doi:10.1017/S1431927618009790
Microsc. Microanal. 24 (Suppl 1), 2018

In Situ Atomic-Scale TEM Observation of Phase Transformation in Two-Dimensional $SnSe_2$ Single Crystals

Sungkyu Kim[1,2], Vinayak P. Dravid[2], Kai He[1,2,*]

[1.] Department of Materials Science and Engineering, Clemson University, Clemson, SC 29634, USA
[2.] Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have been widely used as electrode materials for lithium ion batteries because of their unique layered structures with open space in between to accommodate reversible lithium movement [1]. It is believed that lithiation of these groups of materials would typically start with the initial lithium intercalation process and then proceed through the conversion reactions afterward. To gain the optimized battery performance, a good understanding of the phase transformations during lithiation is necessarily needed, which can be obtained via the advanced in-situ transmission electron microscopy (TEM) methods [2].

Tin diselenide ($SnSe_2$) is a type of TMDs, which has CdI_2-type hexagonal 1T structure (Figure 2a), and its large interlayer spacing of 6.141 nm can easily host lithium ions to insert and extract, leading to a high capacity [3]. It is noted that one of the conversion product, Sn, can further react with lithium via alloying process, which can contribute to extra capacity and may also introduce other unexpected phase transformations, but still lack in details. Therefore, a comprehensive in-situ investigation is required.

Here, we report the atomic-scale direct observation of phase transformation during lithiation and delithiation reactions of single-crystalline $SnSe_2$ using in-situ high-resolution TEM (HRTEM). The $SnSe_2$ nanoflakes were exfoliated from bulk crystals and then transferred onto TEM cell with amorphous carbon support biased with respect to lithium metal. Figure 1 shows the interlayer distance change during lithiation from the cross-sectional view using in-situ HRTEM, which indicates that as lithium inserted into $SnSe_2$ interlayers, the spacing change from 0.61 nm to 0.67 nm to accommodate the volume expansion. Figure 2 shows the atomic structure evolution from pristine $SnSe_2$ (Figure 2a) to lithiated Li_xSnSe_2 phase (Figure 2b), then Li_2Se and Sn composite (Figure 2c and 2d) during lithiation process; and the subsequent recombination to form layered $SnSe_2$ (Figure 2e) during delithiation process. The FFT of HRTEM imaging over the entire observation area clearly indicates the nature of multi-step phase transformation that is in good correlation to the voltage profiles of battery charge-discharge tests shown in Figure 2f. The in-situ HRTEM revealed the reaction pathway through multiple steps, including intercalation, conversion, alloying, and recombination, and provided atomistic mechanism for the lithiation and delithiation processes of $SnSe_2$ nanocrystals. These findings provide valuable insights into mechanistic understanding of other 2D TMD systems as well as Sn-based binary compounds for battery design and applications. [4].

References:

[1] L Peng, *et al*, Adv. Energy Mater. **6** (2016) 1600025.
[2] K He, et al, Nano Lett. **17**, (2017) 5726.
[3] DH Lee, CM. Park, ACS Appl. Mater. Inter. **9** (2017) 15439.

[4] This work made use of the EPIC facility of Northwestern University's NU*ANCE* Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the MRSEC program (NSF DMR-1121262) at the Materials Research Center.

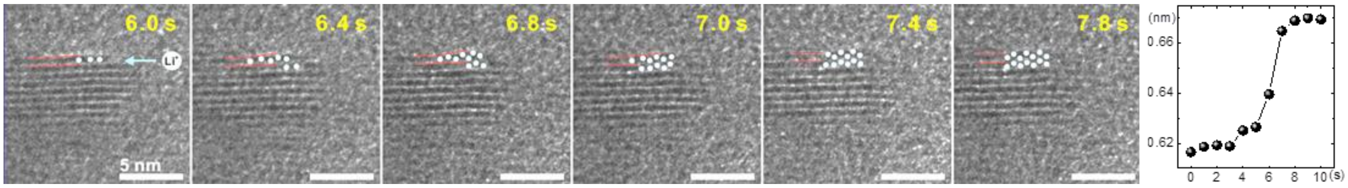

Figure 1. In-situ HRTEM images showing interlayer distance change during lithiation of $SnSe_2$.

