



HAL
open science

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

Viktoriia Saveleva, Kavita Kumar, Pascal Theis, Nicole Segura Salas, Ulrike Kramm, Frederic Jaouen, Frédéric Maillard, Pieter Glatzel

► To cite this version:

Viktoriia Saveleva, Kavita Kumar, Pascal Theis, Nicole Segura Salas, Ulrike Kramm, et al.. Fe-based Single Atom Electrocatalyst Structure Probed by X-ray Emission Spectroscopy. Gordon Research Conference, Feb 2023, Lucca, Italy. , Reactions at Surface Active Sites: From Single Atoms and 2D Materials to Electrified Interfaces, 10.15151/ESRF-ES-799089889 . hal-04005436

HAL Id: hal-04005436

<https://hal.science/hal-04005436v1>

Submitted on 26 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

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

Viktoriia A. Saveleva¹, Kavita Kumar², Pascal Theis³, Nicole Segura Salas³, Ulrike I. Kramm³, Frédéric Jaouen⁴, Frédéric Maillard², Pieter Glatzel¹

¹ ESRF, The European Synchrotron, 71 Avenue des Martyrs, CS40220, 38043 Grenoble Cedex 9, France

² Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France

³ TU Darmstadt, Department of Chemistry, Catalysts and Electrocatalysts Group, Technical University of Darmstadt, Otto-Berndt-Str. 3, 64287 Darmstadt, Germany

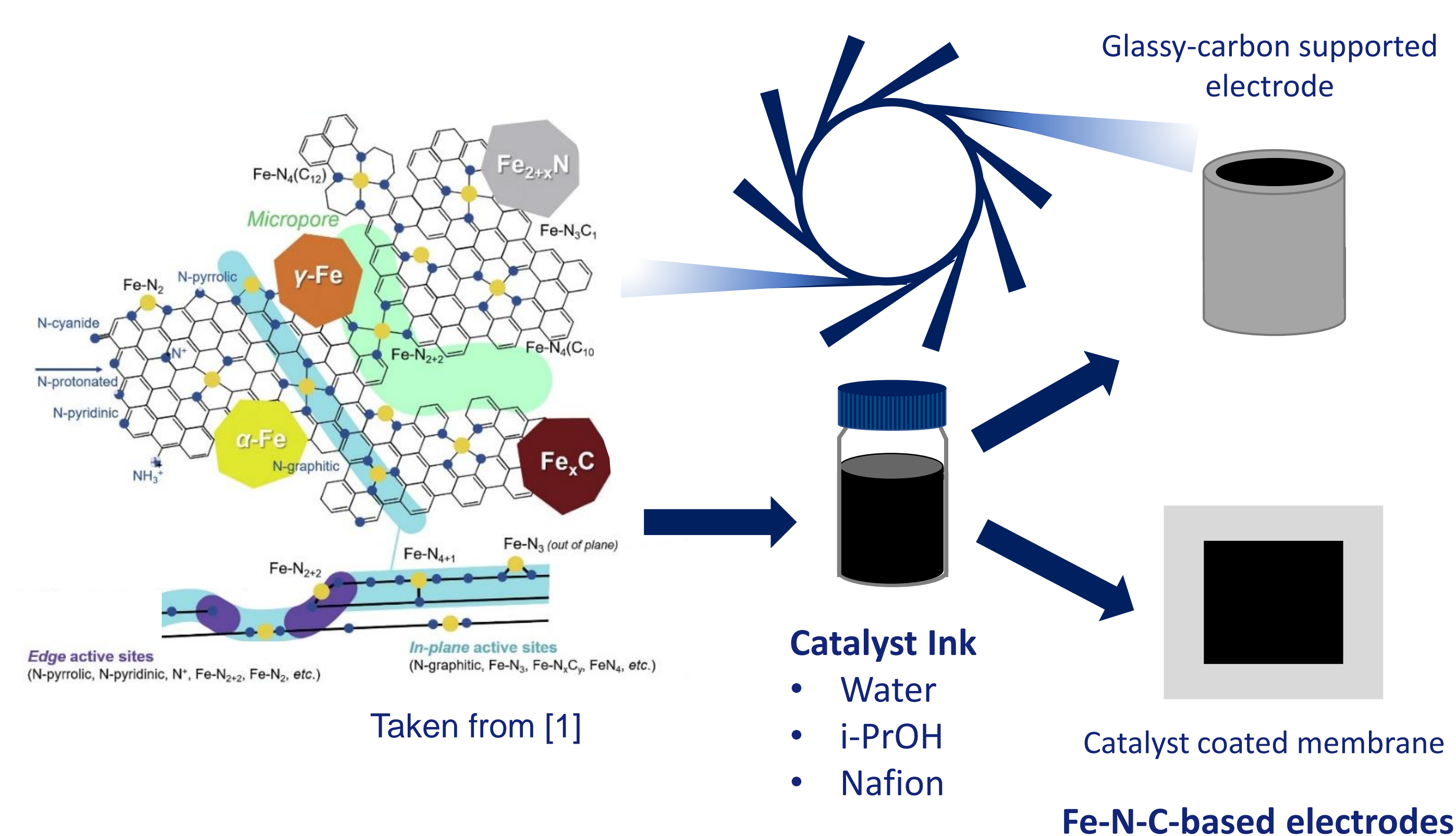
⁴ICGM, Univ. Montpellier, CNRS, ENSCM, 34293 Montpellier, France

