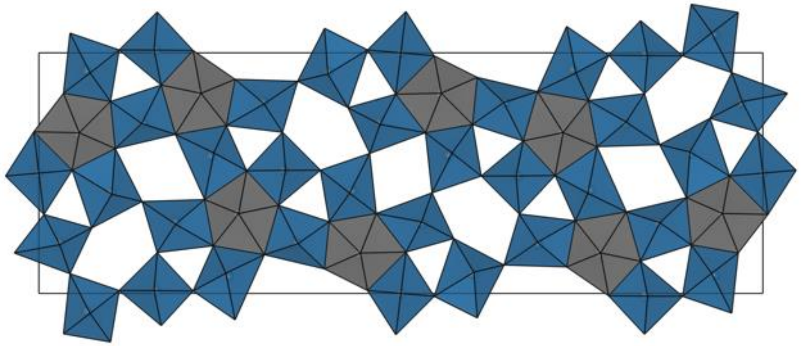

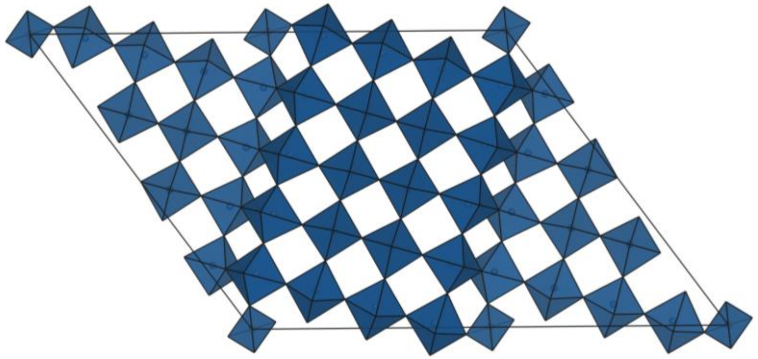

Niobium tungsten oxides for high-rate lithium-ion energy storage

Kent J. Griffith[1*], Kamila M. Wiaderek[2], Giannantonio Cibin[3], Lauren E. Marbella[1#], Clare P. Grey[1]

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[2]X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA

[3]Diamond Light Source, Harwell Science and Innovation Campus, Didcot, UK

[*]Present address: Departments of Materials Science & Engineering and Chemistry, Northwestern University, Evanston, IL, USA

[#]Present address: Department of Chemical Engineering, Columbia University, New York, NY, USA

41st Charles Hatchett Award Seminar, London

Nature **2018**, *559*, 556–563.

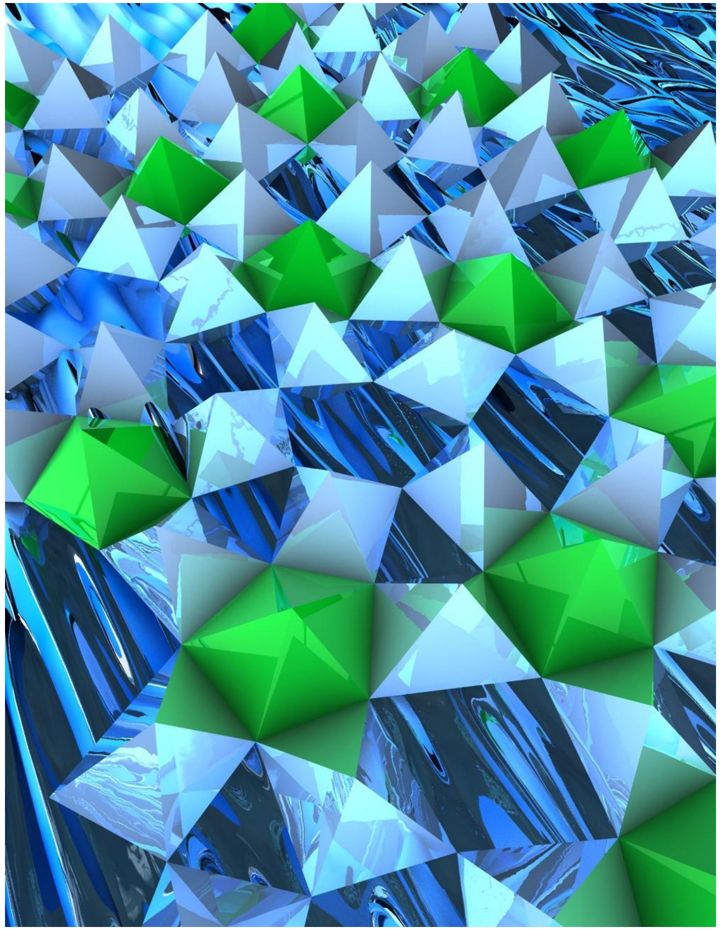
Electrochemical energy storage

UK set to ban petrol and diesel vehicle sales from 2040

£65 million Faraday Institution for advanced batteries

Grid-scale renewables are increasing and require storage/shifting

Personal electronics, power tools, internet-of-things (IoT), robotics



Lithium-ion battery market (cell level)

- 2018 → $31 billion, 160 GWh
- 2025 → $80 billion, 600 GWh
- 2030 → $140 billion, 1200 GWh

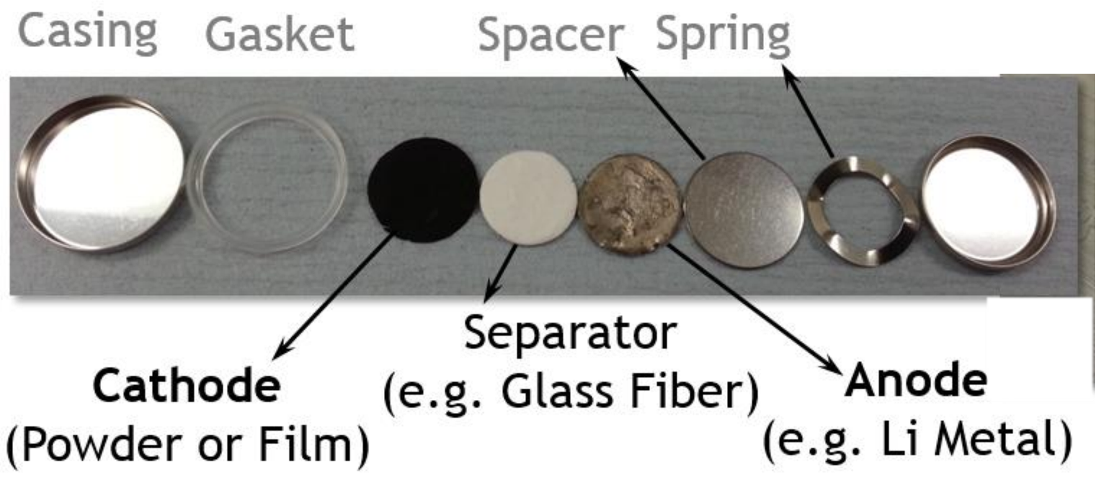
Market data: C. Pillot, Avicenne Energy

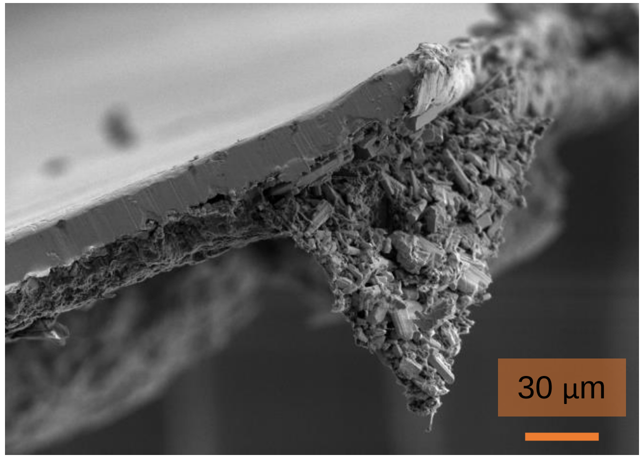
Image: Ella Maru Studio

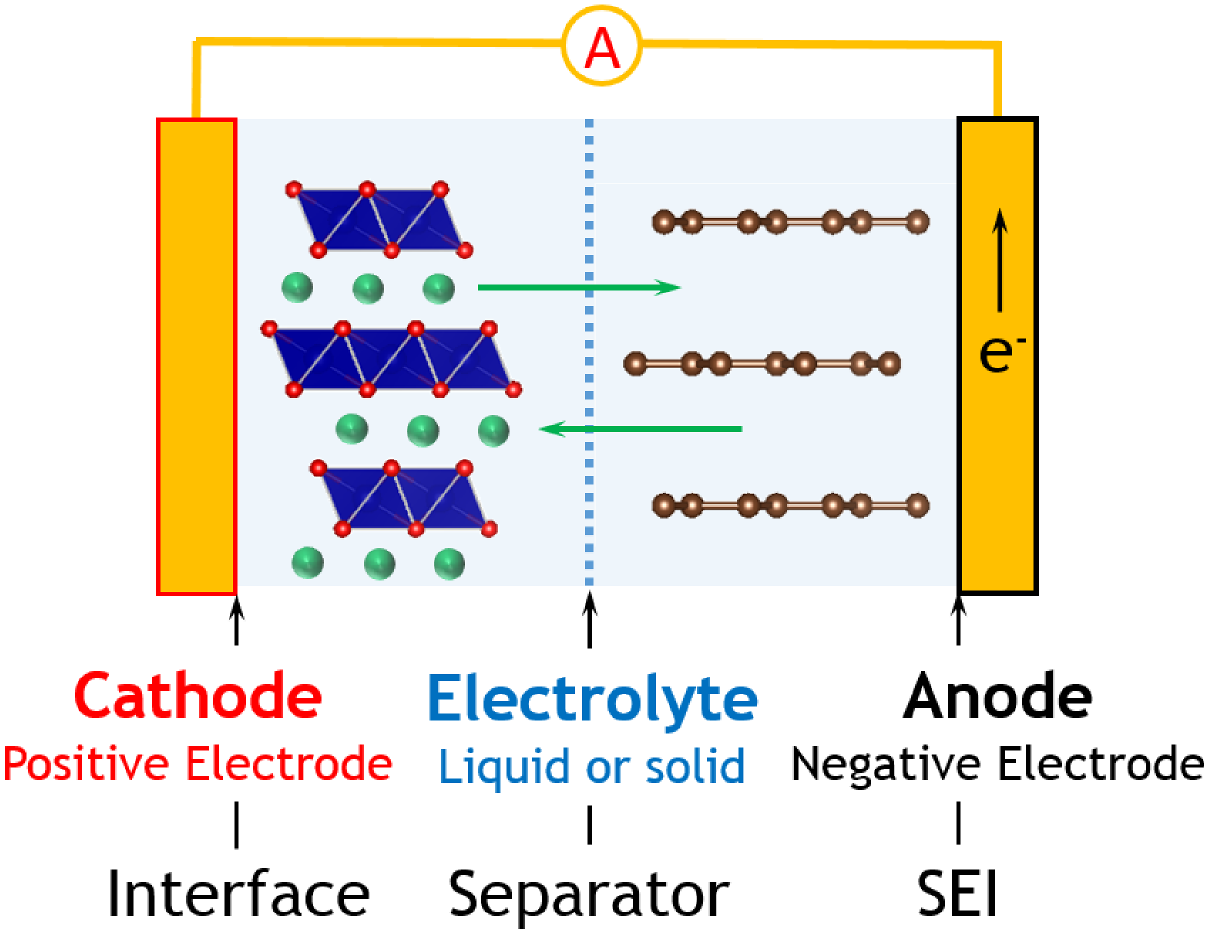
Battery Applications

Images: Toshiba, Chevy Bolt EV, Wall Street Journal, Stanley Black and Decker

Lithium-ion batteries



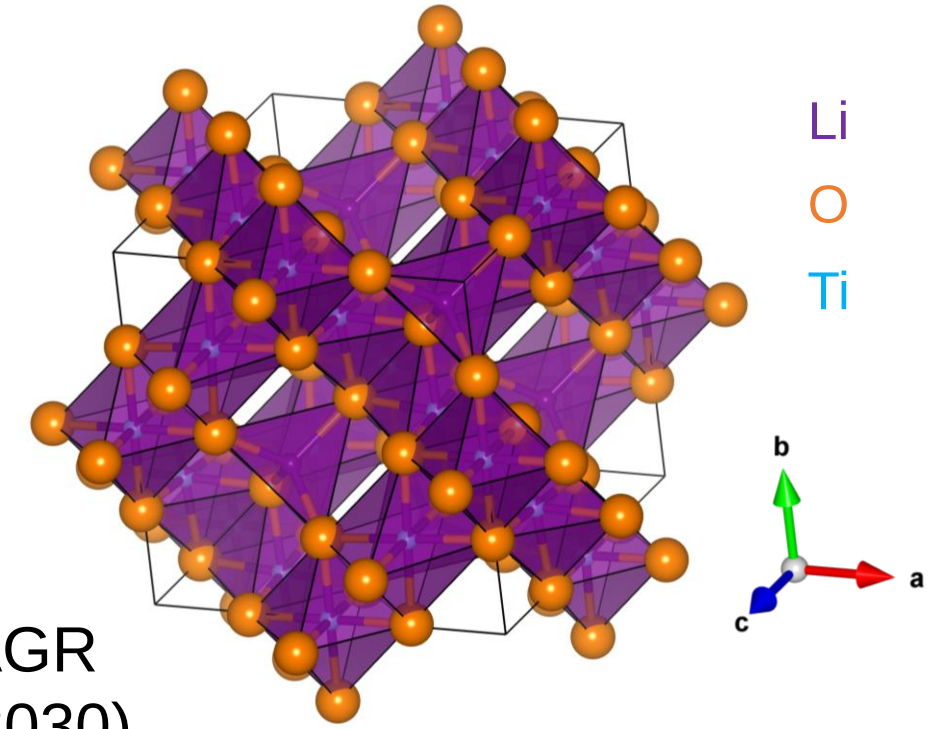




Pecher, O.; González, J. C.; Griffith, K. J.; Grey, C. P. Materials' Methods: NMR in Battery Research. *Chem. Mater.* **2017**, *29*, 213–242.

