Nb-based NASICONs as electrode materials for Sodium-ion batteries

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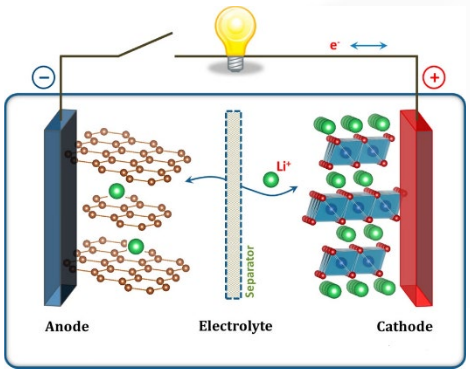
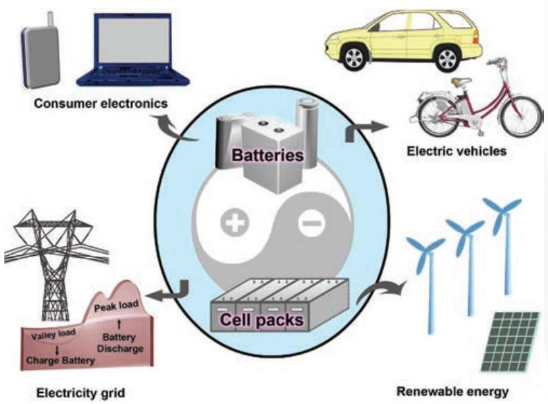
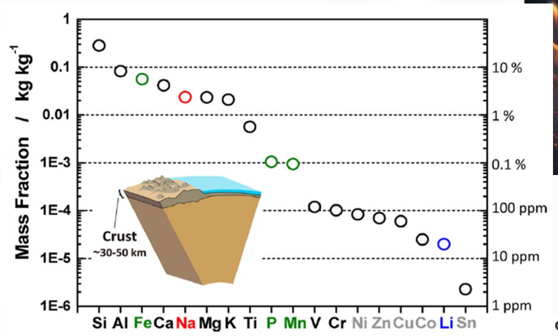
LIBs: a well-known story

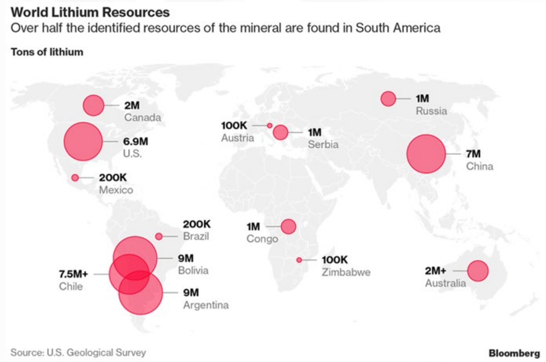
The importance of LIBs

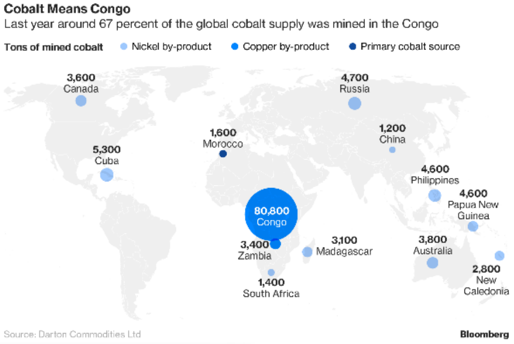




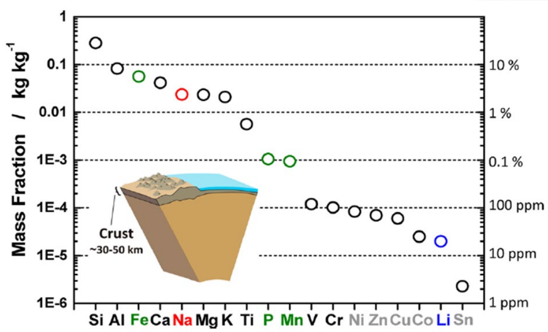
Their criticalities







An alternative: NIBs



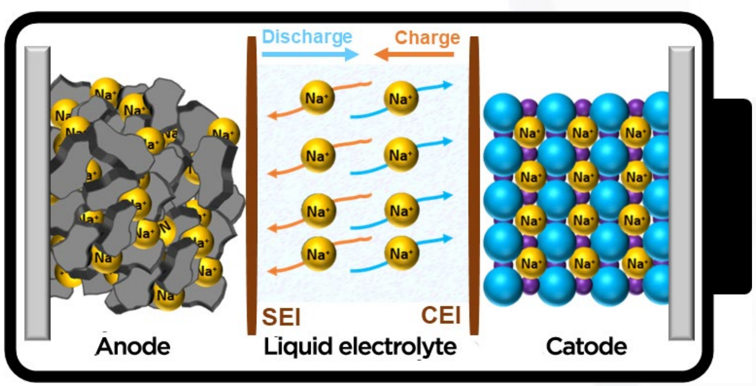
FARADION
Advanced Energy Storage Solutions

中科海钠
HiNa BATTERY

NGK
NGK INSULATORS, LTD.

