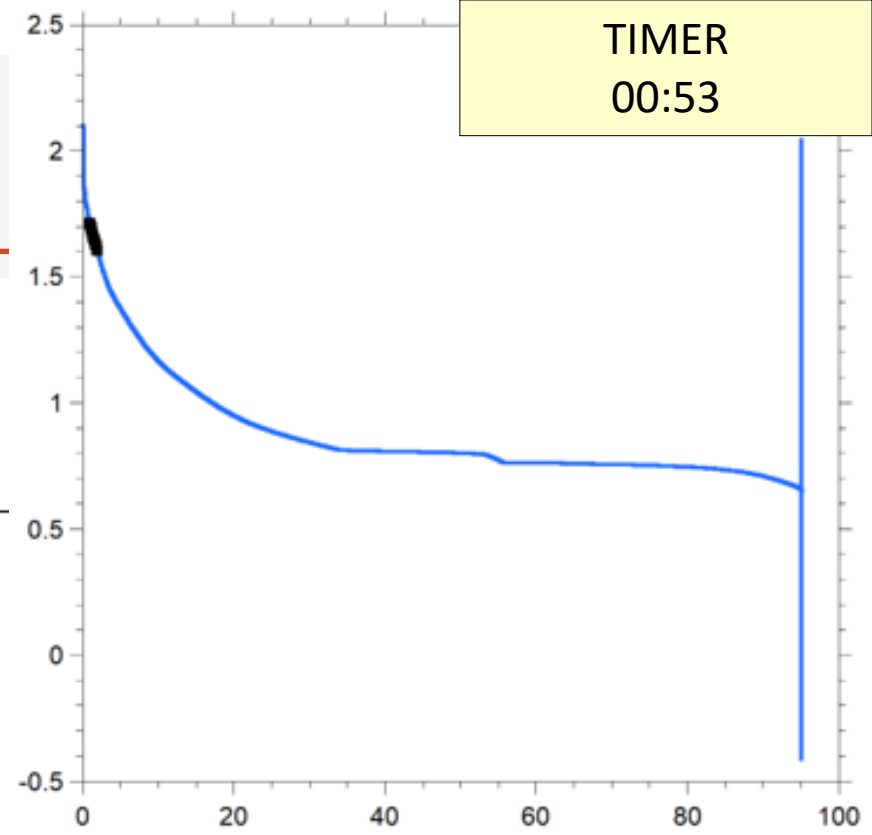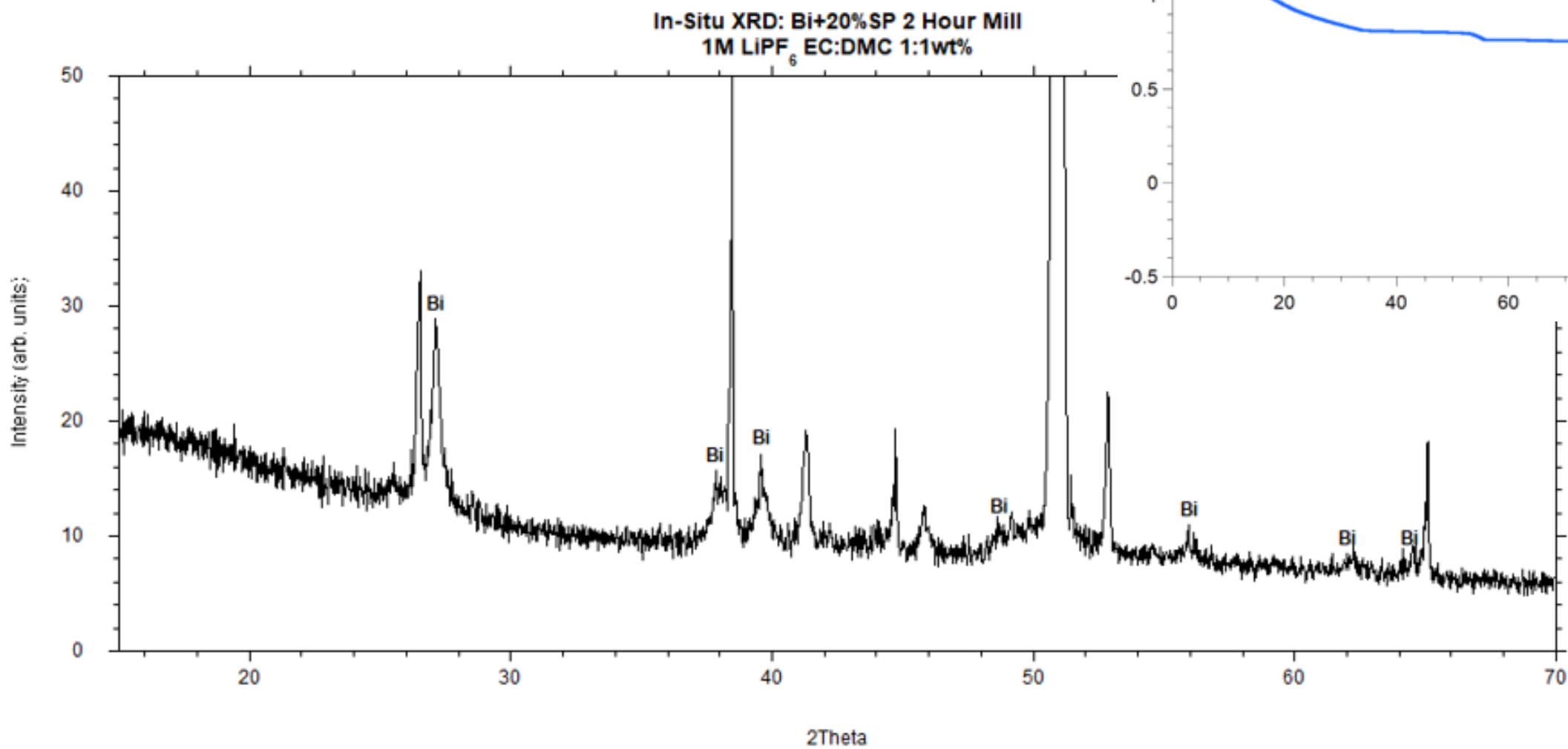X. H. Liu, et al., *ACS Nano*. 6 (2012) 1522-1531