State-of-the-art in high power anodes

Lithium titanate spinel: $Li_4Ti_5O_{12}$, LTO



Voltage vs. Li^+/Li: 1.55 V → safety, lower energy
Max. theoretical capacity (3 Li/5 Ti):
175 $mA{\cdot}h{\cdot}g^{-1}$ (less in practice)
Long cycle life: >15,000 cycles
Limited Li^+ diffusion & e^- conductivity → nanoscale

Commercial: small anode market share but 25% CAGR
4200 tons/y (2018) → 50,000 tons/y (2030)

Improved high-rate anodes are desired for safe, long lasting, fast charging batteries
$TiNb_2O_7$ (Toshiba), crystallographic shear structure

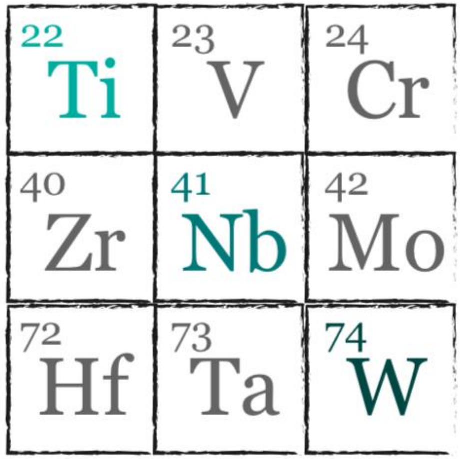
CAGR = compound annual growth rate

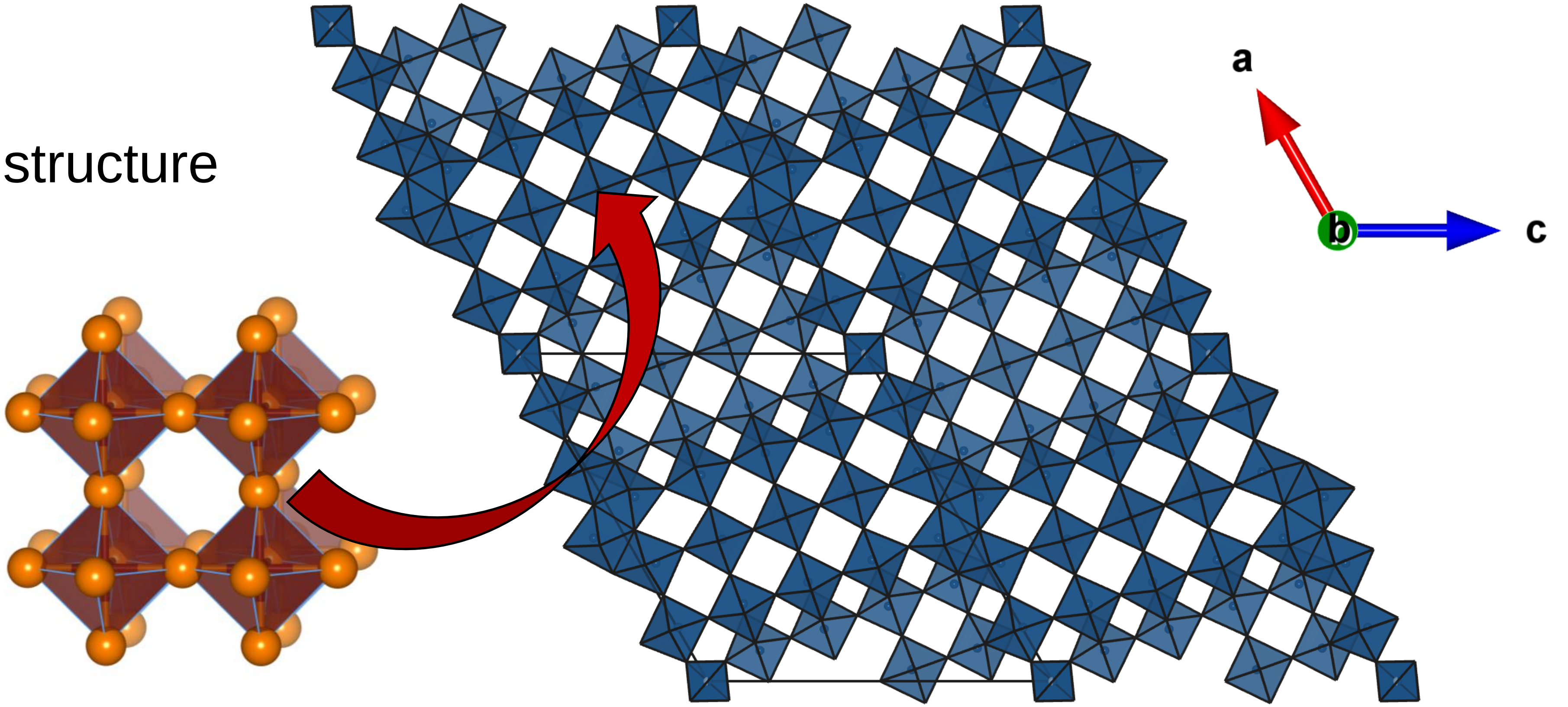
Market data: C. Pillot, Avicenne Energy

New anode materials for high power, fast charging lithium-ion batteries

Niobium-based mixed metal oxides from lessons learnt on Nb_2O_5

H-Nb_2O_5
Wadsley–Roth
crystallographic shear structure
$(4 \times 3)_1$ & $(5 \times 3)_\infty$





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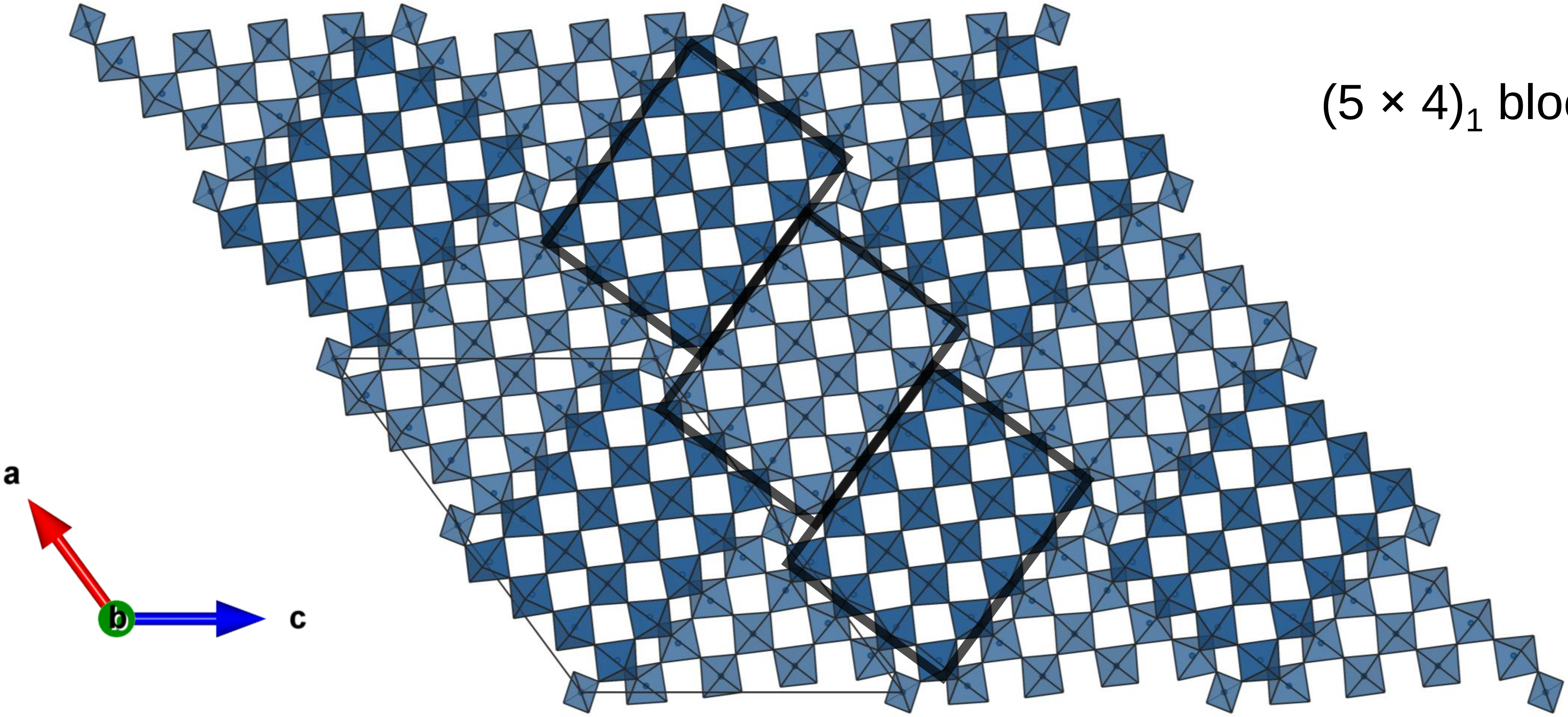
Griffith, Kent. J.; Forse, A. C.; Griffin, J. M.; Grey, C. P. High-Rate Intercalation without Nanostructuring in Metastable Nb_2O_5 Bronze Phases. *J. Am. Chem. Soc.* **2016**, *138*, 8888-8899.

