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Kinetics of Sodium and Selenium Reactions in Sodium Ion Batteries

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Selenium and sulfur, both as chalcogen elements, show similar volumetric capacity as cathode material for both lithium and sodium ion batteries.[1] Additionally selenium has notable higher electrical conductivity than sulfur.[2] In this work, we have investigated the kinetics of sodiation reaction in selenium nanotube as the cathode material for sodium ion battery. We have monitored the microstructure evolution and interface dynamics using *in situ* TEM during sodiation process. A three steps reaction mechanism appears to explain the sodiation process (Figure 1). In the first step, single crystalline selenium nanotube rapidly transforms to an amorphous Na_xSe alloy phase. In the second step with continued charging, the amorphous phase recrystallizes to a polycrystal Na_2Se_2 phase. In the final step near full sodiation, polycrystalline Na_2Se_2 appears to completely transform into Na_2Se phase with high content of Na. Intriguingly, the reaction front region movement is found to be quite different in the different sodiation stages. The solid-state amorphization process quickly finishes due to the high diffusion of sodium ions inside Se nanotube, with the highest nominal speed of ~2.8 nm/s, and the recrystallization processes has a speed of ~1.0 nm/s (Figure 2). Moreover the speed of solid-state amorphization process is nearly 10 times higher than lithiation process when selenium nanotube were tested in lithiation reaction. Molecule Dynamics (MD) calculation shows all the intermediate phases produced in sodiation are good conductor of both electrons and ions. These observations can not only reveal the reaction mechanism and reaction process, but also to provide insights to design novel nanostructure of electrodes with excellent electrochemical performance.

References:
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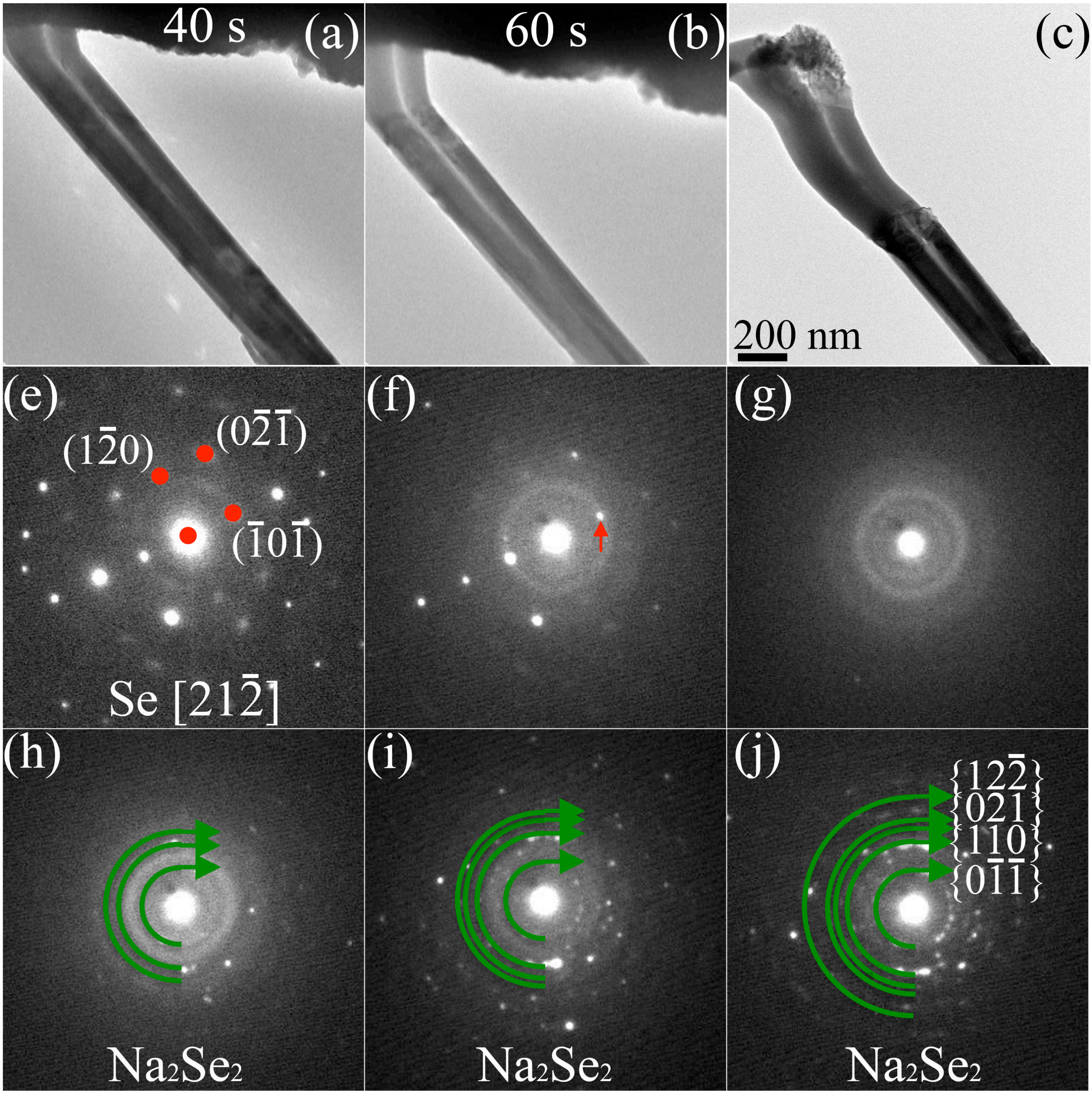