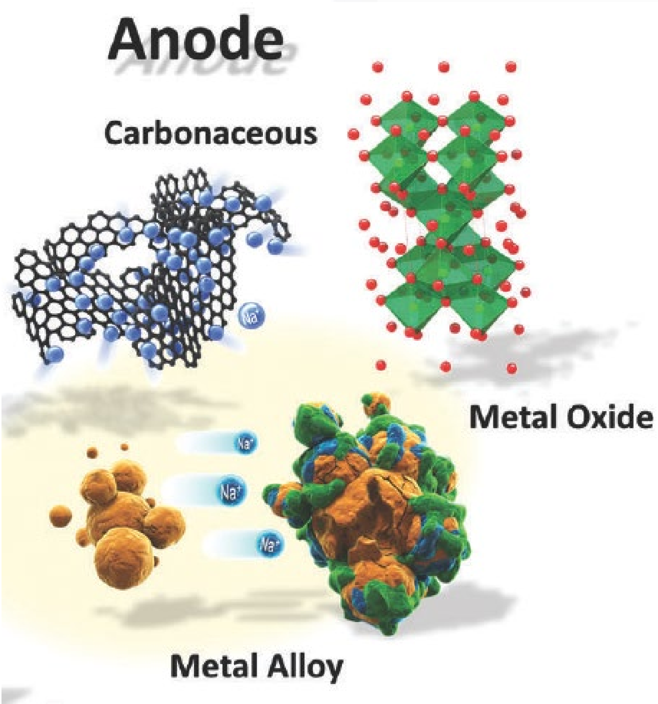
TIAMAT

CATL



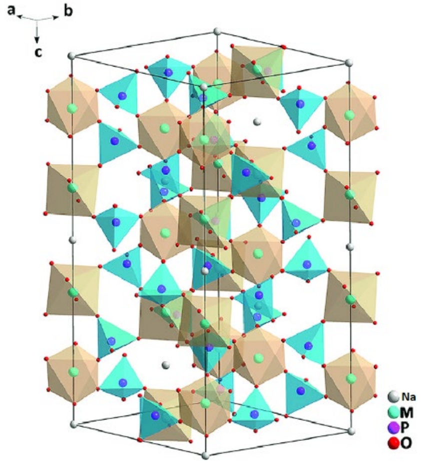
Natron Energy

Anodes for NIBs

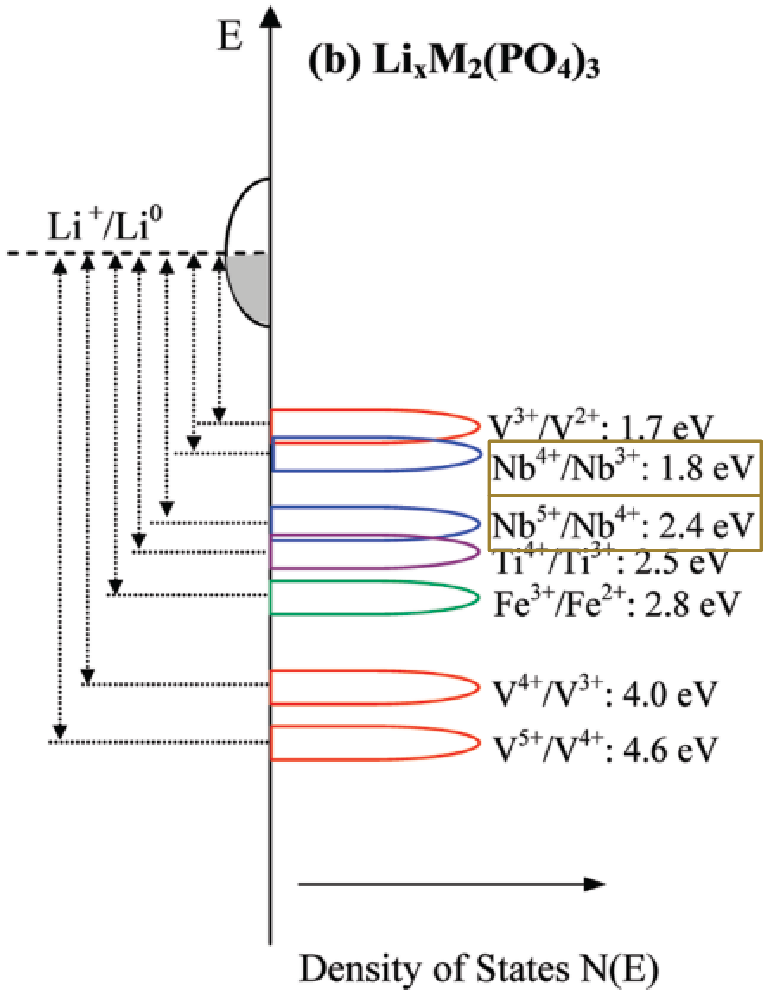


Phosphate-based NASICON

- General formula: $Na_xM_2(PO_4)_3$
- Easy to obtain via solid-state synthesis
- Can store up to 3 – 4 equivalents of sodium (capacities up to 150 – 170 mAh g^{-1})
- Depending on M, the potential can be tuned so to fit the requirements
- Suitable for medium voltage systems (e.g., aqueous batteries)



$Na_xM_2(PO_4)_3$: the choice of M



Niobium:

- can be reduced from Nb^{V} to Nb^{III}, counterbalancing the movement of two sodium ions. In NASICON systems, such redox reactions happens at a relatively low potential
- several of its compounds (like Nb_2O_5) are neither toxic nor hazardous
- abundance on Earth's crust comparable to that of Ni and Cu

Aim of this work

- Synthesize two Nb-based NASICONs: $NaAlNb(PO_4)_3$ and $NaFeNb(PO_4)_3$, named NANP and NFNP
- Study their morphological and electrochemical properties vs Na
- Study the Operando evolution of such materials via XRD and XAS analyses

NASICONs synthesis

$$\frac{1}{2}Na_2CO_3 + \frac{1}{2}Nb_2O_5 + 3NH_4H_2PO_4 + FeC_2O_4/\frac{1}{2}Al_2O_3 \rightarrow NaMNb(PO_4)_3$$