viktoriia.saveleva@esrf.fr

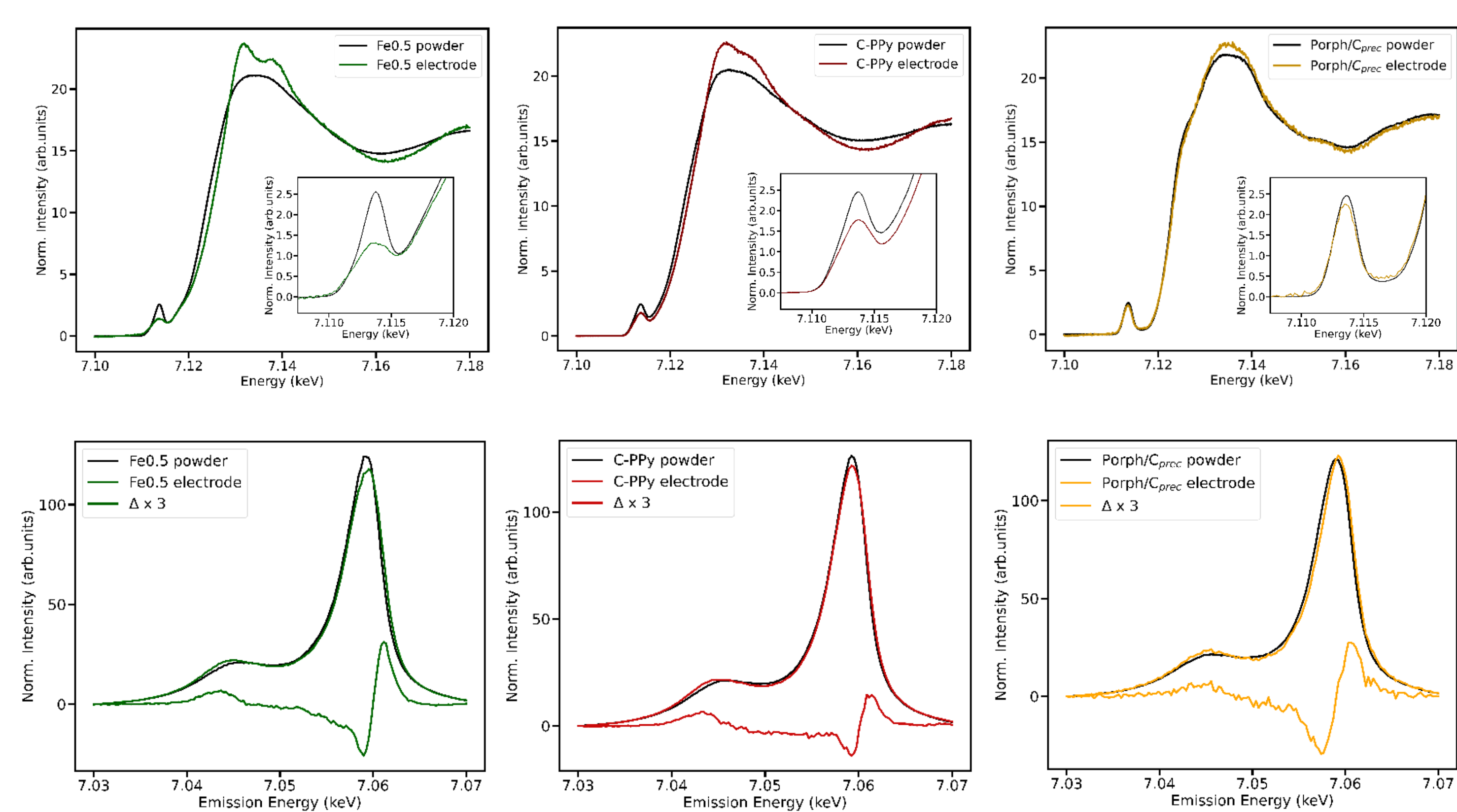
Evaluation of the electrocatalyst performance data includes an electrode preparation step. In this work, we compare the structural composition of several Fe-N-C materials prepared via different synthesis routes and used to electrocatalyze the oxygen reduction reaction in proton-exchange membrane fuel 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



