Controlling Disorder and Lithiation in Wadsley-Roth Shear Phases

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Wadsley-Roth (WR) shear phases are complex crystallographic shear structures that enable fast ionic and electronic transport with minimal structural strain, making them promising candidates for next-generation, fast-charging, durable Li-ion batteries. This work demonstrates the use of careful powder XRD complemented with X-ray absorption spectroscopy (EXAFS and XANES), PDF and TEM, to understand our recent performance gains for WR compositions including $TiNb_2O_7$, $Nb_{12}WO_{33}$, $MoNb_{12}O_{33}$, and $Hf_{0.5}Zn_{0.5}Nb_{11}O_{29}$.[1] Powder diffraction is challenging with monoclinic unit cells of ~4 x 20 x 30Å comprising large corner-shared octahedral blocks with edge-sharing octahedra forming shear planes as shown in Fig. 1. The structural blocks take on many different sizes, for example [3 x 3], [3 x 4], or [4 x 4] octahedra, and we find that both oxygen vacancies and disordered block sizes may significantly improve Li diffusivity and/or overall battery capacities. Perhaps most interesting is the flexibility of the structures which allow reduction under reactive gas and reoxidation to yield controlled quantities and types of defects. We show that in-situ XRD provides direct knowledge of the phase progressions during intentional reduction and reoxidation reactions as well as during synthesis of the target phases from amorphous chemical precursors. Combining EXAFS and XANES measurements with high resolution S/TEM, powder diffraction and some PDF work, we determine the origins of improved performance for several WR phases. For example, poorly crystalline $TiNb_2O_7$ synthesized using chemical methods provides enhanced 10C capacity of 233 mAh/g for specimens characterized by extremely broadened XRD peaks with Nb primarily, but not entirely, in 6-fold coordination.[2] In $Nb_{12}WO_{33}$, partial reduction or reduction-reoxidation treatments were explored for increasing electronic conductivity and Li-ion diffusivity, achieving up to 1.4x improvement. Additionally, controlled kinetically limited crystallization of $MoNb_{12}O_{33}$ enabled the formation of non-equilibrium, defect-rich structures that facilitate transport, yielding remarkable lithiation capacities of 200 and 151 mAh/g at 10C and 20C, respectively, comparable to benchmark anode materials.[3] Direct evidence of mixed structure block sizes in high-performance $MoNb_{12}O_{33}$ comes from microscopy and diffraction studies. These results underscore the importance of disorder and point defects in these complex shear structures and demonstrate some new approaches for controlling and optimizing these phases to yield high-performance battery materials.

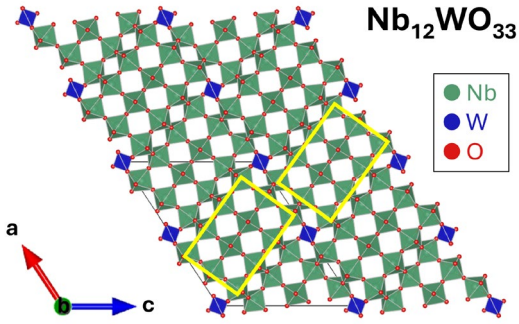


Figure 1: Projection of the best-known model for the WR phase $Nb_{12}WO_{33}$, looking along the direction of continuous tunnels formed by corner-shared NbO_6 octahedra. Yellow boxes show the [3 x 4] block bounded by shear planes.

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[2] Sturgill, C. J.; Milisavljevic, I.; Wechsler, S. C.; Muhit, M. A. A.; zur Loye, H.-C.; Misture, S.; Stefik, M. Tailored $TiNb_2O_7$ Particle Size, Defects, and Crystallinity Accelerate Lithiation. Chemistry of Materials 2025, 37 (2), 624-635. DOI: 10.1021/acs.chemmater.4c02279.

[3] Sturgill, CJ.; Kumar, M.; Karimitari, N.; Milisavljevic, I.; Collins, C. S.; Hegler, A.; Chao, H.-Y. J.; Balijepalli, S. K.; Misture, S. T.; Sutton, C.; et al. Role of Wadsley Defects and Cation Disorder to Enhance $MoNb_{12}O_{33}$ Diffusion. Advanced Energy Materials 2026, 16 (12), e06454. DOI: https://doi.org/10.1002/aenm.202506454.