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Size-controlled Intercalation to Conversion Transition in Lithiation of Transition Metal Chalcogenides – $NbSe_3$

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Transition metal chalcogenides (TMCs) can be used either as intercalation cathodes or as conversion type anodes for lithium ion batteries, for which two distinctively different lithiation reaction mechanisms govern the electrochemical performance of TMCs. Although results[1,2] show the structural changes of TMCs as an intercalation compound during the Li^+ insertion but how layered or tunneled structure of TMCs change/degrade upon the Li^+ insertion and further react with Li^+ to achieve large capacity as a conversion type anode and what controls the transition of lithiation mechanisms are still unclear. Herein, we investigated the lithiation process of $NbSe_3$ ribbons using *in situ* transmission electron microscopy (TEM) and observed a size dependent transition from intercalation to conversion reaction.

Fig. 1A to C show time-resolved TEM images depicting the typical lithiation process for an $NbSe_3$ ribbon with a width of ~300nm. This lithiation process illustrated in Fig. 1D causes the expansion of inter-chain spacing in both x and z directions with the atomic structure in y direction remaining unchanged, and it also causes sliding between chains. We show here the lithiation of this $NbSe_3$ ribbon proceeds dominantly through an intercalation mechanism with the most of chain structure retained. On the other hand, the lithiation process of a much smaller $NbSe_3$ (50.2 nm in width) illustrated in Fig. 1E-F shows the pristine chain structure was fully converted to a nanocomposite structure of small nanoparticles embedded in a matrix. The STEM-HAADF image of Fig. 1G shows the matrix lattice matches well with Li_2Se (111), and the dispersed nanoparticle are Nb metal nanoparticles with a bright contrast (white dash circles).

The schematic in Fig. 2 illustrates the size effect of $NbSe_3$ ribbons on their lithiation mechanisms and highlighting the observed size effect is related to Li^+ diffusion and mechanical confinement. The smaller ones has a large surface-to-volume ratio with more surface defects exposed, leading to much faster Li^+ diffusion through surface and reaction rate. For larger $NbSe_3$ ribbons, it is hard for new phases to nucleate in the limited spacing of layered structures. And as the conversion reaction proceeds, the stress can be generated due volume expansion in the un-reacted area, which retards and/or halts the conversion reaction, leading to a surface-only converted ribbon with most of its layered structure maintained.

References:

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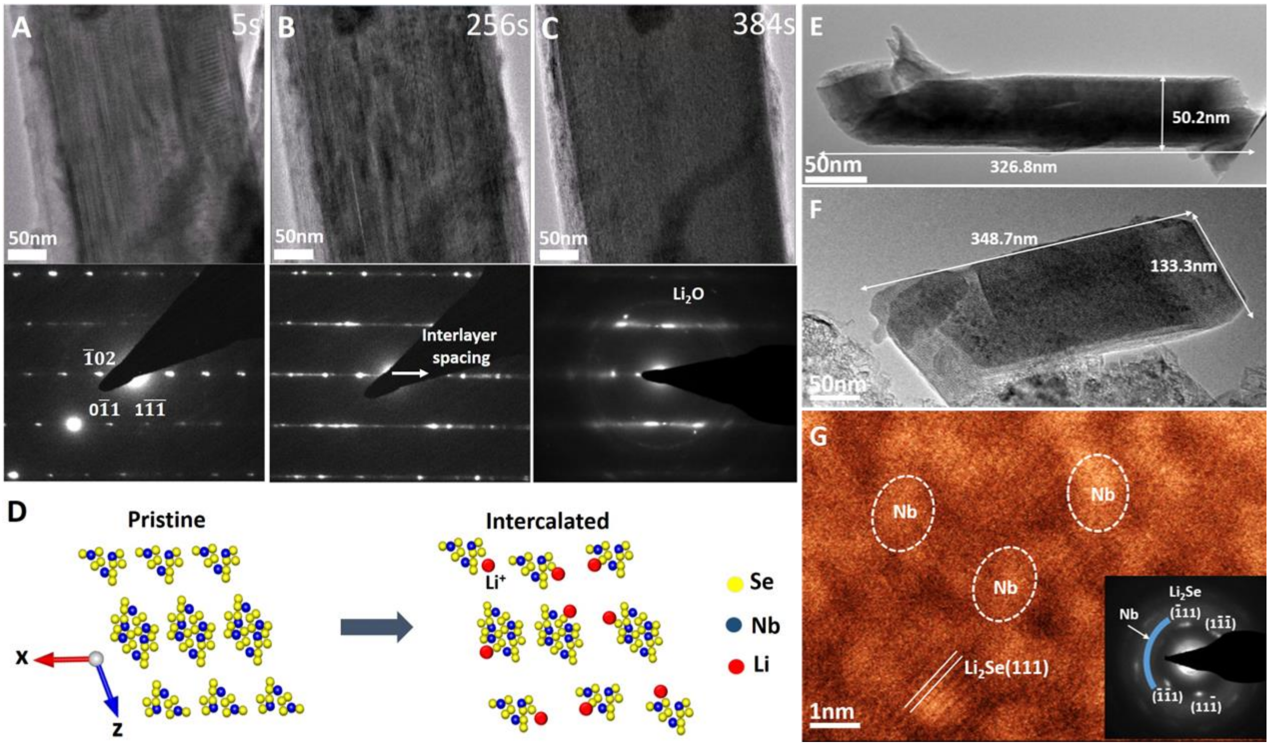

