



Marianne Liebi– Material Science at Large Scale Facilities

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

EPFL Master Course 2025 MSE435

# Battery

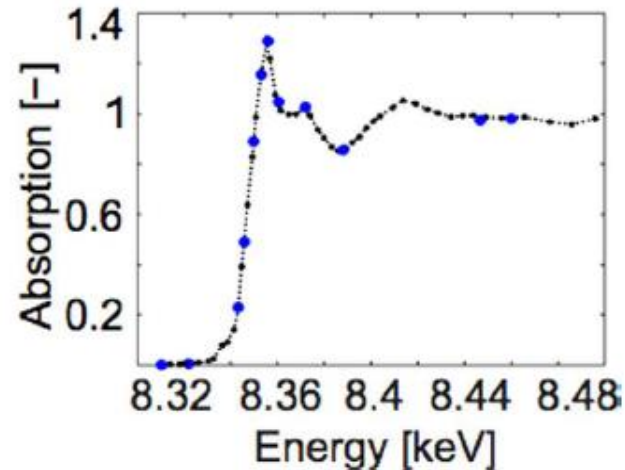
- Study the lithiation kinetics of a commercial, mixed-metal oxide cathode material, nickel cobalt aluminium oxide (NCA), during (dis)charge and its degradation during overcharge.
  
- EXAFS, XANES?

# 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

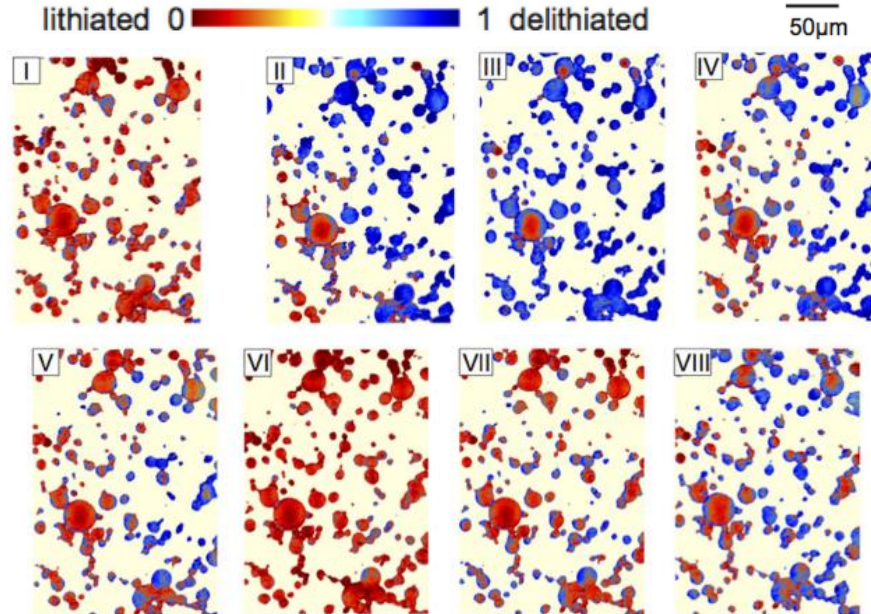
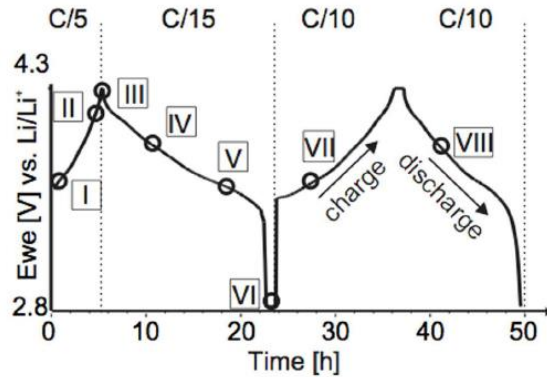
discretized energy resolution