300°C
1°C/min
12 hours

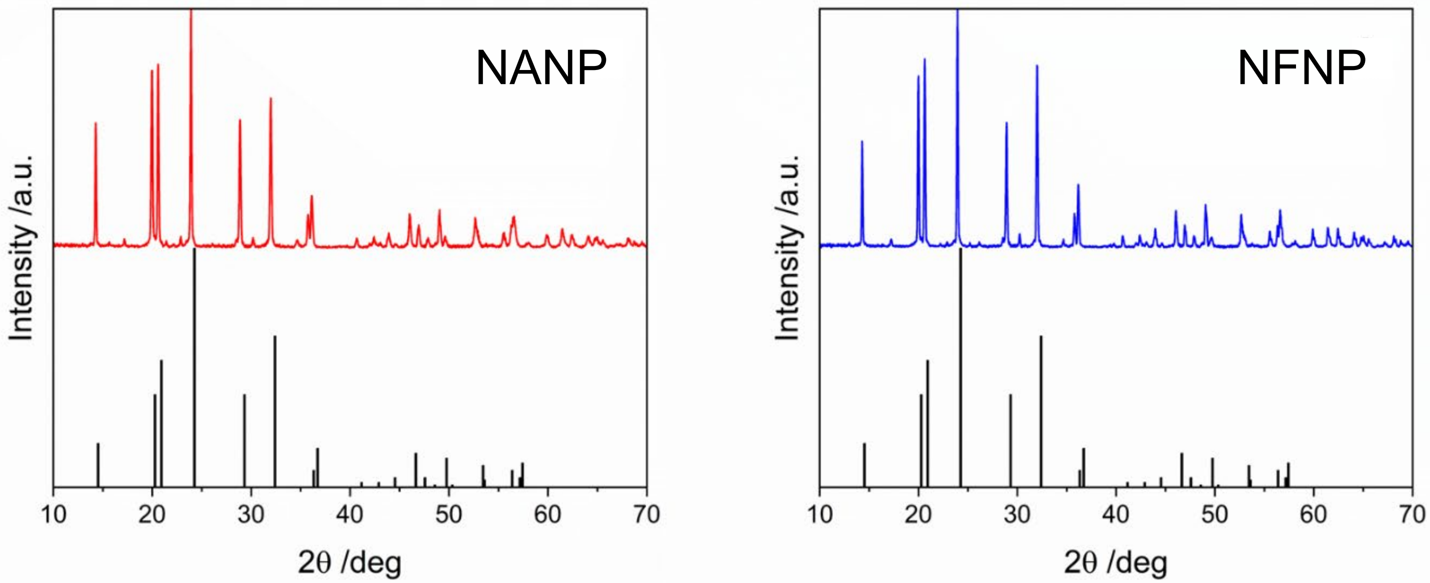
600°C
5°C/min
3 hours

950°C
5°C/min
72 hours

Al

Fe

Diffraction patterns



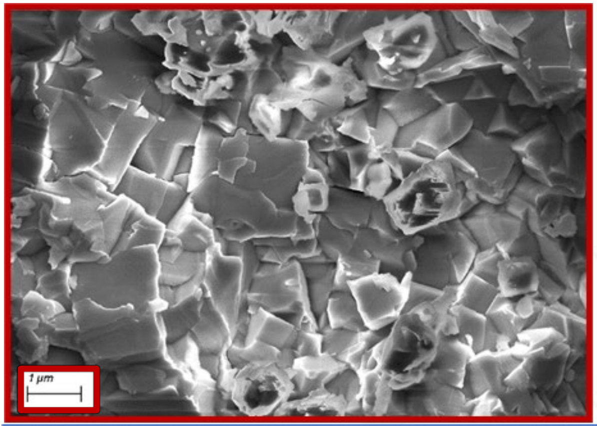
- Both NASICONs present the same structure (space group R-3c)
- Purity of the NASICONs > 97%
- Impurities: mixed oxides – phosphates of the transition metals

From Rietveld Refinement

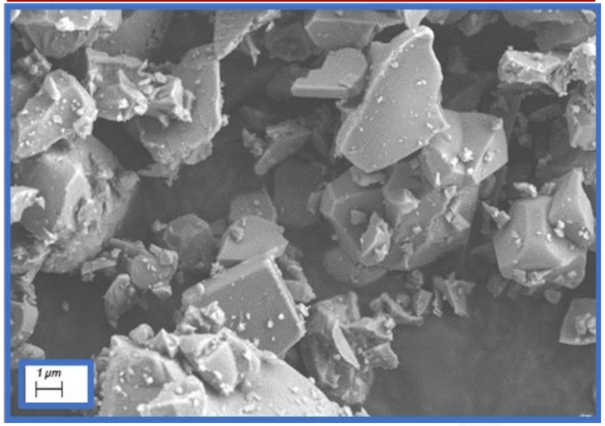
	NANP	NFNP
Na	0.6	0.66
Al/Fe	0.85	0.98
Nb	1.15	1.02