Figure 1. A)-B) Time-resolved TEM images show the lithiation process of a large $NbSe_3$ ribbon. D) Schematic of intercalation of $NbSe_3$. A small pristine D) and lithiated E) $NbSe_3$ ribbon. G) HAADF STEM images of the lithiated small $NbSe_3$ ribbon showing the Nb metal particles embedded in the Li_2Se matrix.

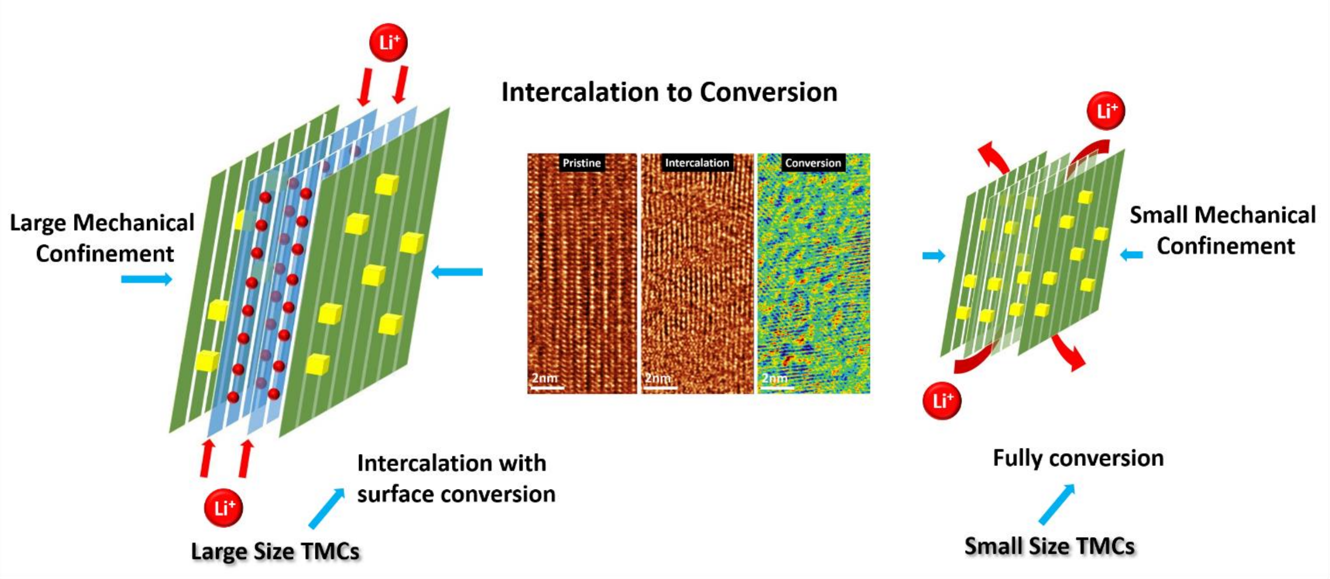

Figure 2. Schematic drawings to illustrate the size effect on the lithiation reaction mechanisms: the large size TMC is dominated by intercalation reaction and the surface region is subjected to conversion reaction; while the small size TMC is fully converted upon lithiation.