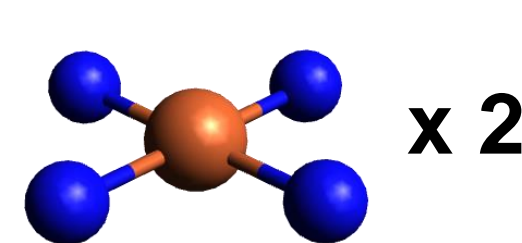
Powder vs Electrode: K β HERFD XANES & XES



Fe-N-C Catalysts Overview

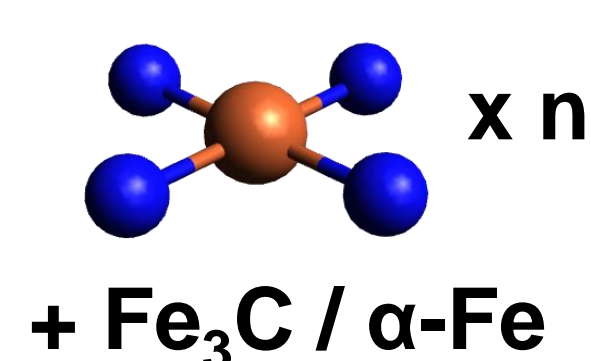
Fe0.5

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



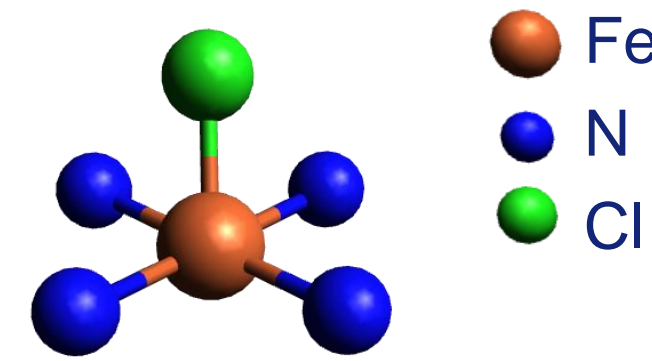
C-PPy

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

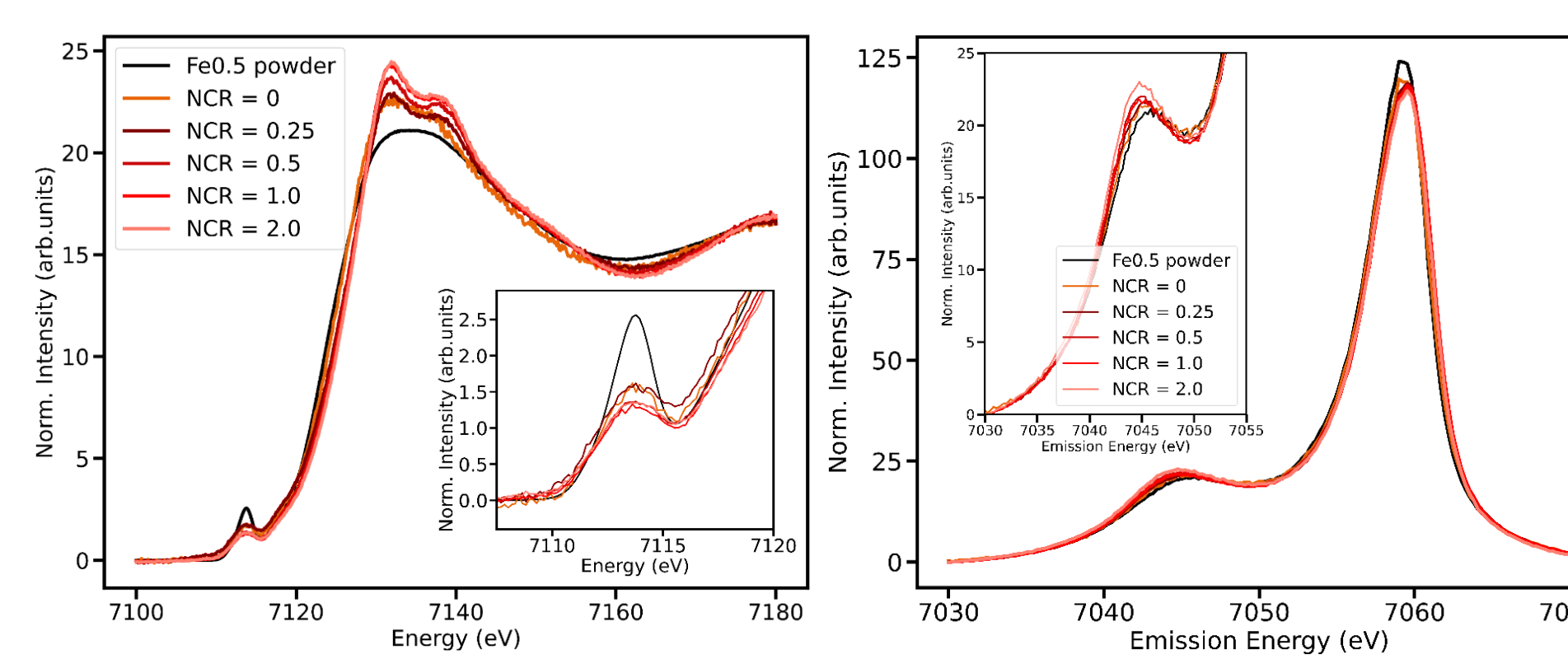


