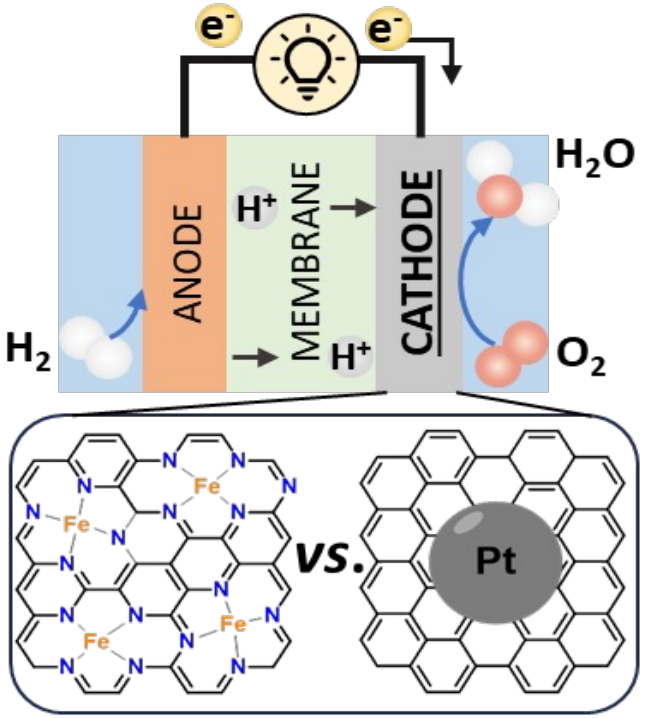
IMPERIAL

Carbon nanomaterials in hydrogen fuel cells

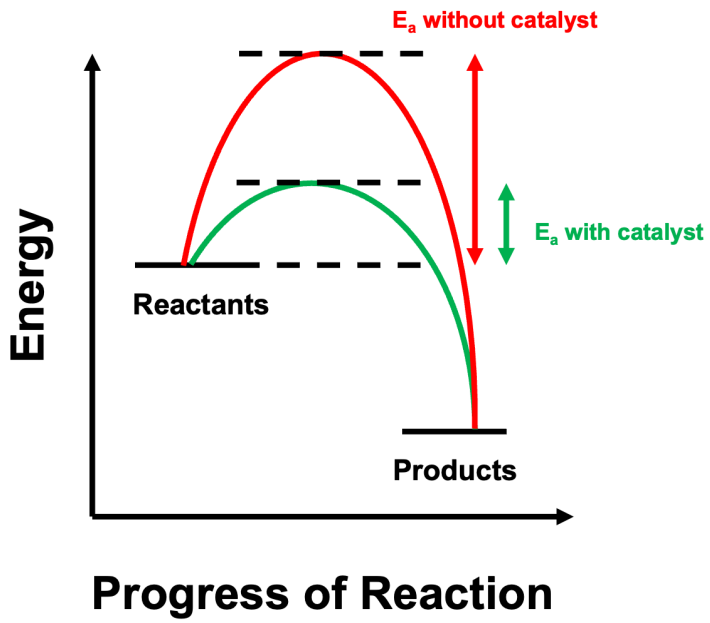
European School on Molecular Nanoscience