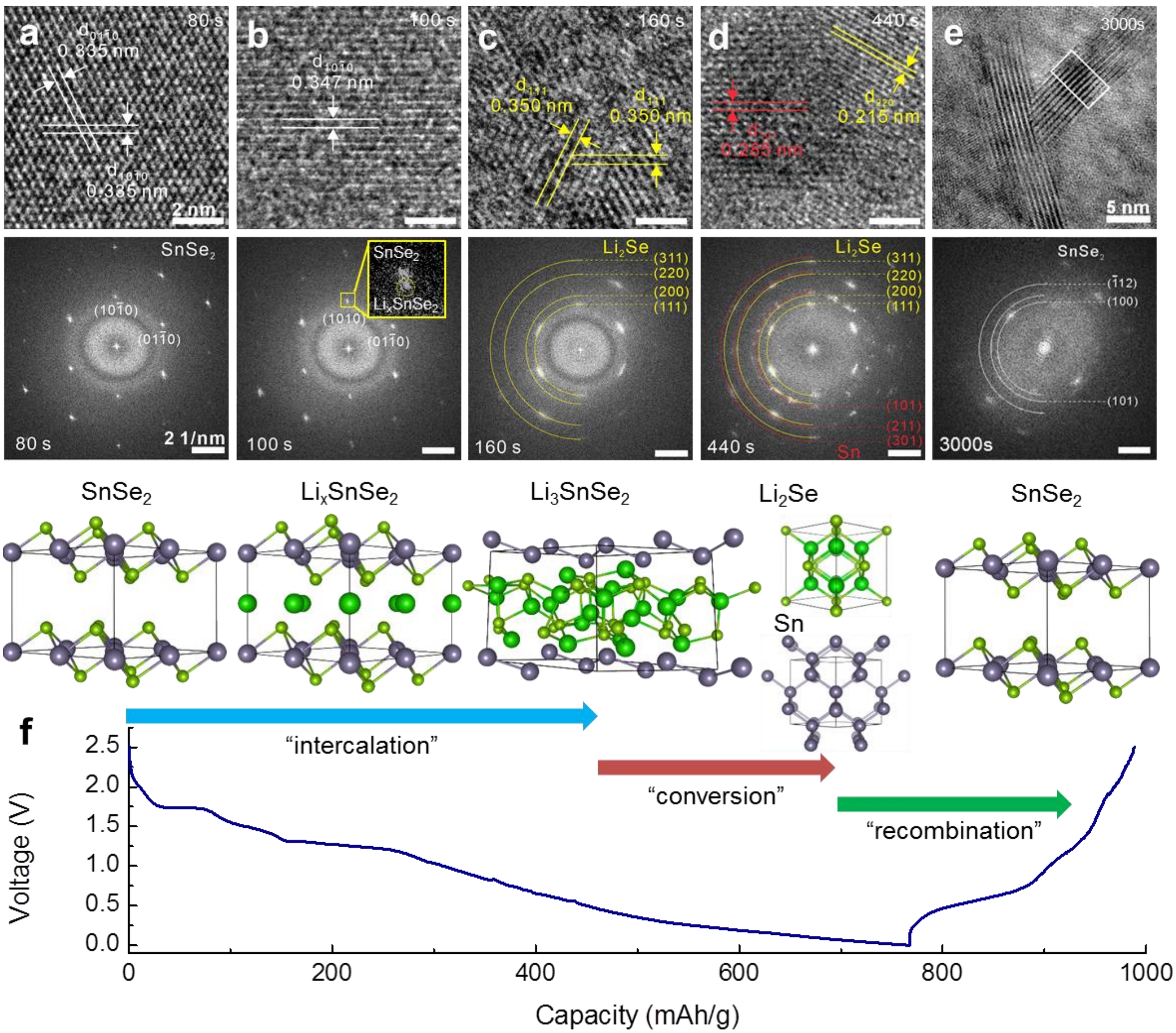

Figure 2. In-situ HRTEM and corresponding FFT images during (de)lithiation process showing (a) pristine $SnSe_2$, (b) lithiated Li_xSnSe_2, composite of (c) Li_2Se and (d) Sn, and (e) delithiated $SnSe_2$, respectively; which are well correlated to (f) voltage profiles of charge-discharge test.

https://doi.org/10.1017/S1431927618009790 Published online by Cambridge University Press