# 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

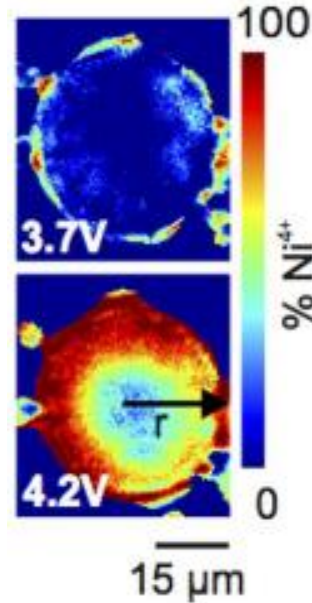
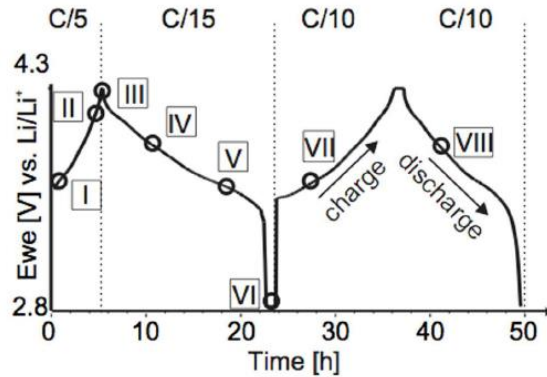
electrochemical cycling profile:



# 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:

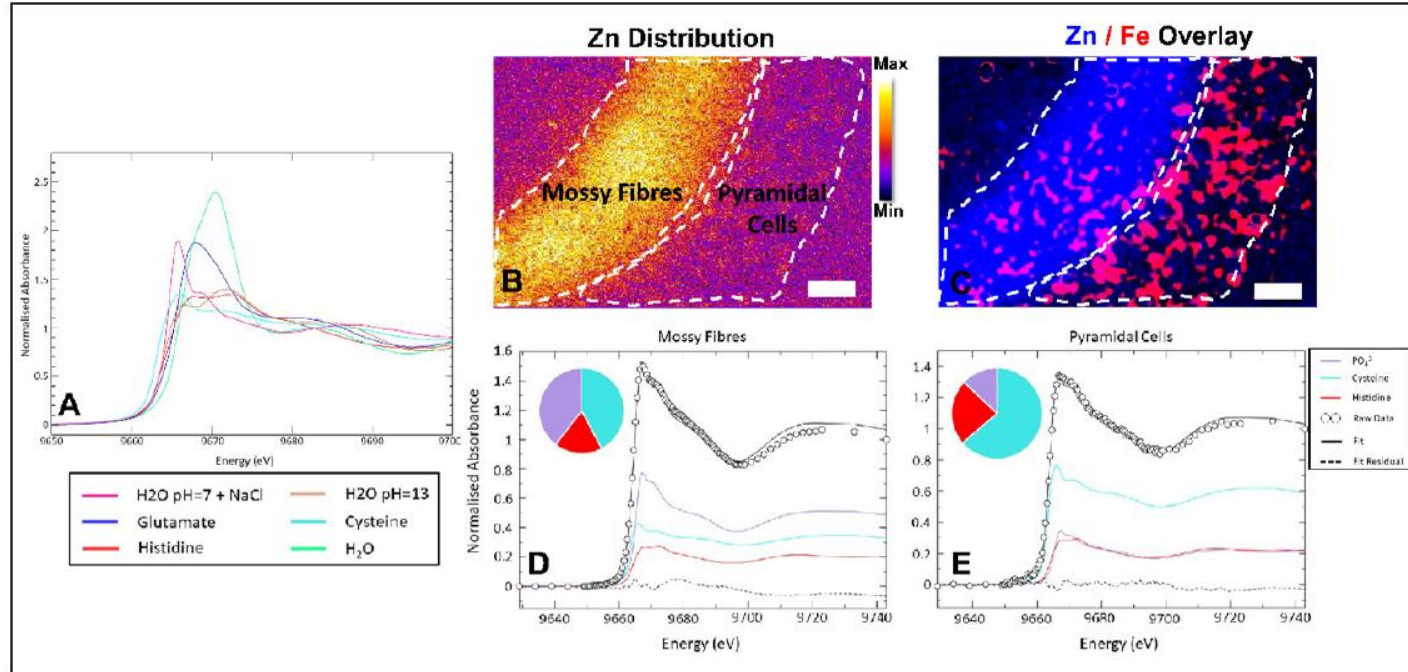


Ni<sup>4+</sup> oxidation maps of a single large particle during charge at 3.7 V and 4.2 V

# 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?

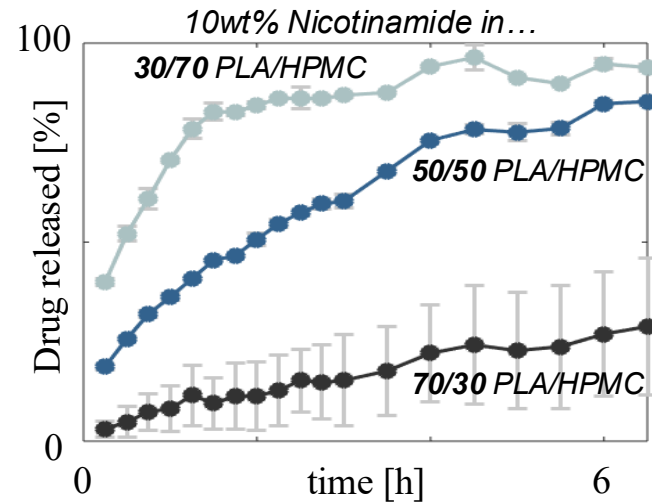
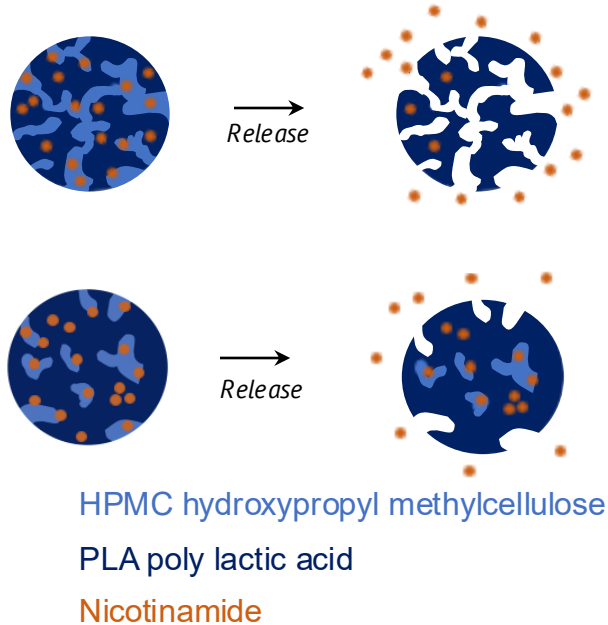
# Brain: different chemical forms of Zn



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

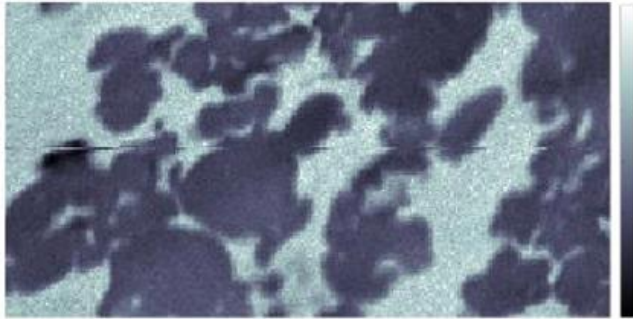
# Pharmaceutical formulations for controlled release