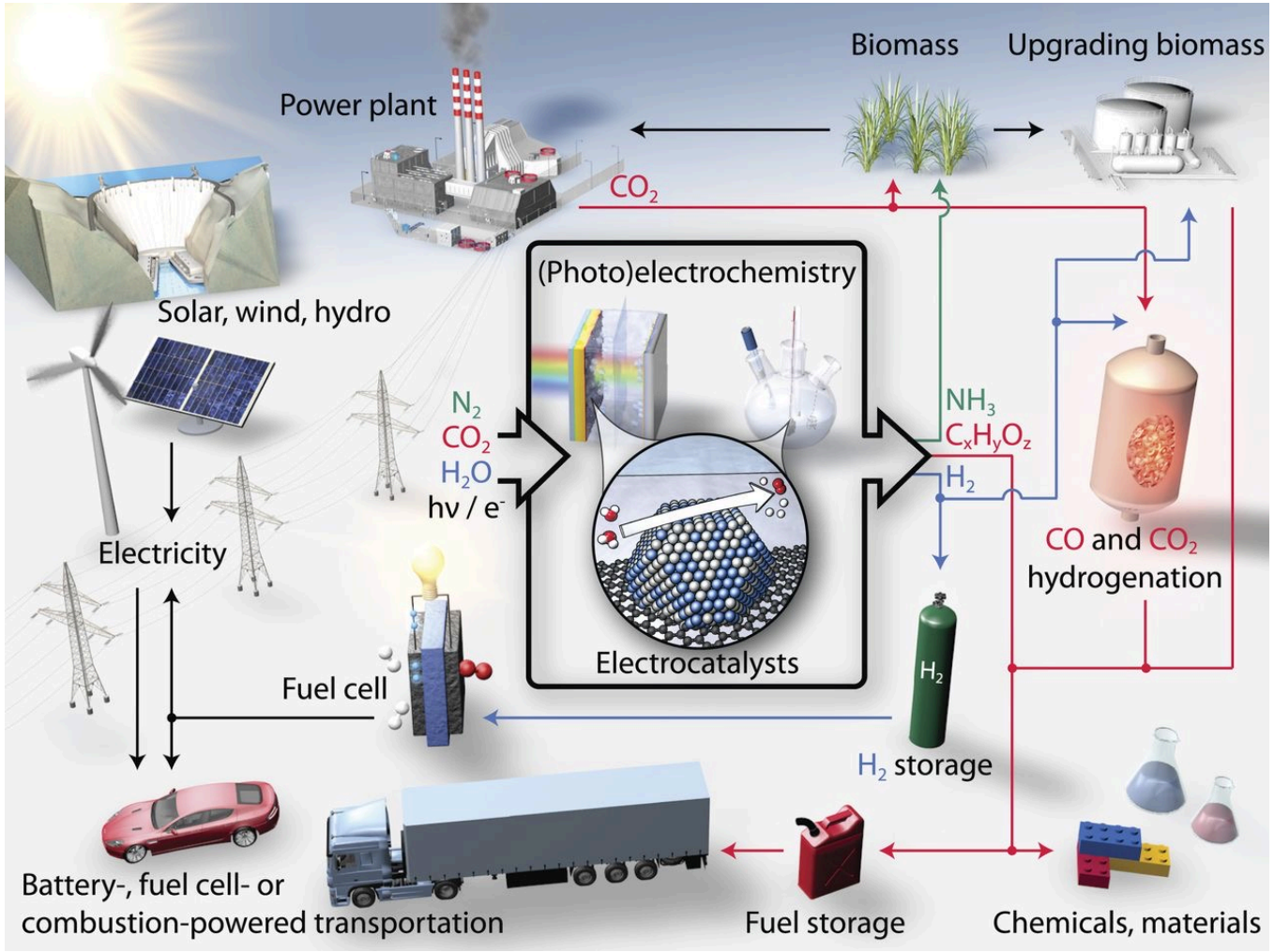


Jesús Barrio Hermida, ICRF
Chemical Engineering Department, Imperial College London
20/05/2025

Role of electrocatalysts in society

Electrocatalysis enables the decarbonization of the transport and chemical industry





Seh, …, Chorkendorff, Norskov, Jaramillo *Science* **2017**

Proton-Exchange Membrane Fuel Cells (PEMFCs)

$$\mathbf{O_2 + 2H_2 \rightarrow\ 2H_2O}$$

Converts chemical energy into electrical energy

Anode (HOR)

$$H_2 \rightarrow 2H^+ + 2e^-$$

Cathode (ORR)

$$O_2 + 4H^+ + 4e^- \rightarrow\ 2H_2O$$

Proton-Exchange Membrane Fuel Cells (PEMFCs)