$Nb_{16}W_5O_{55}$ crystal structure

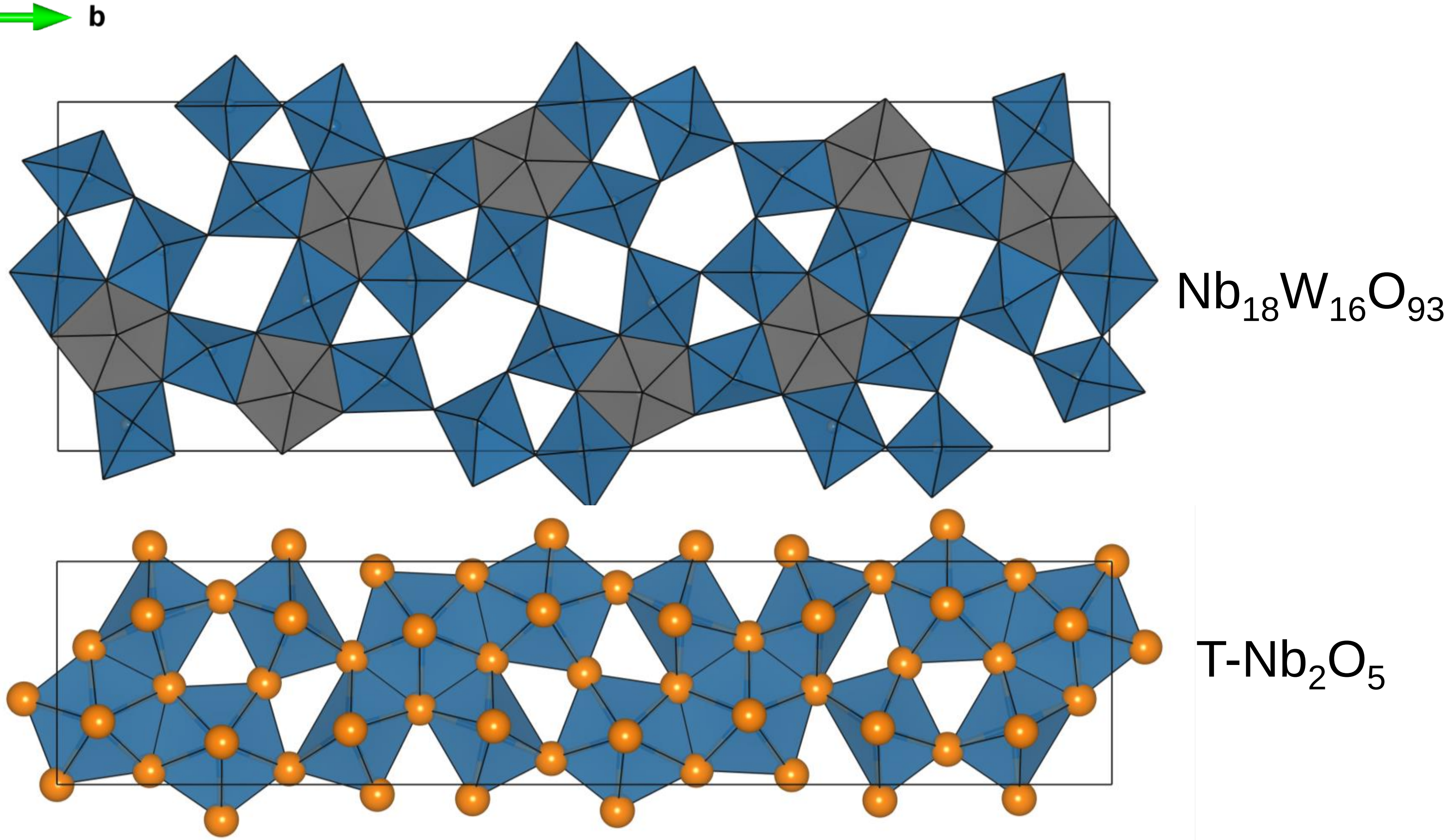


$(5 \times 4)_1$ blocks

Griffith, K. J.; Wiaderek, K. M.; Cibin, G.; Marbella, L. E.; Grey C. P.
Niobium Tungsten Oxides for High-rate Lithium-ion Energy Storage. *Nature*, **2018**, *559*, 556–563.

New anode materials for high power, fast charging lithium-ion batteries

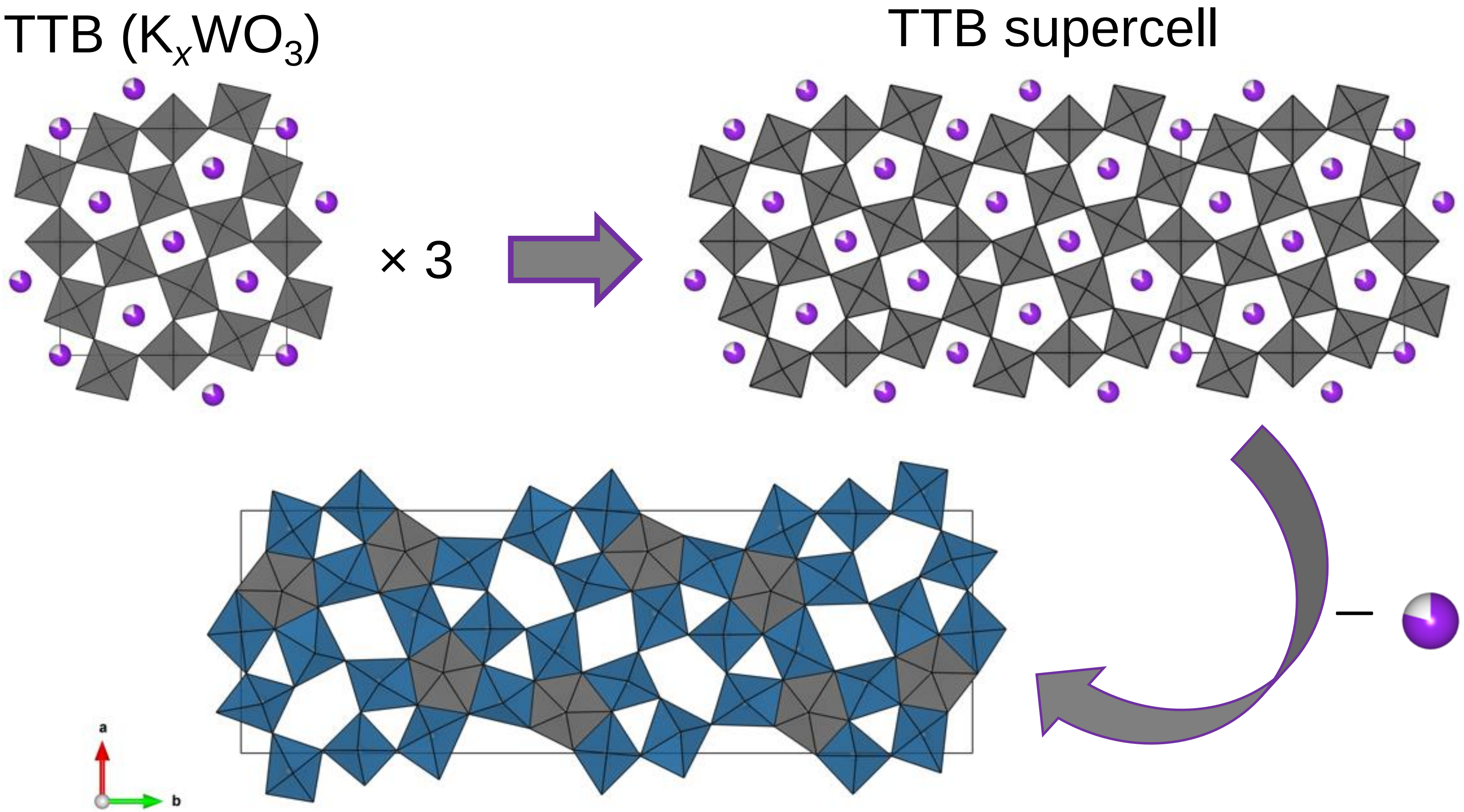
Niobium-based mixed metal oxides from lessons learnt on Nb_2O_5



Griffith, Kent. J.; Forse, A. C.; Griffin, J. M.; Grey, C. P. High-Rate Intercalation without Nanostructuring in Metastable Nb_2O_5 Bronze Phases. *J. Am. Chem. Soc.* **2016**, *138*, 8888-8899.

$Nb_{18}W_{16}O_{93}$ crystal structure

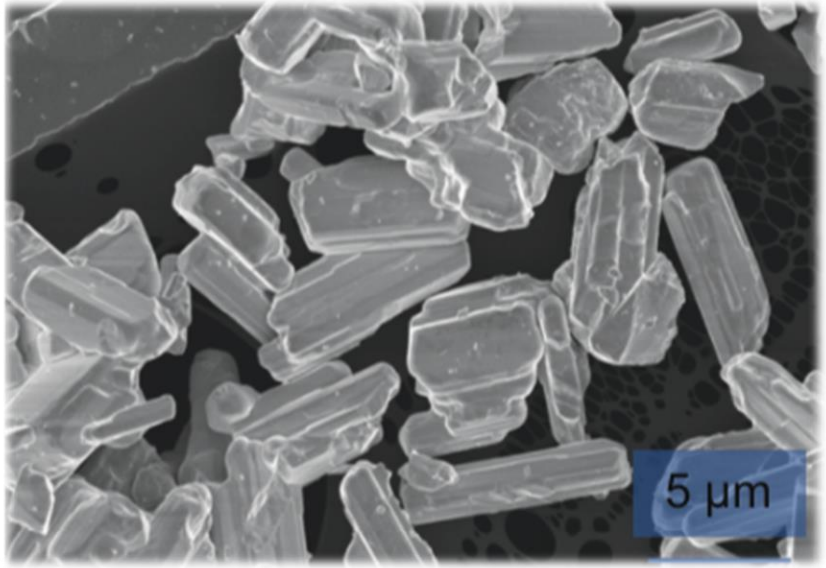
$Nb_{18}W_{16}O_{93}$
a tetragonal tungsten bronze (TTB) derivative



$Nb_{18}W_{16}O_{93}$ - distorted TTB superstructure

Griffith, K. J.; Wiaderek, K. M.; Cibin, G.; Marbella, L. E.; Grey C. P.
Niobium Tungsten Oxides for High-rate Lithium-ion Energy Storage. *Nature*, **2018**, *559*, 556–563.

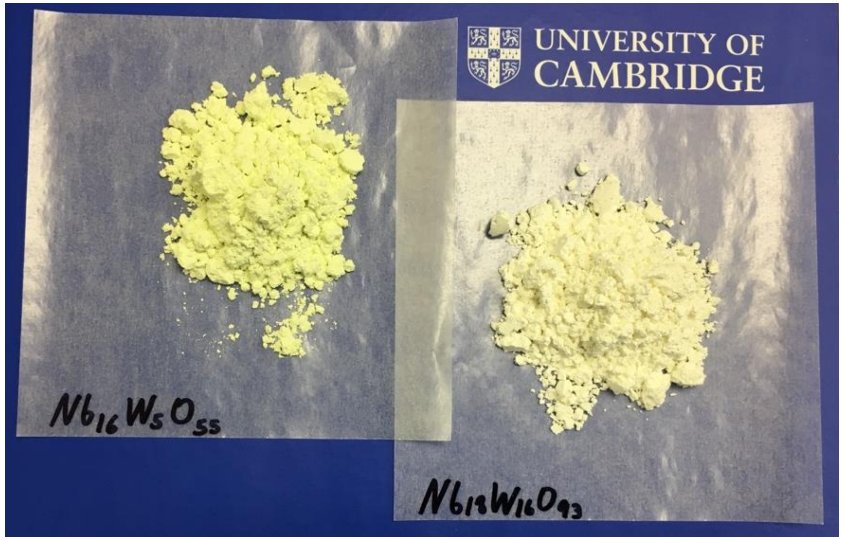
Micrometer-scale bulk particle morphology (for high rates??)



Electrode manufacturing

Standard powder mixing

Standard slurry coating

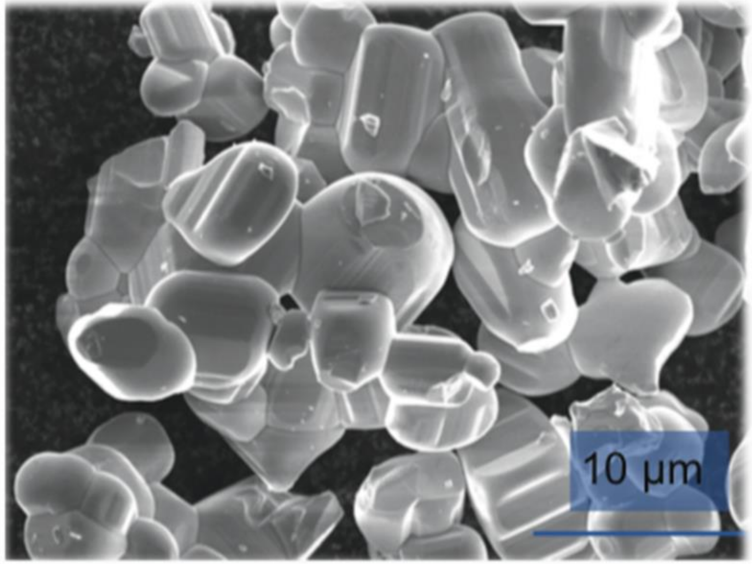


Material synthesis

Scalable

Low manufacturing cost

(Li-free synthesis)

