

## In-situ TEM Study of Coating Layer Function on Silicon Anode Particle for Lithium Ion Battery

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One of the key challenges of Si-based anodes for lithium ion batteries is the large volume change upon lithiation and delithiation, which commonly leads to electrochemi-mechanical degradation and subsequent fast capacity fading. Recent studies have shown that applying nanometer-thick coating layers on Si nanoparticle (SiNPs) enhances cyclability and capacity retention [1]. However, it is far from clear how the coating layer function from the point of view of both surface chemistry and electrochemi-mechanical effect. Herein, we use *in situ* transmission electron microscopy to investigate the lithiation/delithiation kinetics of SiNPs coated with a conductive polymer, polypyrrole (PPy). We discovered that this coating layer can lead to “self-delithiation” or “self-discharging” at different stages of lithiation. We rationalized that the self-discharging is driven by the internal compressive stress generated inside the lithiated SiNPs due to the constraint effect of the coating layer. We also noticed that the critical size of lithiation-induced fracture of SiNPs is increased from  $\sim 150$  nm for bare SiNPs to  $\sim 380$  nm for the PPy-coated SiNPs, showing a mechanically protective role of the coating layer. These observations demonstrate both beneficial and detrimental roles of the surface coatings, shedding light on rational design of surface coatings for silicon to retain high-power and high capacity as anode for lithium ion batteries.

The effect of surface coating on SiNPs on battery performance can be evaluated from the point of view of both electrochemical and mechanical effects. In this work, we investigated the lithiation kinetics and lithiation induced chemo-mechanical fracture of PPy-coated *c*-SiNPs. Our *in-situ* TEM studies along with chemo-mechanical analyses reveal that the surface coating functions in both beneficial and detrimental roles for SiNPs as anodes. Figure 1 depicts the time-resolved bright-field TEM images captured from the Supporting video S1, showing the dynamic morphological changes of three PPy-SiNPs upon lithiation. Conductive polymer PPy with a thickness of  $\sim 7$  nm were conformably attached to the surface of SiNPs with a sharp interface (white dash line), as shown in Figure 2A. After 20 s of lithiation, two SiNPs started to expand and the newly formed *a*-Li<sub>x</sub>Si phase was shown as bright contrast regions between PPy coatings and *c*-Si core in Figure 2B. The PPy coating expanded along with SiNPs, but remained adherent to the newly formed *a*-Li<sub>x</sub>Si phase as the amorphous-crystalline interface (yellow dash line) propagated inward of the SiNPs. We noticed that following 30 s lithiation, the thickness of the *a*-Li<sub>x</sub>Si layer increased to  $\sim 7$  nm (Figure 2C), the amorphous-crystalline interface stopped moving inward, but surprisingly began to move backward, indicating a self-delithiation of the *a*-Li<sub>x</sub>Si and this self-delithiation leads to the lithiated SiNPs to shrink to almost its original size with the *a*-Li<sub>x</sub>Si phase diminished within 10 s. This “lithiation to self-delithiation” cycle, or “fluctuation lithiation/delithiation” repeated multiple times during the lithiation of this cluster of SiNPs, as illustrated in the schematic in Figure 2. This indicates that the fluctuation lithiation/delithiation was not caused by accidental oscillation of the applied external voltage for driving lithiation. Furthermore, this fluctuation lithiation/delithiation phenomenon is only present in the coated SiNPs, indicating the surface coating plays a critical role in the fluctuation, as described next. It should be noted that the PPy coating will be lithiated, which is accompanied by a volume increase. When the PPy is applied as a coating layer on Si

nanoparticle, due to the expansion of Si nanoparticle upon lithiation, the lithiated PPy layer is also stretched. Therefore, upon initial lithiation, it seems that the PPy layer shows no significant change in thickness [2].

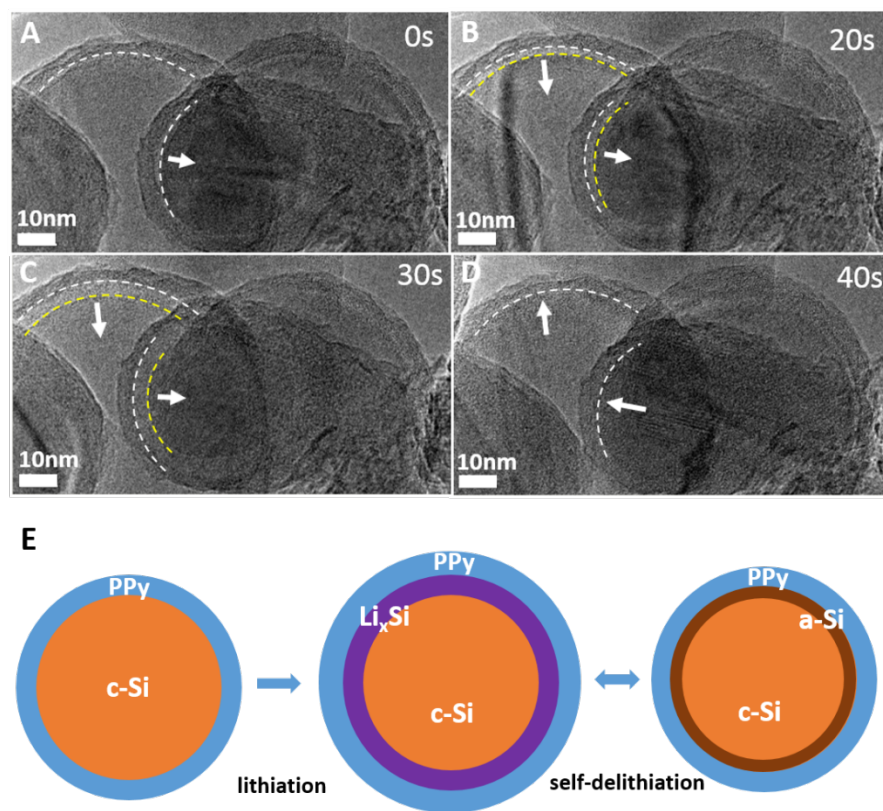
Owing to the constraint effect of the coating layer, large compressive stress may be generated both at the reaction front and in the lithiated shell, which not only retards lithiation, but also causes fluctuant lithiation/delithiation, leading to self-discharge of the battery. On the other hand, the coating layer acts as a mechanical confinement that buffers the volume change of the anode during cycling, rendering the SiNP electrochemi-mechanically more durable. Our findings suggest the significance of the coupled electrochemi-mechanical effects of surface coatings in the design of high-performance Si-based anodes for lithium ion batteries [3].

#### References:

[1] He, Y. et al, (2014), *ACS Nano* 11, 11816-11823.

[2] Luo, L. L. et al, (2015), *Nano Lett.*, 15, 7016-7022.

[3] The work was conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at PNNL.



**Figure 1.** (A-D) Time-resolved TEM images depict the “fluctuation” of two SiNPs during lithiation process. White dash lines in Figures 4A and D indicate the interface between *c*-SiNP and PPy coating, and yellow dash lines in Figures 4B and C indicate the interface between *c*-Si core and *a*-Li<sub>*x*</sub>Si shell. The white arrows show the moving directions of the interface. (E) Schematic of three stages during “fluctuation” lithiation of a coated SiNP. [2].