Morphology and ionic conductivity

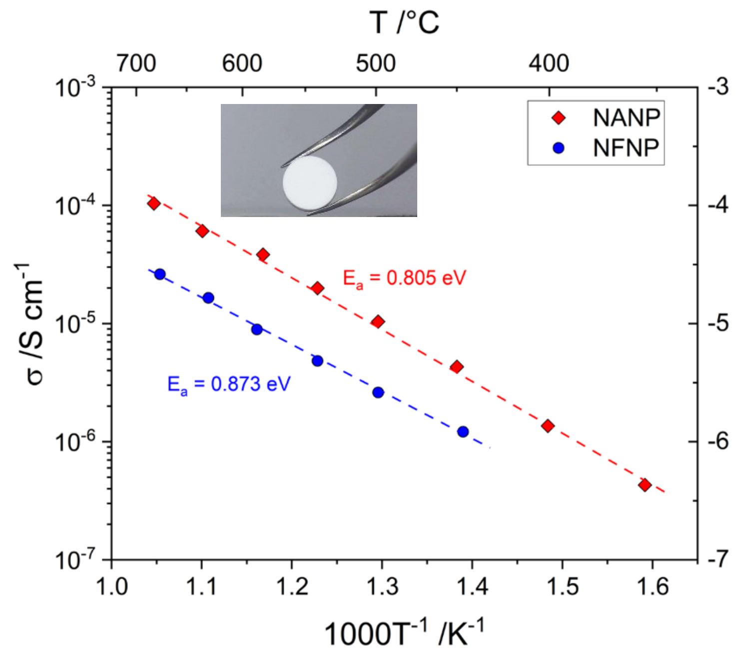
NANP



NFNP

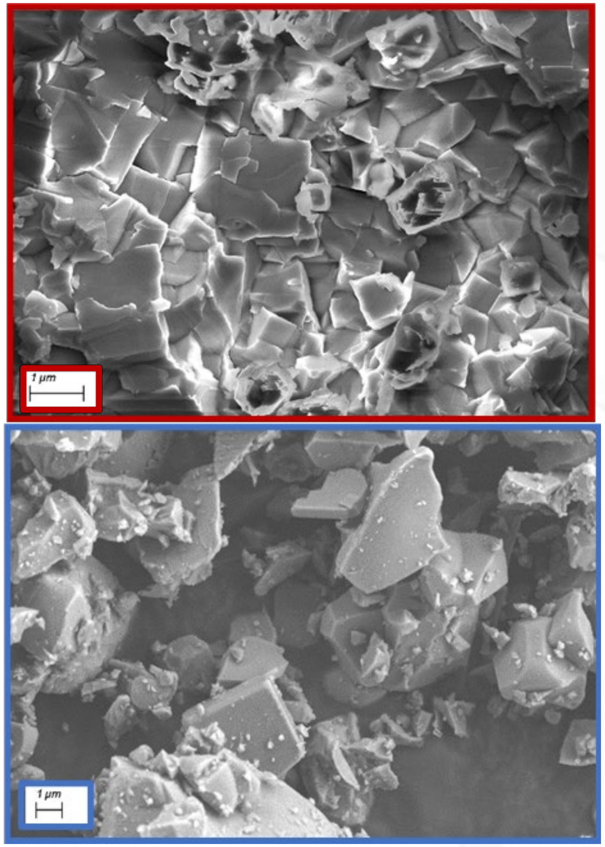


- More or less regular particles of about 2 – 5 µm coalesced together



- Relative densities > 98% for both NASICONs

Morphology and ionic conductivity



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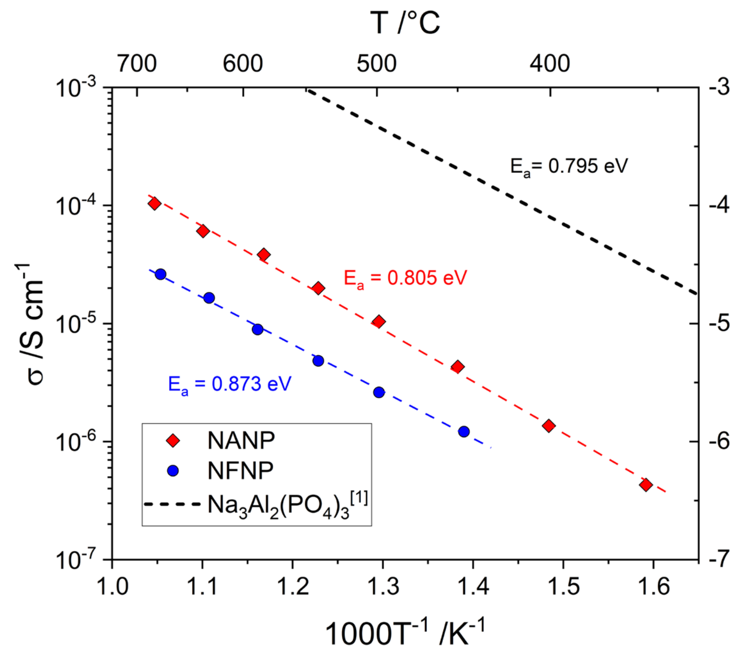

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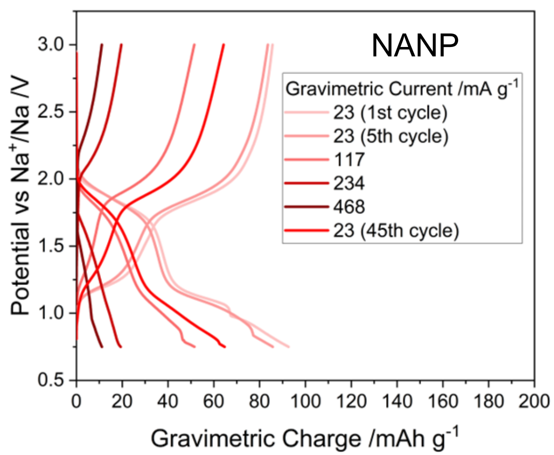
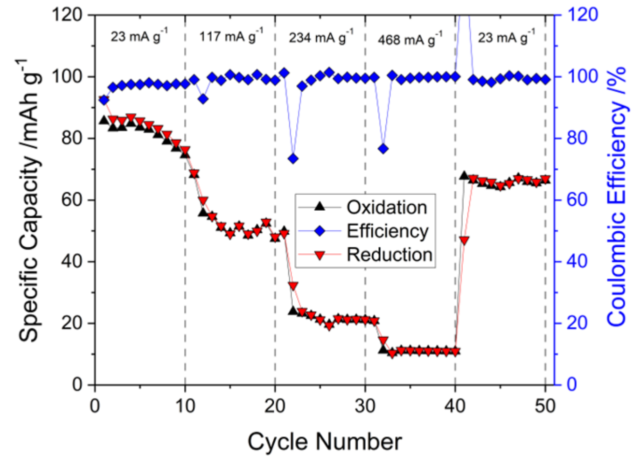
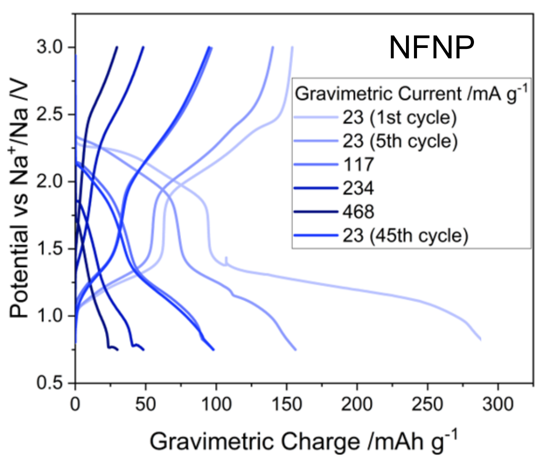
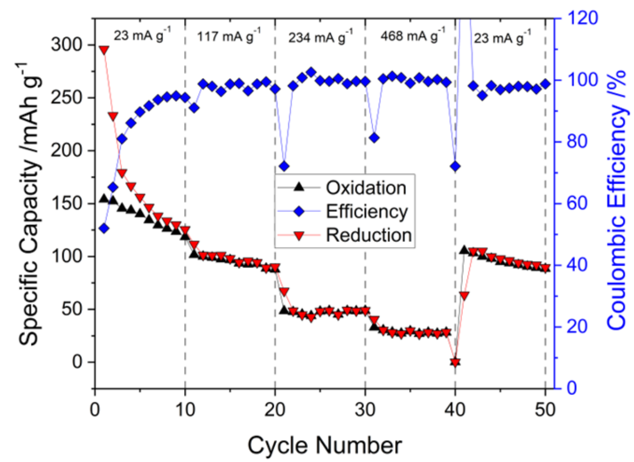
[1]: R. Schimanouchi et al., Mat. Chem. Phys., Vol 238, 2019