Phase separated system higher connectivity for faster release

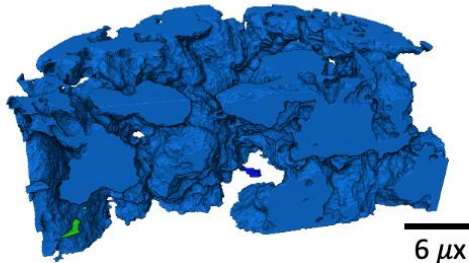


# Pharmaceutical formulations for controlled release

10wt% Nicotinamide  
in 50/50 PLA/HPMC

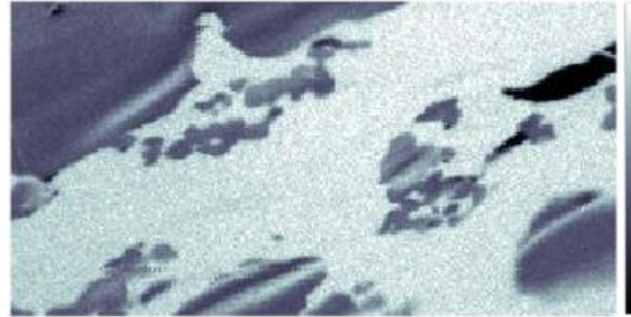


5 μm

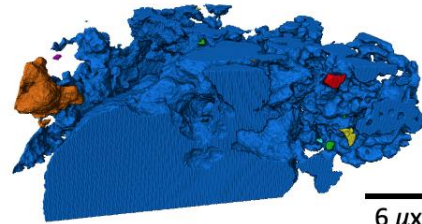


6 μm

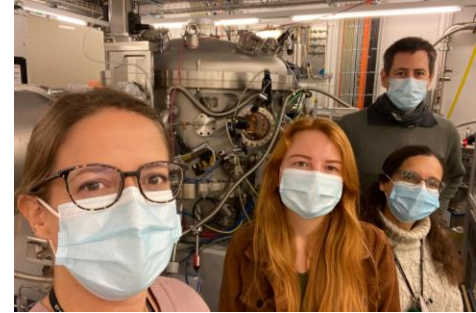
10wt% Nicotinamide  
in 70/30 PLA/HPMC



5 μm



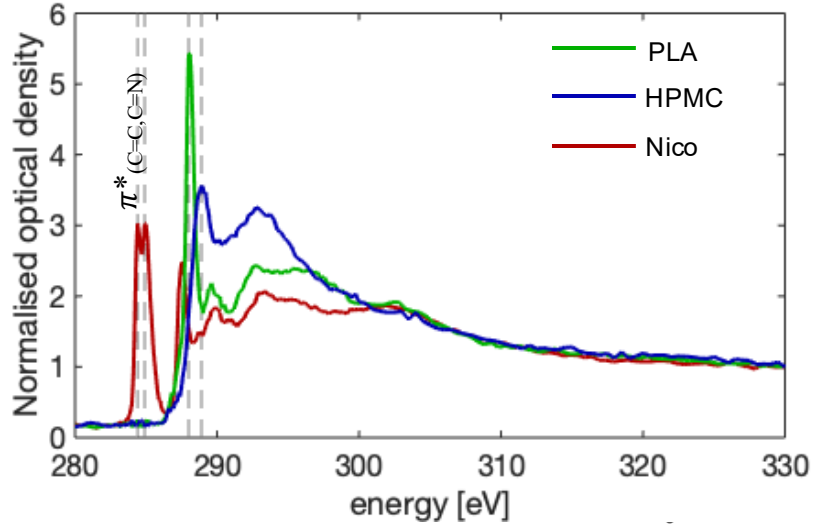
6 μm



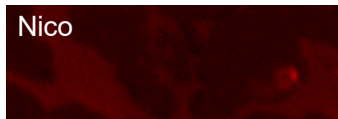
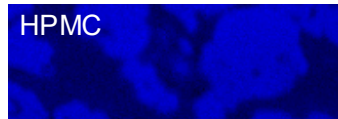
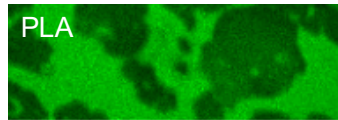
# Pharmaceutical formulations for controlled release