$$\mathbf{O_2 + 2H_2 \rightarrow\ 2H_2O}$$

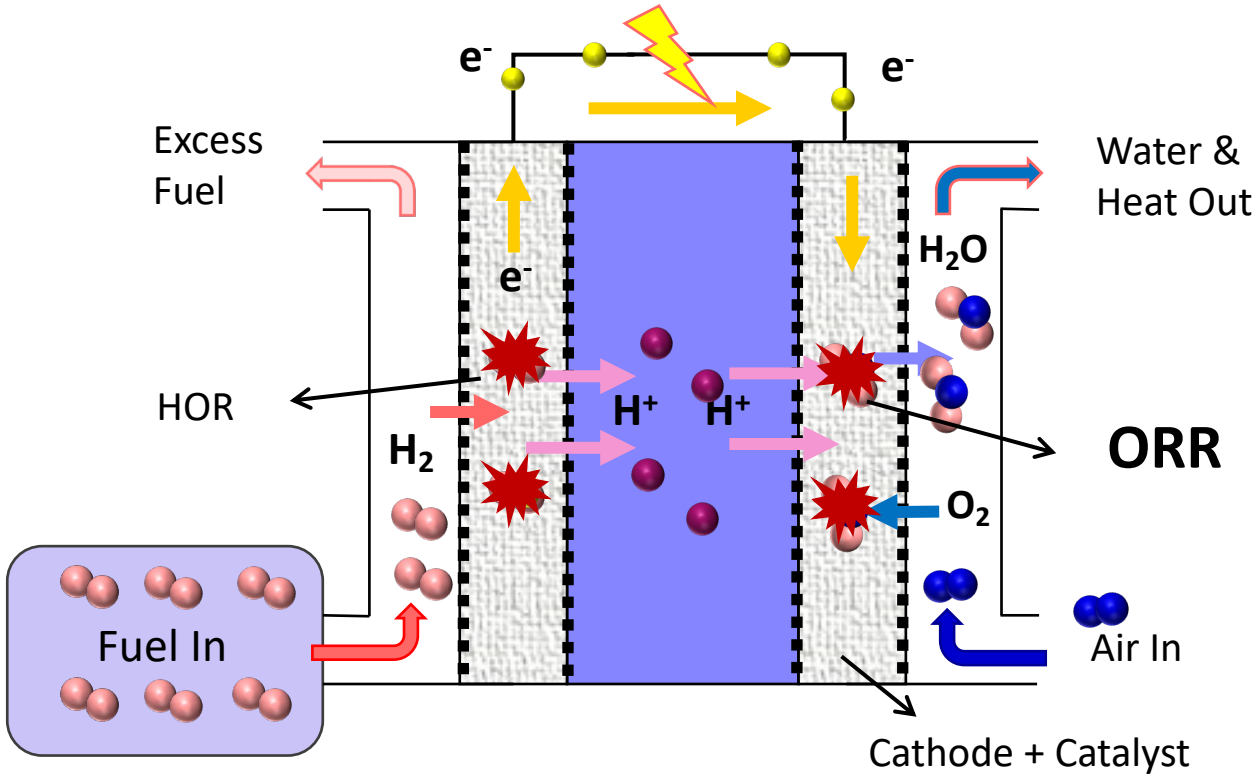
Converts chemical energy into electrical energy

Anode (HOR)

$$H_2 \rightarrow 2H^+ + 2e^-$$

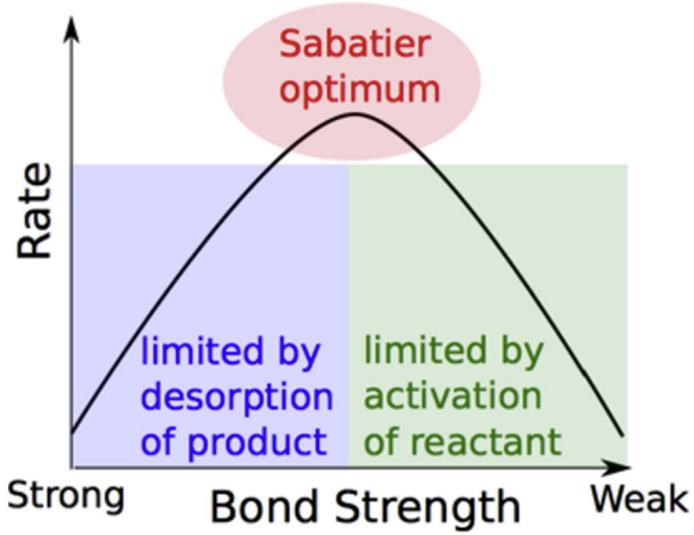
Cathode (ORR)

$$O_2 + 4H^+ + 4e^- \rightarrow\ 2H_2O$$



What does a good catalyst look like?

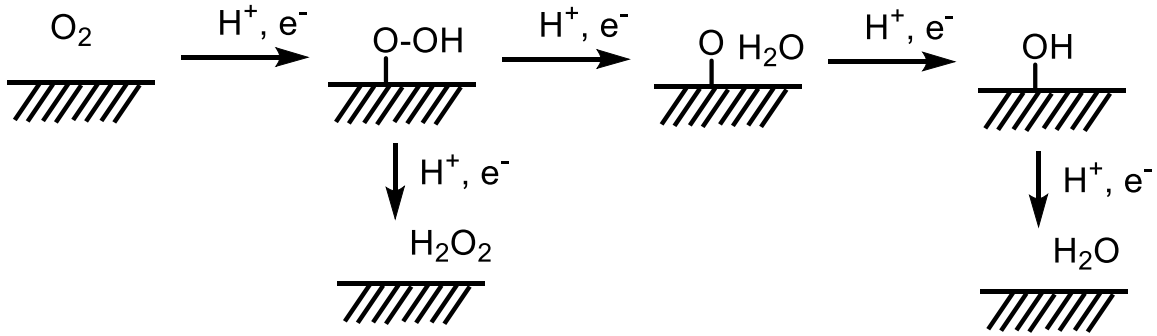
A "**Volcano Plot**" (from the Sabatier principle), shows the catalytic activity as a function of the binding energy of an intermediate



Sabatier Principle:

The most optimal catalyst should exhibit moderate binding to the reaction intermediates (neither too strong nor too weak)