Electrochemical performances

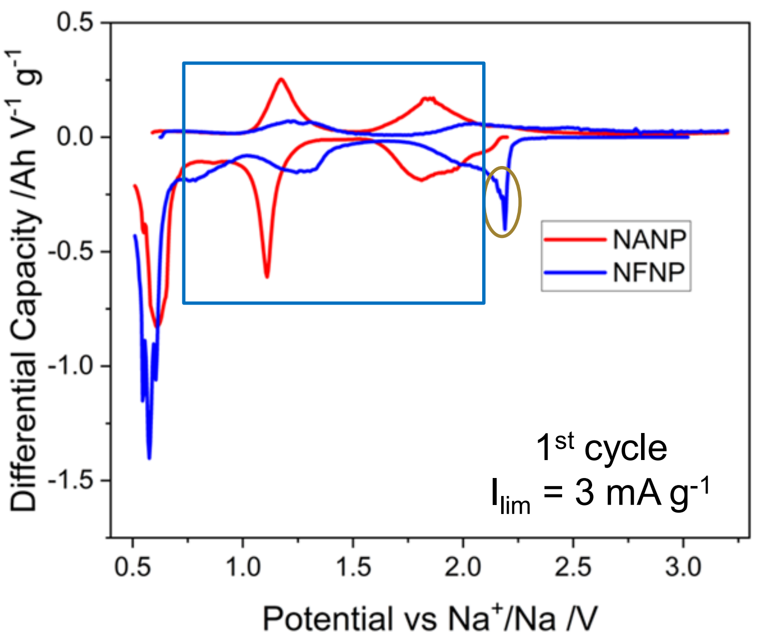




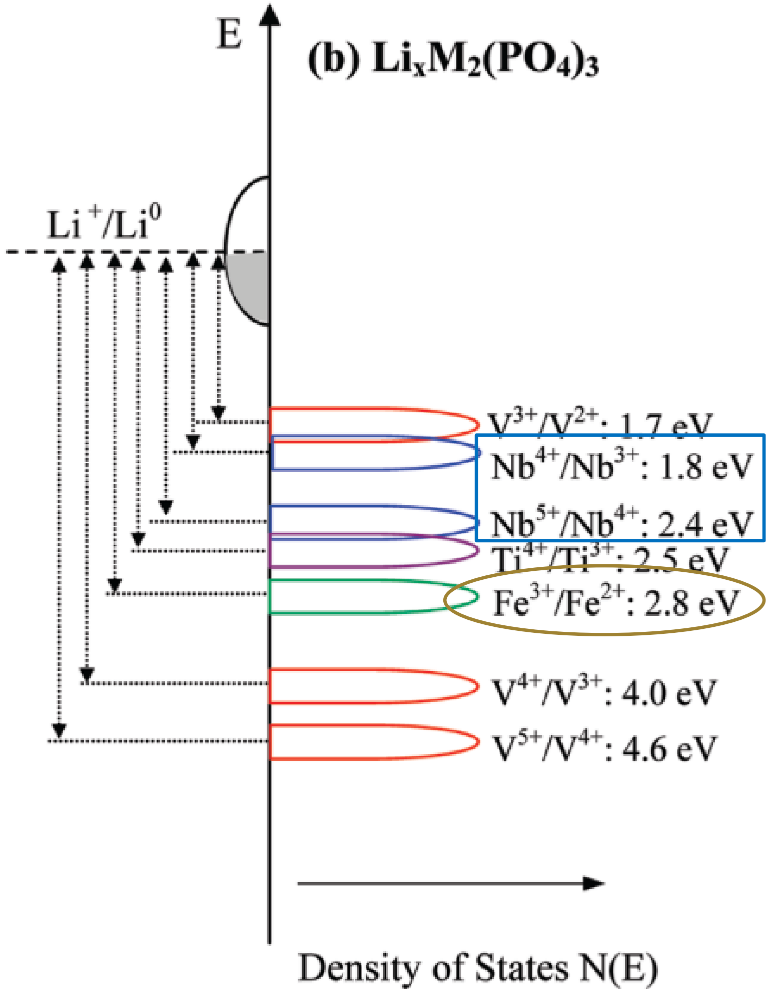




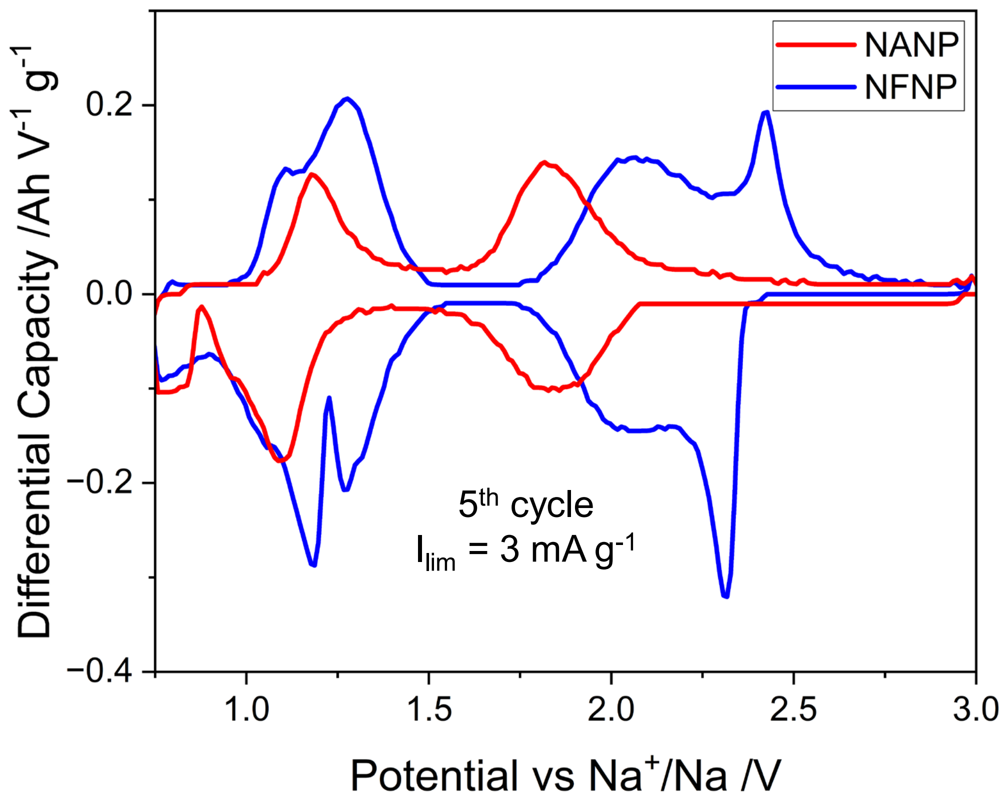
Differential capacity



- In case of NFNP, the first peak is probably related to the $Fe^{III/II}$ reduction
- For both NASICONs, peaks between 2.1 and 0.9 V vs Na^+/Na are likely related to Nb reactions