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

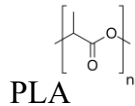
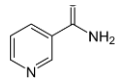
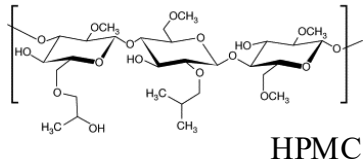
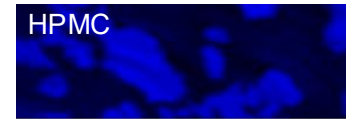
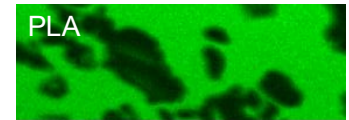
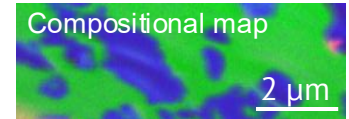
# STXM-XANES: Imaging with chemical contrast



10wt% nico in 50/50 PLA/HPMC

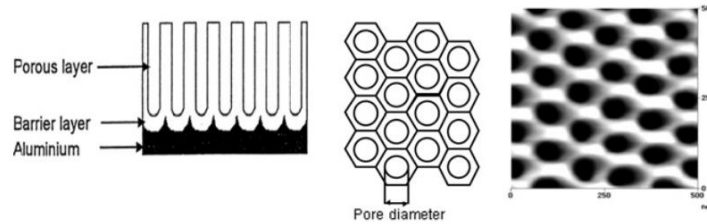


10wt% nico in 70/30 PLA/HPMC



# 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. E et 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?

- **local atomic structure** of the metal nanowire around the absorbing atom, specifically the nearest neighbor interatomic distances and coordination numbers, up to about the fourth nearest neighbors. 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 behavior 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 aluminum backing from the AAO samples to study them by EXAFS.

# Nanowires EXAFS

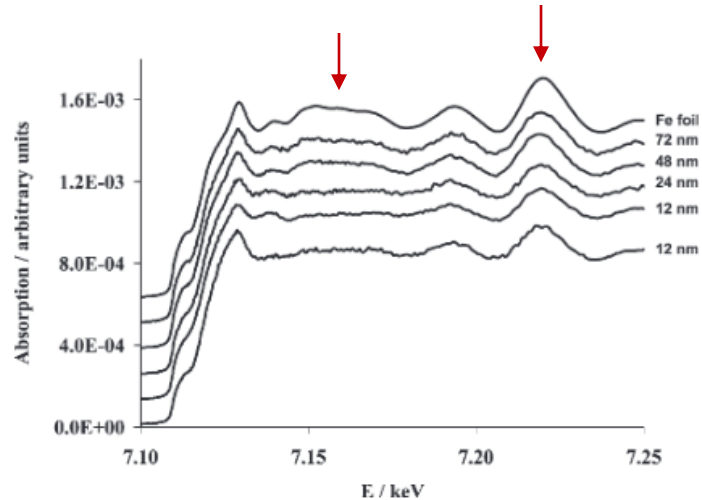
**Table 1** Representative results of Fe K-edge EXAFS refinements of iron nanowires. The results shown from ESRF BM29 are for a separately prepared series of samples; the results for the samples studied on SRS 7.1 were also confirmed on ESRF BM29. Data collection temperatures were 80 K at the SRS and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