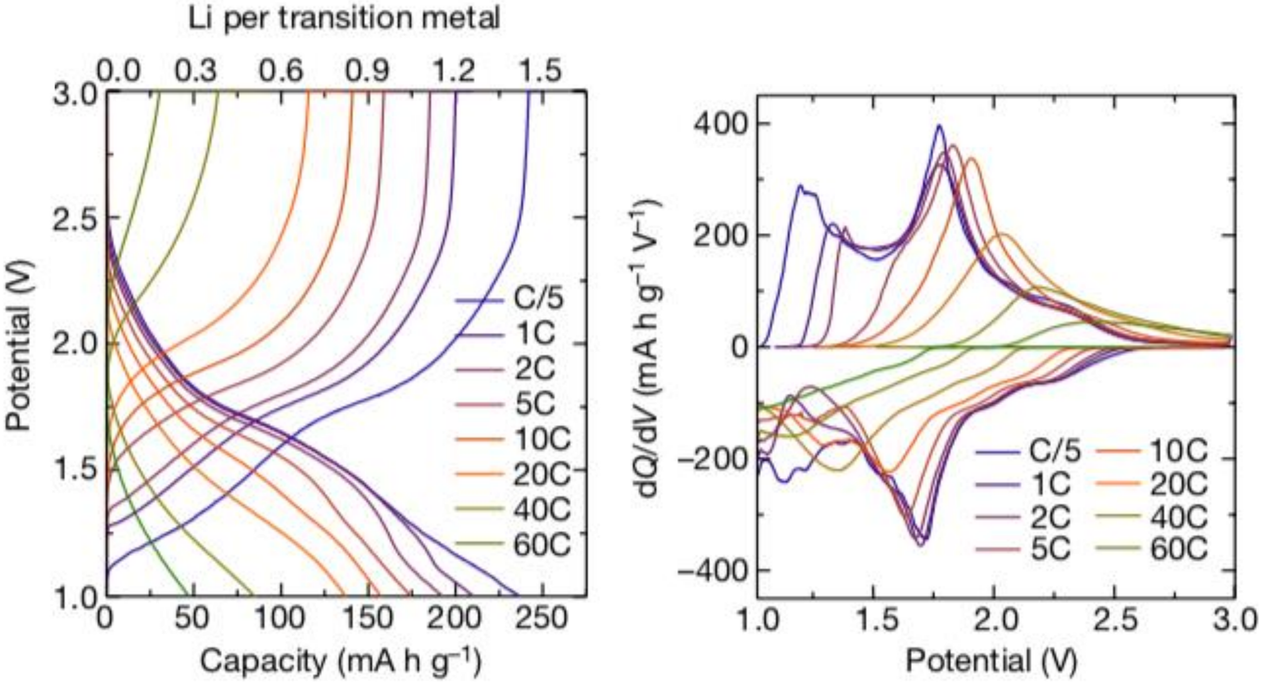


Battery performance

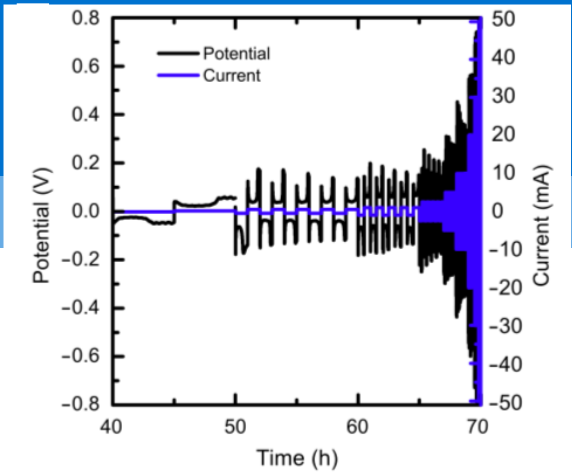
Low surface area = low reactivity

→ long cycle life, high safety

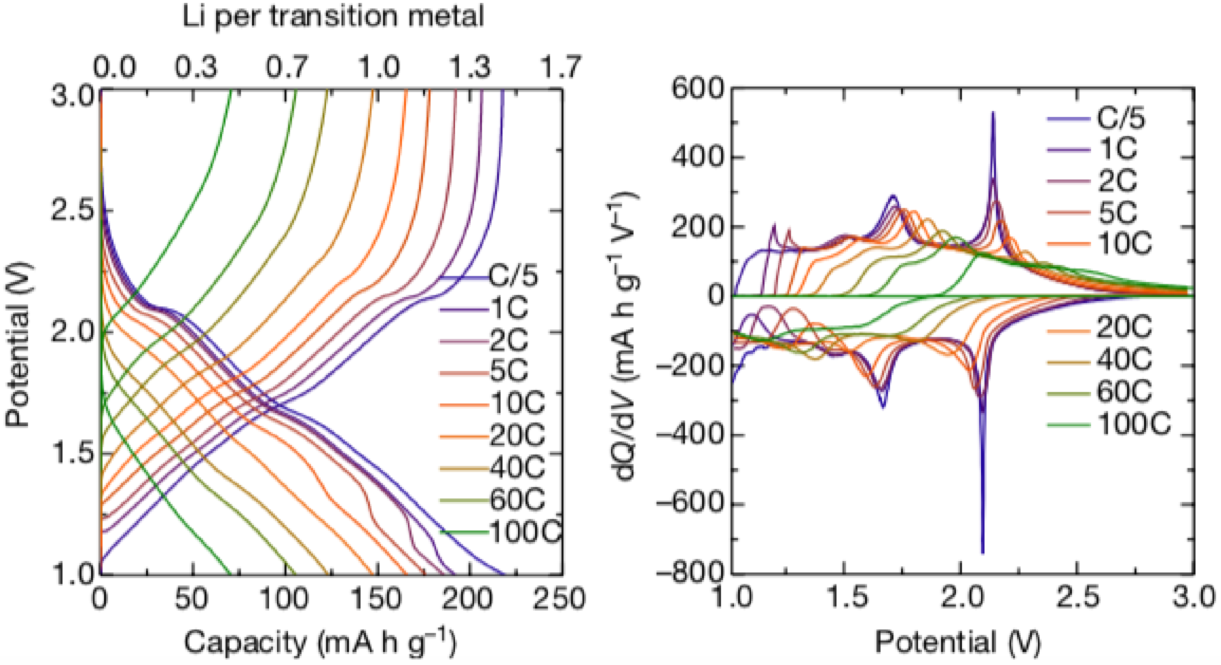
Niobium tungsten oxide electrochemistry



$Nb_{16}W_5O_{55}$



$Nb_{18}W_{16}O_{93}$



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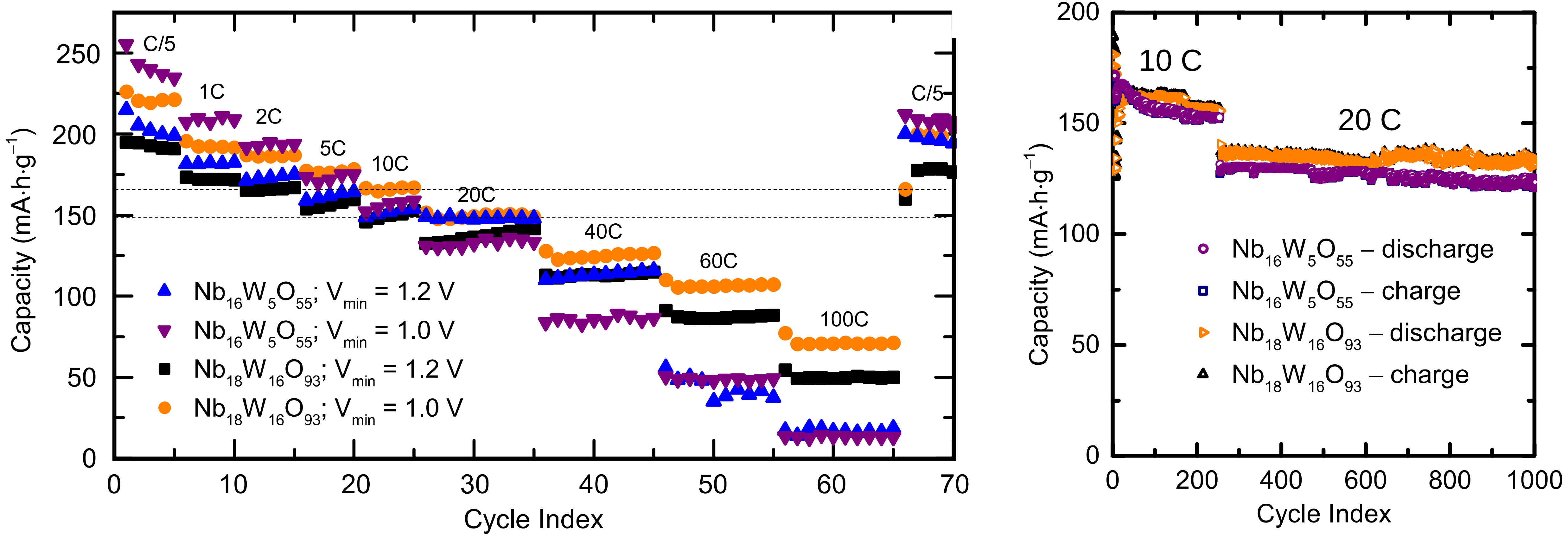
Niobium tungsten oxide electrochemistry



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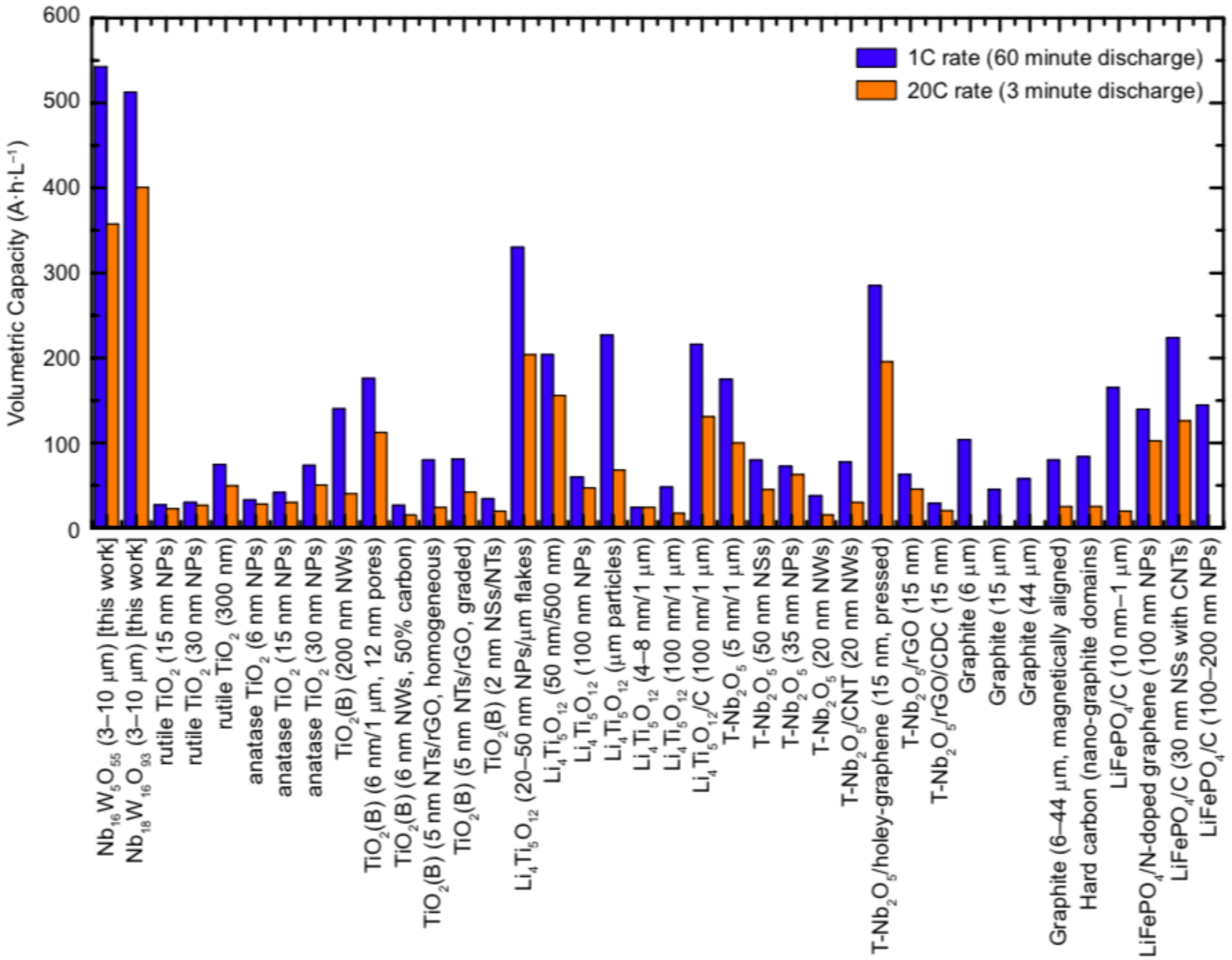
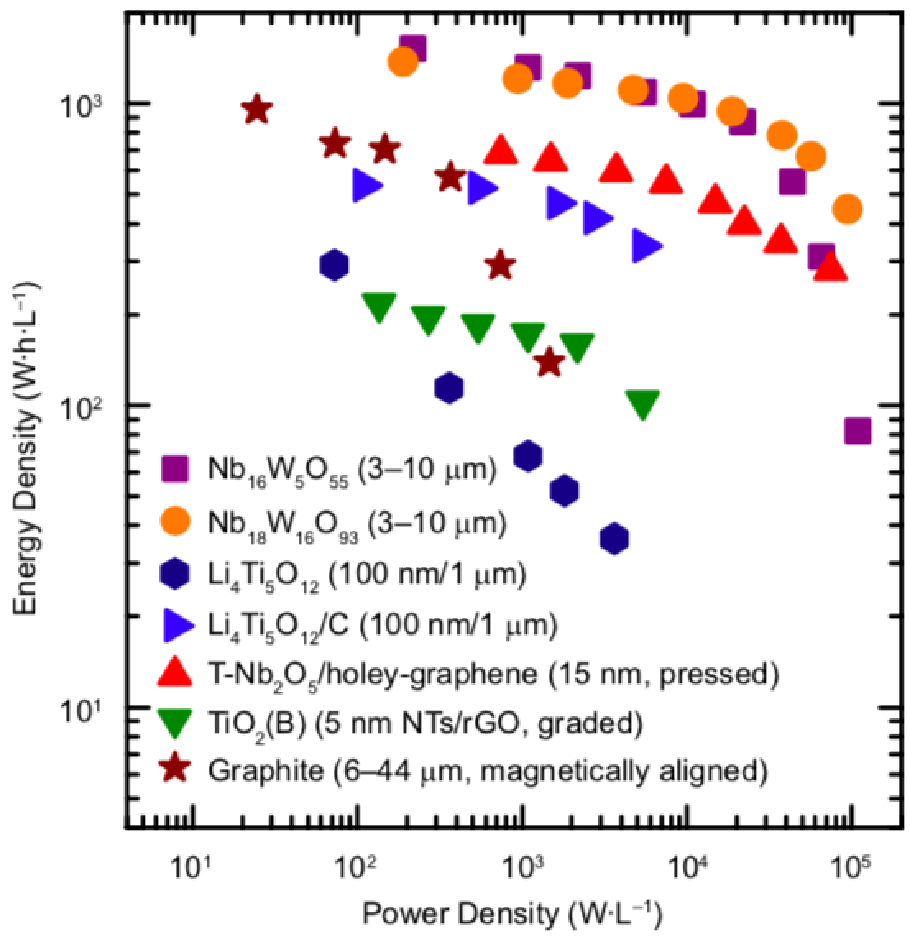
dashed lines = theoretical one electron per transition metal capacity