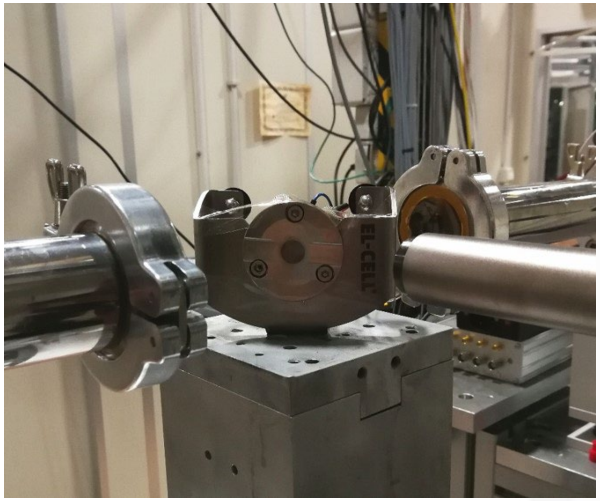


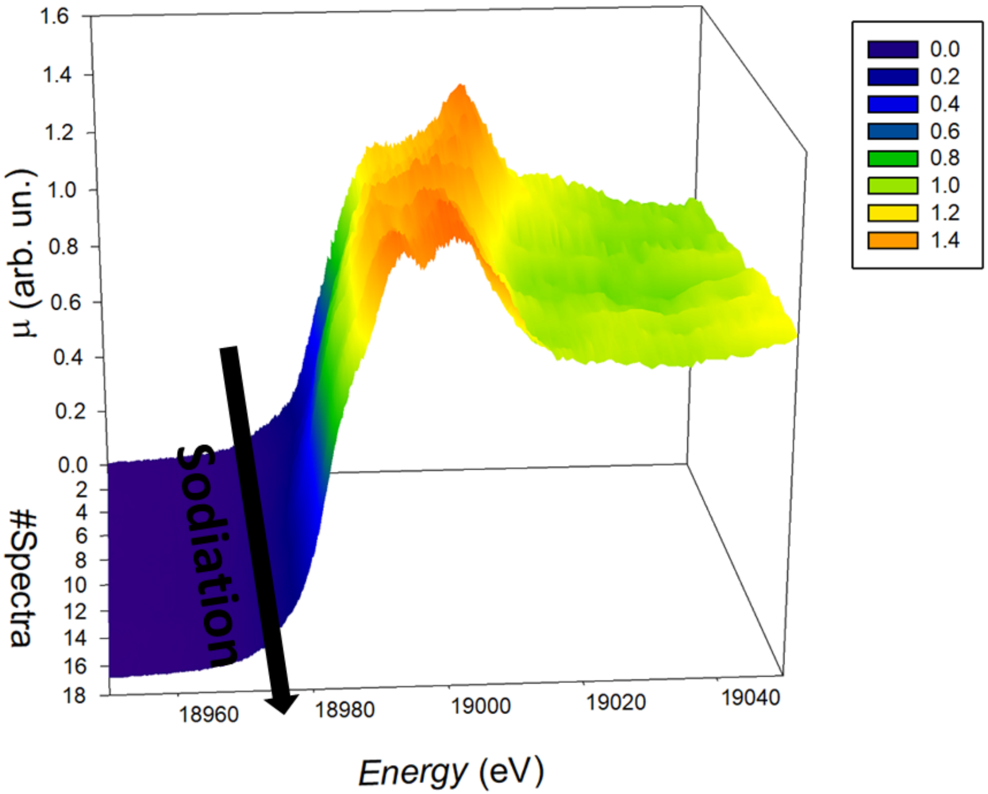
Differential capacity



- In NANP, Nb redox couples operate at lower potentials than in NFNP (1.84 V vs 1.75 V in oxidation)
- After the first cycle $Nb^{IV/III}$ peaks start to separate in two. This is probably due to some kind of degradation of the material

Operando XAS

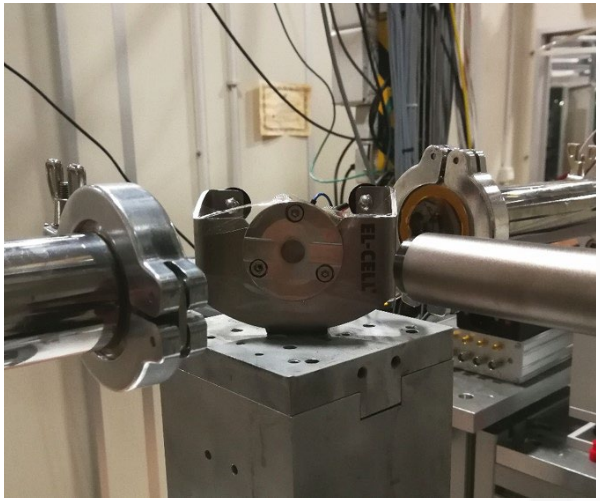


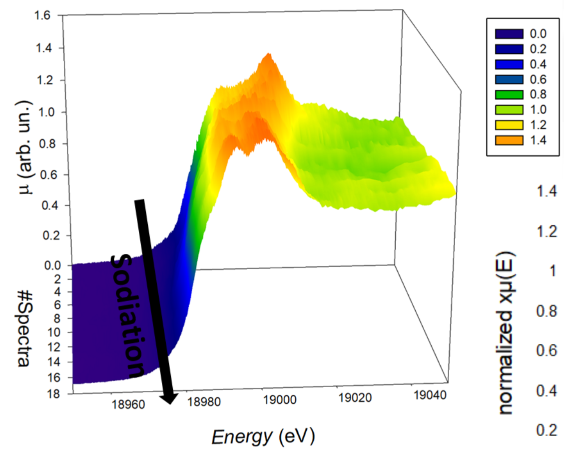


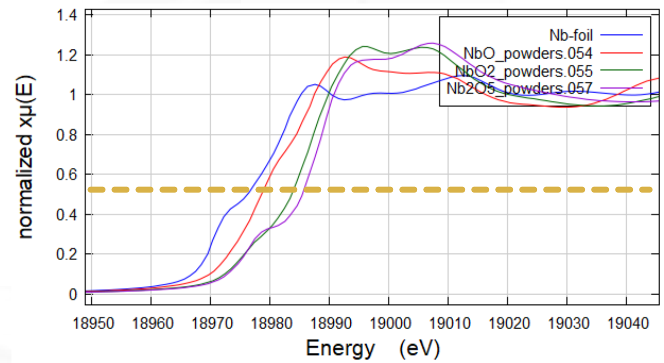
- Experiment performed at Elettra (Beamline: XAS)
- Performed in an optical cell (polyimide window), fluorescence mode

