doi:10.1017/S1431927617010911
Microsc. Microanal. 23 (Suppl 1), 2017

In-situ Electron Diffraction Studies of Sodium Electrochemistry in MoS_2

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MoS_2 is a promising electrode materials for sodium-ion batteries. In the structure of MoS_2, there is adequate "space" between the MoS_2 layers interconnected with weak van der Waals force to accommodate Na ions during charging. It turns out that MoS_2 allows Na ions to intercalate therein without a significant volume expansion (1); which enables MoS_2 to be a promising electrode material for rechargeable batteries (2). However, the number of the electrons can be accommodated in the S-Mo-S layer is limited while the structural framework remains stable. It has been shown that up to 1.5 electrons can be stored per unit formula in MoS_2 before the layered structure collapses (3). Meanwhile, there is a structural transition between trigonal 2H- and octahedral 1T-AMoS_2 (A = Li, Na, K, etc.) accompanied by an electronic state change from semiconducting to metallic observed upon alkali-metal ion's intercalation (4). Recent developments of *in-situ* transmission electron microscopy (TEM), as one unique tool to conduct real time structural measurements under the dynamic electrochemical reaction processes. (5) Such *in-situ* or *in-operando* measurements make it possible to analyze and tackle the intricacies of the sodiation mechanism in electrode materials during charge/discharge cycles.

In general, a large electron beam dose is required to imaging materials structure at atomic resolution, which introduces artificial microstructural changes during the observations. Herein, we applied *in-situ* electron diffraction with a remarkably low electron beam dosage to study the dynamic structural evolution in sodium intercalated MoS_2 crystals during sodiation. The diffraction patterns are then carefully indexed and compared to the DFT calculations to derive the structural evolution at or close-to atomic resolution and unravel the mechanism of MoS_2 sodiation under dynamic conditions.

Figure 1 shows the recorded electron diffraction patterns along with the sodiation process and the illustration of the Na-ion intercalated structures with Na content from 0.125 to 1.75 (the formula of each crystal is labeled). In each indexed pattern, the measured *d*-spacing of three spots are labeled. When Na content reaches 0.375, phase transformation from 2H to 1T occurs with appearance of superlattice spots. When Na content is higher than 1.75, the conversion reaction occurs, leading to the formation of metallic Mo and Na_2S reaction product. The structural models of the Na-intercalated structures are derived from DFT calculations and their simulated electron diffraction patterns are compared to the experimental ones; as shown in Fig.2. Several metastable phases have been identified in the early stage of sodiation in nanostructured MoS_2 crystals. The nano-MoS_2 crystal can host up to 1.75 Na per unit formula before the layered structure collapses. This study provides relevant insights into understanding the sodiation kinetics in typical layered transition-metal dichalcogenide structures, which we believe will be helpful in designing next generation advanced sodium ion batteries of the future [6].

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[6] This work was supported as part of the Center for Electrochemical Energy Science, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences under Award # DEAC02-06CH11357, and the Initiative for Sustainability and Energy at Northwestern (ISEN). This work was also supported by the NU*ANCE* Center at Northwestern University, using the EPIC facility that receives support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF NNCI-1542205); the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. We gratefully acknowledge the computing resources from: 1) the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract DE-AC02-05CH11231. 2) Blues, a high-performance computing cluster operated by the Laboratory Computing Resource Center at Argonne National Laboratory.