Niobium tungsten oxide electrochemistry





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Griffith, K. J.; Wiaderek, K. M.; Cibin, G.; Marbella, L. E.; Grey C. P.
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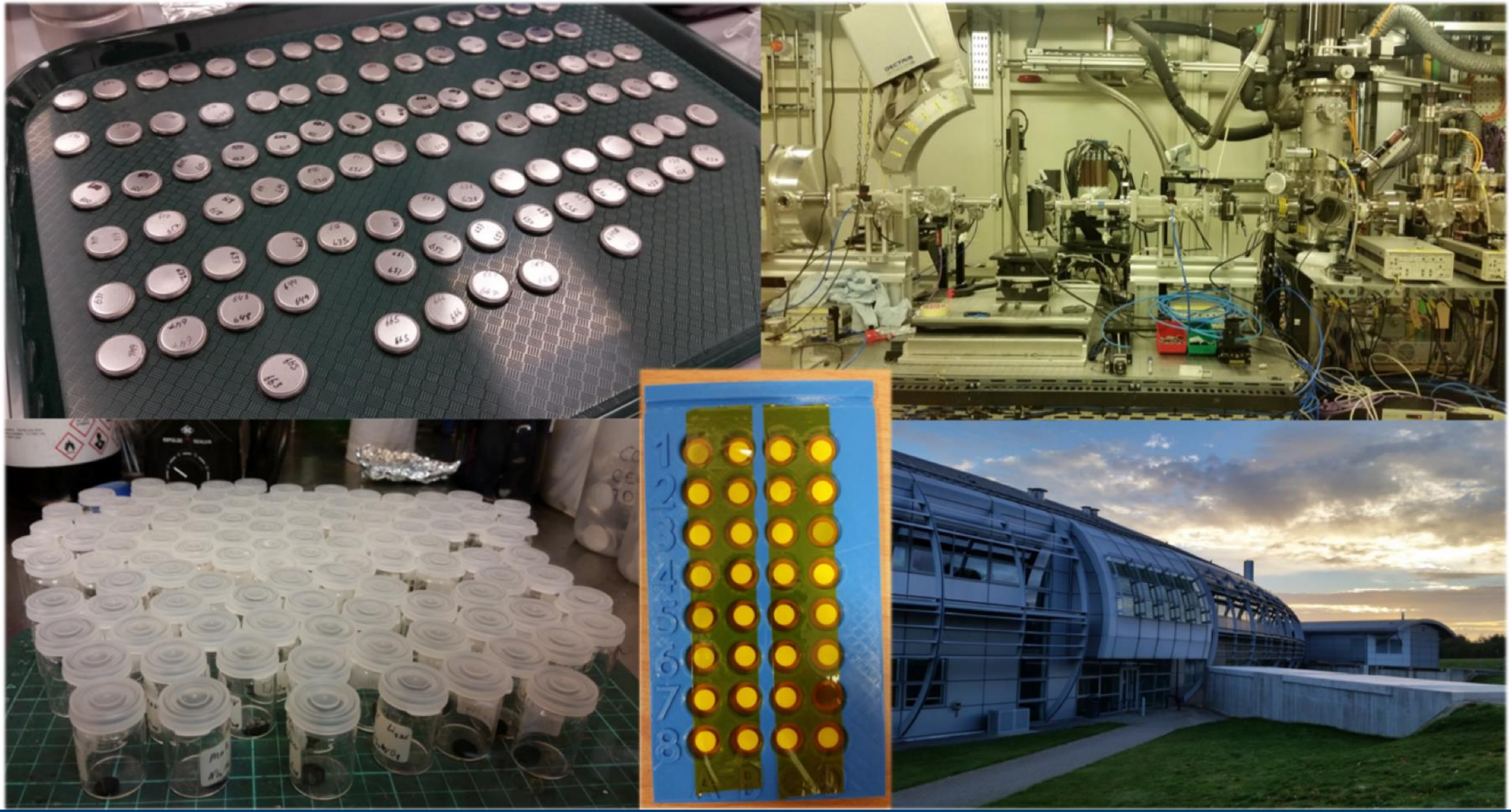
Chemical and structural insights from synchrotron X-rays



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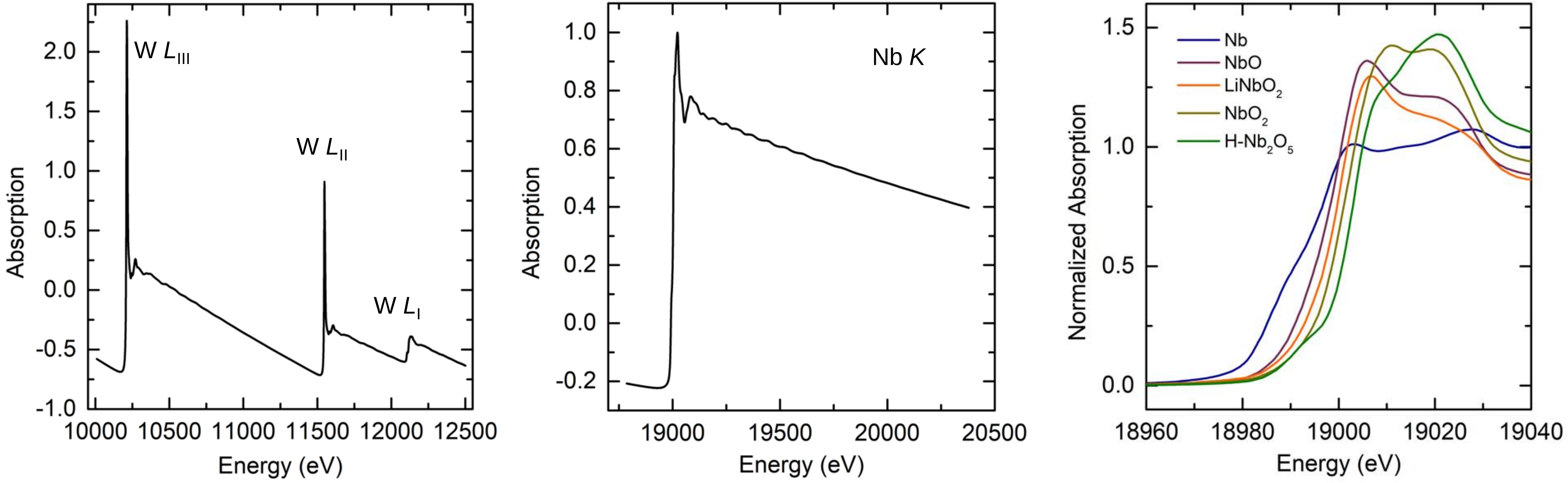
Diamond Light Source, Beamline B18
Principal beamline scientist: Giannantonio Cibin

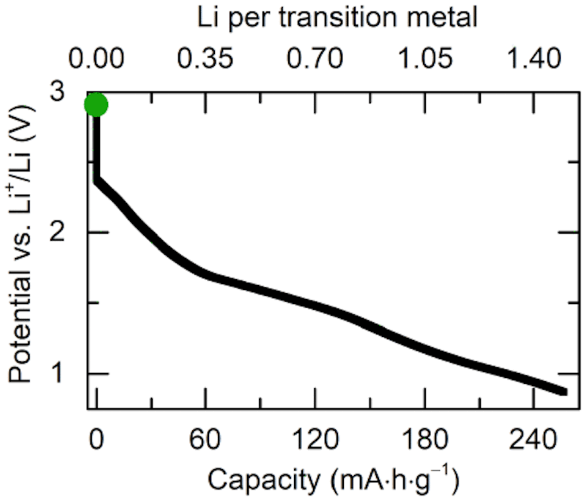
Multi-edge X-ray absorption spectroscopy

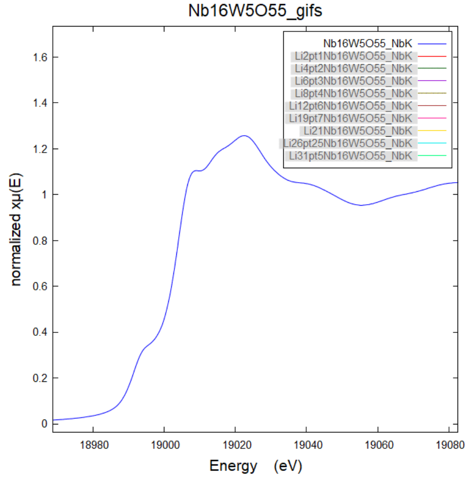


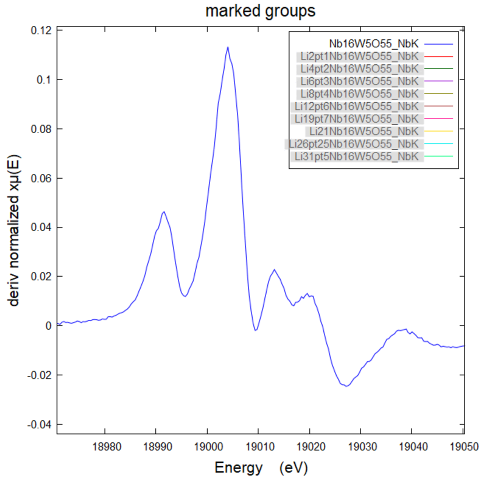
XAS: Element specific, sensitive to bulk, electronic and atomic probe

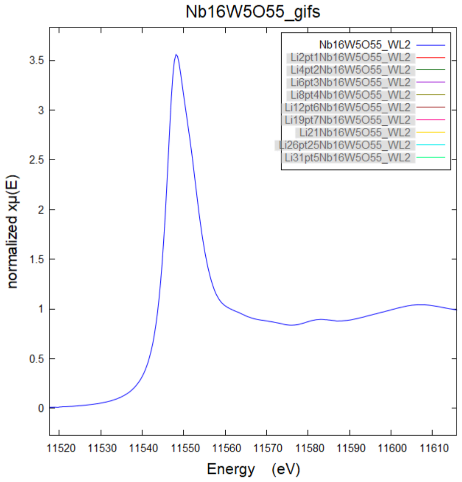
Griffith, K. J.; Wiaderek, K. M.; Cibin, G.; Marbella, L. E.; Grey C. P.
Niobium Tungsten Oxides for High-rate Lithium-ion Energy Storage. *Nature*, **2018**, *559*, 556–563.