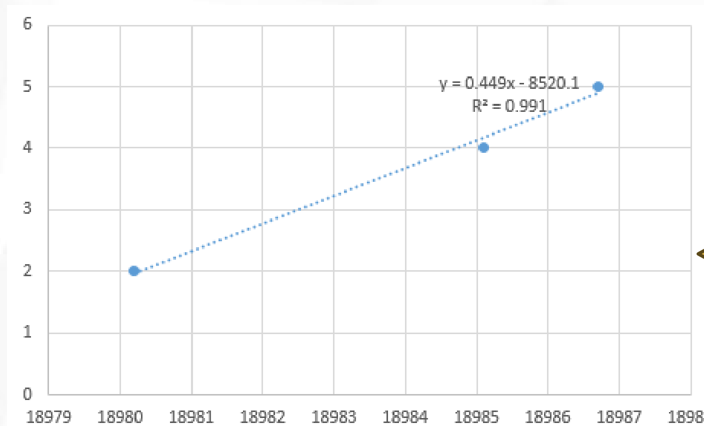
Elettra Sincrotrone Trieste

Operando XAS





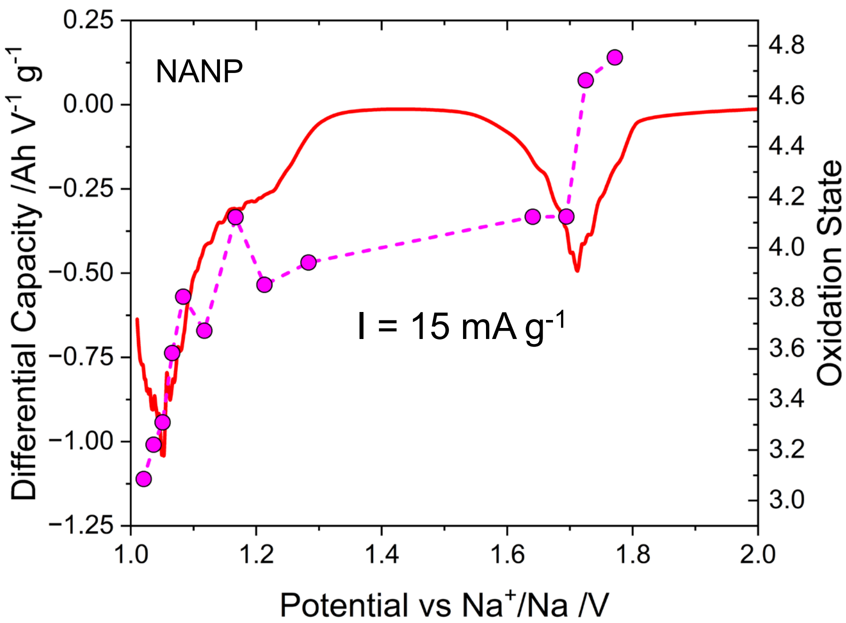


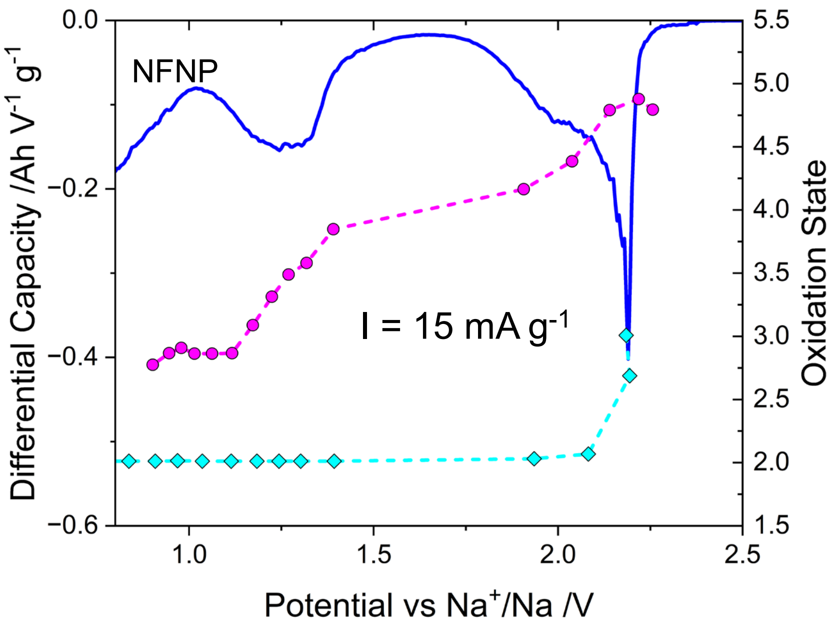


- Shift in spectra's energy is directly proportional to the state of charge of the element
- It is possible to estimate the oxidation state by taking the energy at which a spectrum reaches a precise μ