Figure 2. Electrochemical lithiation of a small SiNP around the critical size showing no fracture. (a) Pristine SiNP with a diameter of about 160 nm. (b–g) Steady lithiation stage without cracking. There was a twin boundary (TB) in the center of the SiNP. Fast swelling along ⟨110⟩ resulted in a bump on the flat (110) plane, which formed a 35° angle with the TB (b). Anisotropic lithiation led to formation of the faceted Si core during the lithiation process (g). (h) Morphology of the fully lithiated particle. The electron beam was blanked during the lithiation process except for a short exposure for imaging. (i) EDP from the fully lithiated particle confirming the formation of polycrystalline $Li_{15}Si_4$ phase (blue lines and indices). The Li_2O phase showing up in the EDP was from the adjacent Li_2O layer (red dashed arcs and indices).
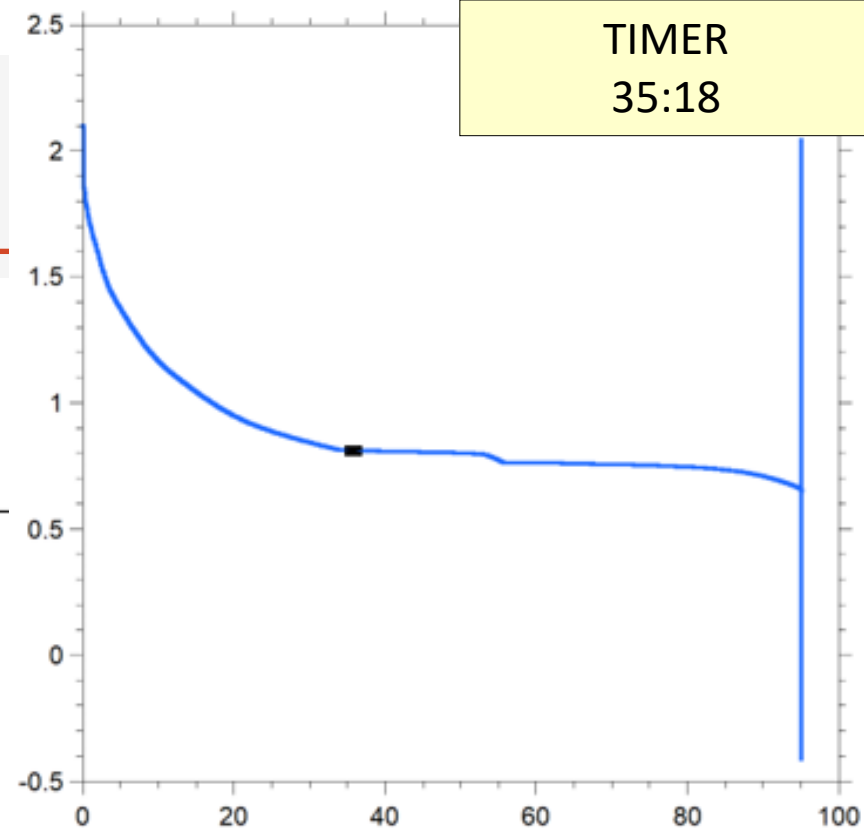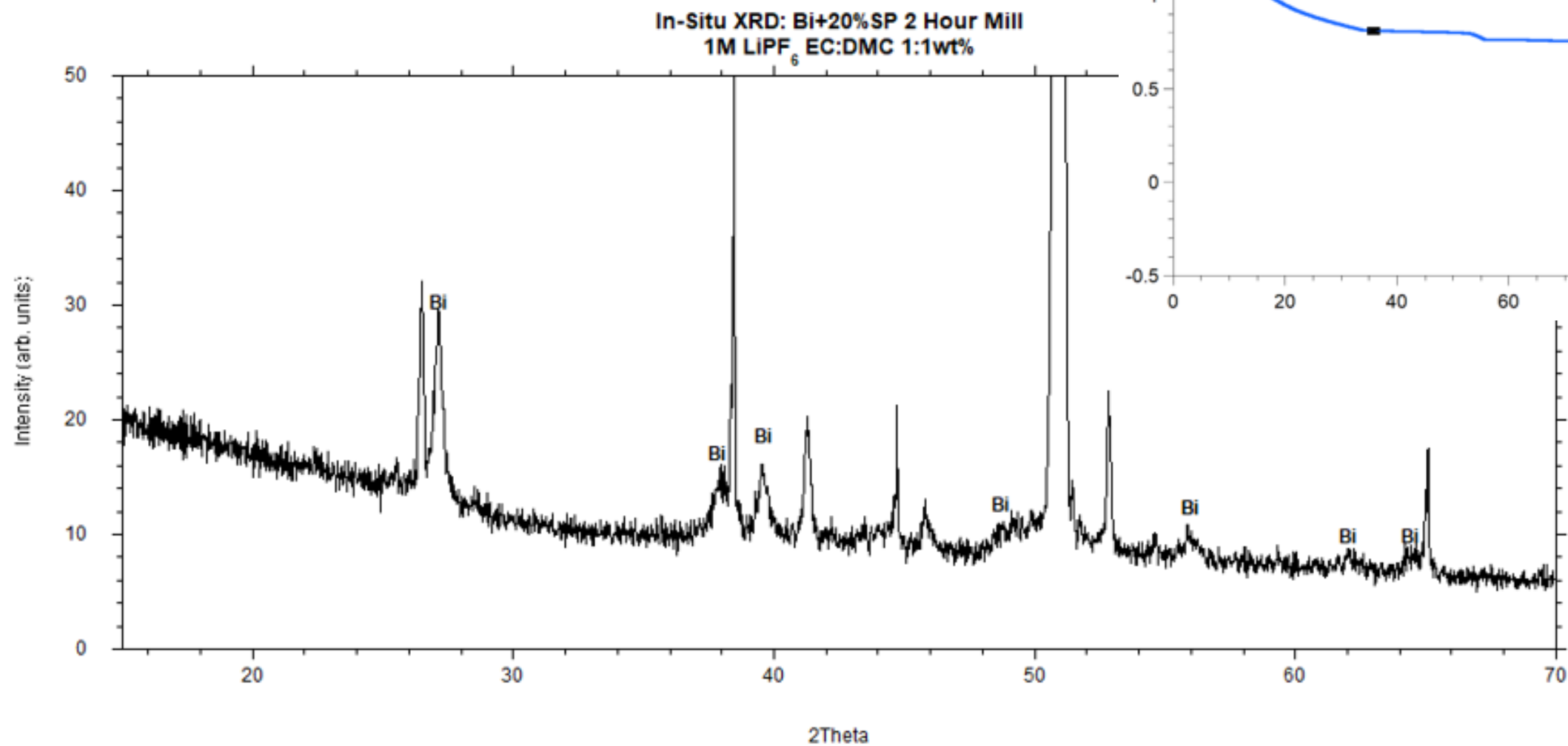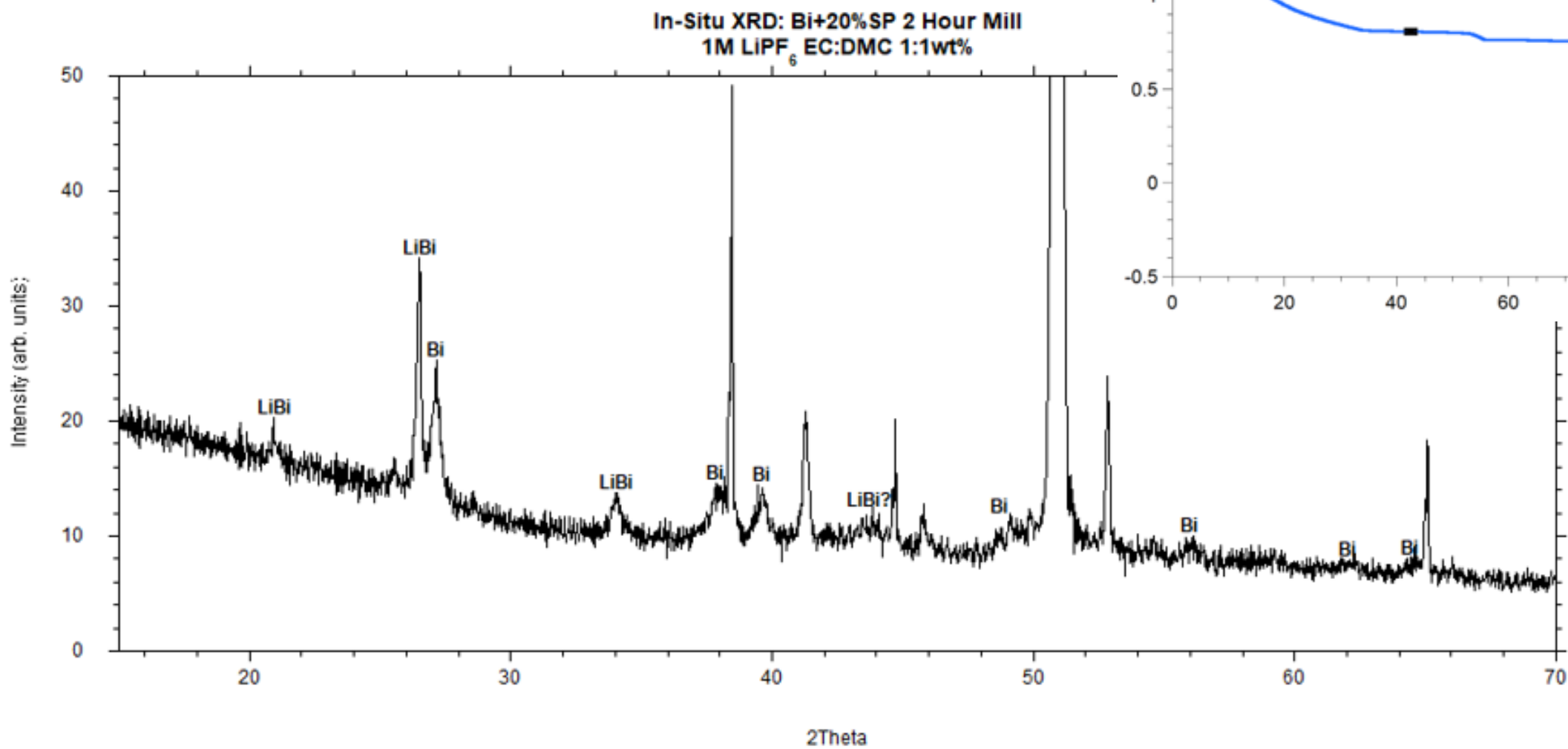
Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%

TIMER
HR:MIN

Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%

TIMER
00:53

Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%

TIMER
35:18

Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%

TIMER
42:00

Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%

Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
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Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%
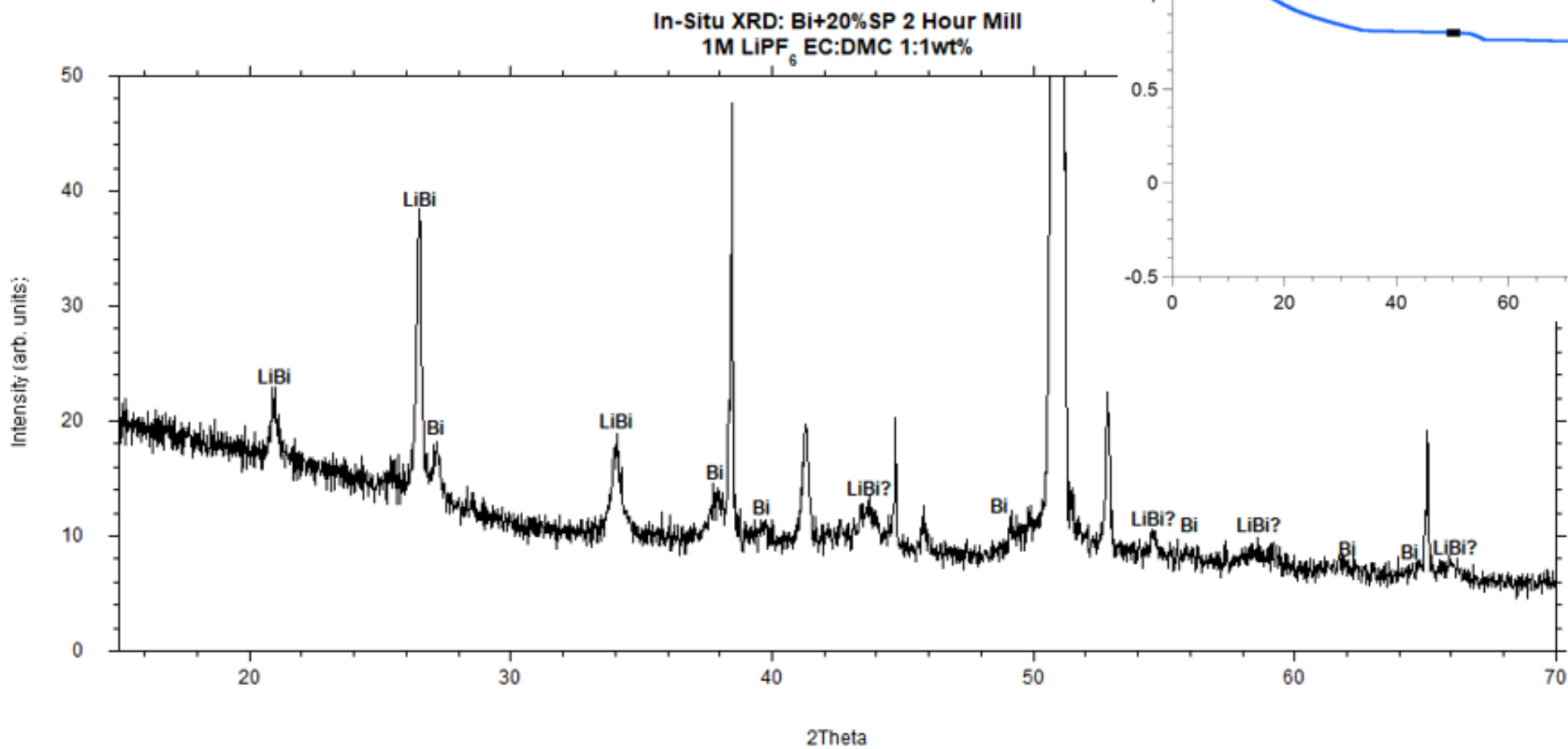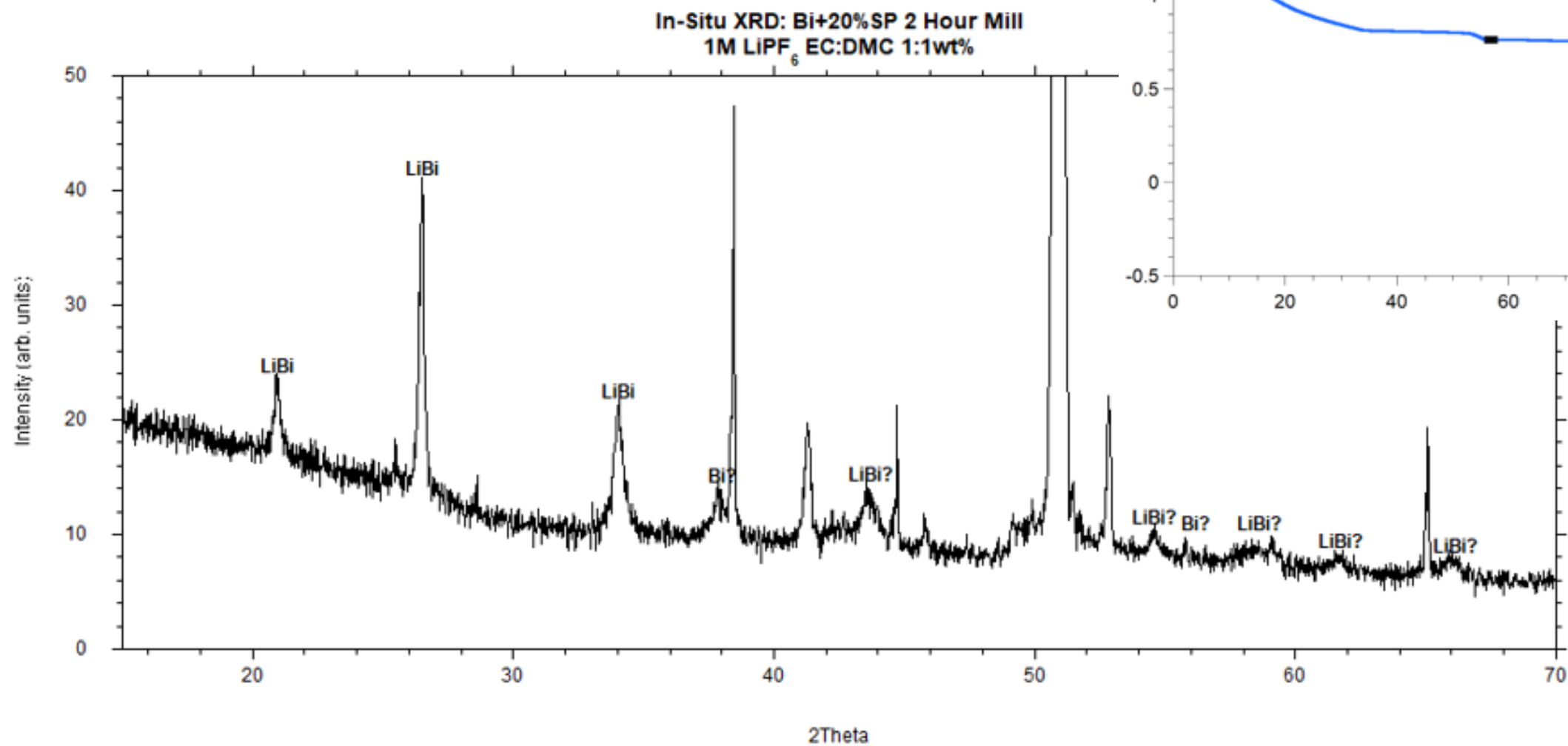
TIMER
68:46