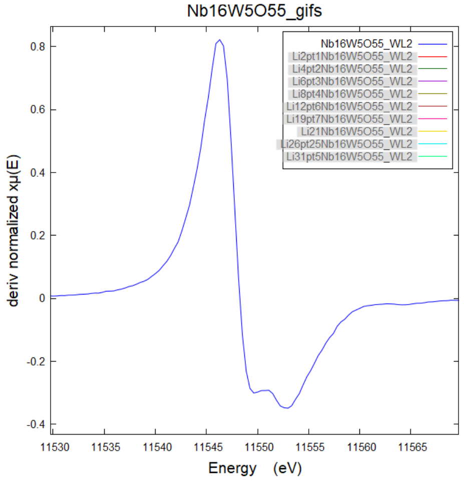
$Nb_{16}W_5O_{55}$ XAS @ Nb *K*, W *L*$_{II}$, W *L*$_I$ edges

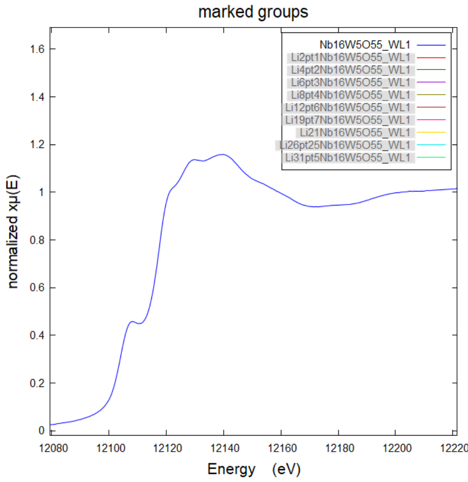


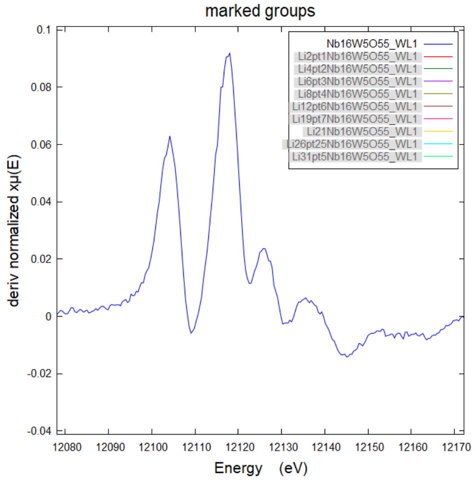




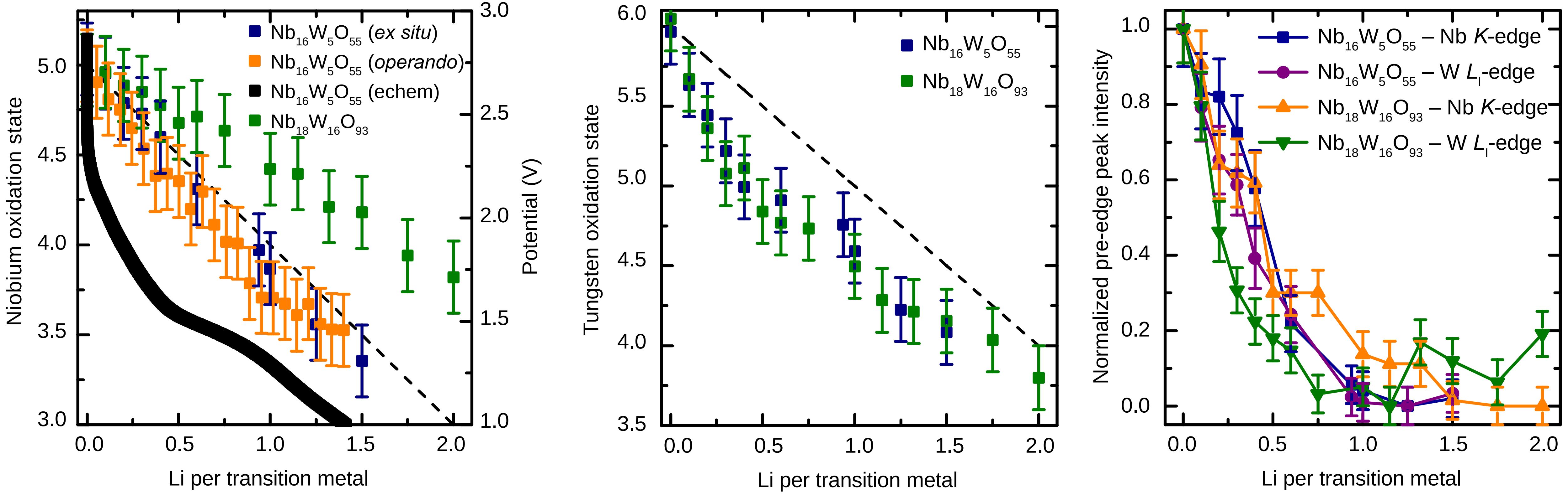




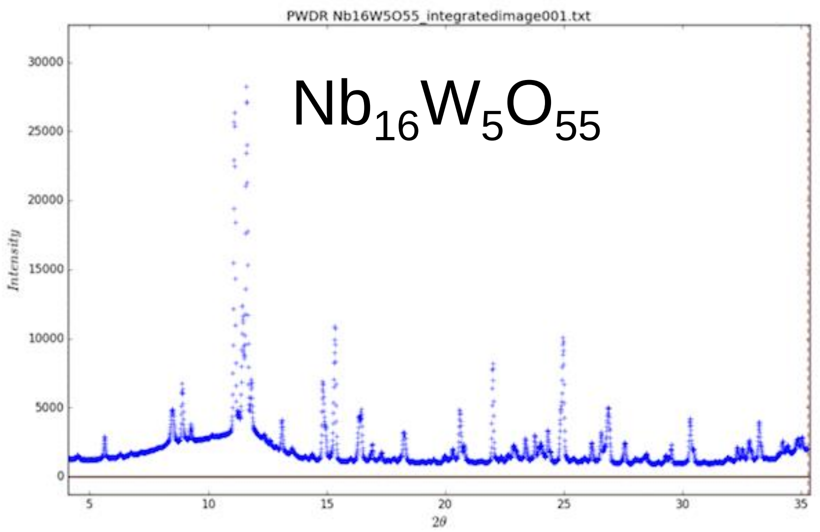


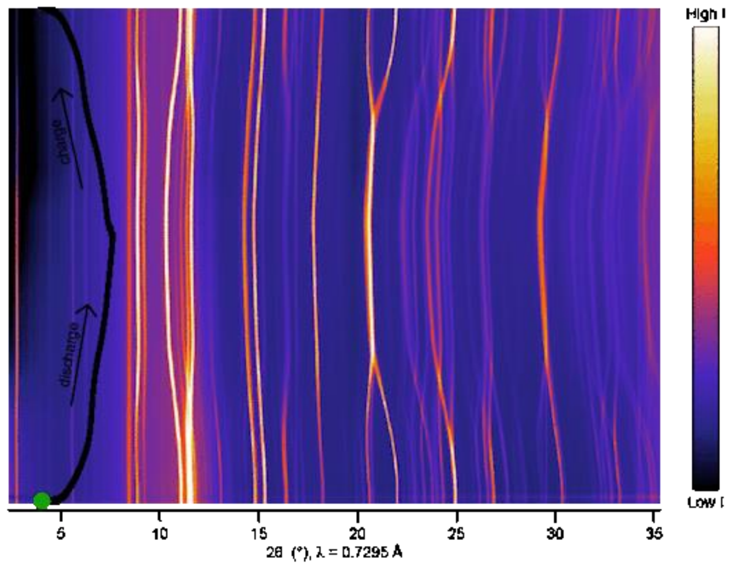


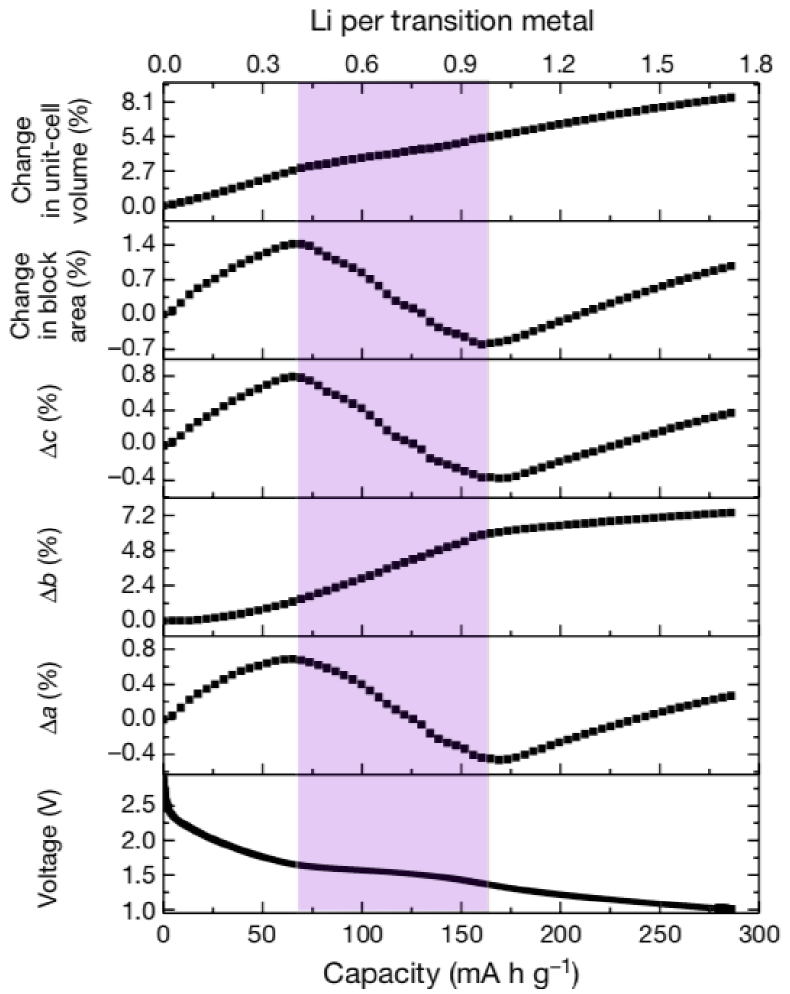
Multi-electron Redox at Nb and W

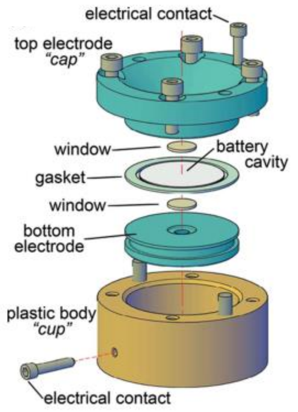


Operando high-rate structure evolution from synchrotron diffraction





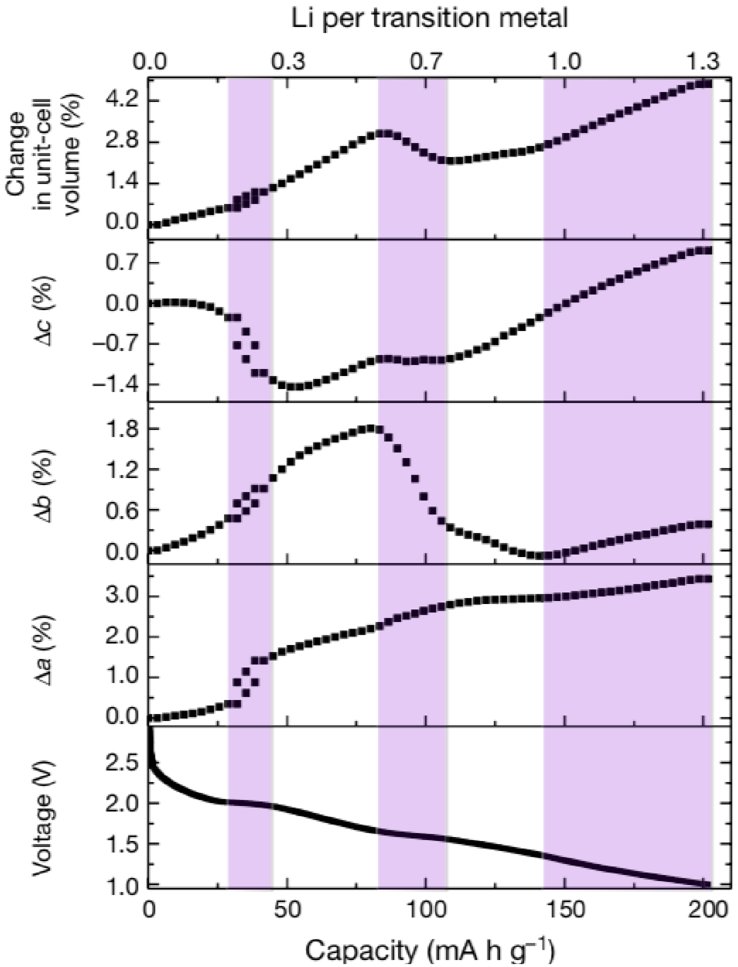




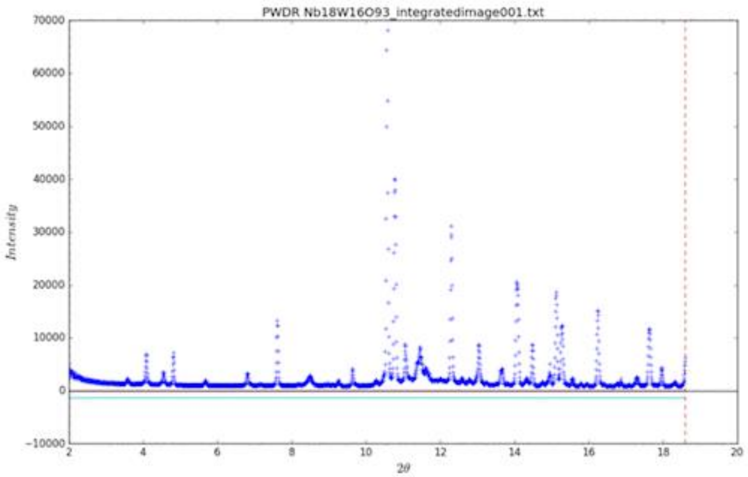
Advanced Photon Source, Argonne National Lab; Beamline scientist: Kamila Wiaderek

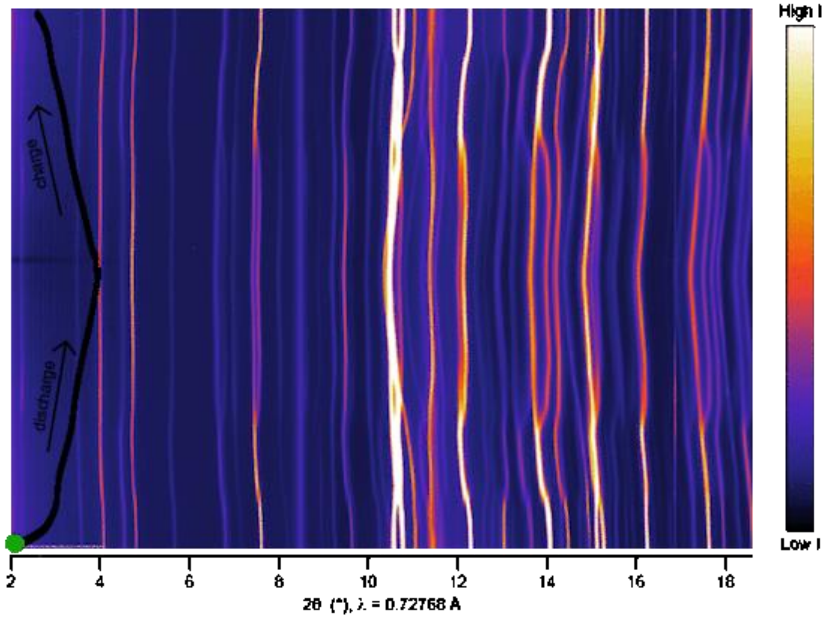
Borkiewicz, O. J.; Shyam, B.; Wiaderek, K. M.; *et al. J. Appl. Cryst.* **2012**, *45*, 1261–1269.