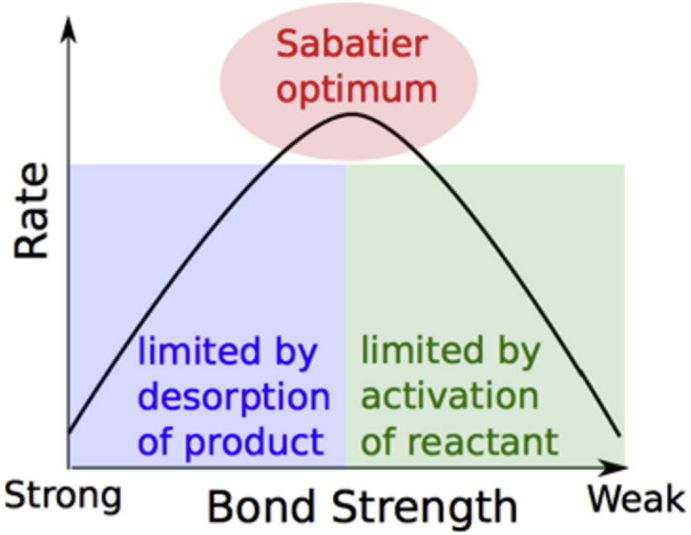
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \; E^0 \; [V \; vs \; RHE] = 1.23$$

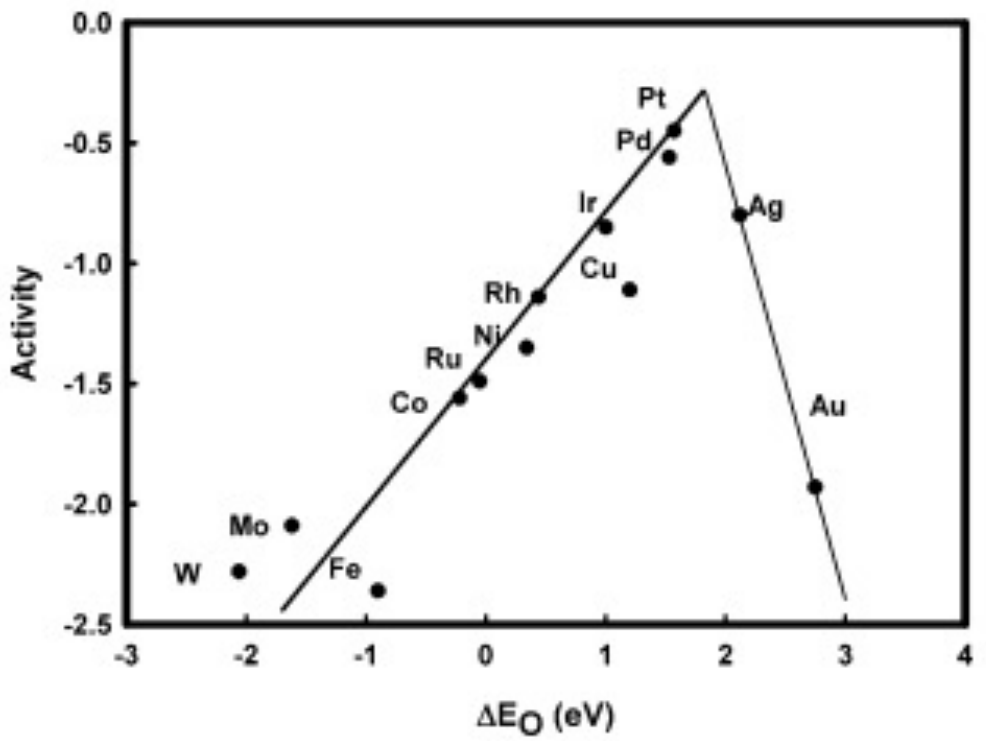


Medford, Vojvodic, Hummelshoj, Voss, Pedersen, Studt, Bligaard, Nilsson, Norskov, *J. Catal* **2015**, 328, 36-42

What does a good catalyst look like?

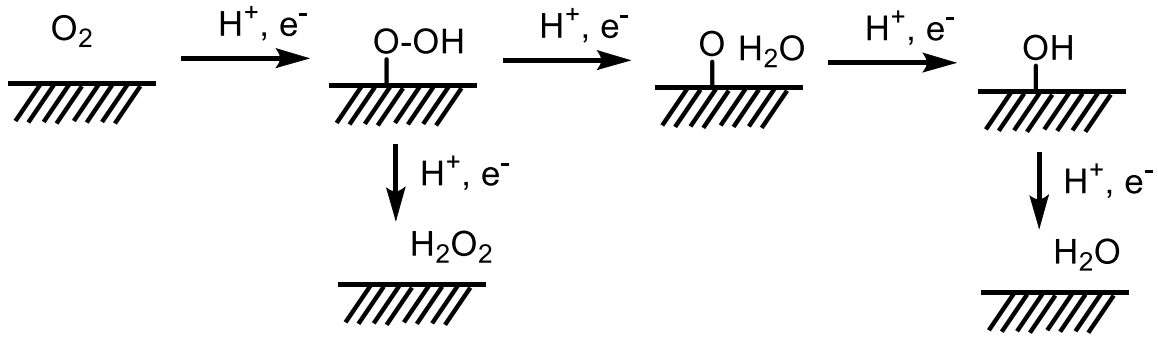
A "**Volcano Plot**" (from the Sabatier principle), shows the catalytic activity as a function of the binding energy of an intermediate





