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Fe-based Single Atom Electrocatalyst Structure Probed by X-ray Emission Spectroscopy

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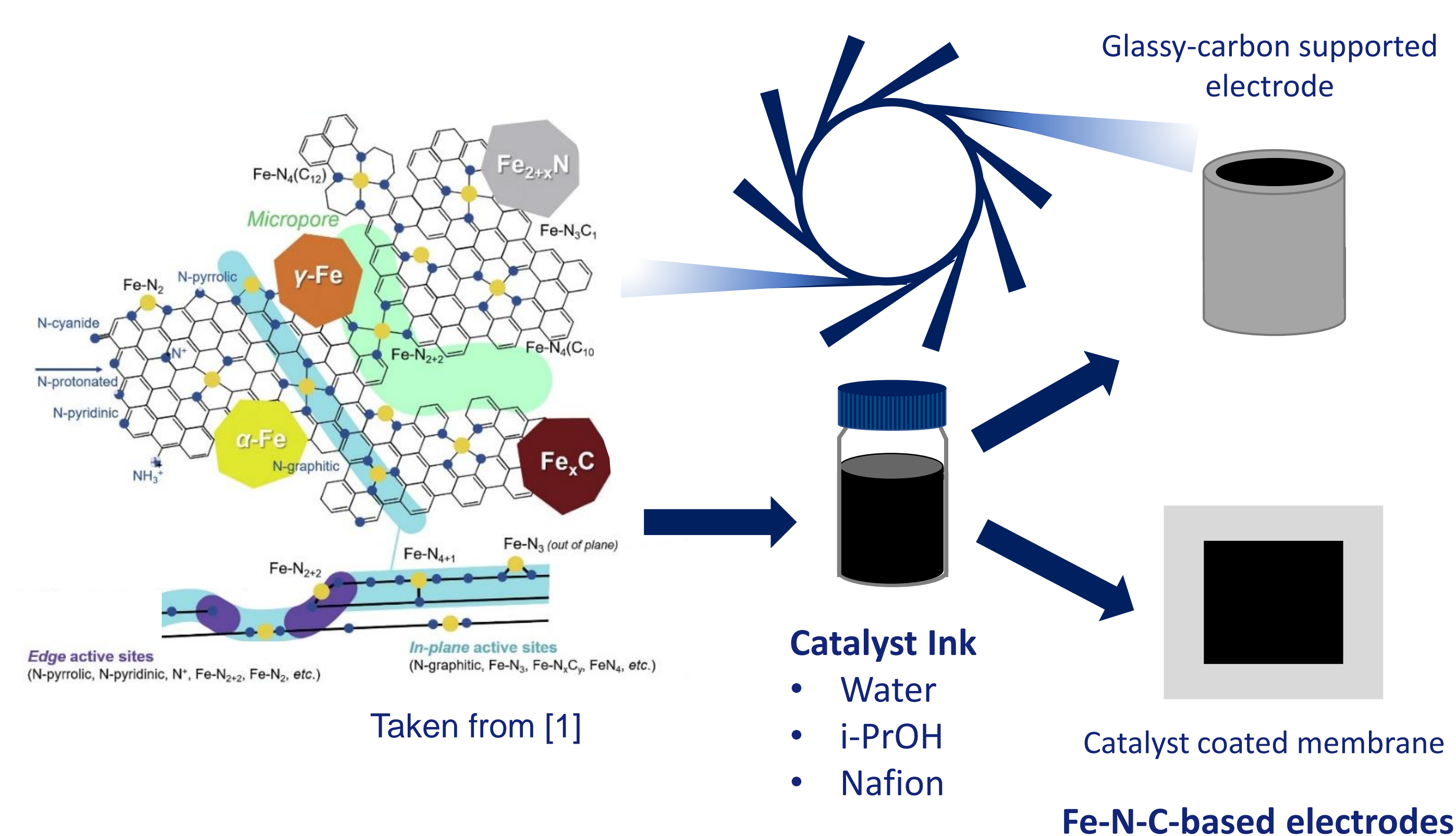
⁴ICGM, Univ. Montpellier, CNRS, ENSCM, 34293 Montpellier, France

