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X-ray Absorption Fine Structure(XAFS): XANES/NEXAFS and EXAFS

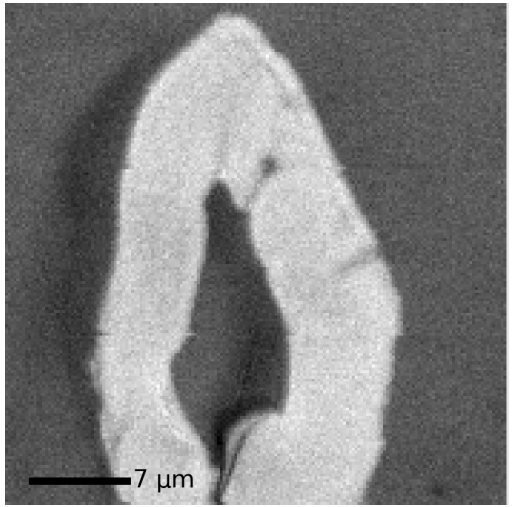
EPFL Master Course 2024 MSE435

STXM: high spatial resolution vs. high energy reolution

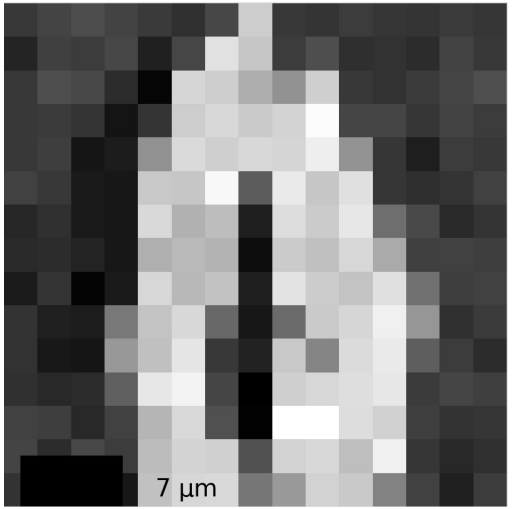
cellulose fibre

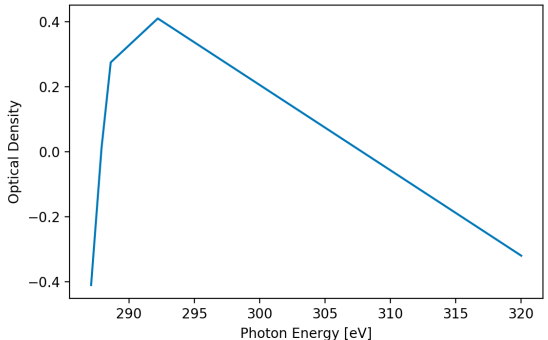
- Trade off between high spatial resolution and high energy resolution

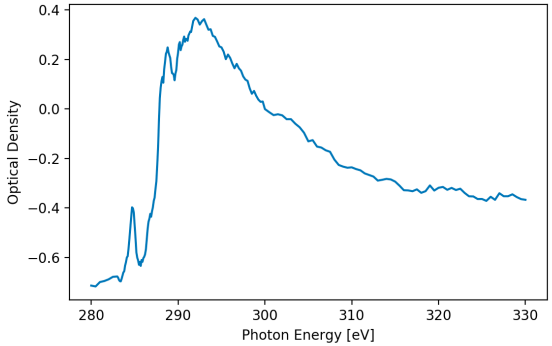
High spatial resolution scan at 287.1 eV