Lithiation of Bi
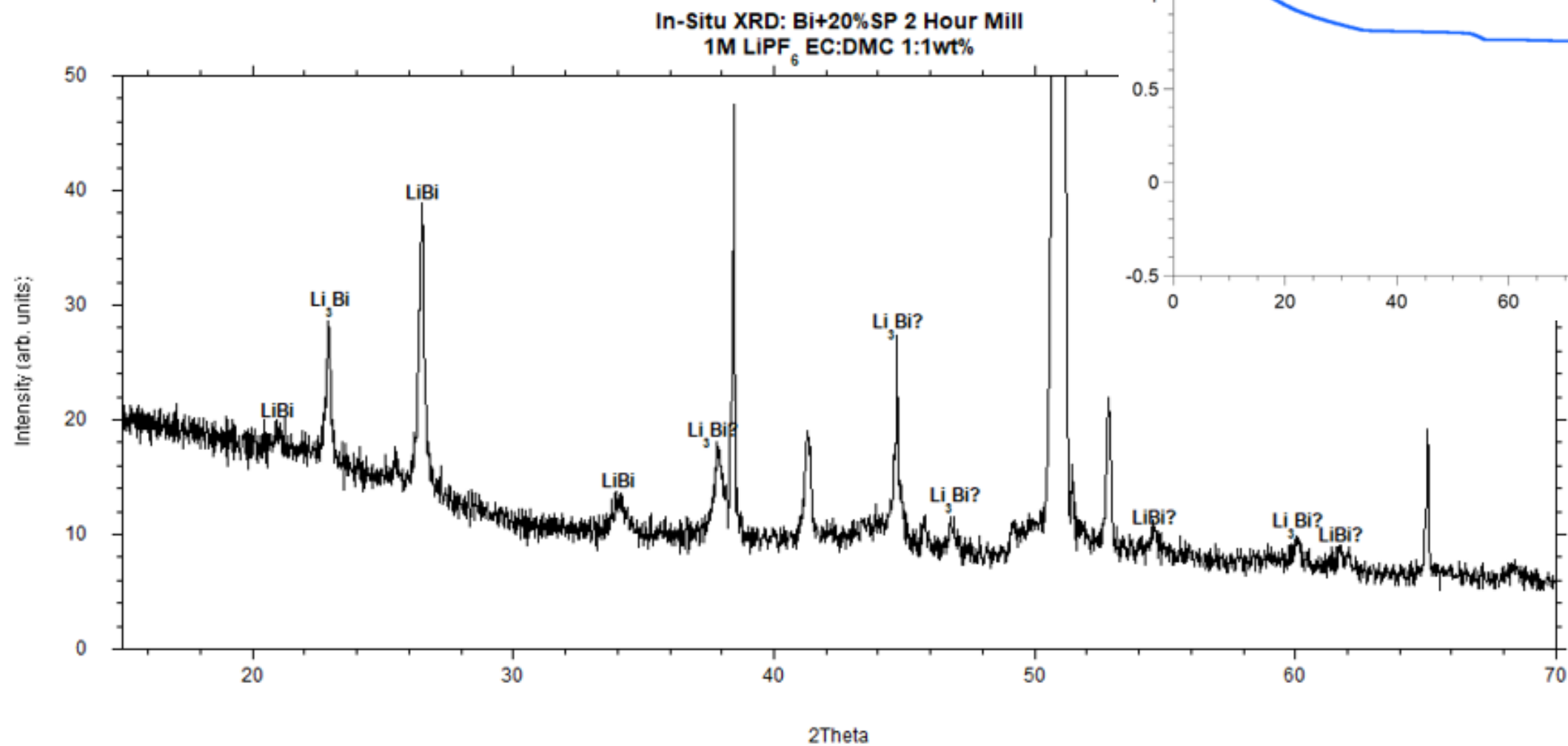
In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%