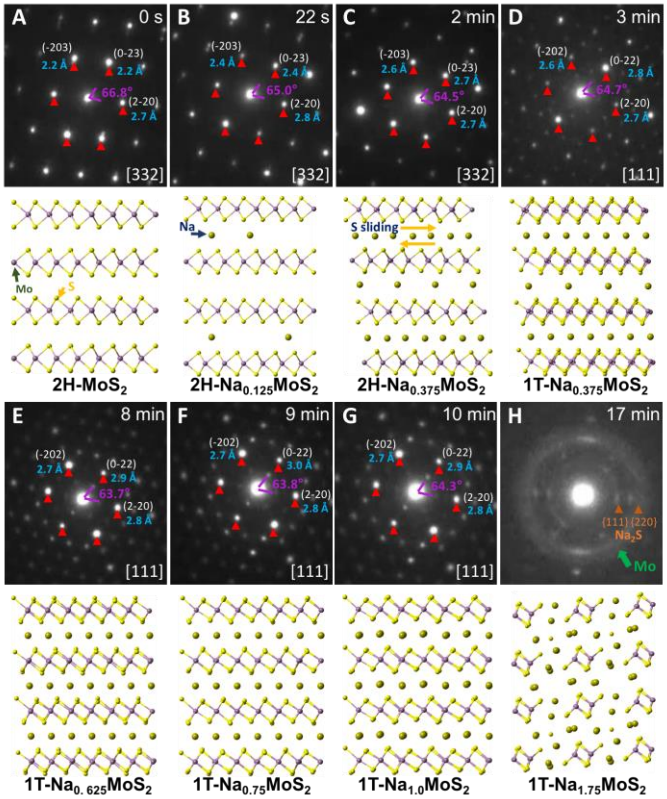

Figure 1. *In-situ* electron diffraction of Na-intercalation into MoS_2. (A) The starting 2H-MoS_2 is identified to be oriented along the [332] zone axis, along with the illustration of the atomic structure (underneath the pattern). (B)-(H) The indexed diffraction patterns and structural illustrations of Na-ion intercalated structures with Na content from 0.125 to 1.75 (the formula of each crystal is labeled), along with the sodiation, while the sodiation time is marked in each pattern. In each indexed pattern, the measured *d*-spacing of three spots are labeled. When Na content reaches 0.375, phase transformation from 2H to 1T occurs with appearance of superlattice spots. When Na content is higher than 1.75, the conversion reaction occurs leading to the formation of Mo and Na_2S.

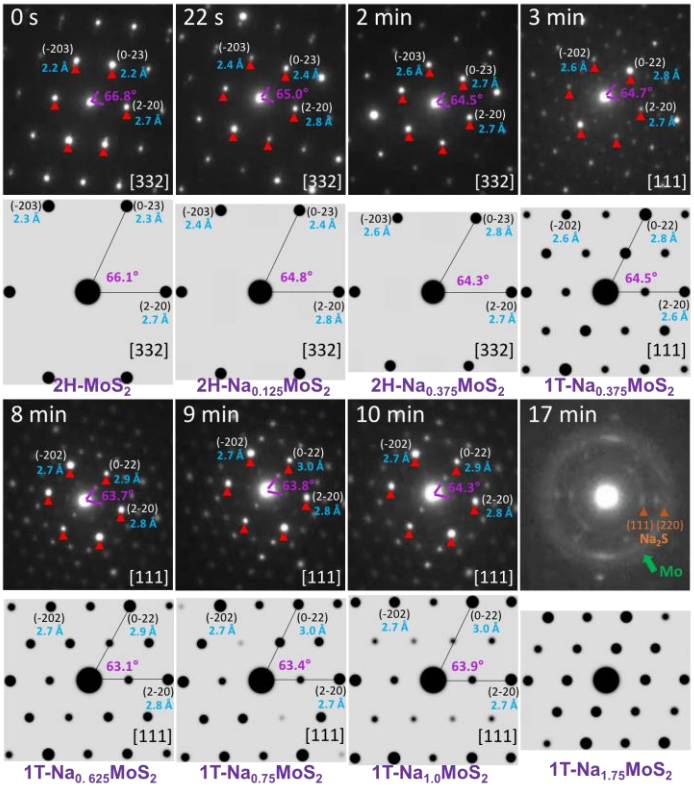

Figure 2. Comparison of experimental electron diffraction patterns to the simulated ones. The experimental selected-area electron diffraction (SAED) patterns of all the intermediate phases appeared in the sodium insertion process are compared to the simulated ones calculated by DFT.

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