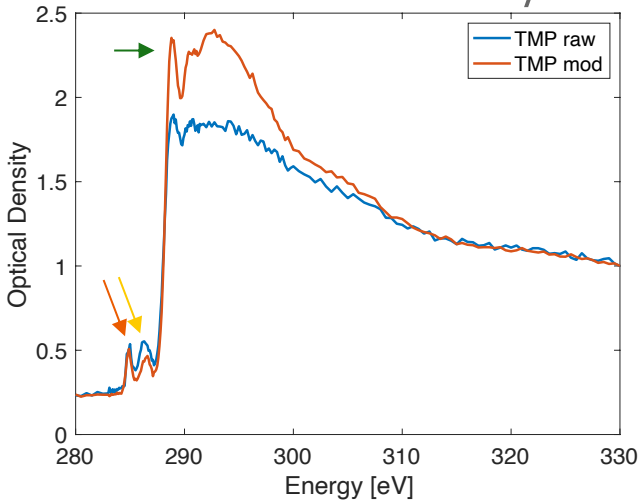
Low spatial resolution scan at 287.1 eV

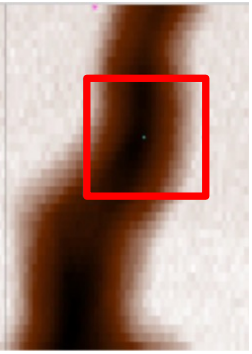




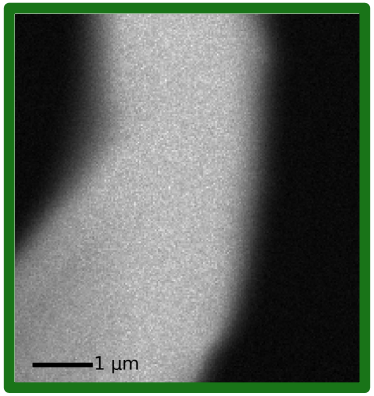


STXM/XANES lignin on fibers

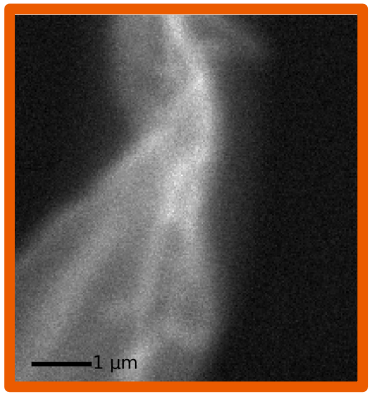




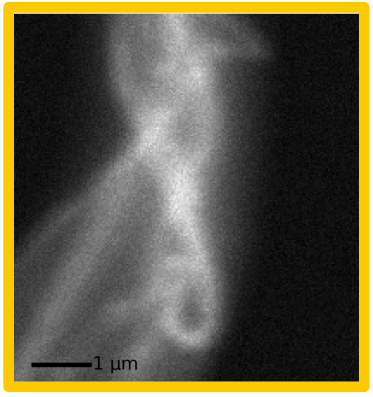
288.9 eV (cellulose)



284.9 eV (lignin)



286.2 eV (lignin)



Battery

- Study the lithiation kinetics of a commercial, mixed-metal oxide cathode material, nickel cobalt aluminium oxide (NCA), during (dis)charge and its degradation during overcharge.

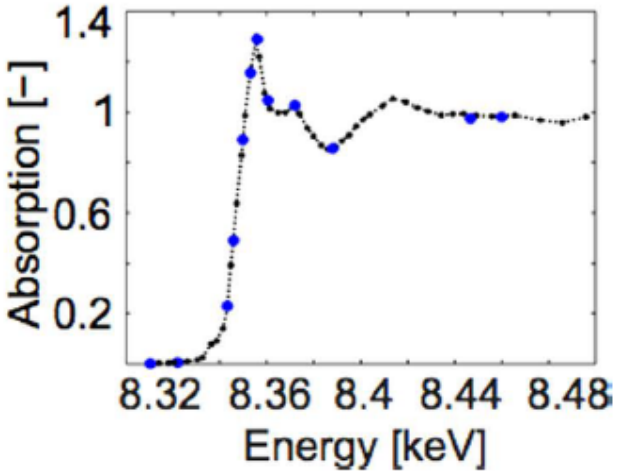
- EXAFS, XANES, other technique?

Lithiation Dynamics in Transition Metal Oxide Particles

insights into the lithiation kinetics of a commercial, mixed-metal oxide cathode material, nickel cobalt aluminium oxide (NCA), during (dis)charge and its degradation during overcharge

challenge: fast enough (<5min), low dose to prevent radiation damage to look at multiple cycles

discretized energy resolution

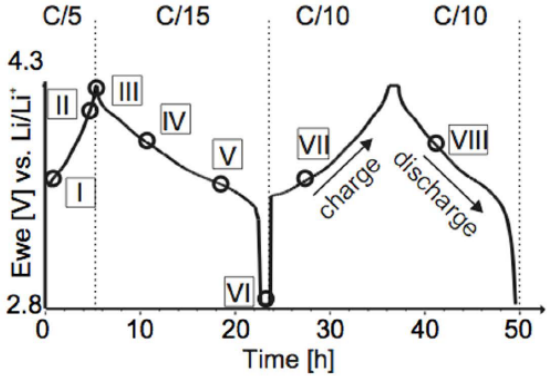


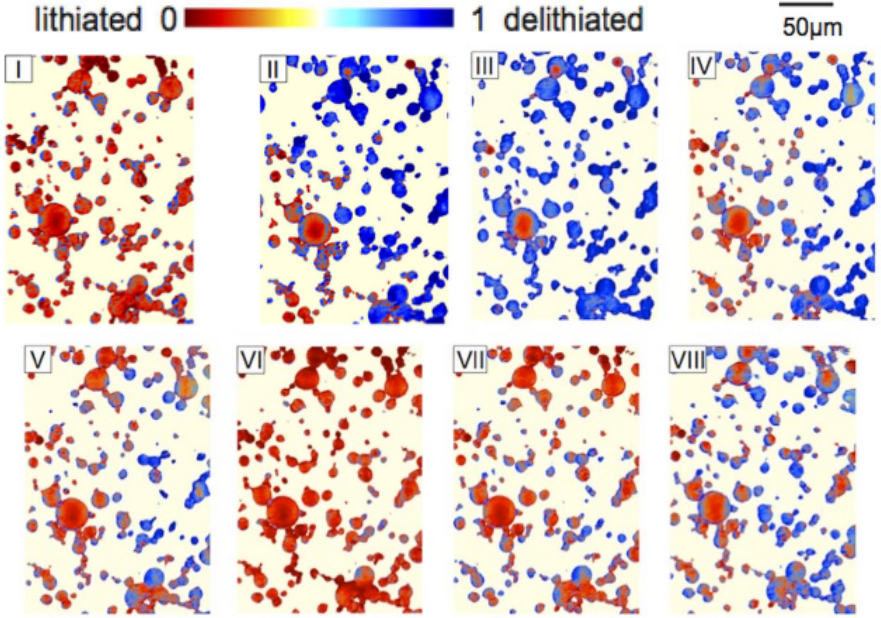
L. Nowack, D. Grolimund, V. Samson, F. Marone, and V. Wood, "*Rapid Mapping o*
Metal Oxide Particles with Operando X-ray Absorption Spectroscopy" Sci. Rep., v

Lithiation Dynamics in Transition Metal Oxide Particles

insights into the lithiation kinetics of a commercial, mixed-metal oxide cathode material, nickel cobalt aluminium oxide (NCA), during (dis)charge and its degradation during overcharge

electrochemical cycling profile:





L. Nowack, D. Grolimund, V. Samson, F. Marone, and V. Wood, "*Rapid Mapping of Lithiation Dynamics in Transition Metal Oxide Particles with Operando X-ray Absorption Spectroscopy*" Sci. Rep., vol. 6, no. 1, p. 21479, 2016.

