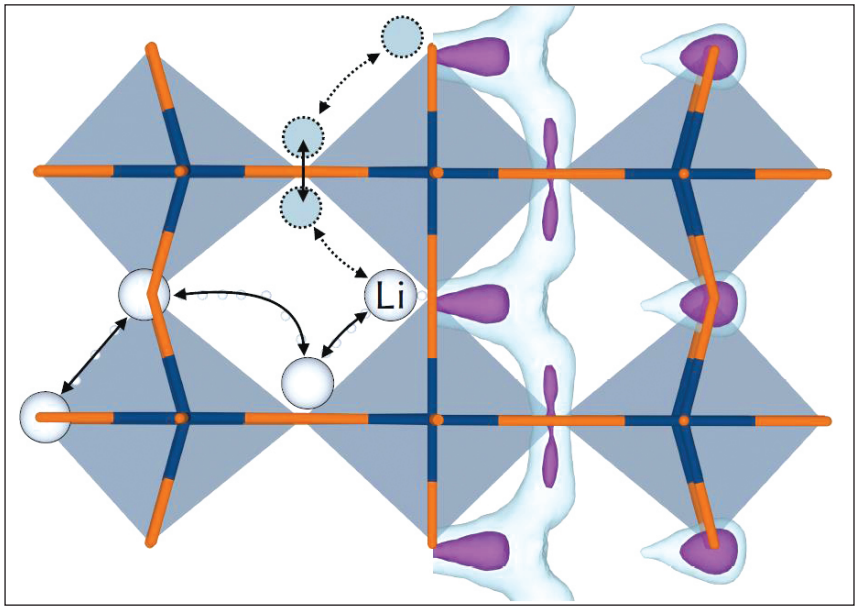
Energy Focus

Computational insights describe diffusion of lithium through novel battery anodes



Two complementary computational techniques describe the ion diffusion mechanisms and provide structure–property relationships of lithium-ion diffusion in niobium tungsten oxide anodes. Credit: Can Koçer.

Electrode materials constitute the most crucial elements of a lithium-ion battery, controlling the amount of energy that it can store, and how quickly power can be released. The anode, which intercalates lithium ions into its structure during charging, is a particularly stubborn roadblock on the arduous path toward higher electrochemical capacities of these devices. Graphite, the state-of-the-art material for these negative electrodes, cannot rapidly accommodate a significant amount of lithium safely. In response, researchers have fielded numerous novel materials structures that aim to maximize capacities of anodes. These alternatives must overcome slow diffusion of lithium through their structures during intercalation. Lithium ions must be able to rapidly permeate the anodes in order for electrodes to charge efficiently.

An emerging crystal structure family of niobium tungsten oxides is a system of interest for high-rate anodes. This material, which exhibits a planar configuration with systematic arrangements of oxygen vacancies that form so-called "crystallographic shear structures," includes $Nb_{12}WO_{33}$, $Nb_{14}W_3O_{44}$, and $Nb_{16}W_5O_{55}$. These ceramics have very large unit cells and low symmetries. Subsequently, lithium pathways through these tortuous structures are very complicated and proceed through a series of windows, cavities, and tunnel types. Nevertheless, these open framework structures offer significant promise to rapidly and efficiently lithiate, and they caught the attention of a research team from the University of Cambridge. In collaboration with scientists from Northwestern University and the University of Birmingham, they completed a computational analysis of the lithium diffusion through these complex structures. Their findings appeared in a recent issue of *Chemistry of Materials* (doi:10.1021/acs.chemmater.0c00483).

Can Koçer, the lead author of the article, highlights the novelty of the anode materials: "Wadsley-Roth phases [a crystal structure of niobium tungsten oxide] are a very interesting class of materials, and are still relatively unexplored. We have made good progress in terms of understanding how these materials work at the atomistic level, and why they show such excellent performance."

The research team used a combined approach of elastic band calculations—through density functional theory—and molecular dynamics to account for different lithium concentrations. Their computational approach identified specific types of tunnels in the structures as the most probable ion intercalation pathways. The calculations accounted for different anode material stoichiometries and lithium concentrations to derive ranges of activation barriers. The researchers were able to predict high diffusion coefficients of ions through different categories of cavity-like tunnels that permeate ceramic anodes, which promise to rapidly lithiate at excellent rates that match those of the best available solid electrolytes.

Koçer further comments on the constrained one-dimensional lithium diffusion pathway through the structures: "The crystallographic structure is key to understanding the diffusion mechanism. We were able to show conclusively that the lithium motion is constrained to occur along one direction, in parallel one-dimensional tunnels. Lithium ions can jump from one tunnel to another, leading to the idea of a 'multi-lane highway' for lithium ions, which we were able to put on a more quantitative footing. Motion in the tunnels is rapid due to very low energy barriers. In addition, we were able to identify other types of processes that occur in the structure, for example certain transitions into specific sites that act like parking spots for lithium, away from the tunnels."

These results build upon prior work of this research team, which had previously described the viability of these crystallographic shear phases as lithium-ion battery anodes. Their nuclear magnetic resonance capabilities probe both long-range and local motion of lithium through these materials, and future measurements will provide important insights into ion hopping and kinetic barriers. This computational effort is one of the first trailblazers to provide insight into a previously unexplored structure and corresponding lithiation process, and the team's discoveries will pave the way for these emerging complex materials to gain prominence as promising energy-storage anodes in the future.

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