

## Similarities and Differences in Kinetics and Dynamics During Li and Na Transport in MoS<sub>2</sub> Nanostructures

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The emerging large-scale applications, particularly in electric vehicles and grid storage, necessitate development of new generation battery systems other than LIBs due to the limited natural abundance and uneven global distribution of lithium. Various alkali-metallic ion batteries thereby have been proposed as candidates, including Na, K, and Mg. Among of them, sodium-ion batteries (NIBs) have attracted much attention due to the low cost, large abundance, wide and uniform distribution around the earth of sodium. However, owing to the larger radius and heavier mass of Na ions, the Na ion diffusion and reaction kinetics may significantly differ from that of Li. For example, graphite is the most commonly used anode in LIB anode, but is no longer suitable for NIBs because of limited space for accommodating Na ions. Therefore, the major challenge for NIBs development is to find appropriate electrode materials with high capacity and good reversibility. Probing the Li and Na ionic transport in the same electrodes should be helpful to understand the similarities and differences between Na and Li, and thereby to search suitable electrode materials based on the knowledge of the current LIBs technologies.

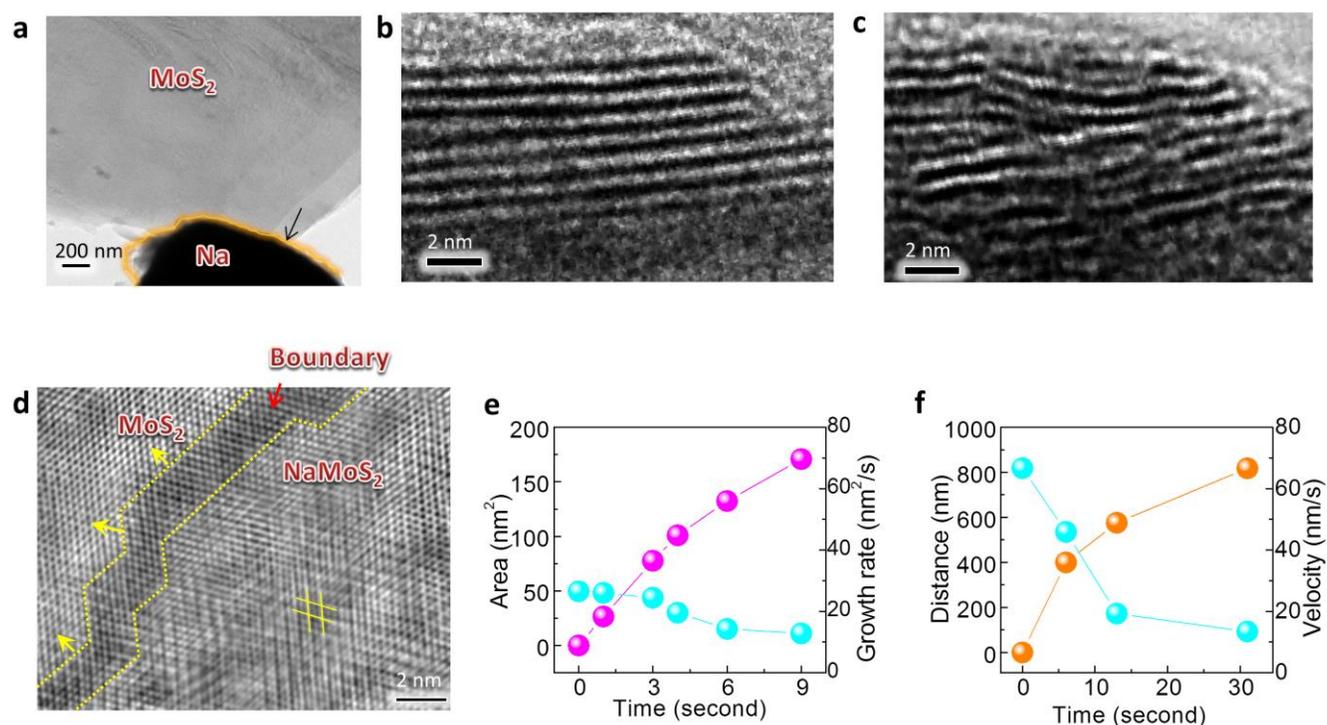
Here, we quantitatively compare the Na ion transport kinetics and dynamics in MoS<sub>2</sub> with behaviors of Li by using in situ TEM method. The experimental setup in Figure 1a consists of a few-layer sheet of MoS<sub>2</sub> and Na counter electrode, which was fabricated in an Ar-filled glove box and subsequently transferred into the TEM chamber. The pristine MoS<sub>2</sub> nanosheet has a trigonal prismatic (2H) structure. In Figure 1b, the (001) planes in the pristine MoS<sub>2</sub> nanosheet are parallel to each other and the layer distance was 0.615 nm. After Na intercalation in Figure 1c, the Na intercalated phase—NaMoS<sub>2</sub>—is formed and the layered structure is broken into tiny “nanodomains” with typical size of ~5 nm separated by the “cracks”. The phase boundary of MoS<sub>2</sub> and NaMoS<sub>2</sub> during Na intercalation can be tracked in real-time with high resolution in Figure 1d. Such two-phase reaction mode in Na-MoS<sub>2</sub> system is also confirmed by our electron diffraction and in agreement with a previous XRD study [1]. The width of phase boundary in Figure 1d is measured to be ~2 nm. The area of the Na-intercalated domain (i.e. NaMoS<sub>2</sub>) is plotted as a function of time to estimate the Na migration rate of boundary and Na ion diffusivity in MoS<sub>2</sub>. The measured reaction rate in Figure 1e is ~3-7 nm/s (10-50 nm<sup>2</sup>/s). Compared to lithium diffusion in MoS<sub>2</sub> ~30-70 nm/s in Figure 1f [2], Na diffuses much slower. The sluggish kinetics for Na intercalation is likely due to a larger radius (0.116 nm for Na<sup>+</sup> and 0.076 nm for Li<sup>+</sup>) [3] and heavier mass for Na compared to that for Li, thus slowing down the ionic transport within MoS<sub>2</sub>.

In summary, some similarities and differences between the sodium intercalation and lithium insertion we can be summarized. Similar to Li, Na ions can also be intercalated and diffuse in MoS<sub>2</sub> to form NaMoS<sub>2</sub>. After Na insertion, many defects occur and break the layered structure into small segments. The formation of high density of “crack” defects can relax the strain that results from the lattice expansion due to Na insertion. Furthermore, both the Na- and Li-ion intercalation can trigger a phase transition from 2H-MoS<sub>2</sub> to 1T-NaMoS<sub>2</sub> and 1T-LiMoS<sub>2</sub>. One remarkable difference between the Na and Li intercalation in MoS<sub>2</sub> is the velocity of the phase boundary (ionic diffusivity), originating from the larger radius and heavier mass of Na-ion which slows down the Na ions diffusion. Our study provides useful

information to search suitable materials for NIBs. [4]

#### References:

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**Figure 1.** (a) Experimental setup. (b) High-resolution image of the edge of pristine MoS<sub>2</sub> nanosheet. (c) Same region after Na-ion insertion. (d) Phase boundary of NaMoS<sub>2</sub>/MoS<sub>2</sub>. (e) Area of the sodium-intercalated domain and growth rate are plotted as a function of time. (f) Distance of the lithium-intercalated domain and velocity are plotted as a function of time.