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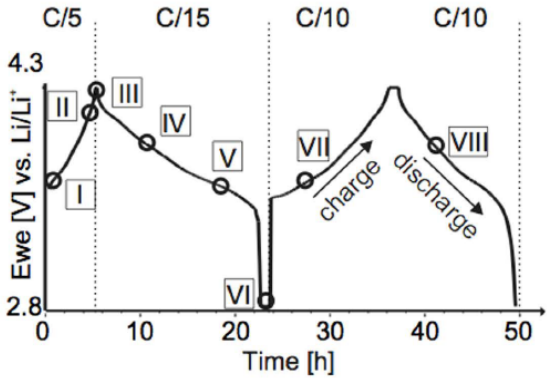
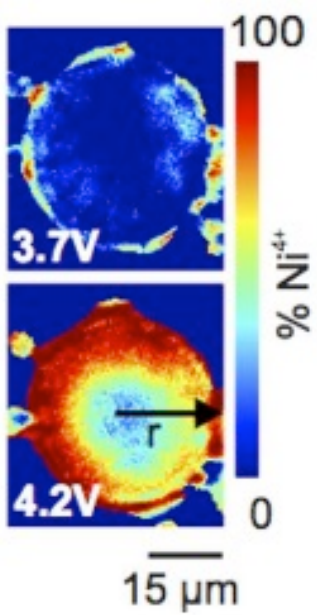




Ni^{4+} oxidation maps of a single large particle during charge at 3.7 V and 4.2 V

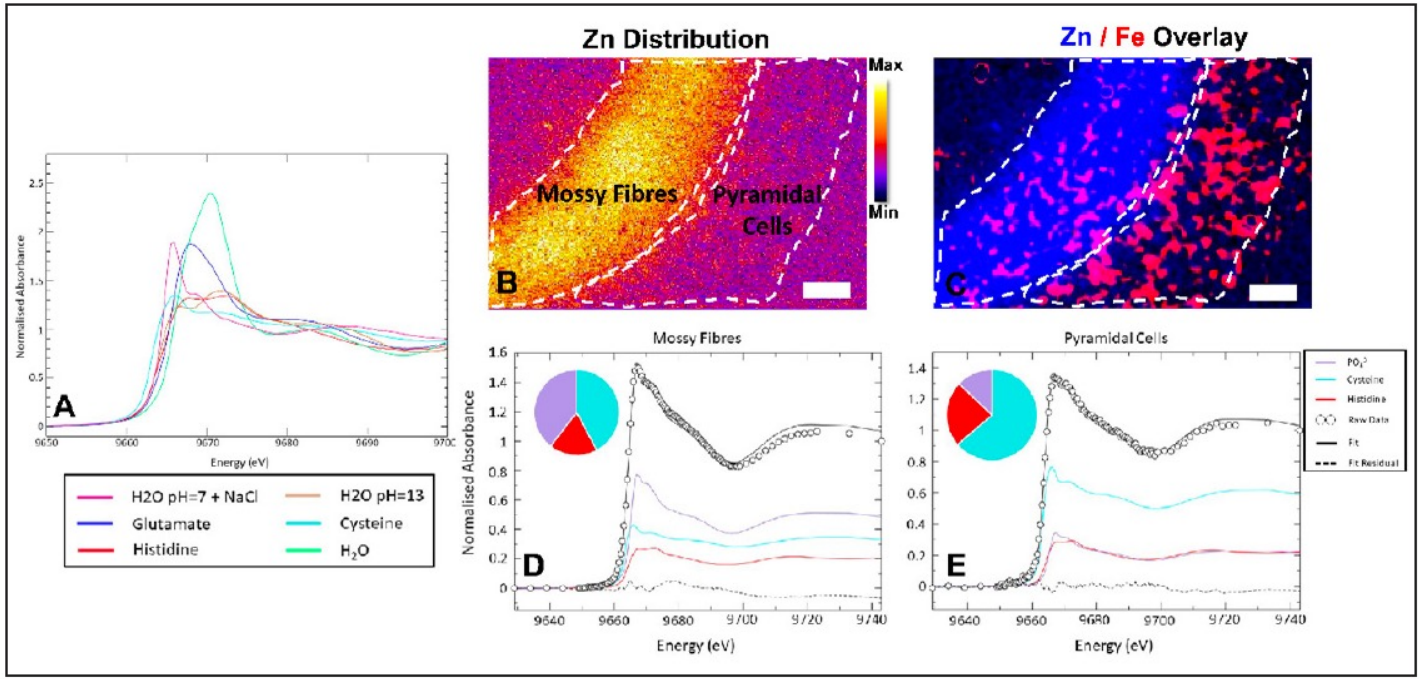
L. Nowack, D. Grolimund, V. Samson, F. Marone, and V. Wood, "*Rapid Mapping of Lithiation Dynamics in Transition Metal Oxide Particles with Operando X-ray Absorption Spectroscopy*" Sci. Rep., vol. 6, no. 1, p. 21479, 2016.