Figure 1. The local morphology and structure analysis of one selenium nanotube with partial sodiation. (a-b) In-situ sodiation process of the one single selenium nanotube. (c) The morphology of the partially sodiated selenium nanotube. (e-j) The electron diffraction patterns are taken from the different phase region and the interface between two adjacent phases. The partially sodiated selenium nanotube shows the three sodiation stages in one nanotube. The unreacted region, amorphous region and the recrystallized region.

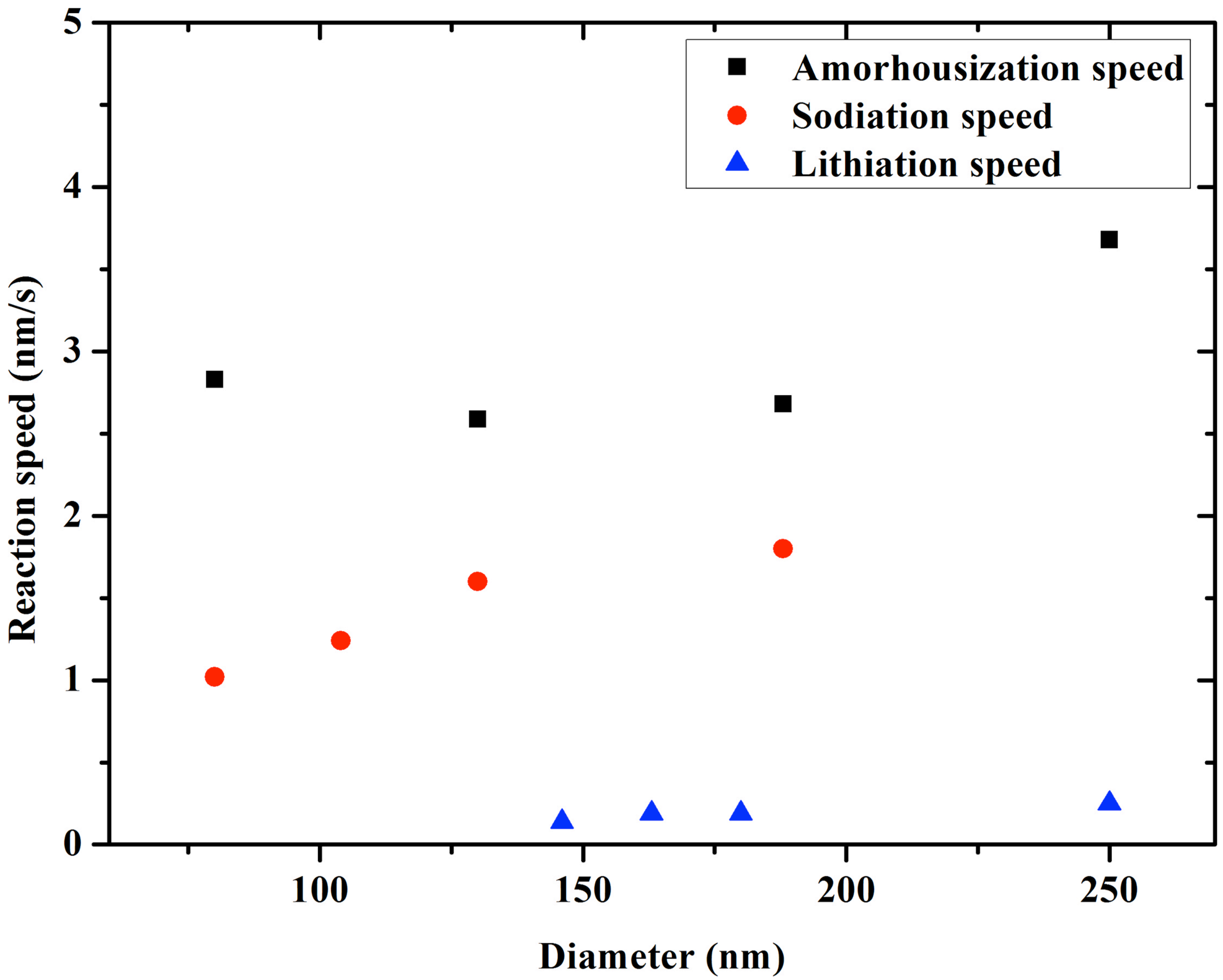

Figure 2. The reaction speed of different diameter selenium nanotubes. The solid-state amorphization stage with the highest reaction speed of ~2.8 nm/s; and the total speed of sodiaton process has a speed of ~1.3 nm/s, due to the lower speed of recrystallization stage in the whole sodiation process. The average lithiation speed is ~0.23 nm/s.