Porph/C_{prec}

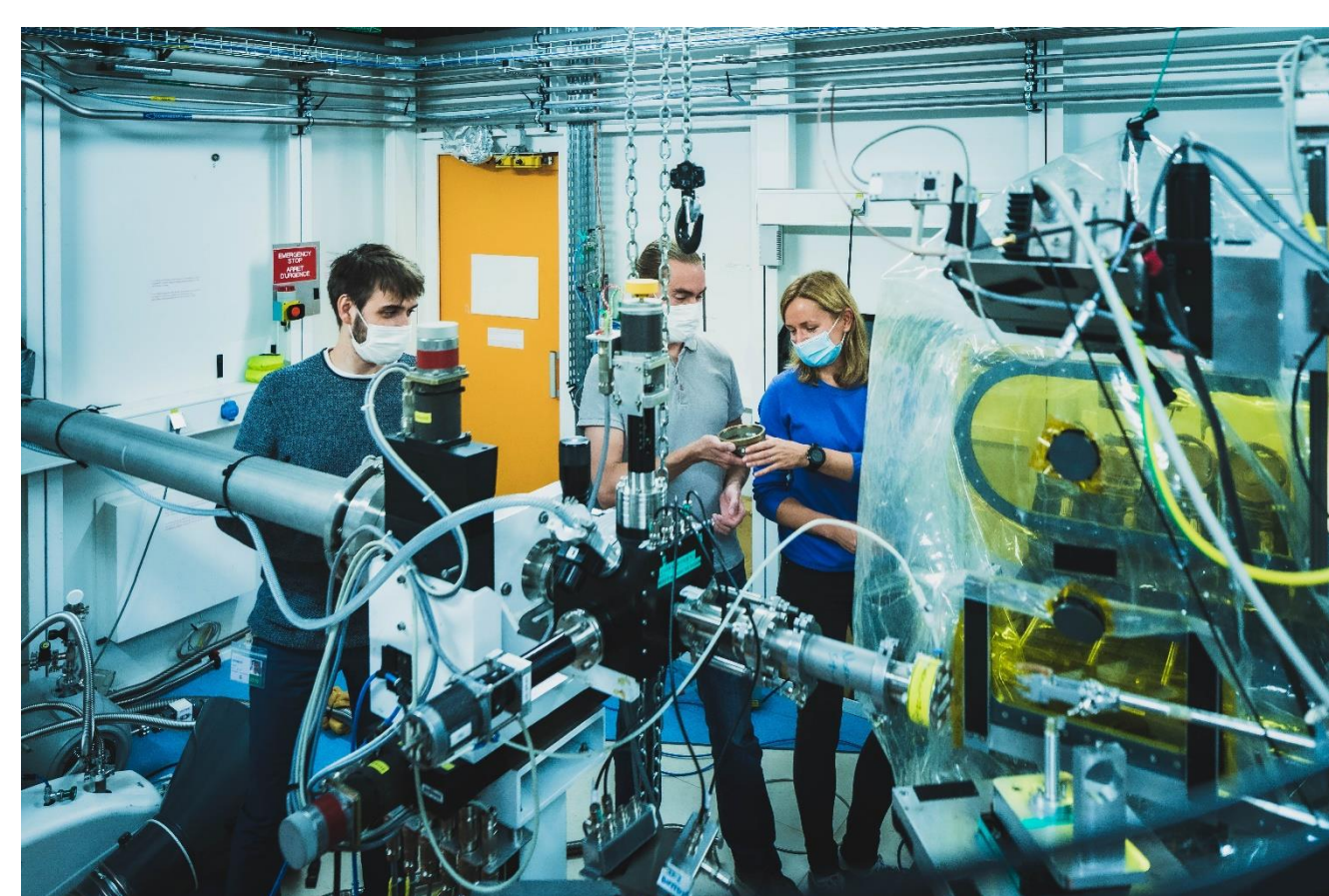
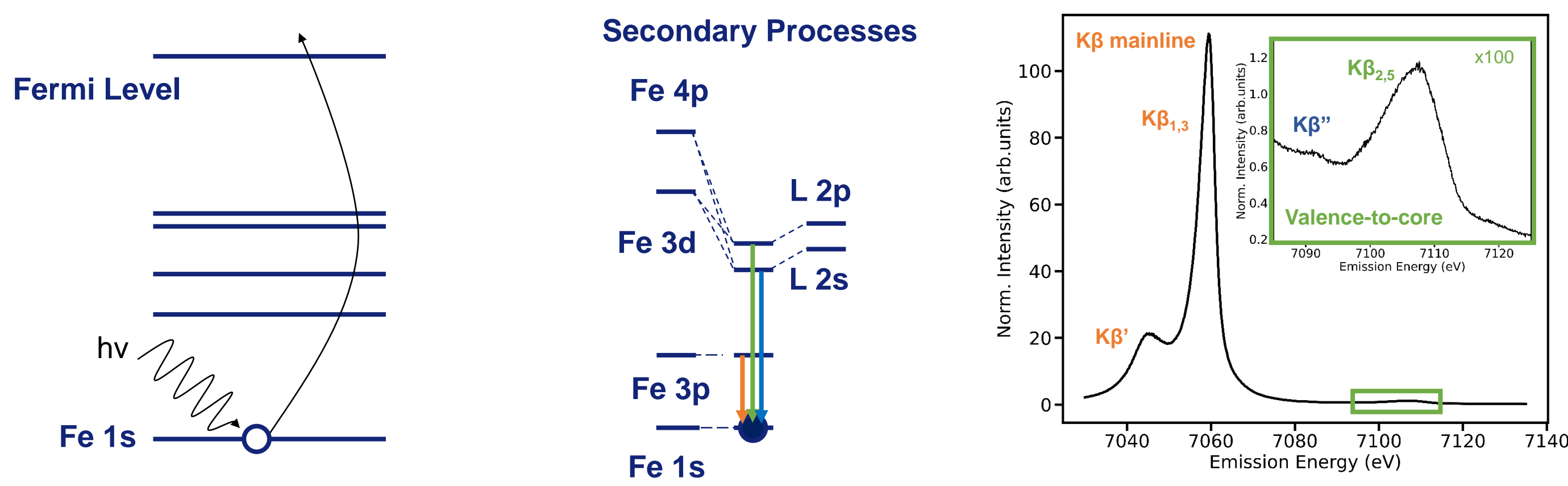
- Porphyrin-based
- FeTMPPCI / Carbon
- Reference [4]