Operando high-rate structure evolution from synchrotron diffraction



$Nb_{18}W_{16}O_{93}$





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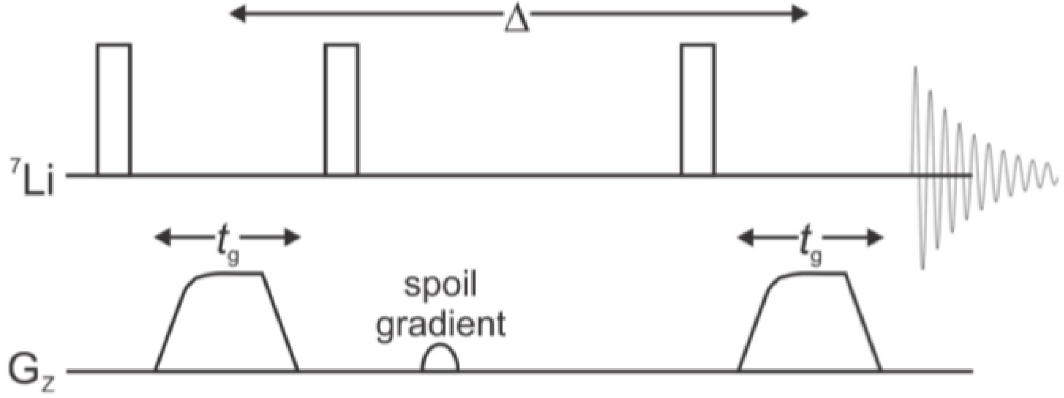
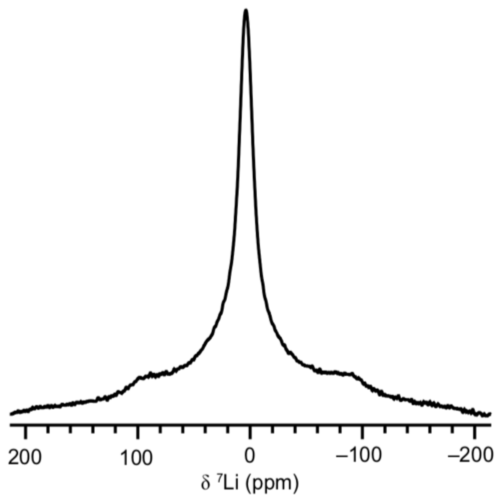
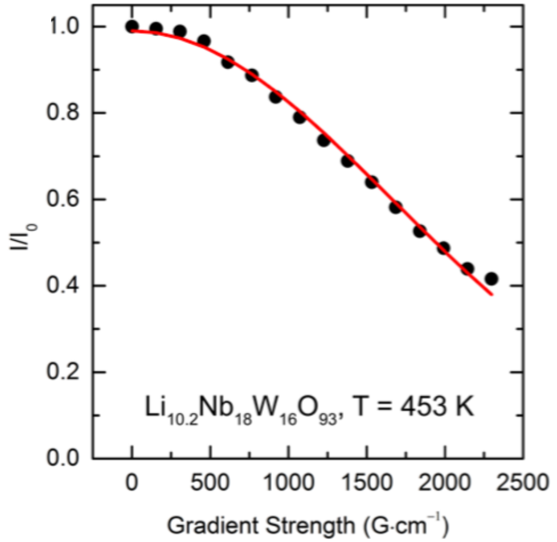
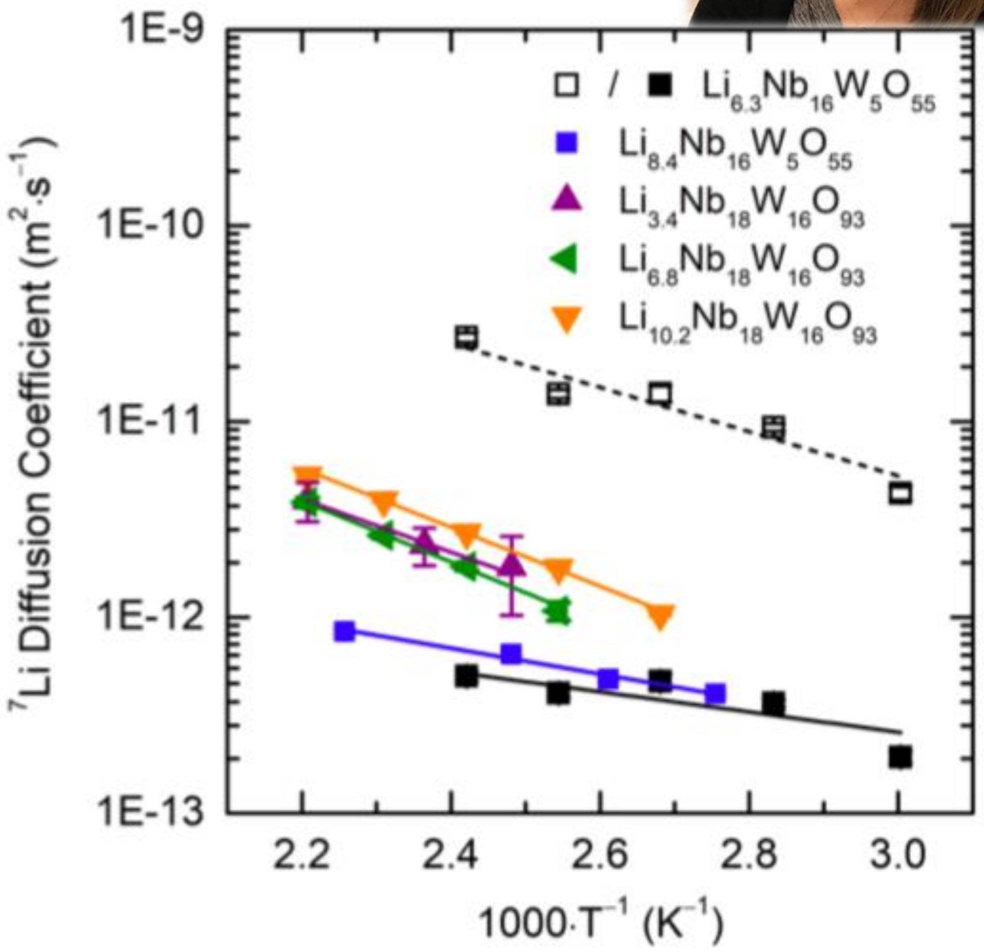
Pulsed field gradient NMR Spectroscopy









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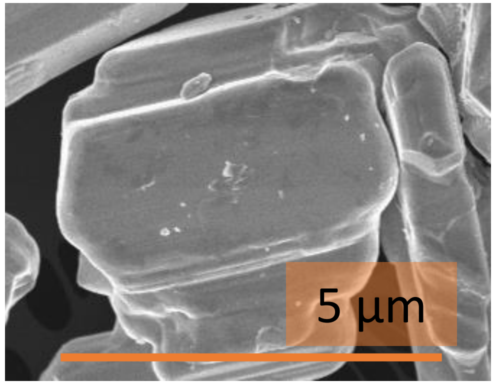
Niobium tungsten oxides

D_{Li} (298 K) ~ 10^{-13} $m^2 \cdot s^{-1}$; E_a ~ 0.2–0.3 eV

Putting diffusion coefficients into context

	Diffusion Length (μm)		
D_{Li} ($m^2·s^{-1}$)	1C (3600 s)	20C (180 s)	60C (60 s)
$1.0×10^{-12}$	150	33	19
$1.0×10^{-14}$	15	3.3	1.9
$1.0×10^{-16}$	1.5	0.33	0.19
$1.0×10^{-18}$	0.15	0.033	0.019
$1.0×10^{-20}$	0.015	0.0033	0.0019