TIMER
76:33

Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%

Lithiation of Bi

In-Situ XRD: Bi+20%SP 2 Hour Mill
1M LiPF$_6$ EC:DMC 1:1wt%
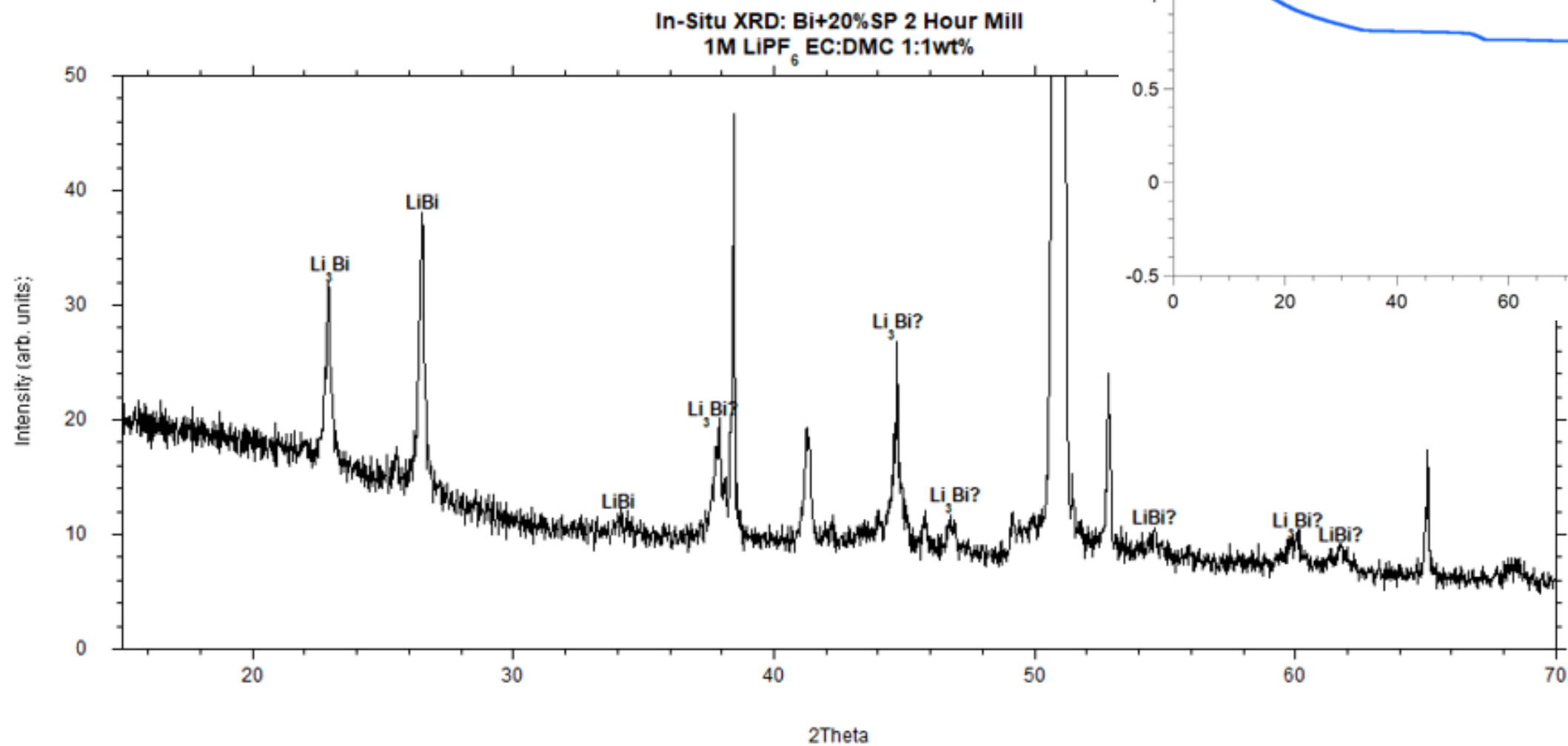
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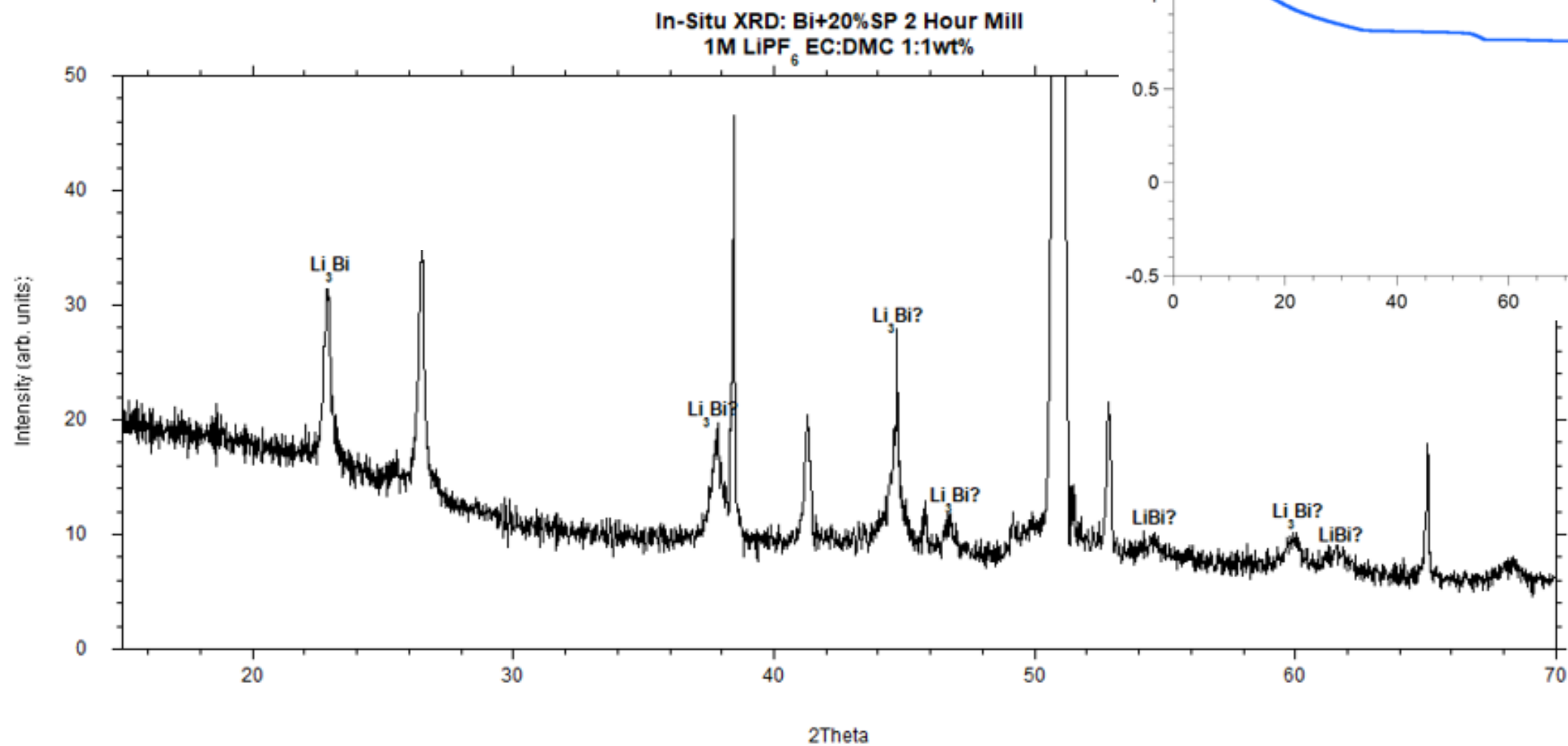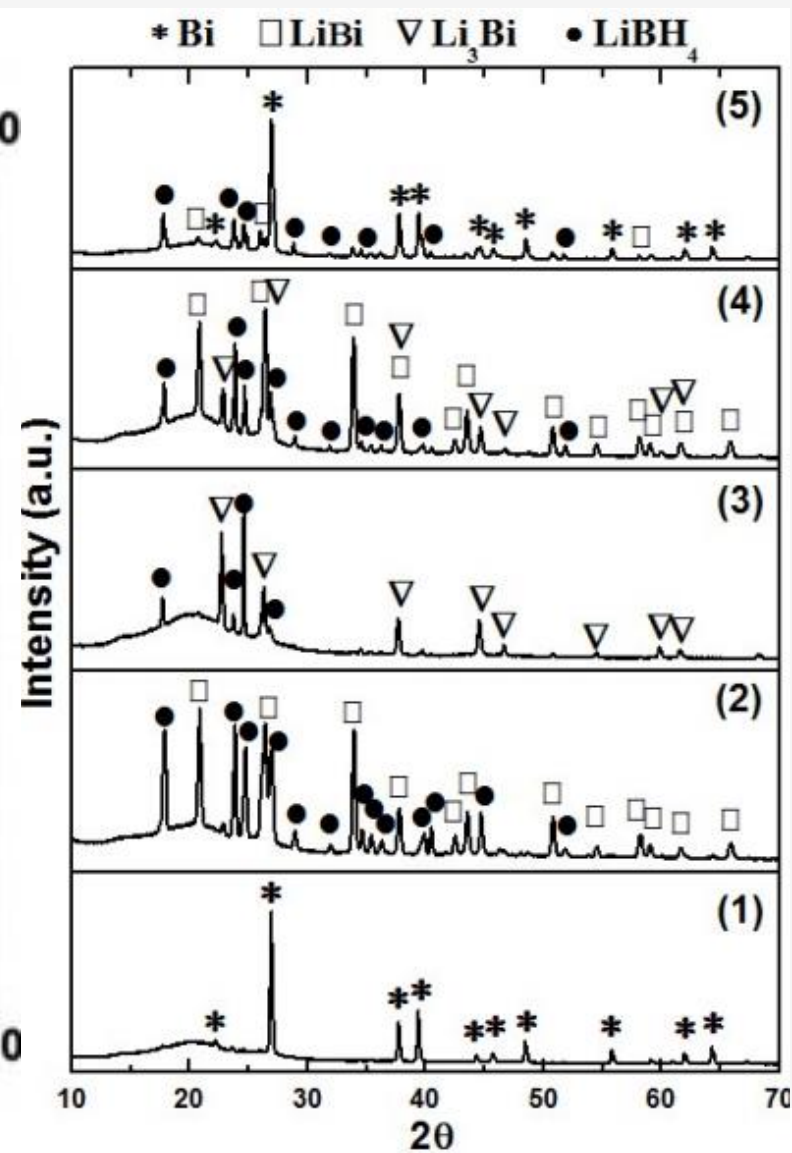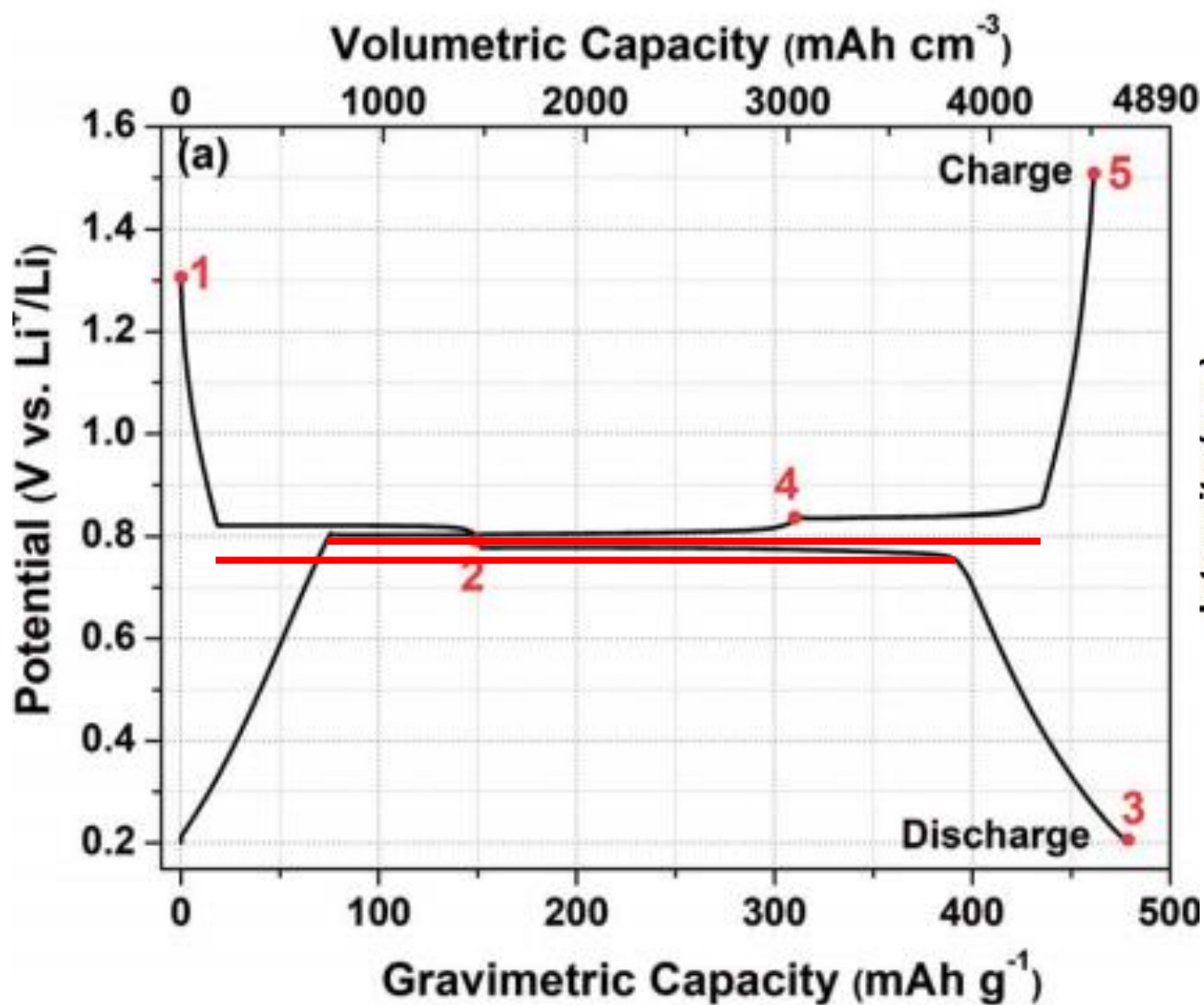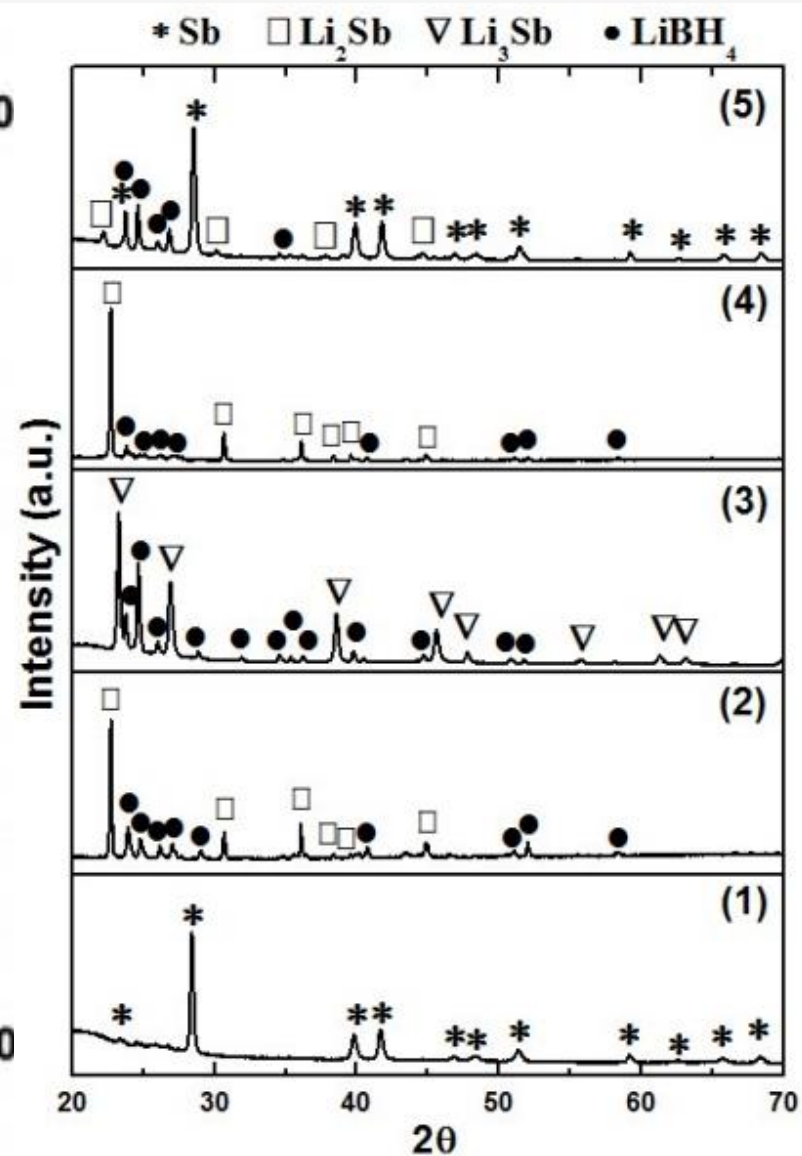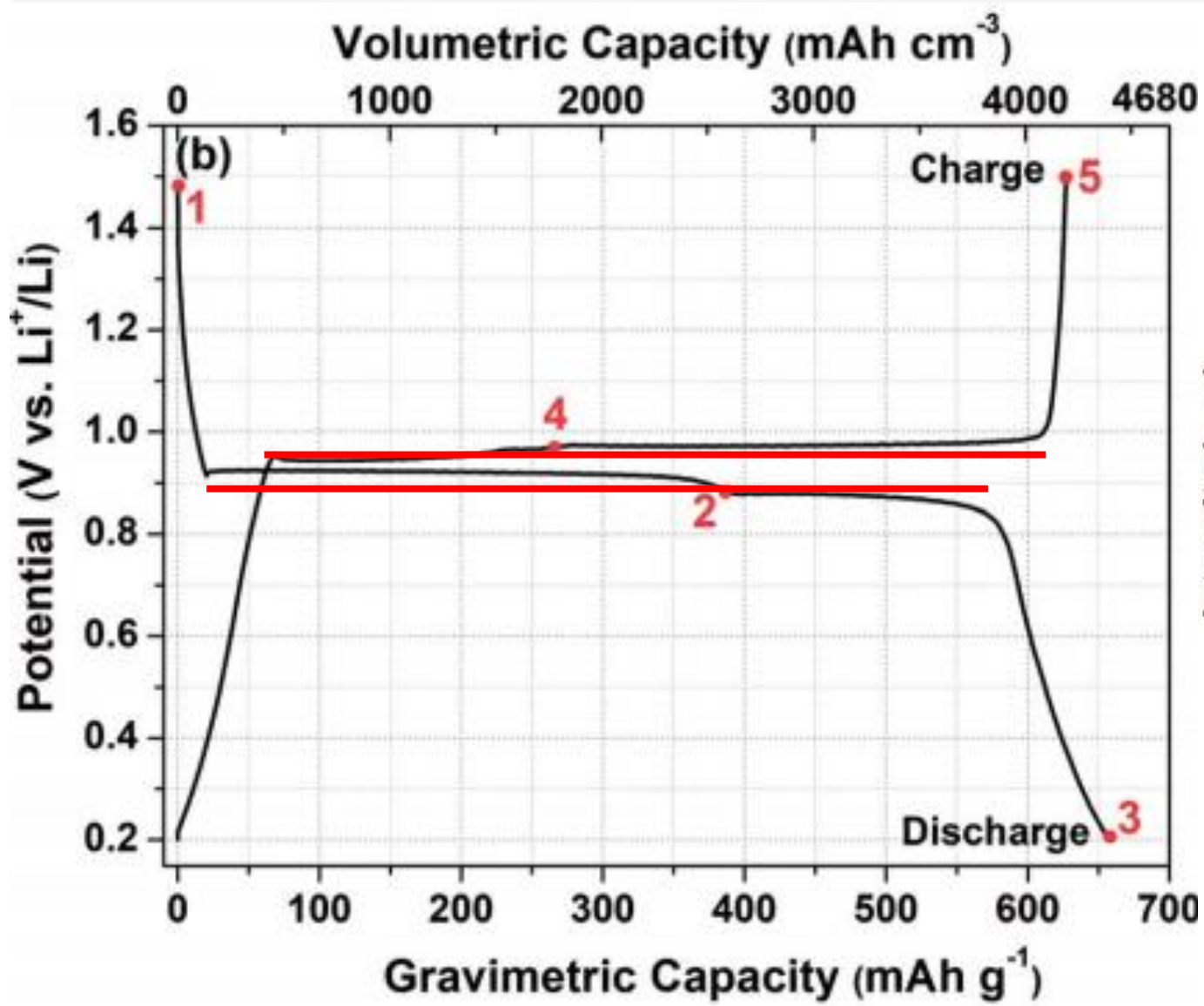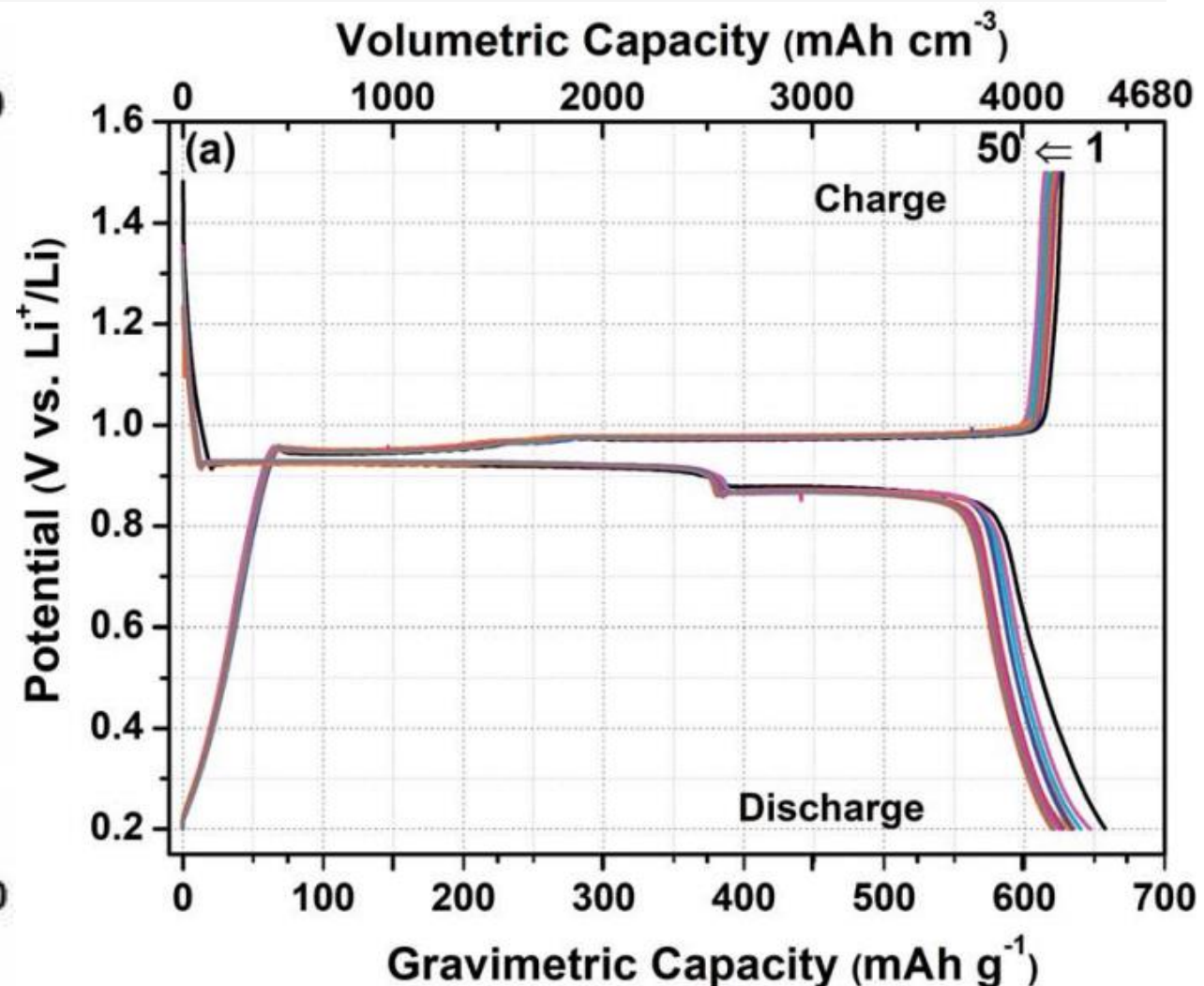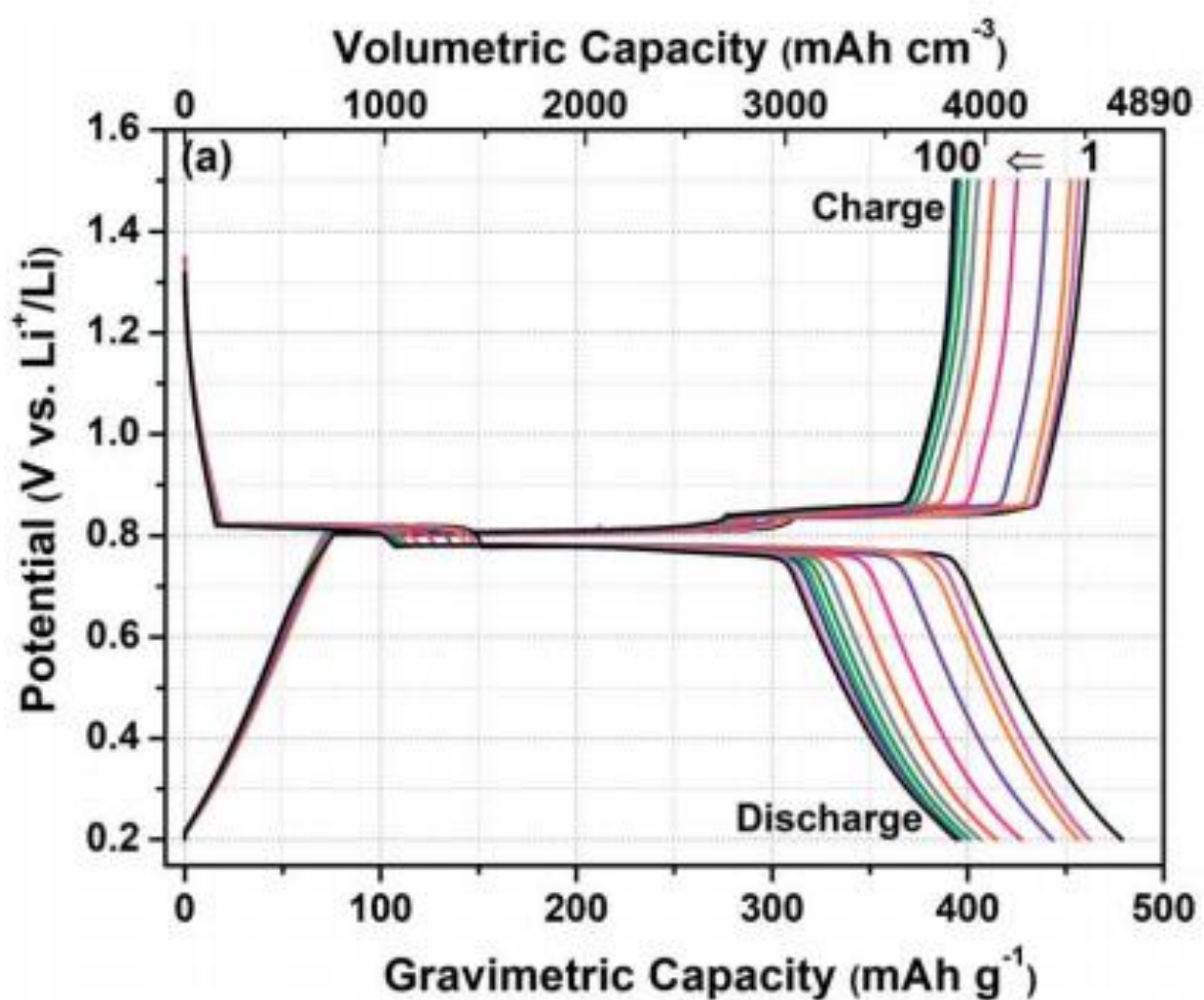
Paper Results

