Wadsley-Roth
Crystallographic Shear Phase Oxides for Battery Applications

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Wadsley-Roth Crystallographic Shear phases are a family of chemistries constructed from transition metal octahedra sheared along different axes.

“3 by 3 “ Wadsley Roth phase constructed with 3 by 3 octahedral blocks.
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"3 by 3" Wadsley Roth phase constructed with 3 by 3 octahedral blocks.
The history of Wadsley-Roth chemistries and their usages as battery electrode materials

- These phases were first synthesized by Wadsley and Roth in the 1960s
- Cava performed a study of lithium insertion into differing Wadsley Roth phases
- Wadsley-Roth phases can be placed into 3 types, E, T, M

Schematics of Wadsley-Roth phases synthesized by Cava for which he did lithium insertion tests

Expanded the definitions of Wadsley-Roth phases to group by structure type and unique Li sites for experimentally synthesized phases.
These blocks can be constructed by shifting block of octahedra in different ways

Type $E_1 \ [nxm]$
These blocks can be constructed by shifting block of octahedra in different ways

Type T \([n \times m]\)
E1 type structures and are the most prevalent of the Wadsley-Roth phases but there is a large variety.
What is a rechargeable battery?

Lithium-ion battery anodes suffer from low power density and safety issues


Lithium intercalation into graphite at variable c-rates for the first cycle, normalized

Lithium dendrite formation on a lithium anode
Why are Wadsley-Roth phases being examined for lithium-ion battery applications?

Operates at 1-2V vs Li/Li+ -> Low SEI/dendrite formation  
High power density

Crystal structure for one of the phases of the Wadsley-Roth structure, TiNb$_2$O$_7$

Crystal structure for the Wadsley-Roth phase, PNb$_9$O$_{25}$

Why are Wadsley-Roth phases being examined for lithium-ion battery applications?

Variable rate cycling data for the Wadsley-Roth phase structure, TiNb$_2$O$_7$\(^6\)

Variable rate cycling data for the Wadsley-Roth phase structure, PNb$_9$O$_{25}$\(^7\)


What types of Li sites are stable in these Wadsley-Roth phases?

Type E₁

Type T
How do Li Site stabilities differ between structures?

Li ion sites present are structure dependent

Type $E_0[n\times \infty]$

Type $E_1[n\times m]$

Type $M[n\times m]$

Type $E_0[n\times m]$

Type $T[n\times m]$

Type $E_1[n\times m]$
Li diffusion at the dilute limit in TiNb$_2$O$_7$ and Nb$_{12}$WO$_{33}$ is anisotropic

- As determined by Kocer et. al, diffusion in the T[4x3] block structure Nb$_{12}$WO$_{33}$, NEB studies indicate lower kinetic energy barriers for the window sites. A similar finding occurred for TiNb$_2$O$_7$.
- The paper also shows that kinetic energy barriers between face sharing Ps sites is very high, indicating there may be anisotropic diffusion of Li.

If window sites show the lowest kinetic energy barriers, why isn’t ReO$_3$ used as an anode material?
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Li does not reversibly intercalate into ReO$_3$ since insertion of Li is followed by twisting of the ReO$_3$.

Octahedral Rotations in ReO$_3$ upon Li insertion$^9$

Wadsely-Roth phases are stabilized by their edge-sharing octahedra
Wadsley-Roth phases can be synthesized with differing block sizes, ways that the blocks are shifted and degrees of disorder.

Parameters that can change in Wadsley-Roth phases:
- Block size
- TM Disorder
- Cation Species
- Structure type

“3 by 3 “ Wadsley Roth phase constructed with 3 by 3 octahedral blocks.
Differentiating structural properties by transition metal disorder

Type $E_0[nxm]$  
Type $E_0 [nx\infty]$  
Type $E_1 [nxm]$  
Type $T [nxm]$  
Type $M[nxm]$
How can disorder affect battery performance?

Higher energy set of TiNb$_2$O$_7$ orderings
Differentiating structural properties by structure type

Type $E_0[nxm]$  
Type $E_0[nx\infty]$  
Type $E_1[nxm]$  
Type $T[nxm]$  
Type $M[nxm]$
Voltage and Site occupancy show significant differences as we vary WR structure type

Conclusions

- Different Wadsley-Roth phases are oxides with crystallographic shear along a block of transition metal octahedra.
- Different sets of Wadsley-Roth phases can be differentiated by the relative shifts of their “blocks” and the size of the sets of corner sharing octahedra units.
- Synthesized WR phases used for battery applications tend to be of the E1[nxm] structure type.
- SOJT distortions are generally seen on the edges of the blocks when the transition metals are fully oxidized.
- Disorder may be a method for tuning site occupancies and therefore the voltage profile.
- Different structure types show differences in voltage profile though work still needs to be done to deconvolute this affect from the affect from disorder.
Questions?
Back up slides
General Methodology: We can examine 0K thermodynamic properties and electronic structure using density functional theory (DFT) calculations as training data.

=Li

=Li coordinated by 4 oxygens

=Li coordinated by 5 oxygens

=TMO$_6$ octahedra where TM means transition metal

Density functional theory (DFT)

Convex hull

Formation Energy (eV)

Li composition

Voltage

Capacity (mAh/g)

And many other electronic and structural properties
The DFT training data can be used to fit an equation called a cluster expansion that can be used to examine thermodynamic properties at finite temperature.

\[ E(\vec{\sigma}) = V_0 + \sum_a V_a \phi_a(\vec{\sigma}) \quad \text{with} \quad \phi_a(\vec{\sigma}) = \prod_{j \in a} \sigma_j \]

\[ Z = \sum_{\sigma} e^{-\frac{E(\vec{\sigma}) - \mu_i N_i}{k_B T}} \]

\( \vec{\sigma} \) is a vector of occupation variables where \( \vec{\sigma} = \sigma_1, \sigma_2, \ldots, \sigma_N \).

A caveat on Li site stabilities

- In some structures there is a high energy minima that is five coordinated between sets of octahedra.