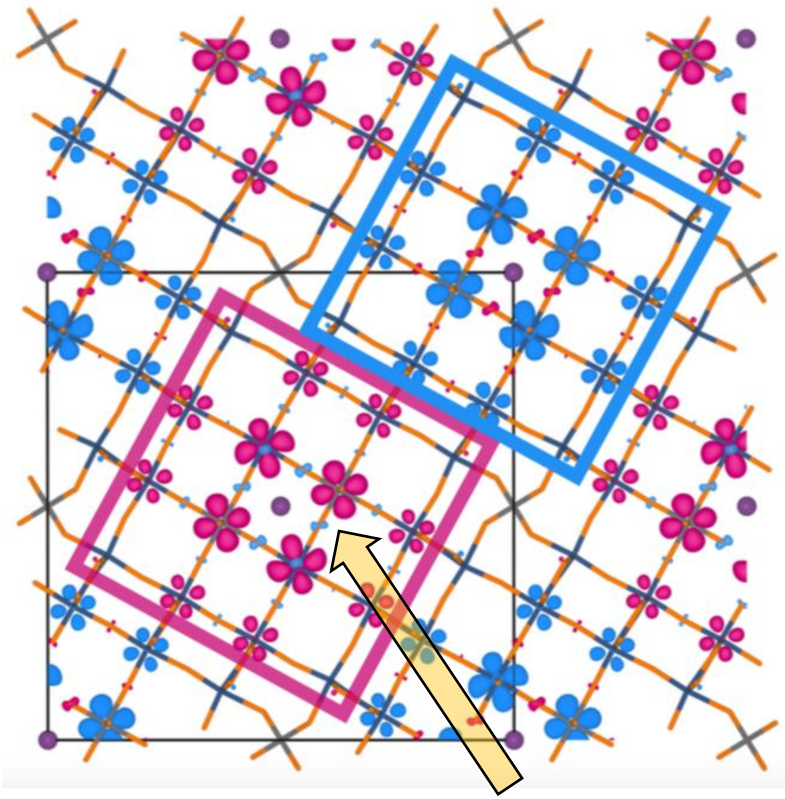
Liquid electrolytes are 10^{-10}–10^{-12} $m^2·s^{-1}$

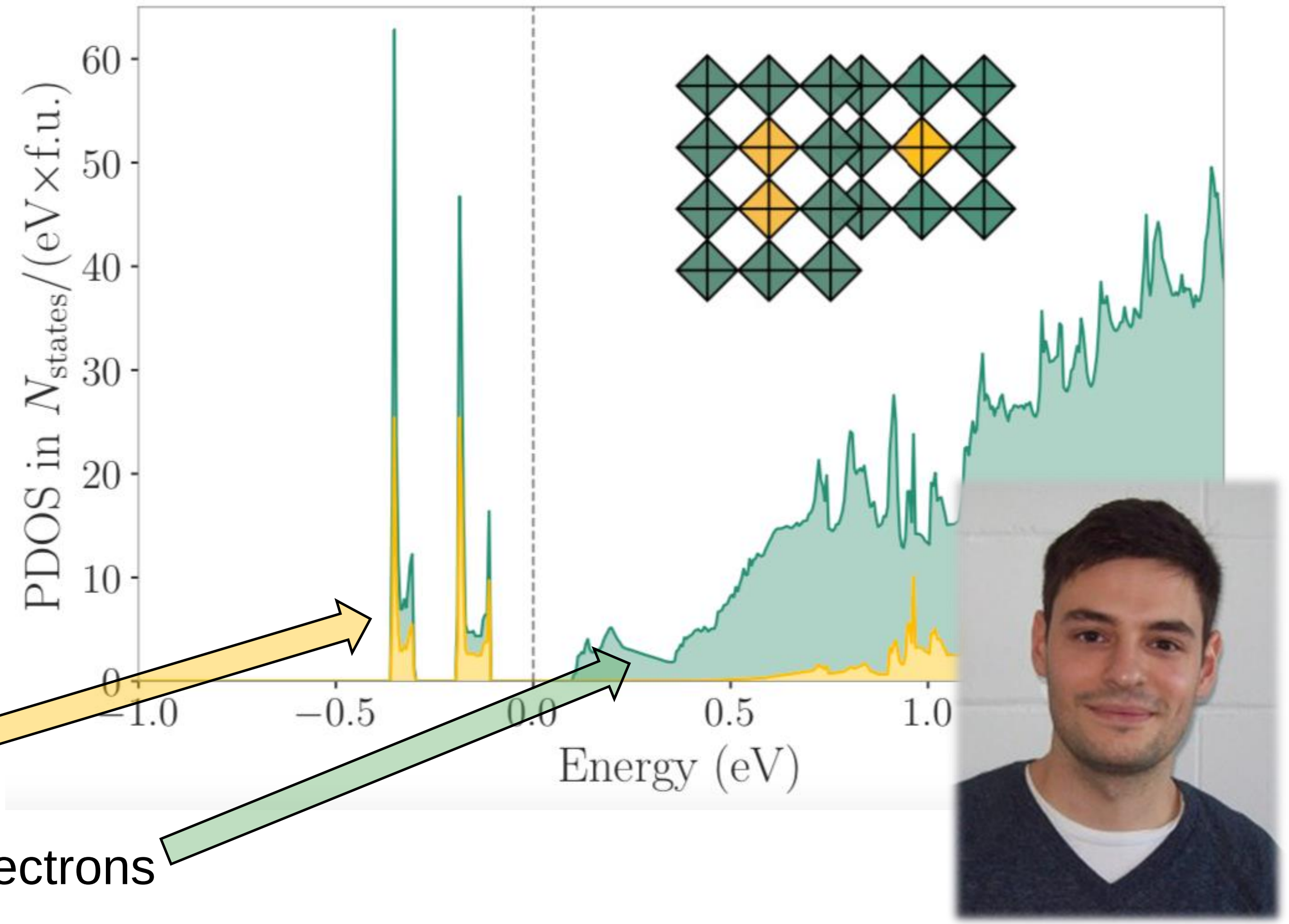
Compound	Structure Type	D_{Li} ($m^2·s^{-1}$)	T (K)	Tech-nique	Reference
$Li_{10}GeP_2S_{12}$, Li_7GePS_8, $Li_{10}SnP_2S_{12}$ $Li_7P_3S_{11}$, & $Li_{11}Si_2PS_{12}$	Thio-LISICON	1–5 $×10^{-12}$	298	PFG NMR	Kuhn et al. (2013), (2014), Hayamizu et al. (2013)
β-Li_3PS_4	Thio-LISICON	$5.4×10^{-13}$	373	PFG NMR	Gobet et al.
$Li_{0.6}[Li_{0.2}Sn_{0.8}S_2]$	Layered (O1)	2–$20×10^{-12}$	298	PFG NMR	Holzmann et al.
$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$	NASICON	$2.9×10^{-13}$	311	PFG NMR	Hayamizu et al.
$Li_{6.6}La_3Zr_{1.6}Ta_{0.4}O_{12}$	Garnet	$3.5×10^{-13}$	353	PFG NMR	Hayamizu et al.
Graphite (Stage I)	Graphite	1–$2×10^{-15}$	298	NMR relaxn.	Langer et al.
$Li_4Ti_5O_{12}$	Spinel	$3.2×10^{-15}$	298	$μ^+$-SR	Sugiyama et al.
$LiMn_2O_4$	Spinel	$1×10^{-20}$	350	NMR relaxn.	Verhoevenm et al.

Niobium tungsten oxides

D_{Li} (298 K) ~ 10^{-13} $m^2·s^{-1}$; E_a ~ 0.2–0.3 eV

Insights from electronic structure calculations



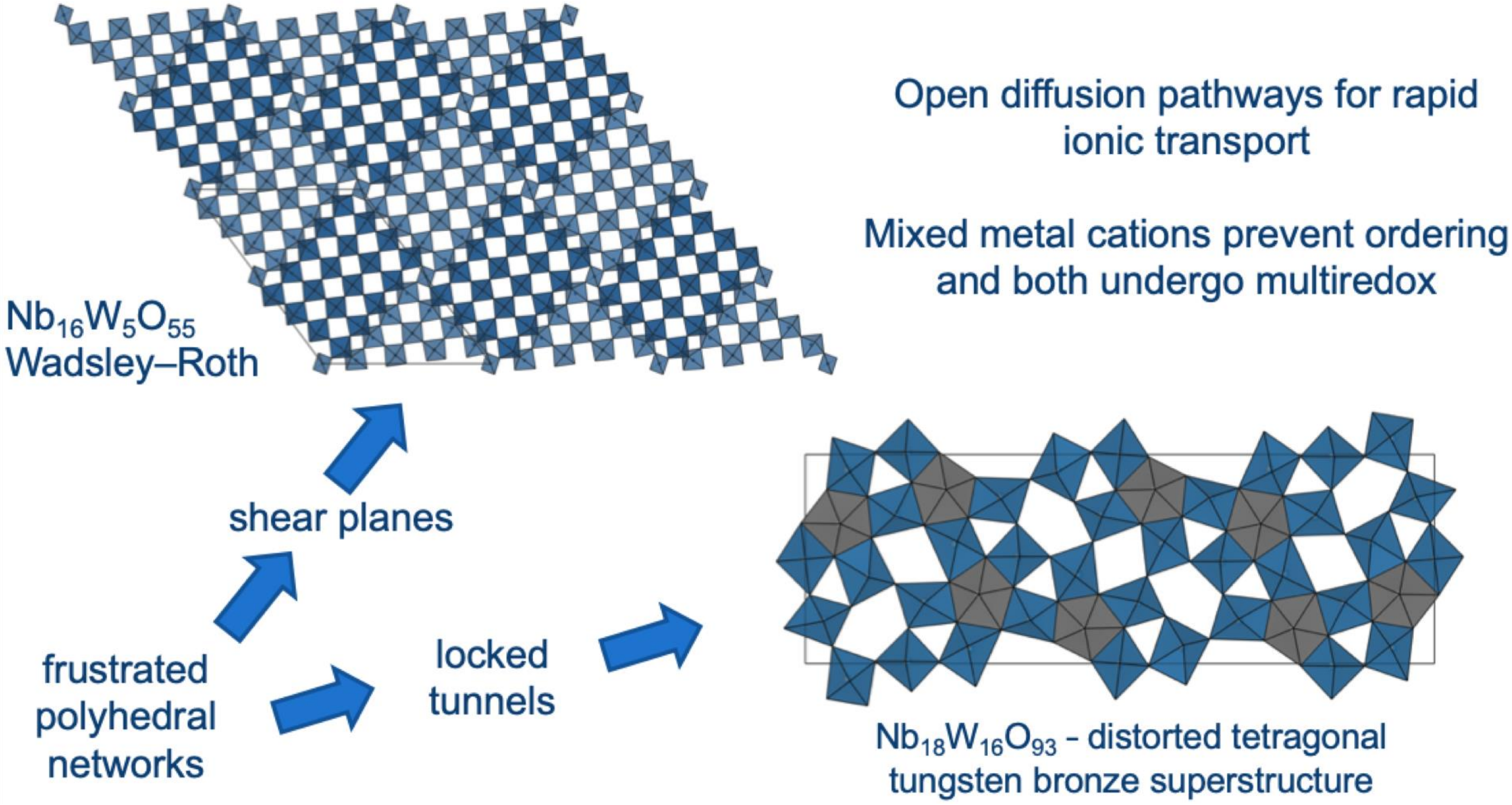


Center of blocks → localized electrons

Crystallographic shear planes → conduction electrons

1) Koçer, Can P.; Griffith, Kent J.; Grey, Clare P.; Morris, Andrew J. *Phys. Rev. B* **2019**, *99*, 075151.
2) Koçer, Can P.; Griffith, Kent J.; Grey, Clare P.; Morris, Andrew J. Cation Disorder and Lithium Insertion Mechanism of Wadsley–Roth Crystallographic Shear Phases from First Principles. arXiv: 1906.04192

Mechanism of high-rate Li intercalation in niobium tungsten oxides



<u>Translation to full cells</u>

High energy – Ni-rich NMC
87% $Q_{retention}$ at 5C for 500 cycles, full SOC cycling

Longest life – $LiFePO_4$
89% $Q_{retention}$ at 10C for 1000 cycles, full SOC cycling

Impedance rise from cathode
→ NWO is very stable

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1) Griffith, K. J.; Wiaderek, K. M.; Cibin, G.; Marbella, L. E.; Grey C. P. *Nature*, **2018**, *559*, 556–563.
2) Kim, Yumi; Griffith, Kent J.; Lee, Jeongjae; Jacquet, Quentin; Rinkel, Bernardine L. D.; Grey, Clare P. High Rate Lithium Ion Battery with Niobium Tungsten Oxide Anode. *In preparation.*

Acknowledgements

Clare Grey

Lauren Marbella

Kamila Wiaderek, Giannantonio Cibin, Anatoliy Senyshyn

John Griffin, Alex Forse

Can Koçer, Martin Mayo, Matthew Evans, Chris Pickard, Andrew Morris

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