Paper Results
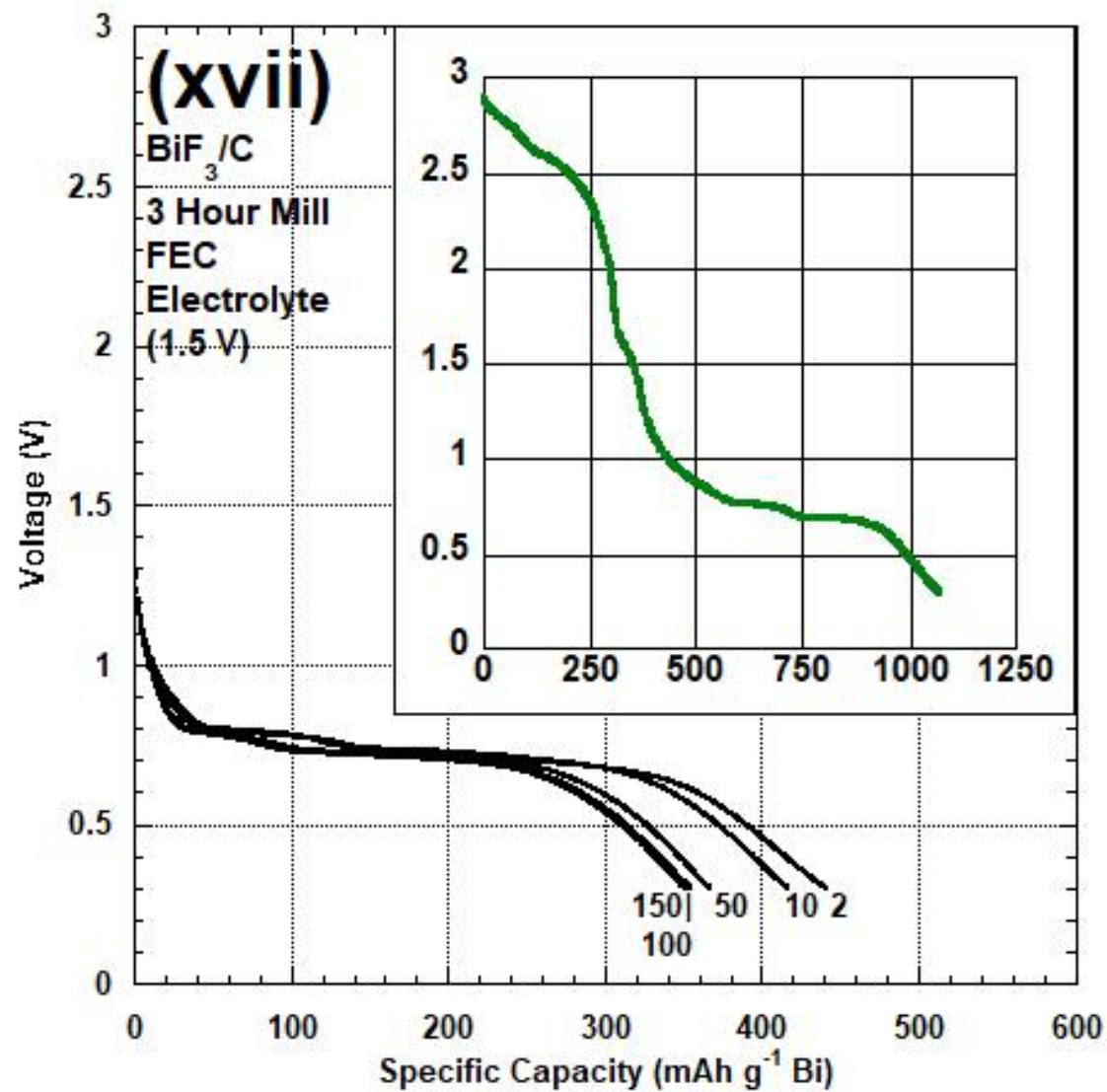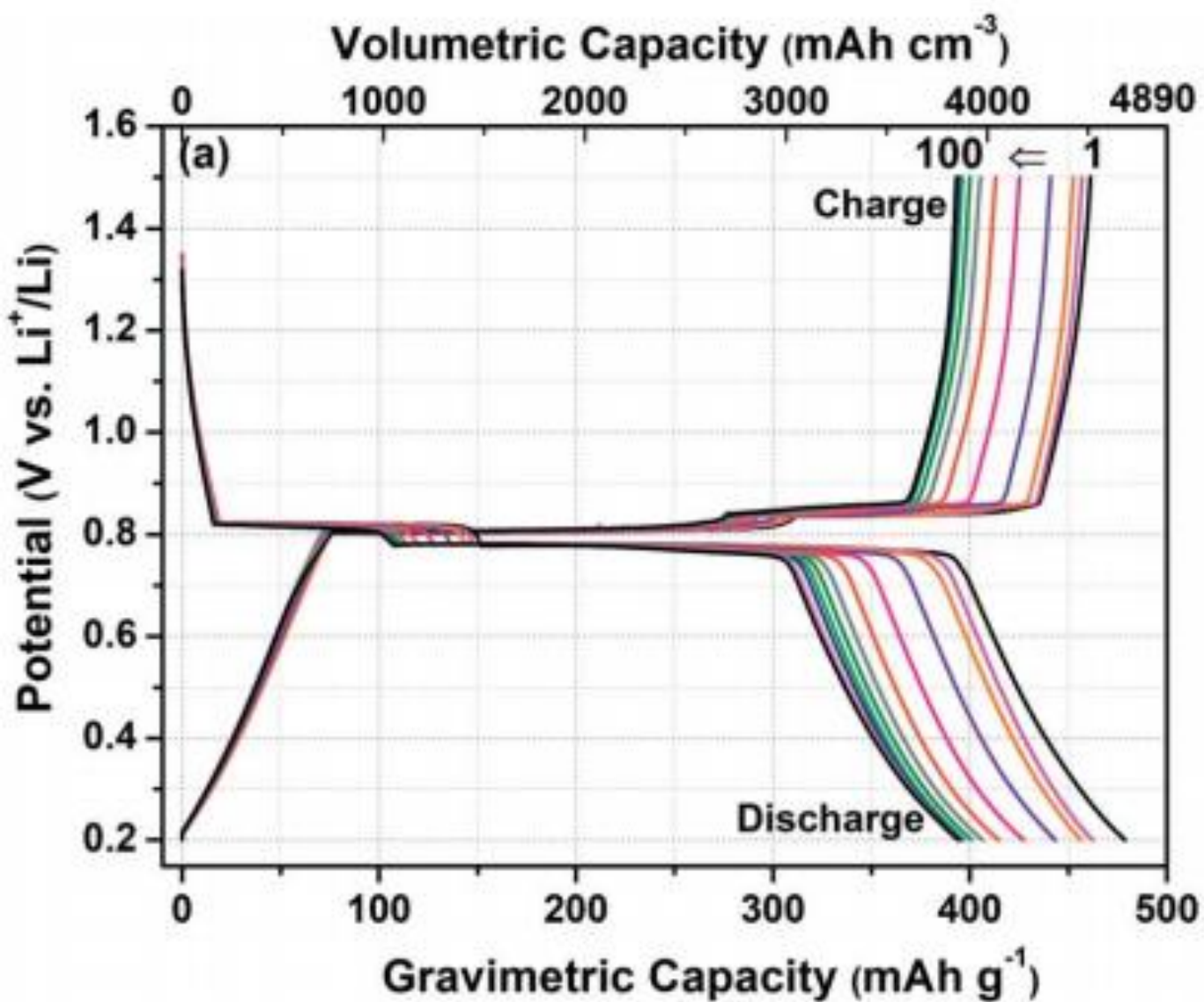
Questions