Elettra Sincrotrone Trieste

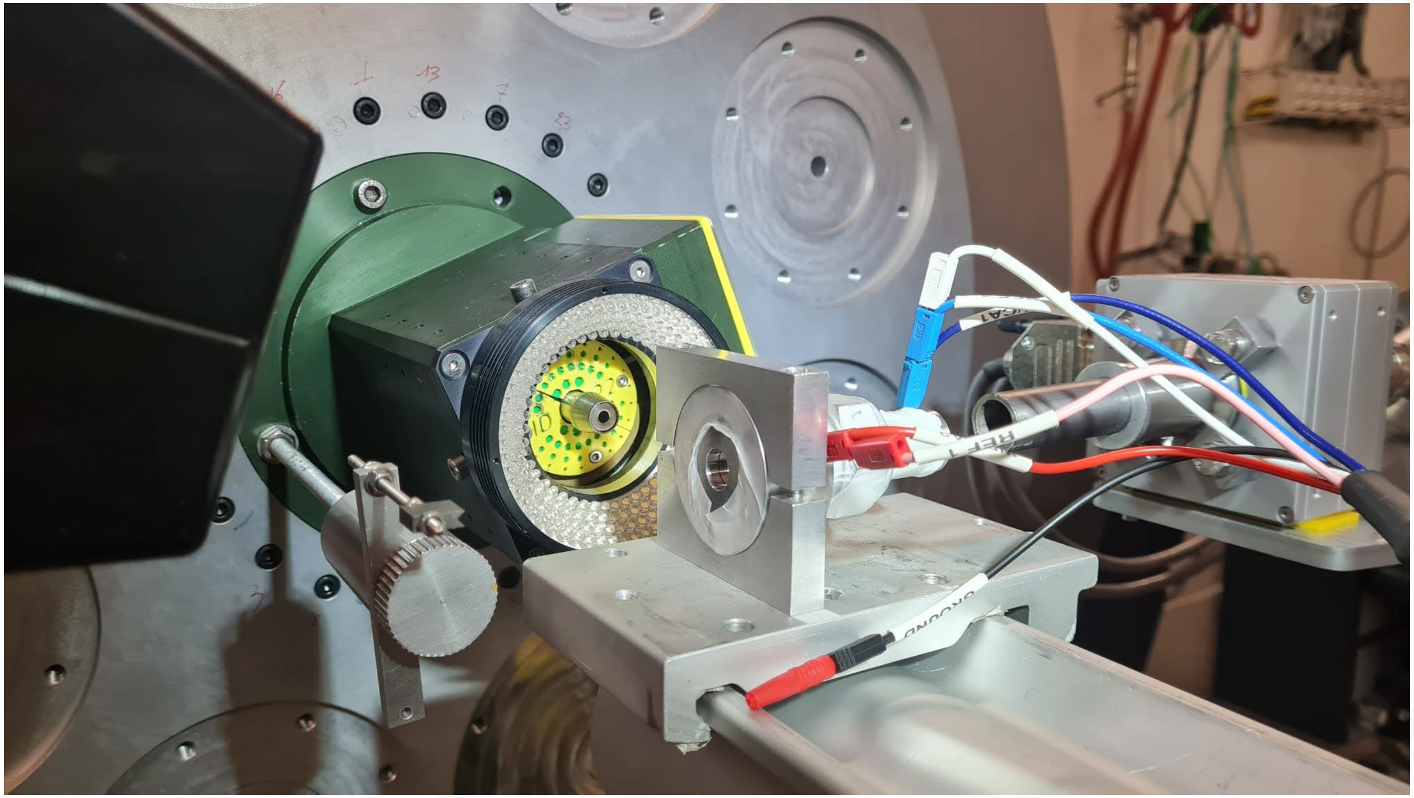
Operando XAS





- In both cases, Nb gets reduced in conjunction with the two peaks between 0.9 V and 2.1 V vs Na^+/Na
- Iron gets reduced only around 2.1 V vs Na^+/Na

Operando XRD: NFNP



- Experiment performed at ESRF (ID22) on a homemade transmission cell (beryllium windows)
- Electrochemical test: charge and discharge (15 mA g^{-1})
- Diffraction analyses at 0.35 Å

ESRF The European Synchrotron

IWES GISEL 2024

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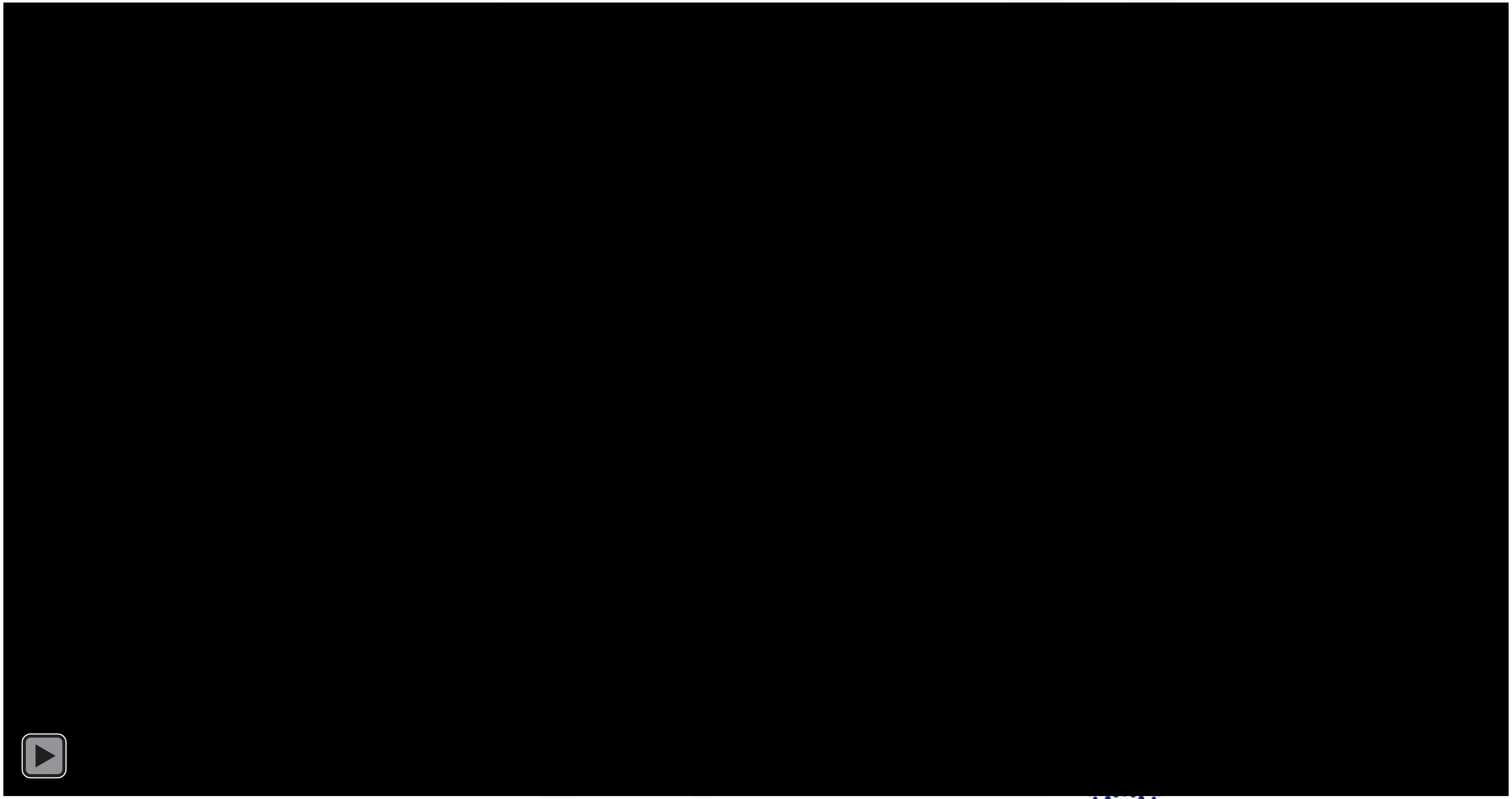
Operando XRD: NFNP



Conclusions

- Nb-based NASICONs can be easily synthesized with different transition metal elements to tune the operative potential
- Niobium preserves its redox reactions, but the potential at which they happen depends on the nature of the other transition metal
- $NaMNb(PO_4)_3$ are able to store around 2 Na^+, but are generally quite unstable and tend to evolve to other structures

Next steps

- Have a better understanding on the effect of the element M in the energy levels of $NaMNb(PO_4)_3$
- Try to stabilize the Nb-based NASICONs so to reduce their irreversible phase transitions (e.g., encapsulating in scaffolds, stabilizing coatings)
- Evaluate the effect of other elements rather than just Al and Fe

Thank you!

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