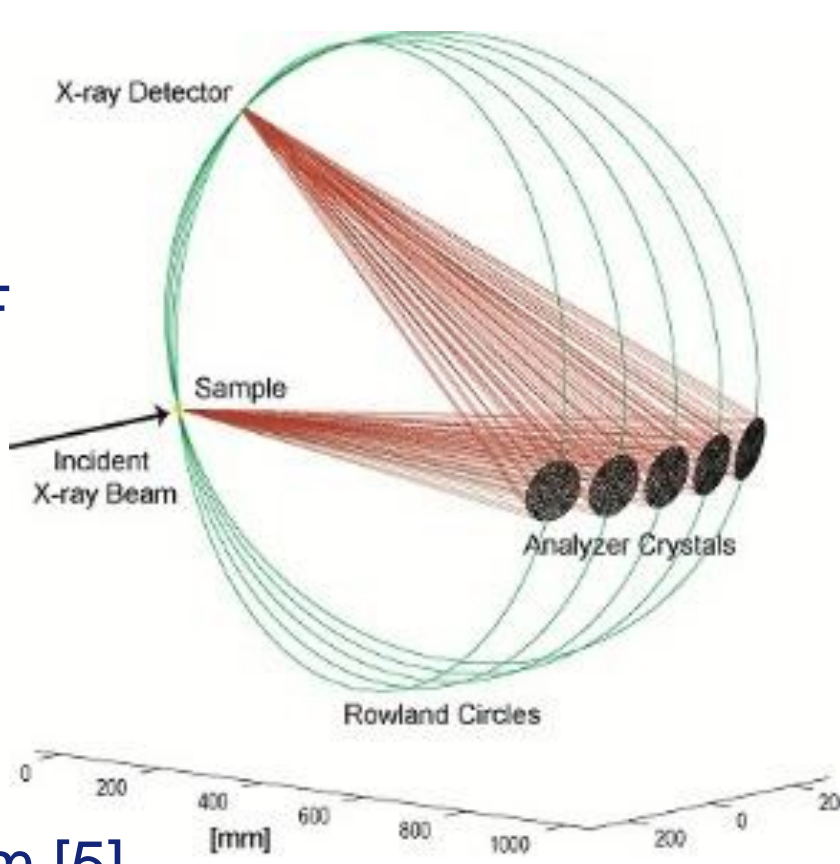
Role of Nafion ionomer



X-ray Absorption & Emission Spectroscopies



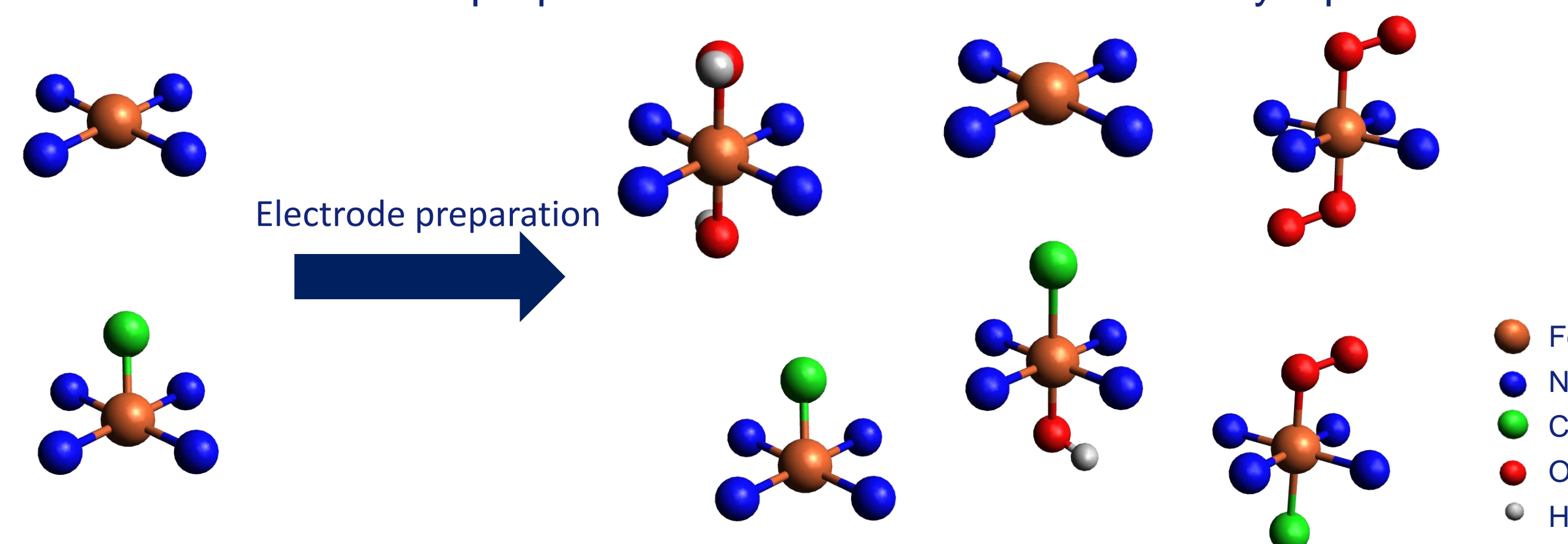
Beamline ID26, ESRF
DCM: 2 x Si 111
Analyzer Crystals:
5 x Ge 620



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

1. Asset, T. and Atanassov, P. Iron-Nitrogen-Carbon Catalysts for Proton Exchange Membrane Fuel Cells, *Joule*, **2020**, *4*, 33–44.
2. Kumar, K.; et al. Physical and Chemical Considerations for Improving Catalytic Activity and Stability of Non-Precious Metal Oxygen Reduction Reaction Catalysts, *ACS Catal.* **2018**, *8* (12), 11264–11276.
3. Scharf, J.; et al. Relation between half-cell and fuel cell activity and stability of FeNC catalysts for the oxygen reduction reaction, *SusMat* **2022**, *2* (5), 630–645.
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.
5. Ducotté, L.; et al. Mechanical aspects of the ID26 emission spectrometer II: improving stability for a large instrument by the use of multiple air pad supports, *Diamond Light Source Proceedings* **2010**, *1* (Issue MEDSI-6), 26.

Acknowledgment

We acknowledge the European Synchrotron Radiation Facility for provision of beamtime at ID26 beamline (DOI: 10.15151/ESRF-ES-799089889). P.T. and U.I.K. acknowledge financial support by the BMBF young researcher group FeNC-StRedO (funding number 03XP0092). F.M., F.J. and K.K. gratefully acknowledge financial support from the French National Research Agency through the ANIMA (grant number ANR-19-CE05-0039) and the DEEP (grant number ANR-21-CE05-0021) projects.