	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 $\mu$ m foil	Stacked membranes with Al backing	Stacked membranes with Al backing	Pressed pellet	Pressed pellet	Pressed pellet	Pressed pellet
$E_0$ /eV <sup>b</sup>	-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 <sup>c</sup>	2.857 (3)	2.857 (3)	2.856 (3)	2.858 (4)	2.863 (3)	2.859 (3)	2.863 (3)
$N_i$ (fixed parameter) <sup>d</sup>	8*	8*	8*	8*	8*	8*	8*
$R_i$ /Å <sup>e</sup>	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

<sup>a</sup> Esd's in the final digits are given in brackets. <sup>b</sup>  $E_0$  = contribution of the wave vector of the zero photoelectron relative to the origin of  $k$ . <sup>c</sup>  $a$  = cell parameter. <sup>d</sup>  $N_i$  = number of atoms in the  $i$ th shell. <sup>e</sup>  $R_i$  = radial distance of atoms in the  $i$ th shell/Å. <sup>f</sup>  $A_i$  = Debye-Waller term of the  $i$ th shell ( $A = 2\sigma^2$  with  $\sigma$  = Debye-Waller factor)/Å<sup>2</sup>

# 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.”

# Titanium aluminum nitride (TiAlN) coating

- $Ti_{1-x}Al_xN$  coatings used for turning of stainless steel
- 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 subsequent formation of wurtzite (w) AlN
- EXAFS, XANES?

# 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.

# TiAlN coating - EXAFS

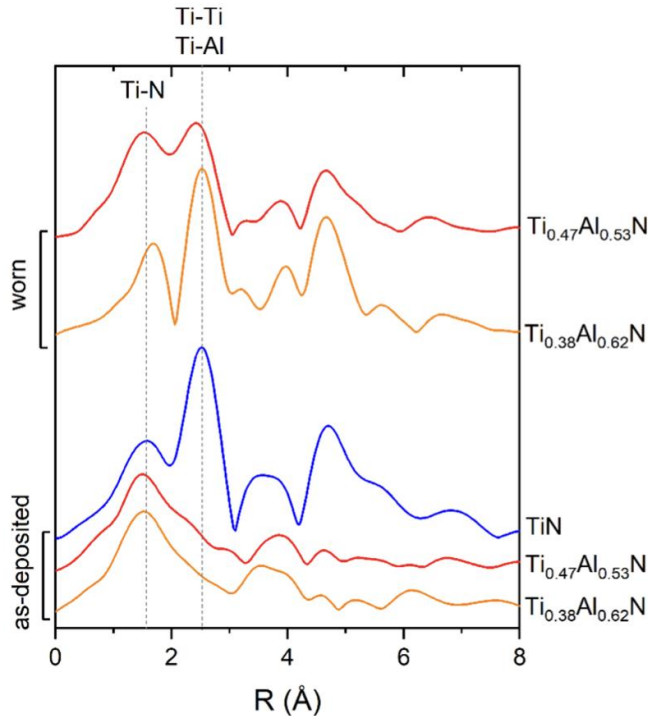
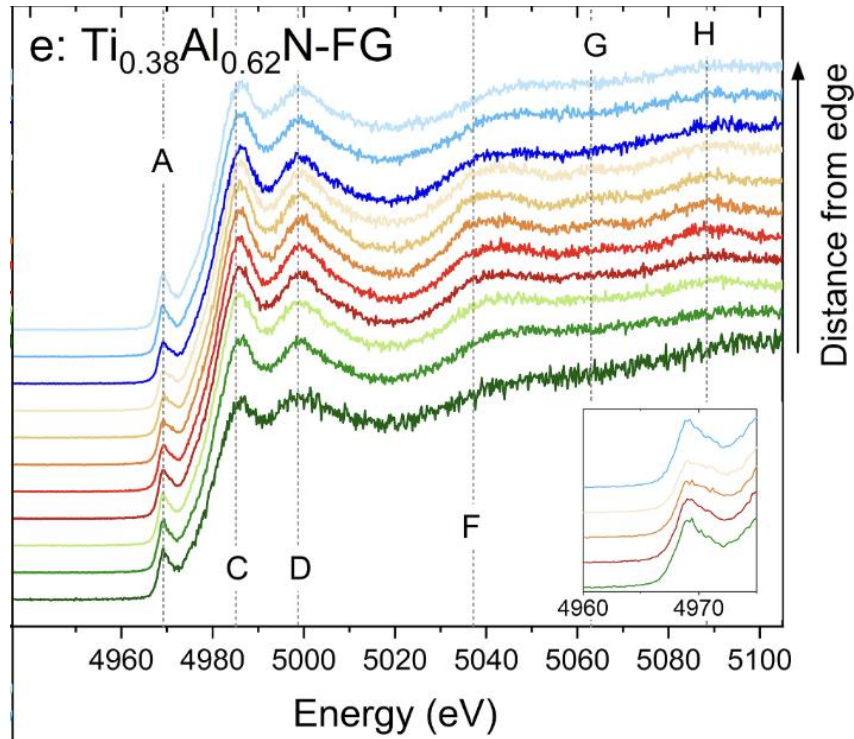