Brain

- Study the difference in coordination environment of Zn in different areas of the brain. This can give hints to which enzymes Zn is used as Co-factor.

- EXAFS, XANES, other technique?

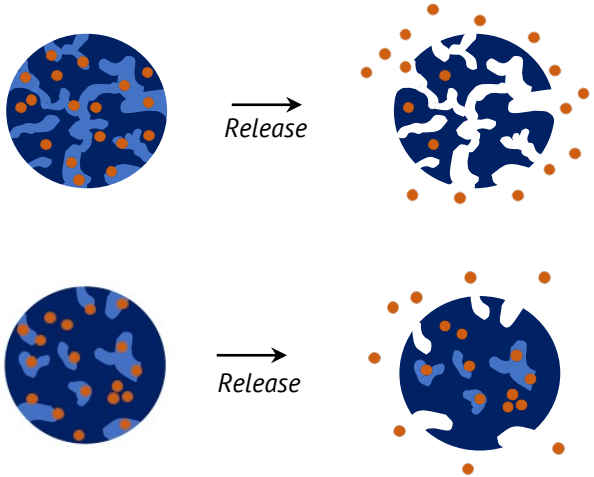
Brain: different chemical forms of Zn



Hollings and Hackett, *Spectroscopy Europe/World* 2022, 34, 4

Pharmaceutical formulations for controlled release

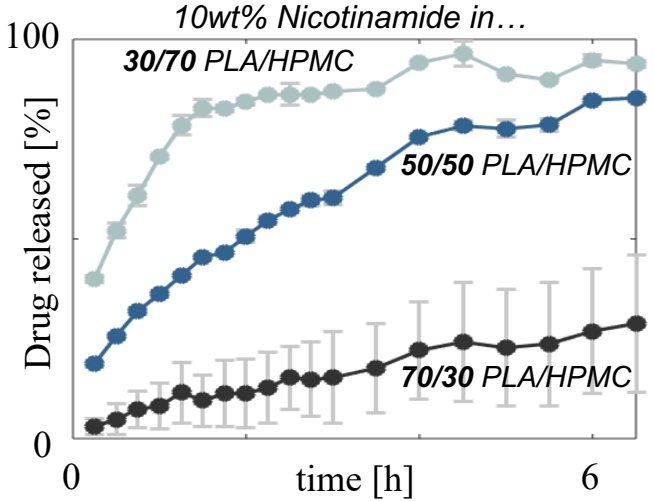
Phase separated system higher connectivity for faster release



HPMC hydroxypropyl methylcellulose

PLA poly lactic acid

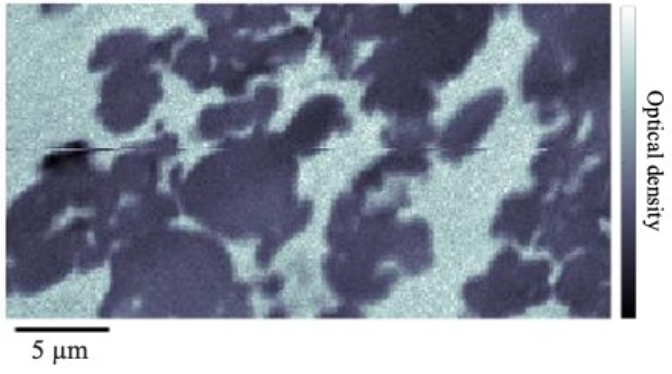
Nicotinamide



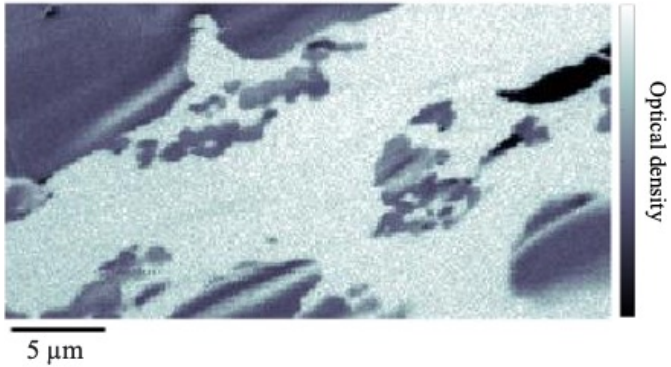
Olsson, M., Nilsson, R. Björn, L. Lilja, V., Krupnik, L. Chen, Y, Naidjonoka, P. Diaz, A., Holler, M., Watts, B., Larsson, A., Liebi, M. , Matic A. *Commun Mater,2024 5(1), 231.*

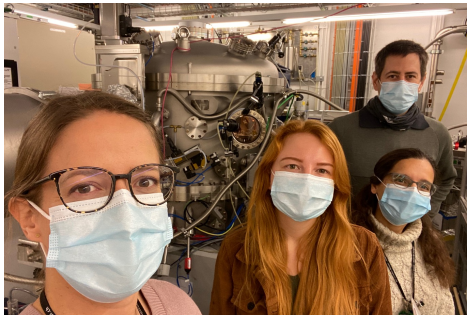
Pharmaceutical formulations for controlled release