Sabatier Principle:

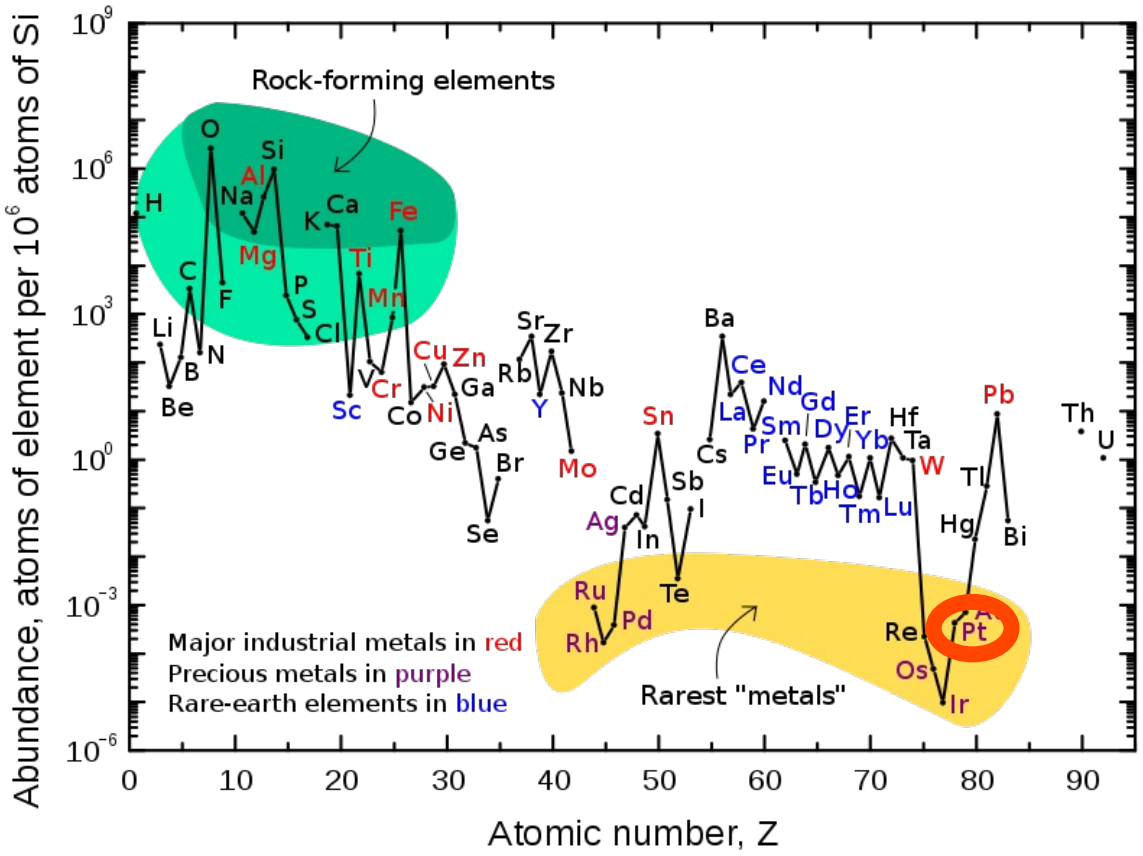
The most optimal catalyst should exhibit moderate binding to the reaction intermediates (neither too strong nor too weak)



Medford, Vojvodic, Hummelshoj, Voss, Pedersen, Studt, Bligaard, Nilsson, Norskov, *J. Catal* **2015**, 328, 36-42