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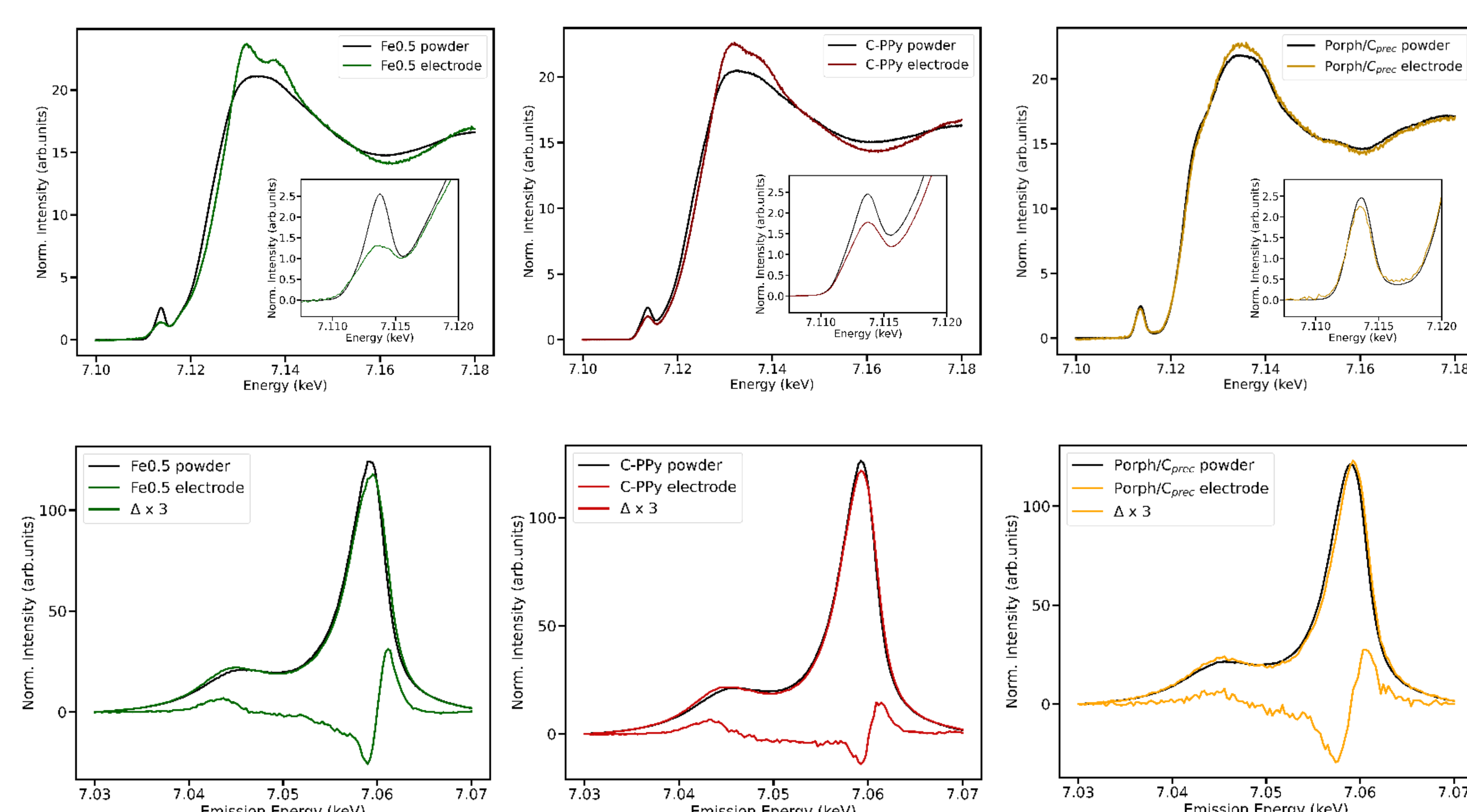
Evaluation of the electrocatalyst performance data includes an electrode preparation step. In this work, we compare the structural composition of several Fe-N-C materials prepared via different synthesis routes and used to electrocatalyze the oxygen reduction reaction in proton-exchange membrane fuel cells, before and after catalyst layer preparation using high energy resolution fluorescence detected X-ray absorption (HERFD XANES) and X-ray emission spectroscopies (XES). The measurements were performed at beamline ID26 of the European synchrotron (ESRF).