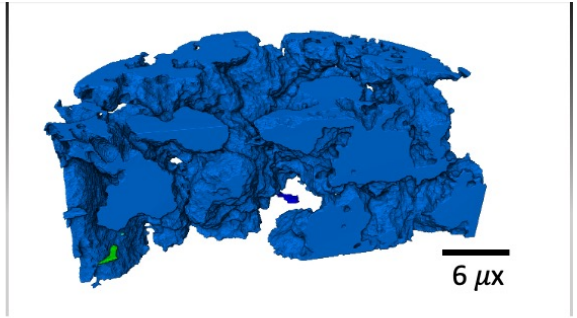
10wt% Nicotinamide
in 50/50 PLA/HPMC

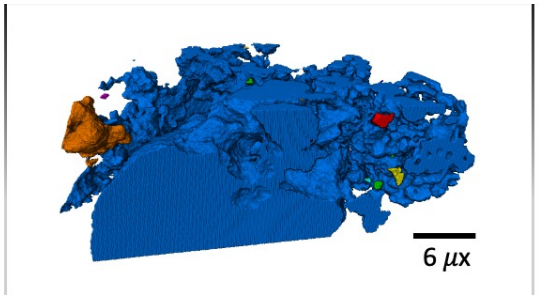


10wt% Nicotinamide
in 70/30 PLA/HPMC









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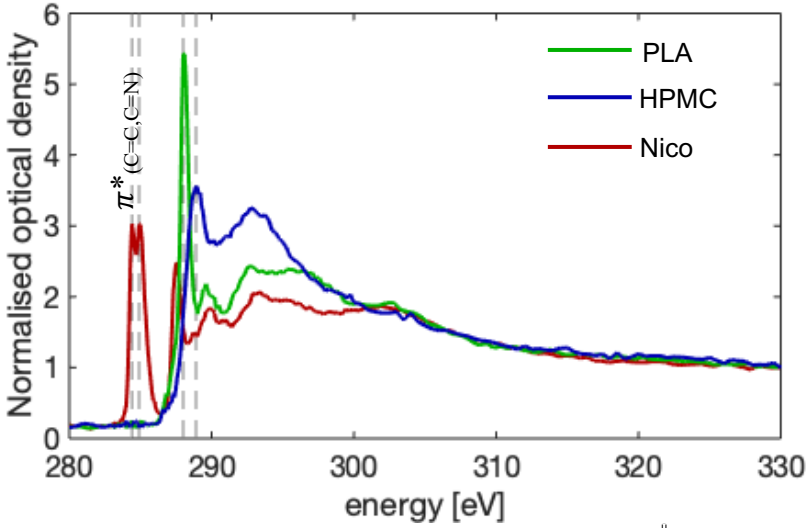
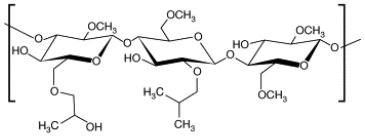
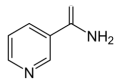
Pharmaceutical formulations for controlled release

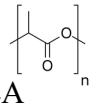
- in which polymer phase does the active compound of the formulation (nicotinamide) sit?
- XANES, EXAFS, other technique?

STXM-XANES: Imaging with chemical contrast

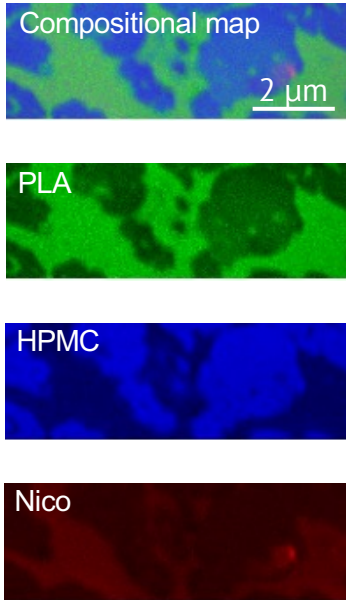




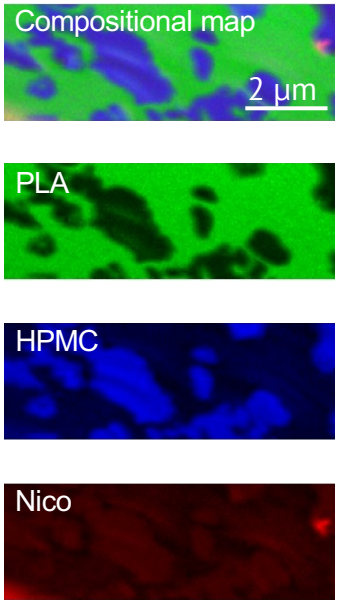




10wt% nico in 50/50 PLA/HPMC



10wt% nico in 70/30 PLA/HPMC



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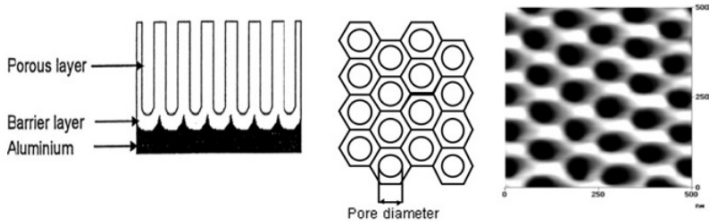
Nanowires

- Nanowires are produced inside mesoporous alumina membranes, which contain hexagonal arrays of parallel non-intersecting cylindrical pores perpendicular to the membran surface, and can be used as templates for the electro-chemical production of nanowires.



Benfield, R. Eet al (2004). *Faraday Discussions*, *125*(0), 327–342.

- Study if the structure between iron nanowire and bulk iron is different with respect to anisotropy of bond lengths, oxidation state and orientation of crystal lattice

EXAFS, XANES, other technique?