About Platinum

Platinum is very expensive and not sustainable

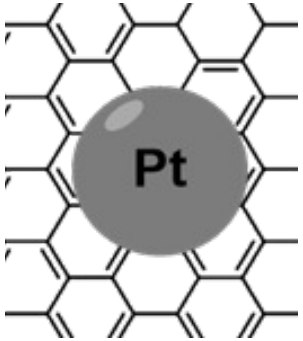


Reich, Vasconcelos, *Elements.* **2015**, 11, 305-310

Vesborg, Jaramillo, *RSC Adv.* **2012**, 2, 7933-7947

The catalysts account for 41% of the cost of a fuel cell

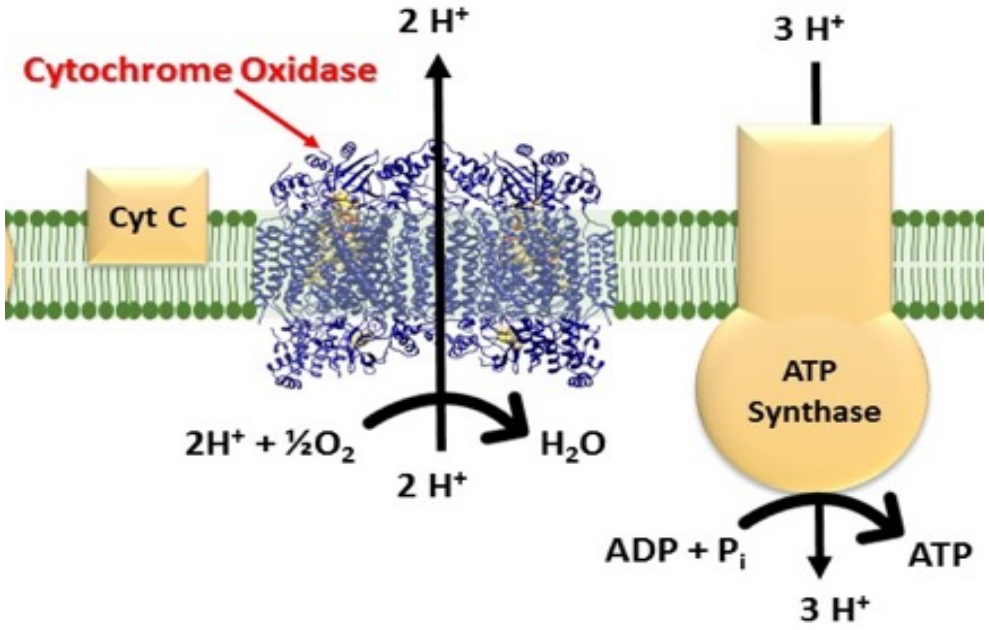
Most of this cost comes from the platinum contained in both the oxygen reduction and hydrogen oxidation catalyst



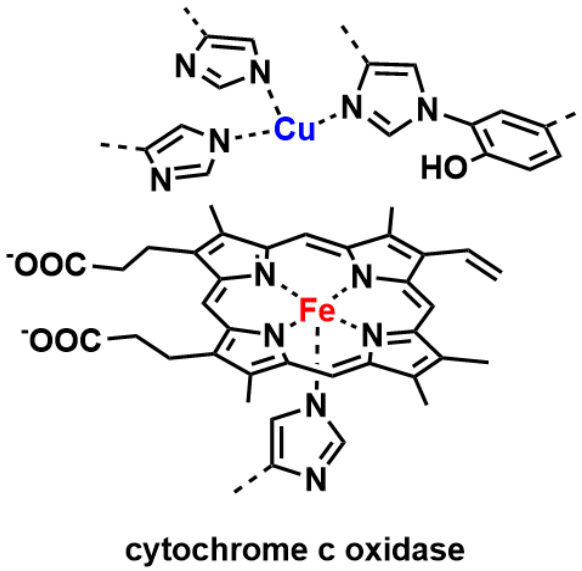
Thompson, Papageorgopoulos et al., *J. Power Sources*, 2018

Platinum-free materials: Bio-inspired catalysts, the case of Cytochrome C

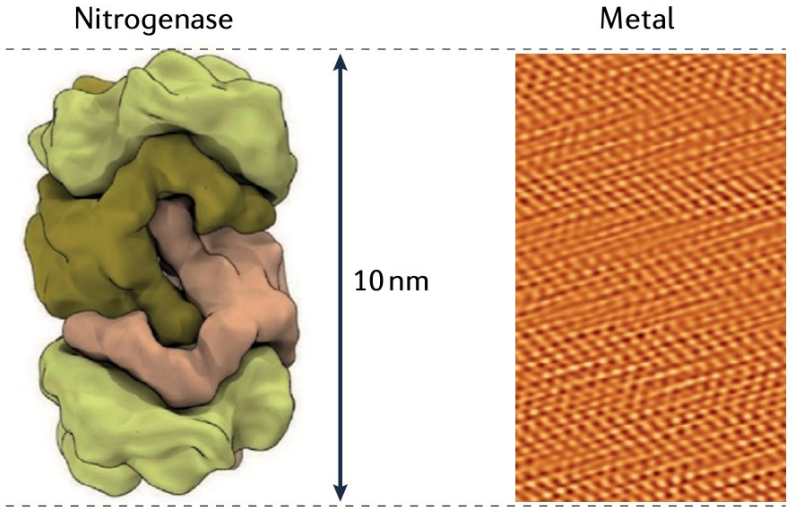
The process of cellular respiration involves the red-ox reaction of hydrogen and oxygen to water.
In the cell, this step is carried out by the cytochrome oxidase