- **What was the anode composition?**

- **What is the benchmark for the observed performance?**

- **Why did Sb perform better than Bi?**

- **What is reacting below the Bi's lithium alloying voltage?**

- **Why does Sb not fully lithiate?**

- **Why is there diffusion of Bi with cycling?**

Press

Composite material - 40 MPa

Electrolyte ($LiBH_4$) - 10 MPa

Li Foil
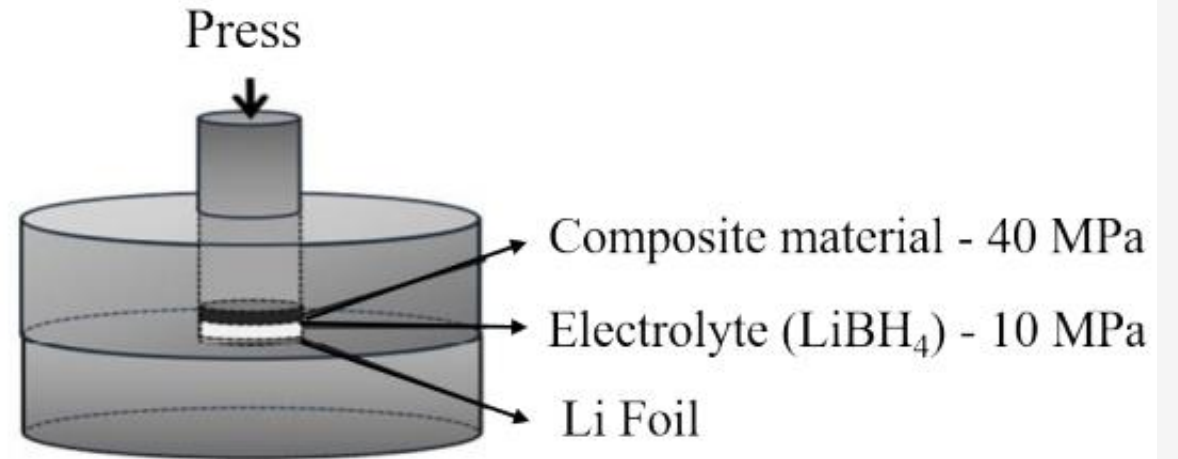
Schematic diagram of the coin cell fabrication

Questions: What is the anode composition?

- **A anode composition with 40% active material (Bi/Sb) is below par**

- Such a composition has more leeway with Sb since it has a larger gravimetric capacity, but wouldn't work for Bi

Experimental Details

Two coin cells constituting of Bi-$LiBH_4$-AB|$LiBH_4$|Li & Sb-$LiBH_4$-AB|$LiBH_4$|Li have been fabricated to perform the electrochemical tests. The commercially available bulk Bi (Alfa aesar 99.999%), and Sb (Rare Metallic Co. Ltd. 99.9%) were used as received, whereas as-purchased $LiBH_4$ (Sigma Aldrich, 95%) and acetylene black (AB) were dried under vacuum at 200°C for 24 hr before using these for the preparation of negative electrode material. $LiBH_4$ and AB were used to enhance the ionic and electrical conductivity of the anode materials. The negative electrodes were prepared by ball milling of Bi/Sb, $LiBH_4$ and conductive carbon (acetylene black AB) in 40:30:30 weight ratio for 2hrs with one hr milling and 30 min rest pattern. The ball milling was carried out in a hardened stainless steel ball of 7 mm in diameter. The milling of 200 mg anode material was performed with 10 SS balls at 370 rpm using Fritsch P7. To measure the electrochemical performance of Bi/Sb anode material, a coin cell was fabricated using a three-layer pellet. *Li*-foil on SS plate was used as the first layer, working as cathode. The second layer was prepared by spreading the solid electrolyte $LiBH_4$ (80 mg) on the Li-foil and applying a pressure of 10 MPa for 5 min. Then the prepared anode composite powder (10 mg) was spread on the two-layered pellet and pressed with 40 MPa pressure for 5 min. Then, this 3-layer pellet was placed in a coin cell and sealed with Perfluoroalkoxy (PFA) gasket. A charge-discharge analyzer (HJ1001SD8, Hokuto Denko Co.) was used to observe the electrochemical performance

# Questions: What is the benchmark for the observed performance?

- **The observed performance is great, but what is contributing to that kind excellent cyclability?**

- The pure powders were milled, which would have reduced the crystallite size and make the samples more resistant to fracture.