EXAFS

- local atomic structure of the metal nanowire around the absorbing atom, sspecifically the nearest neighbour interatomic distances and coordination numbers, up to about the fourth nearest neighbours. Small structural differences between the nanowires and the corresponding bulk metals can therefore be studied. Account can also be taken in the data analysis of any asymmetry in the bond length distribution, giving important insight into the vibrational behaviour of the nanowires. Because of the use of monochromatic radiation, EXAFS is element-selective, and consequently well suited to samples containing more than one type of metal atom. Additionally, it is not necessary to remove the aluminium backing from the AAO samples to study them by EXAFS.

Benfield, R. Eet al (2004). *Faraday Discussions*, *125*(0), 327–342.

Nanowires EXAFS

Table 1 Representative results of Fe K-edge EXAFS refinements of iron nanowires. The results shown from ESRF BM29 are for a separately prepared series of samples; the results for the samples studied on SRS 7.1 were also confirmed on ESRF BM29. Data collection temperatures were 80 K at the SRS and 30 K at the ESRF[a]

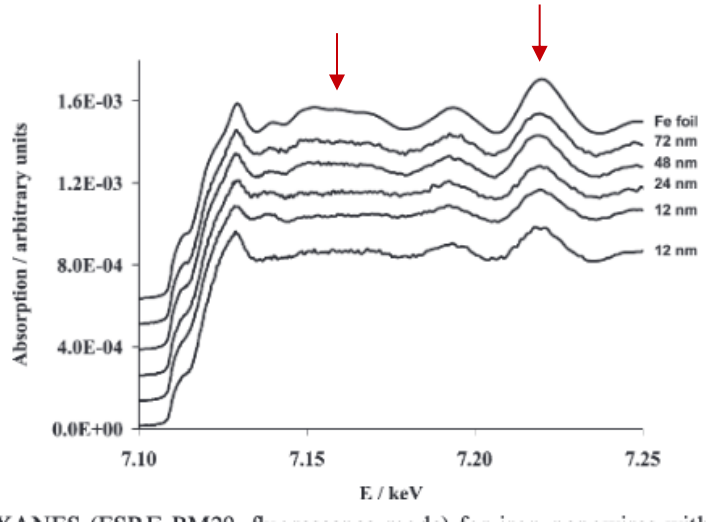
	Bulk iron	Fe-nanowires in 12 nm pores	Fe-nanowires in 24 nm pores	Fe-nanowires in 24 nm pores	Fe-nanowires in 12 nm pores	Fe-nanowires in 48 nm pores	Fe-nanowires in 72 nm pores
Synchrotron	SRS 7.1	SRS 7.1	SRS 7.1	SRS 7.1	ESRF BM29	ESRF BM29	ESRF BM29
Sample form	4 μm foil	Stacked membranes with Al backing	Stacked membranes with Al backing	Pressed pellet	Pressed pellet	Pressed pellet	Pressed pellet
E_f/eV[b]	−14.3 (6)	−4.0 (6)	−4.4 (6)	−6.1 (9)	−5.5 (9)	−4.8 (9)	−14 (1)
Lattice symmetry	bcc	bcc	bcc	bcc	bcc	bcc	bcc
a/Å[c]	2.857 (3)	2.857 (3)	2.856 (3)	2.858 (4)	2.863 (3)	2.859 (3)	2.863 (3)
N_1 (fixed parameter)[d]	8*	8*	8*	8*	8*	8*	8*
R_1/Å[e]	2.474 (5)	2.474 (5)	2.473 (5)	2.475 (7)	2.480 (5)	2.476 (5)	2.480 (5)
A_1[f]	0.005 (1)	0.007 (1)	0.006 (1)	0.008 (2)	0.001 (2)	0.001 (1)	0.005 (2)
A_2	0.007 (1)	0.007 (1)	0.006 (1)	0.006 (2)	0.004(3)	0.002 (2)	0.010 (1)
A_3	0.009 (1)	0.008 (1)	0.008 (1)	0.009 (3)	0.006 (4)	0.004 (2)	0.011 (1)
A_4	0.009 (1)	0.012 (2)	0.012 (2)	0.010 (3)	0.002 (2)	0.001 (1)	0.005 (2)
A_5	0.010 (1)	0.010 (1)	0.009 (1)	0.010 (2)	—	—	—
A_6	0.010 (2)	0.012 (3)	0.011 (3)	0.012 (6)	—	—	—
R-factor (%)	28.4	29.7	27.9	32.4	27.1	21.2	24.2

[a] Esd's in the final digits are given in brackets. [b] E_f = contribution of the wave vector of the zero photoelectron relative to the origin of k. [c] a = cell parameter. [d] N_i = number of atoms in the ith shell. [e] R_i = radial distance of atoms in the ith shell/Å. [f] A_i = Debye–Waller term of the ith shell ($A = 2\sigma^2$ with σ = Debye–Waller factor)/Å^2

Benfield, R. Eet al (2004). *Faraday Discussions*, *125*(0), 327–342.

XANES

- XANES can characterise the chemical bonding environment of the absorbing atom, and can give a measure of the real oxidation state of the metal atoms in the nanowires. This allows any chemical oxidation of the nanowires to be detected and also permits study of possible electron density transfer between the nanowires and their supports.