Overview



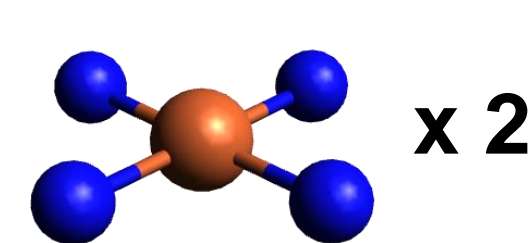
Powder vs Electrode: K β HERFD XANES & XES



Fe-N-C Catalysts Overview

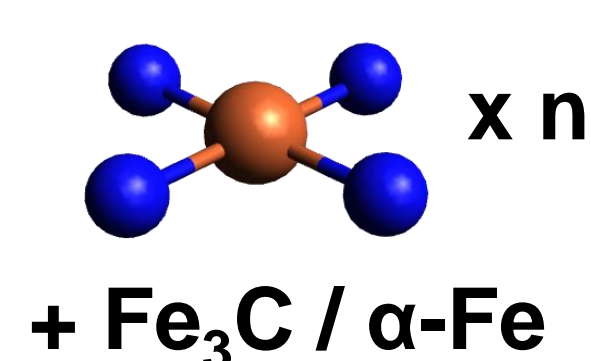
Fe0.5

- MOF-based
- ramp pyrolysis synthesis
- Reference [2]



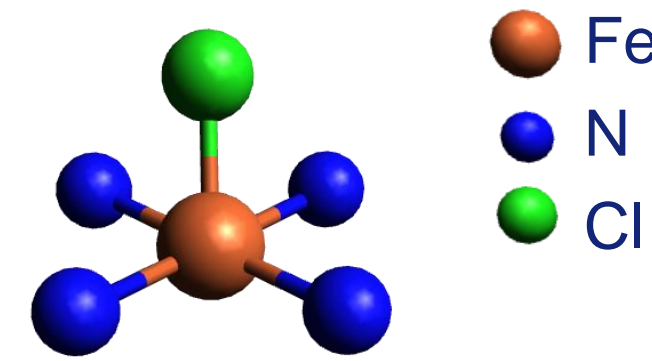
C-PPy

- polypyrrole-derived
- ⁵⁷Fe-N-C
- Reference [3]