- Two hours of milling would definitely improve cycling

- Is the buffering not just a result of so much $LiBH_4$ and C?

Experimental Details

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Questions: Why did Sb perform better than Bi?

- **Authors claim the coulombic efficiency of Sb was worse and attributed that to its larger volume expansion but the alloying reaction of Sb is invariant after 50 cycles! The lost capacity comes from outside the alloying region below 0.6 V**

- **Conversely for Bi, the alloying reaction weaken with each cycle, with about 100 mAh g^{-1} being provided outside that range, consistently**
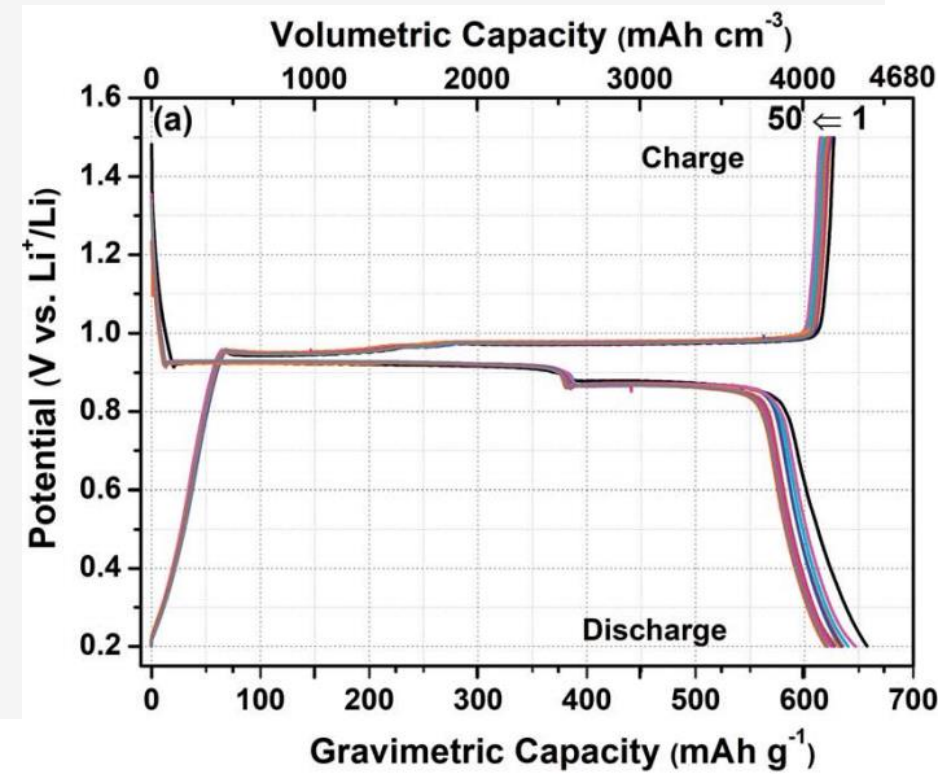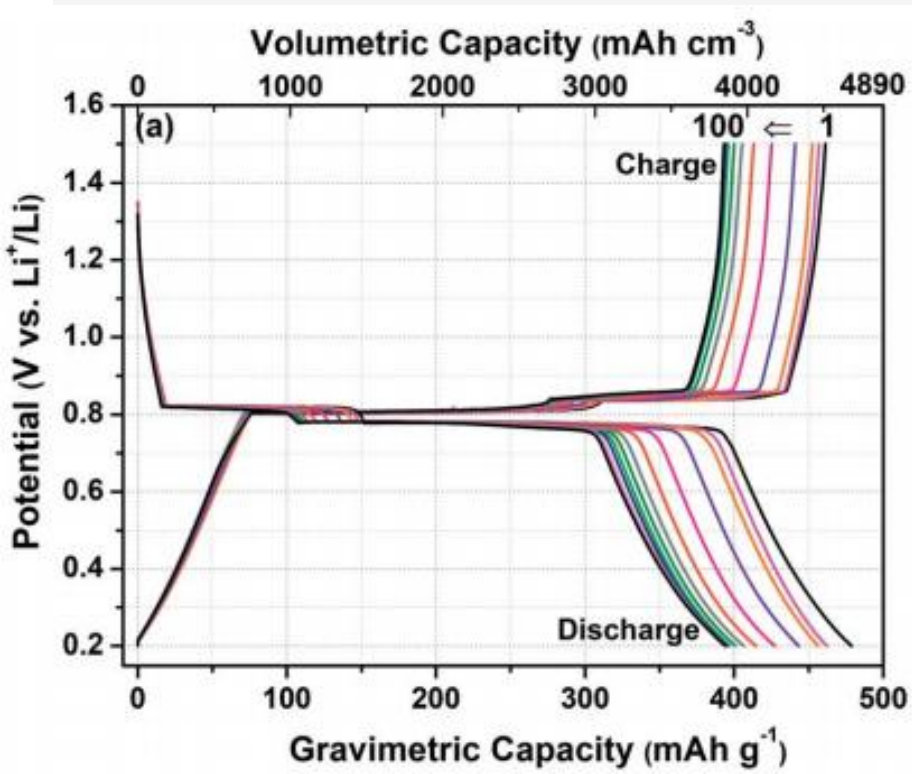
Questions: What is reacting below Bi's lithium alloying voltage?

- **Cyclic voltammetry can be used to ID reactions at different voltages, you force a potential difference across your cell and any reaction at that voltage generates a current response**

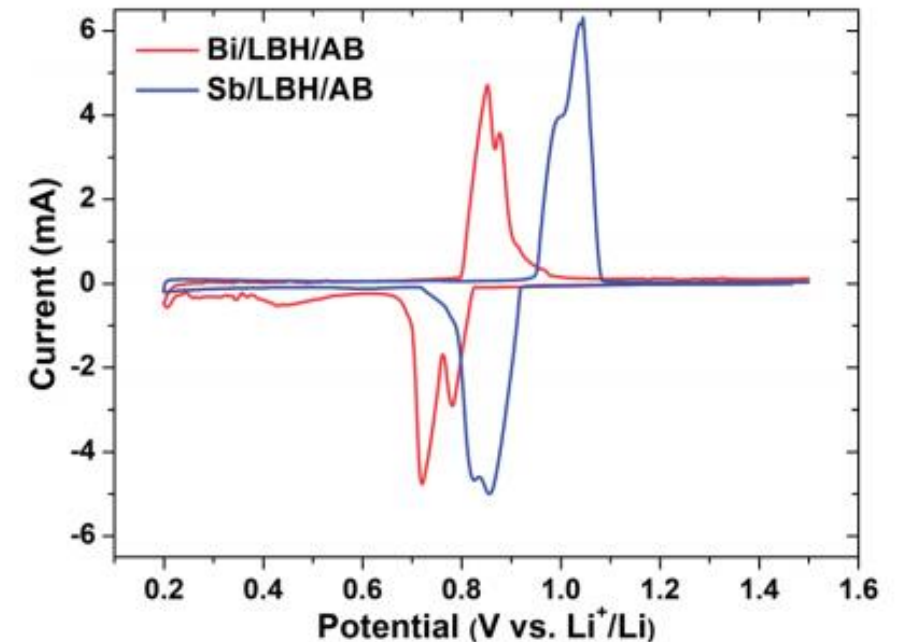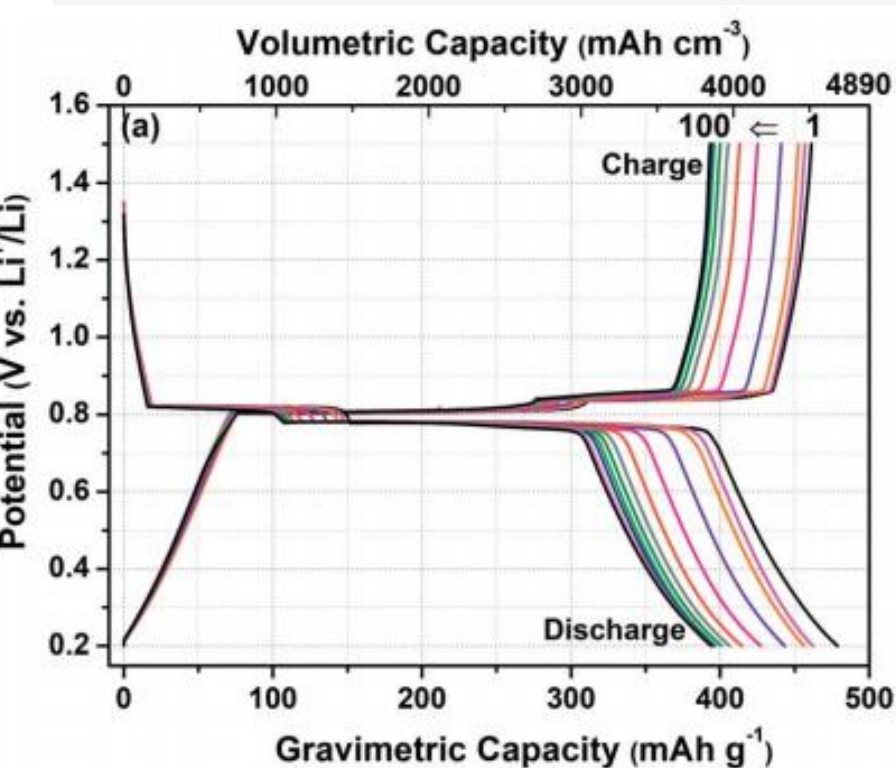- **There appears to be Bi induced reaction at 0.4 V, so what are the products?**

Fig. 1 Cyclic voltammograms of Bi and Sb composite electrode scanned at 0.1 mV s⁻¹.