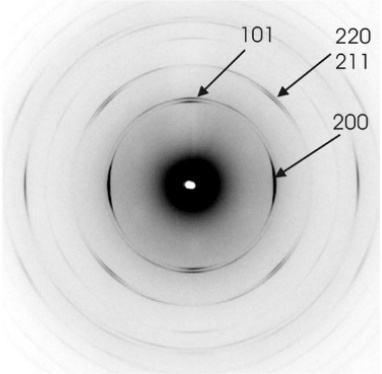
This is a strange observation, and at first we suspected it to be an artefact […] Although we are unable to offer a full interpretation of this XANES behaviour, it is clear evidence that the electronic structure of the iron nanowires varies systematically with the pore diameter.

Benfield, R. Eet al (2004). *Faraday Discussions*, *125*(0), 327–342.

XRD/WAXS

- WAXS allows to study the well-defined Bragg peaks from a crystalline material to give the overall **lattice structure** and an independent measurement of **metal-metal distances** extending to much longer range than EXAFS. Additionally, the width of the diffraction peaks directly gives the **size of the individual crystallites** in the polycrystalline nanowires **through the Scherrer equation.**
- WAXS is **not element-specific**, it is necessary to remove the aluminium backing from the AAO membranes, because otherwise the Al lattice dominates the diffraction pattern.
- Using 2D detector allows to study the **preferred orientations of the nanowire lattices** within the AAO pores.

There is some preferred orientation of the c-axis perpendicular to the pores, and this is strongest in the smallest pore diameters



tin nanowires

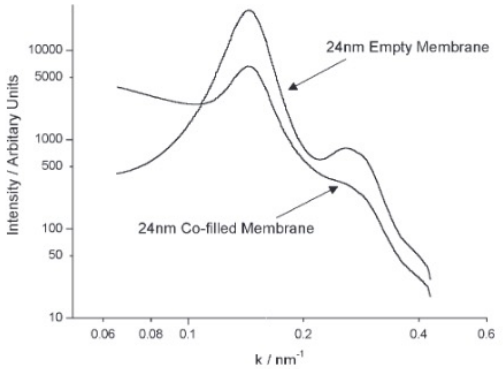
Benfield, R. Eet al (2004). *Faraday Discussions*, *125*(0), 327–342.

SAXS

SAXS has the potential to characterise the structures of these membranes on several different length scales**: pore diameter, pore separation, pore length and aspect ratio, pore continuity and variation of pore diameter along the length**.

SAXS of membranes containing nanowires can show the **extent to which the pores are filled**, because incomplete filling gives a three-phase heterogeneous system (alumina, nanowire and void). Any spontaneous organisation of the filled pores into superlattices will be shown.

Additionally, the technique of **anomalous small-angle X-ray scattering (ASAXS)**, which studies changes in SAXS intensity profiles as the X-ray energy is varied across an absorption edge of an element, can isolate the scattering due to fluctuations in concentration of that element contained in nanowires within the pores.



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Titanium aluminum nitride (TiAlN) coating

- Ti1-xAlxN coatings used for turning of stainless steal
- Investigate structural changes in study worn tools, expecting to find TiN rich areas which happen due to spinodal decomposition of face centered cubic (fcc) TiAlN phase and subsequesnt formation of wurtzite (w) AlN

- EXAFS, XANES or other technique?

TiAlN coating

- We have previously observed that **XRD is not sensitive enough** to detect the initial stage of decomposition because of the small difference in lattice parameter between the as formed cubic phase AlN and TiN-rich domains. X-ray absorption near-edge structure (**XANES**) **and** extended x-ray absorption fine structure (**EXAFS**) are, on the other hand, **more sensitive to the short-range order** compared to diffraction as they probe the local environment, which changes character at early stages of decomposition.

Rogström L., *et al* Applied Surface Science 612 (2023) 155907

TiAlN coating - EXAFS

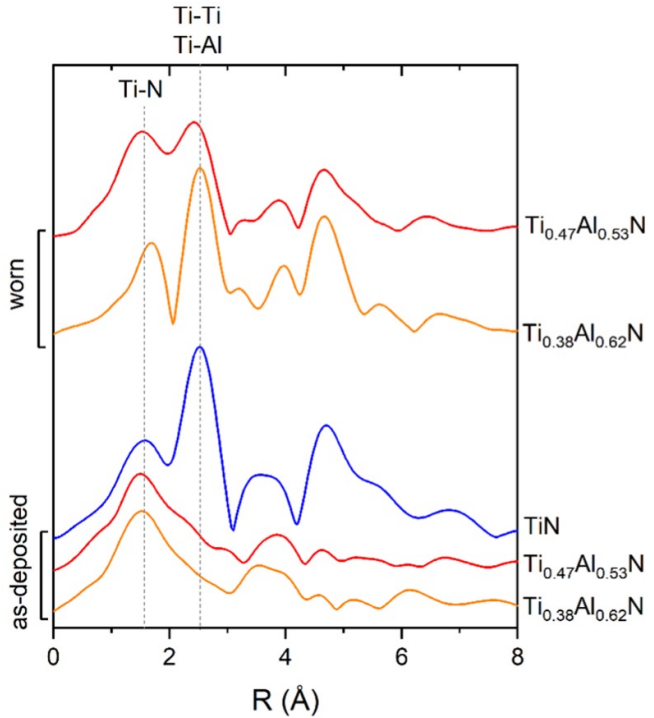

Fig. 4. Fourier transform obtained from the k^2-weighted EXAFS oscillations $\chi(k)$ of selected as-deposited and worn samples.

there is a clear peak from the Ti-Ti/Ti-Al pairs around 2.5 Å (3 Å in Table 2 after phase shift). The appearance of this peak for the worn samples suggests that the Ti-Ti and Ti-Al phase contributions to the total signal has a more uneven share of Ti and Al compared to the as-deposited samples where this peak is suppressed.