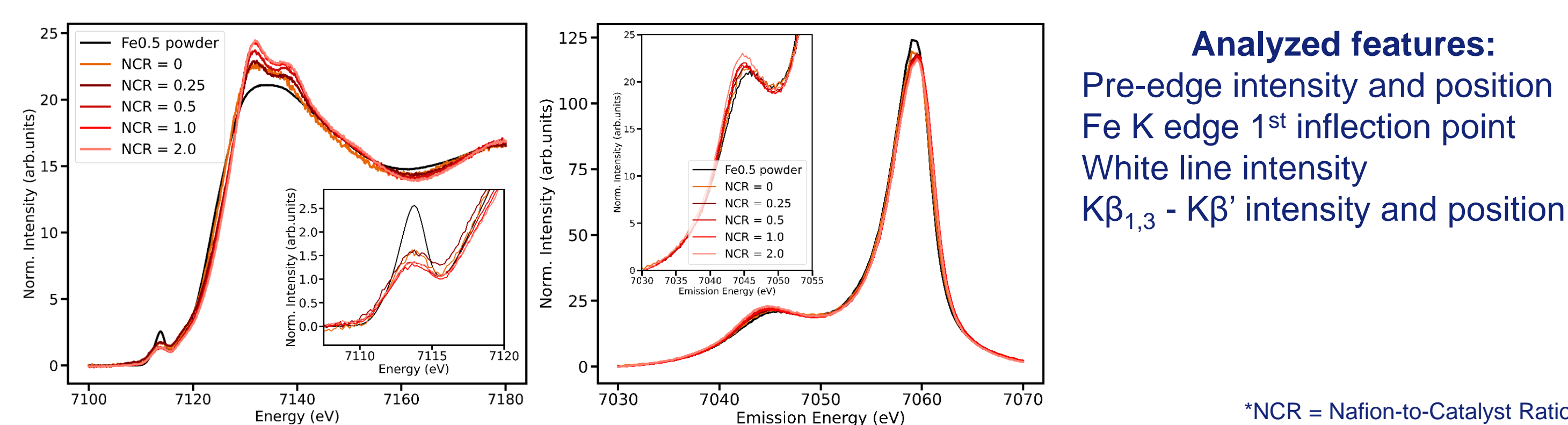


Porph/C_{prec}

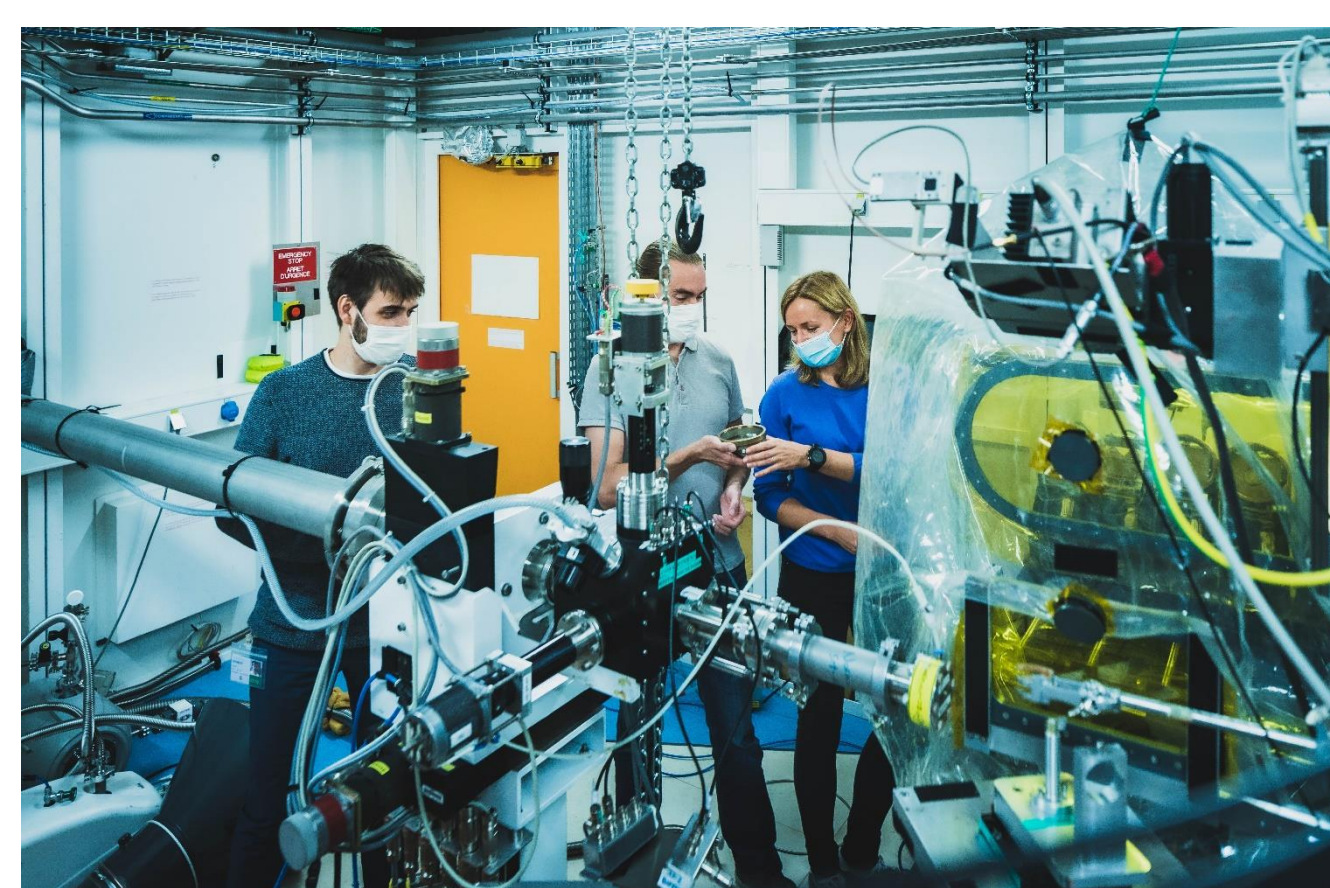