Fig. 4. Fourier transform obtained from the  $k^2$ -weighted EXAFS oscillations  $\chi(k)$  of selected as-deposited and worn samples.

there is a clear peak from the Ti-Ti/Ti-Al pairs around 2.5  $\text{\AA}$  (3  $\text{\AA}$  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.

# 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

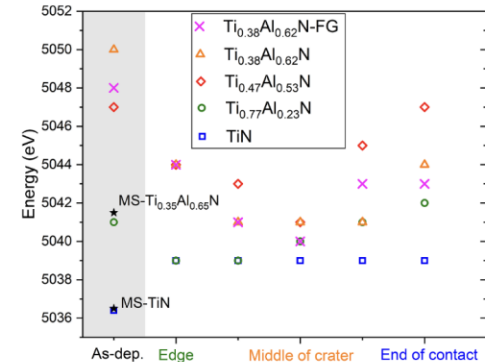
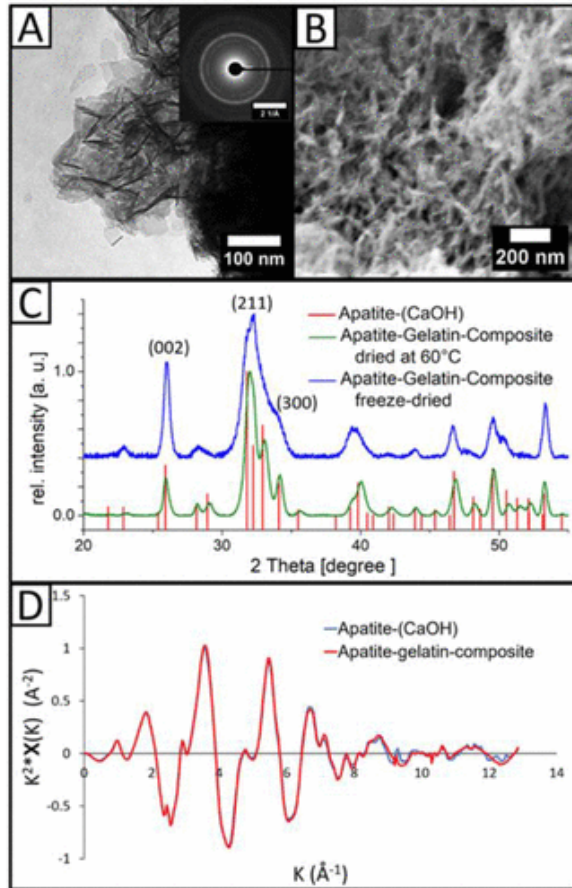


Fig. 6. Position of feature F for the as-deposited coatings and selected positions on the worn edge. The black stars mark the values for the MS reference samples.

# Teeth

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

# Dentine replacement material



apatite-gelatin nanocomposite material

$k^2$ -weighted K-space EXAFS signal

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