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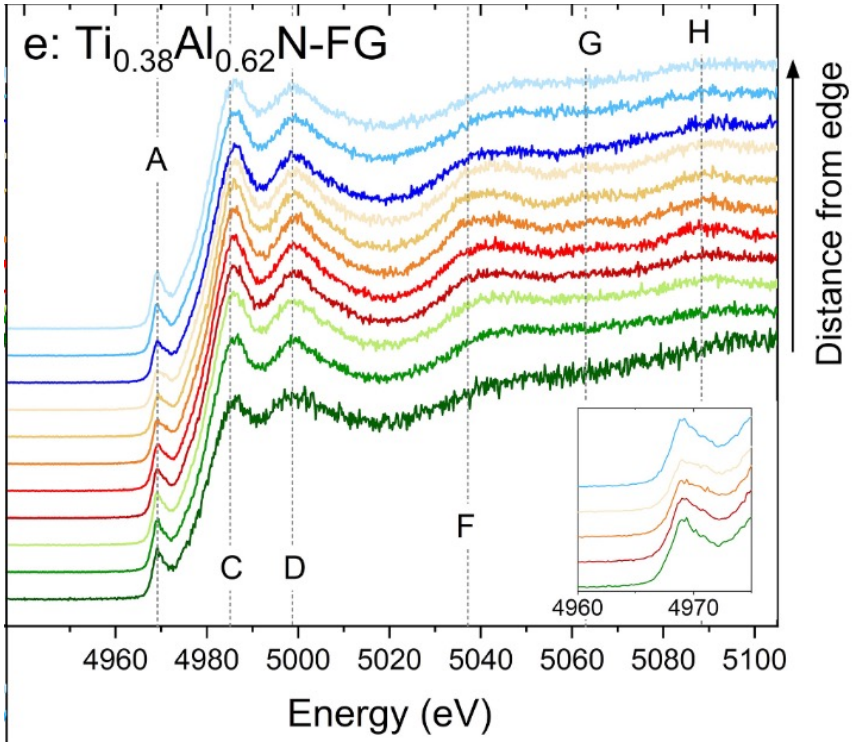
TiAlN coating - XANES



feature F shifts to lower energies in the middle of the contact length (orange) compared to the region closest to the edge (green) and the end of the contact (dark blue).

In agreement with previous studies, the position of feature F is dependent on the Al content of the fcc phase

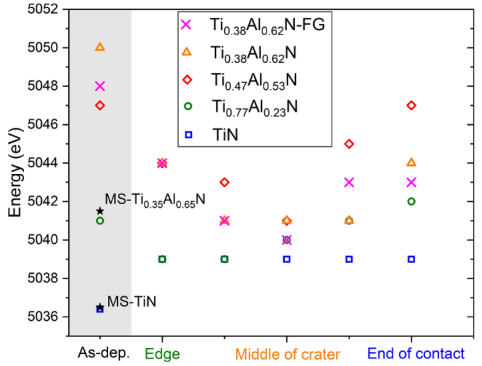


Fig. 6. Position of feature F for the as-deposited coatings and selected positions on the worn edge. The black stars mark the values for the MS reference samples.

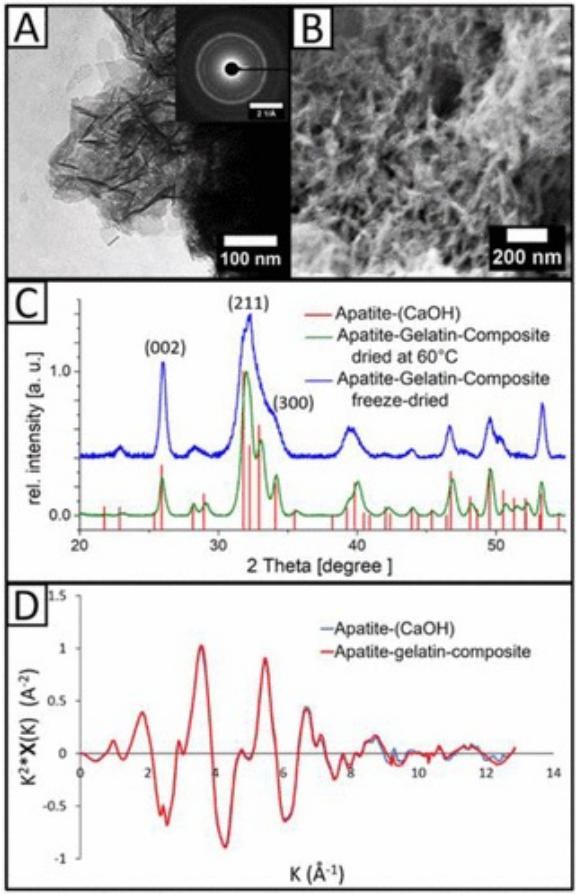
Rogström L., *et al* Applied Surface Science 612 (2023) 155907

Teeth

- Test in a dentine replacement material if the mineral phase is hydroxyapetite and if its short-range order is changed by the cross-linking of gelatine.

- EXAFS, XANES, or other technique?

Dentine replacement material



apateite-gelatin nancomposite material

k^2-weighted K-space EXAFS signal

→ EXAFS shows that the mineral in the nanocomposite is apatite-C

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