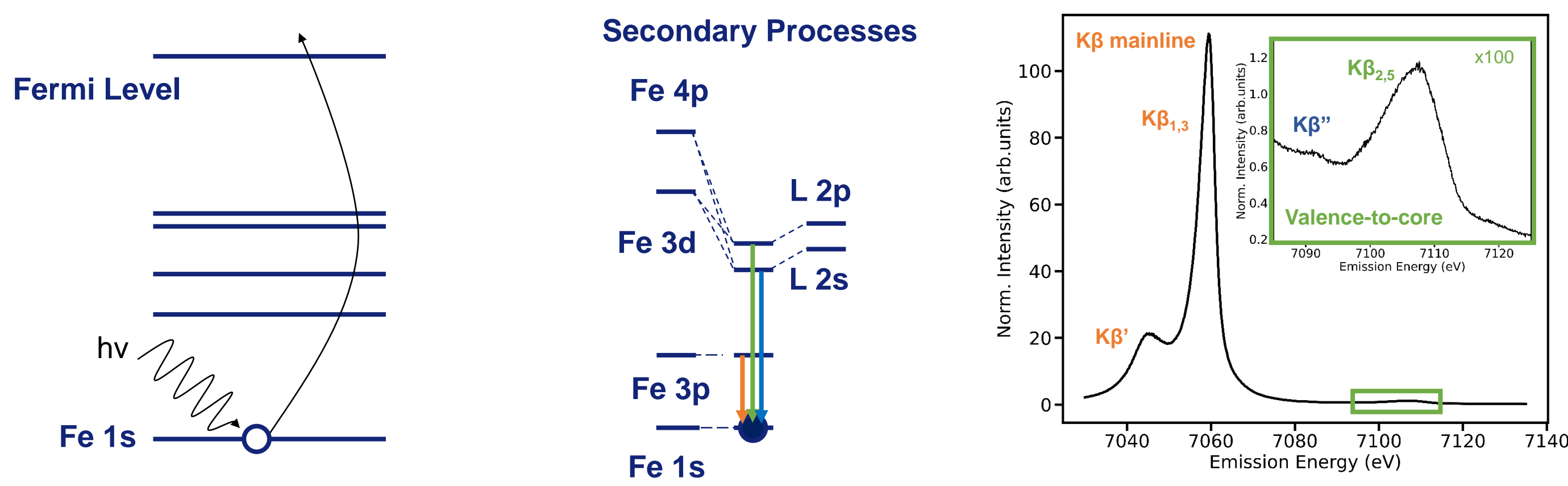
- Porphyrin-based
- FeTMPPCI / Carbon
- Reference [4]