Pedersen, Barrio, …, Stephens. *Adv. Energy Mater.* **2022**

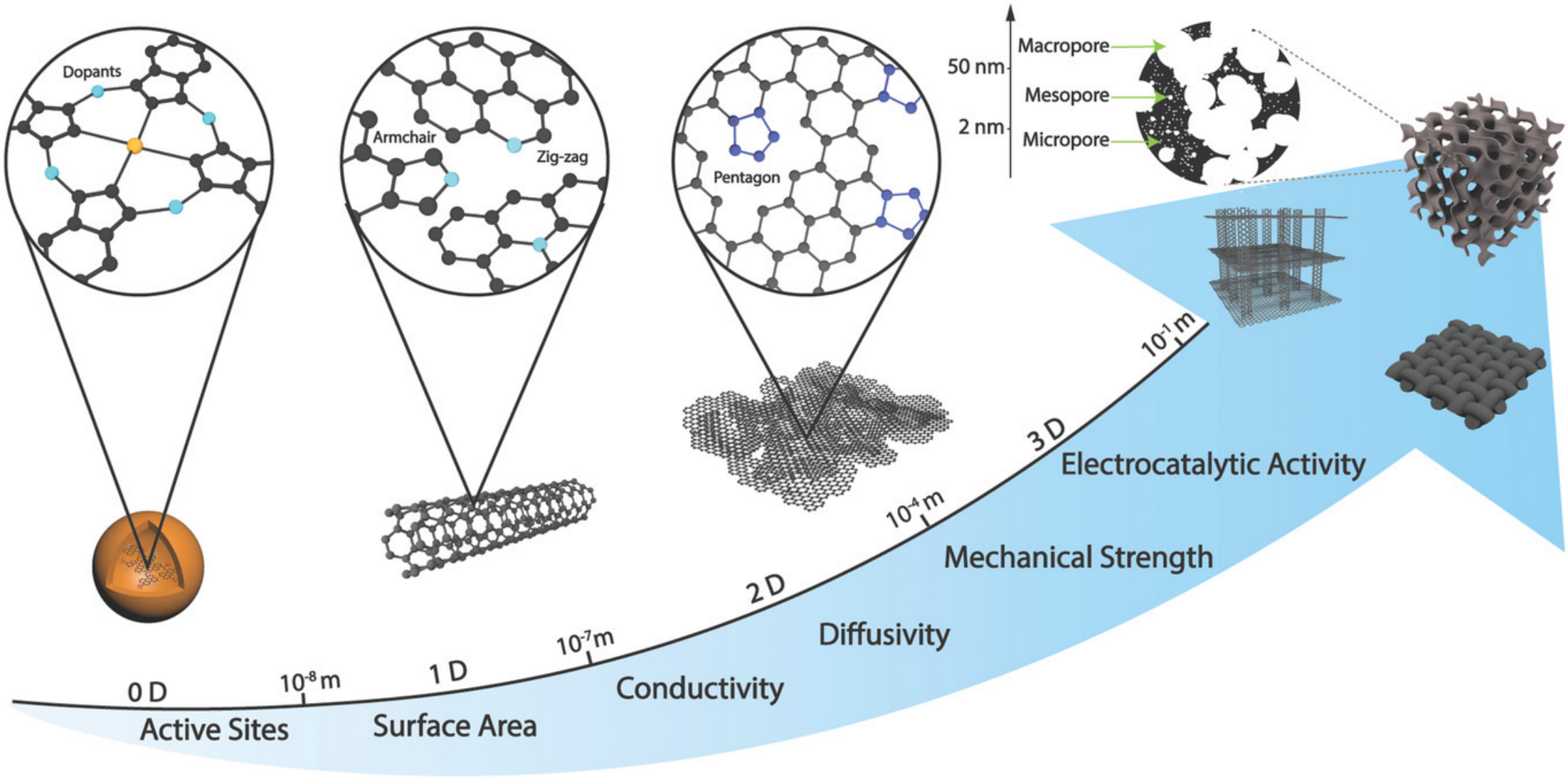


cytochrome c oxidase



Westhead, Barrio,…, Stephens *Nat. Chem. Rev*. **2023**

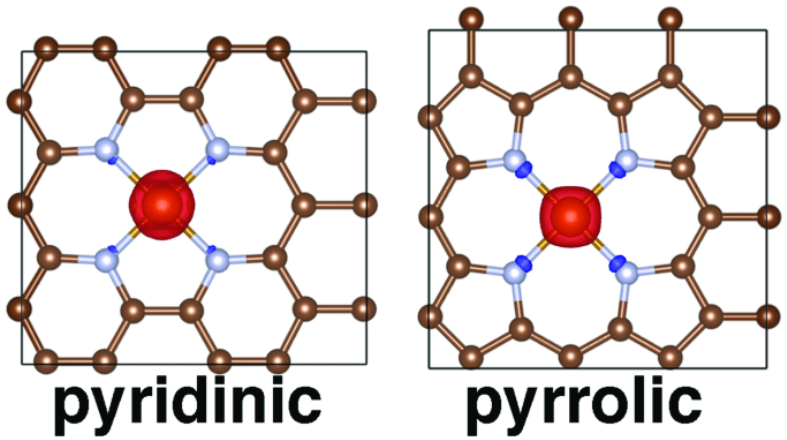
Carbon supported single site catalysts