# Questions: Why does Sb not fully lithiate?

- **Typically, you achieve full lithiation of the metal on initial discharge but that wasn't the case, why is that so?**

- **Why was the Sb only shown to 50 cycles? Presumably because it has a much larger capacity and took about twice as long for a single cycle, assuming both sets were run simultaneously**
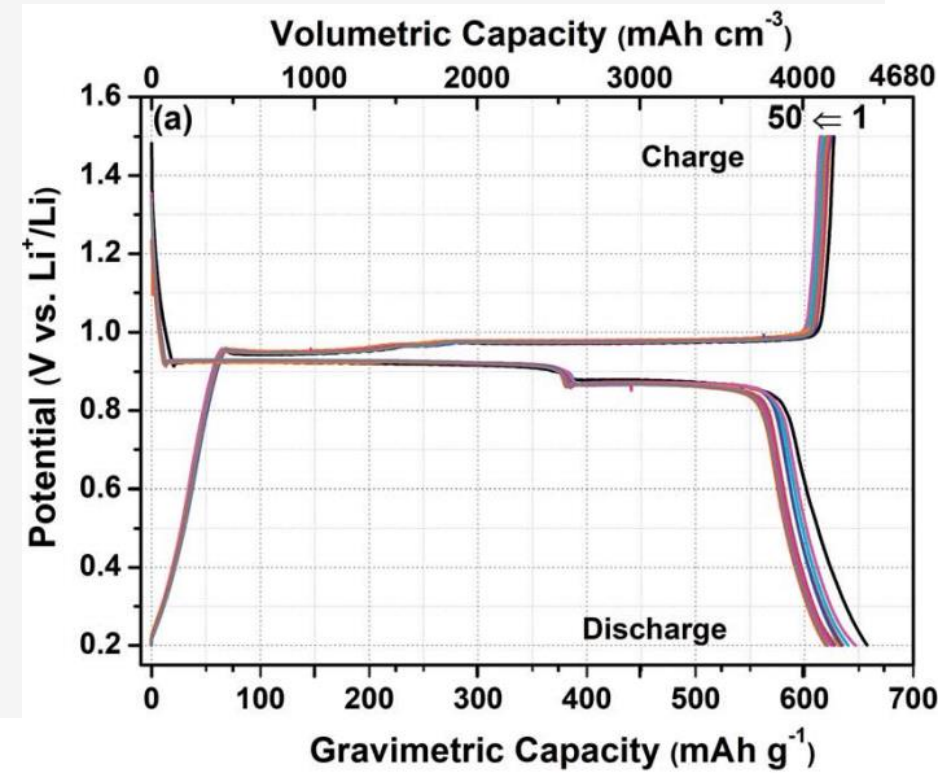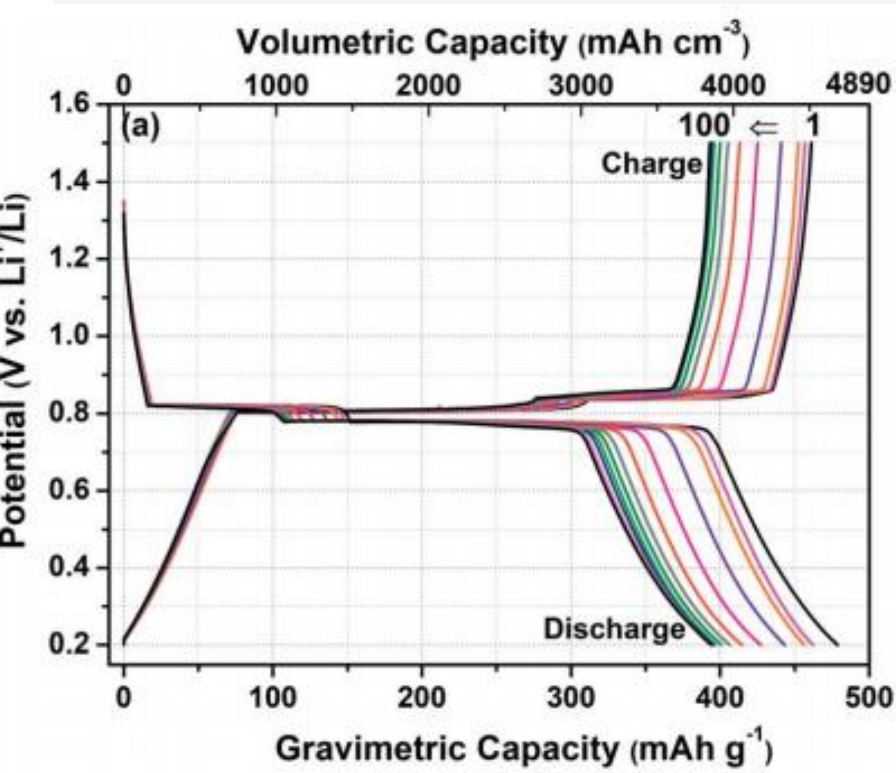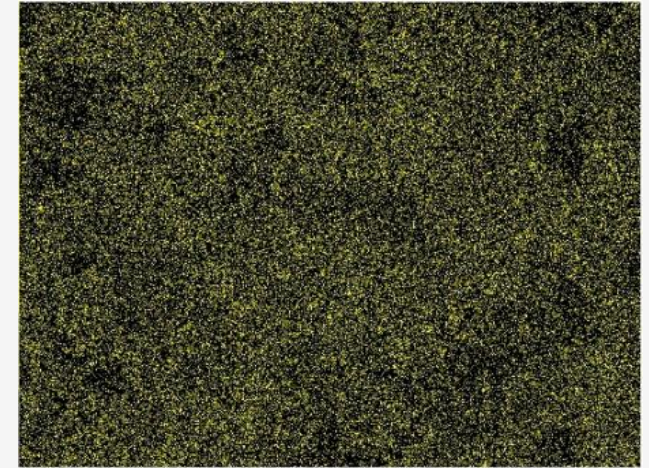
Questions: Why is there diffusion of the metals with cycling?

- Is the movement a result of plastic flow in the lithiated phases

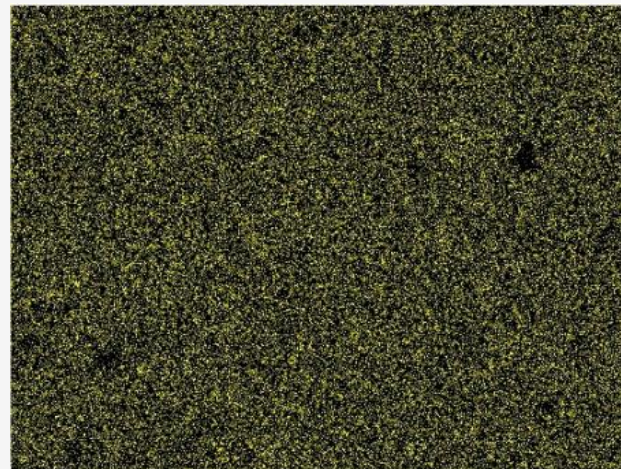- 120C seems too low a temperature for simple diffusion
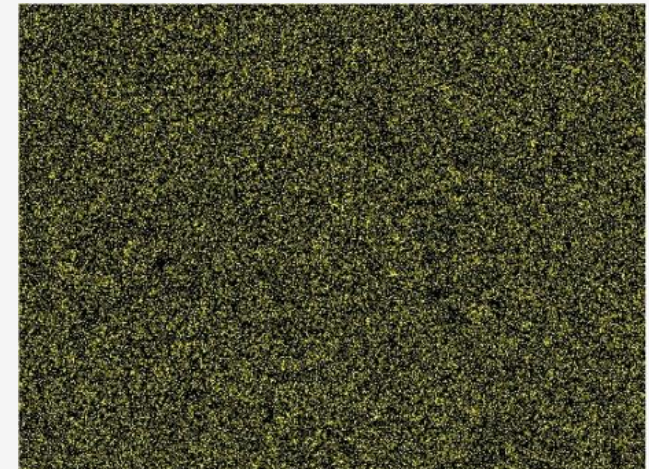
Bi before cycling
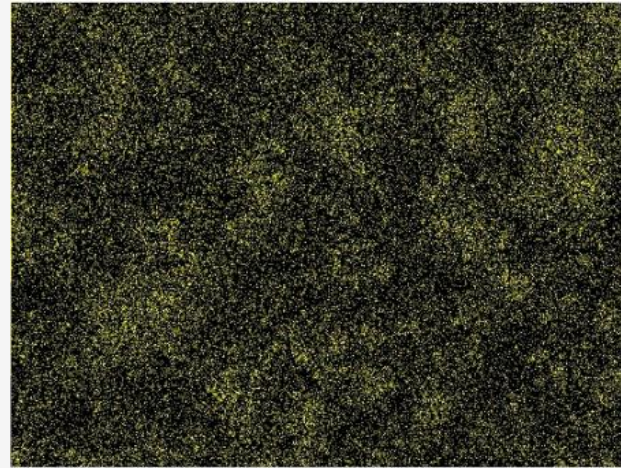
Bi after cycling

Sb before cycling

Sb after cycling

Physics Questions

- Why is the ionic conductivity of Li_3Bi so high?

- How does the [relativistic contraction](#) of the Bi atom affect the behavior of the Li-Bi structures? Does it provide some explanation for its catalytic nature?

[P. Pyykko. *Annu. Rev. Phys. Chem 63* (2012) 45-64](#)

eV, depending on the stoichiometry, in both phases. The mobility of lithium in "Li_3Bi" is about 500 times greater than in "Li_3Sb" with a lithium deficit. The ionic conductivity in "Li_3Sb" increases from about 10^{-4} Ω^{-1} cm^{-1} in the vacancy transport region to about 2×10^{-3} where transport is probably by interstial motion at 360°C. For "Li_3Bi" a practically constant value of nearly 10^{-1} Ω^{-1} cm^{-1} is found at 380°C. The

[W. Weppner and R. A. Huggins. *Journal of Solid State Chemistry.* 22 (1977) 297-308](#)
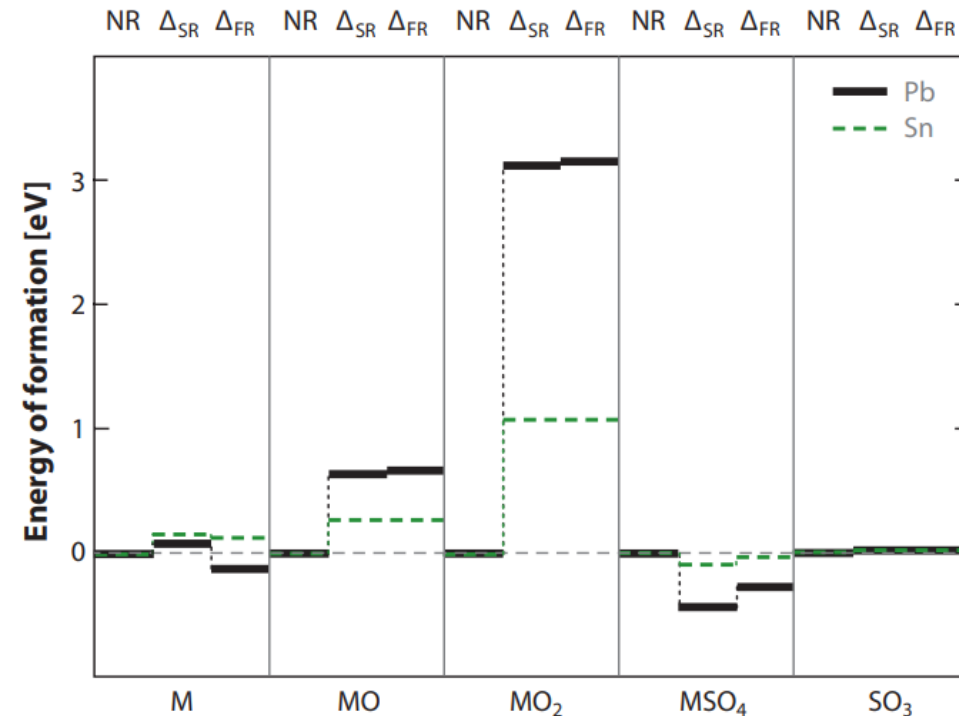

Figure 4

The nonrelativistic (NR), scalar relativistic (SR), and fully relativistic (FR) energy shifts (in electron volts) for the solids involved in the lead-acid-battery reaction (Equation 14). Values for both M = Sn (*green*) and M = Pb (*black*) are given. Figure reproduced with permission from Reference 80, copyright APS.

Thank You!

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