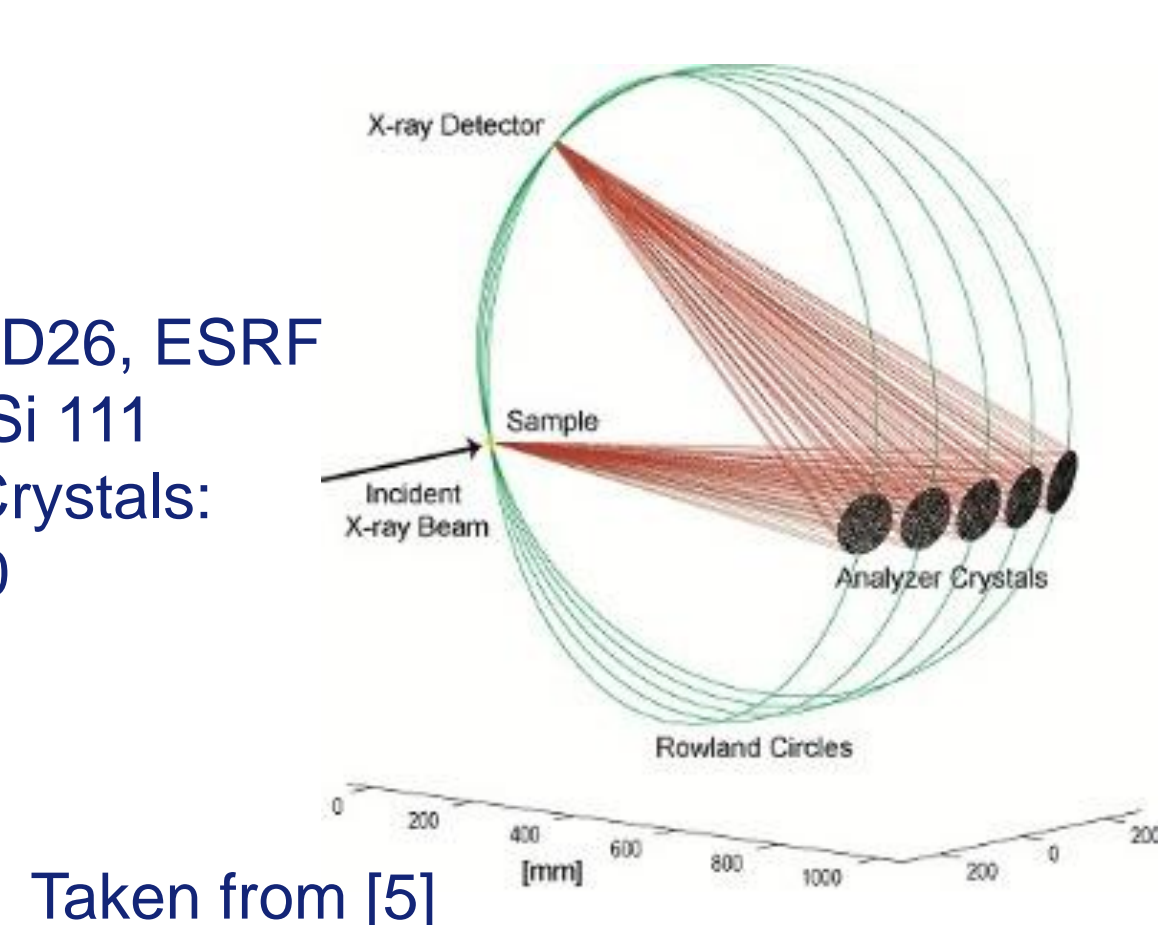
Role of Nafion ionomer



X-ray Absorption & Emission Spectroscopies



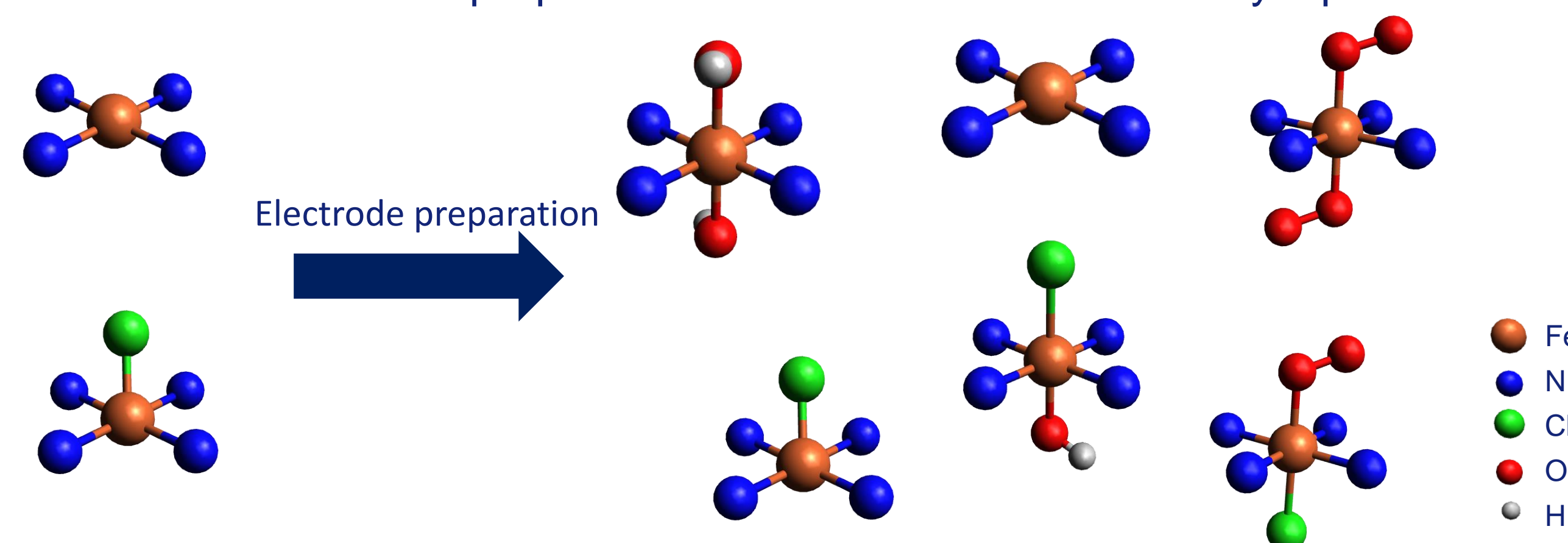
Credits photo: S. CANDE / ESRF



Conclusions

- FeN_x sites structure partially evolves from square planar (or square pyramidal) to octahedral by adding -O₂ / -OH bond(s)
- This change is universal for Fe-N-C materials, the magnitude of change varies with catalyst initial composition
- Nafion presence enhances the formation of oxygenated ligands in the ink.

This aspect should be taken into account when discussing the catalyst structure – activity – stability/durability correlation(s) as well as analyzing *in situ/operando* measurements performed on these materials, where one should consider the electronic state of Fe in the prepared electrode and not in the catalyst powder.



References

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4. Paul, S.; et al. Influence of the metal center in M–N–C catalysts on the CO₂ reduction reaction on gas diffusion electrodes, *ACS Catal.* **2021**, *11* (9), 5850–5864.
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