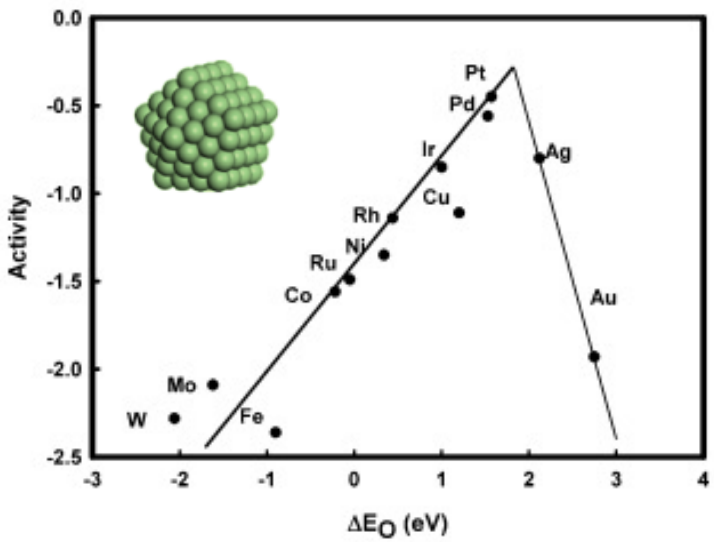


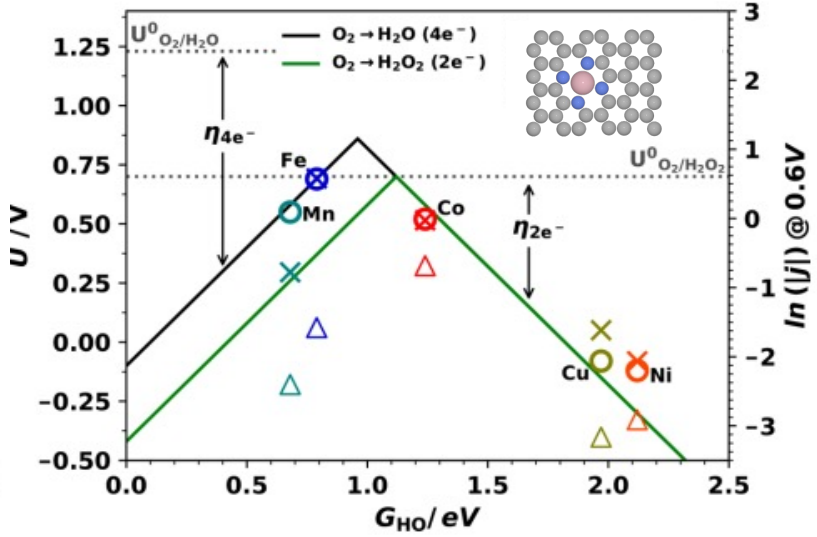
Jorge, Jervis, Prakash, Qiao, Feng, Ngoc Tran, Titirici. *Adv. Energy Mater.* **2020**, 10, 1902494

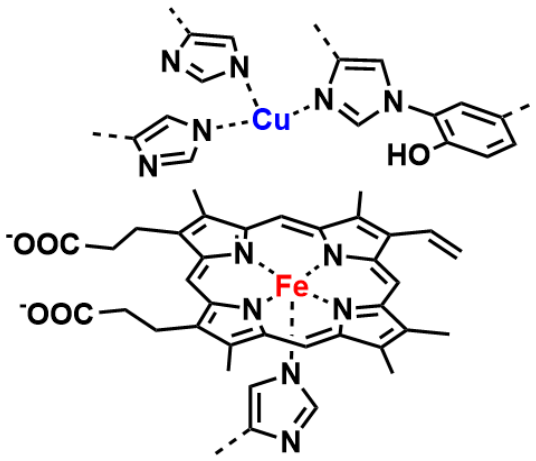
Platinum-free catalysts: Fe-N-C materials (FeN_4)

The FeN_4 site

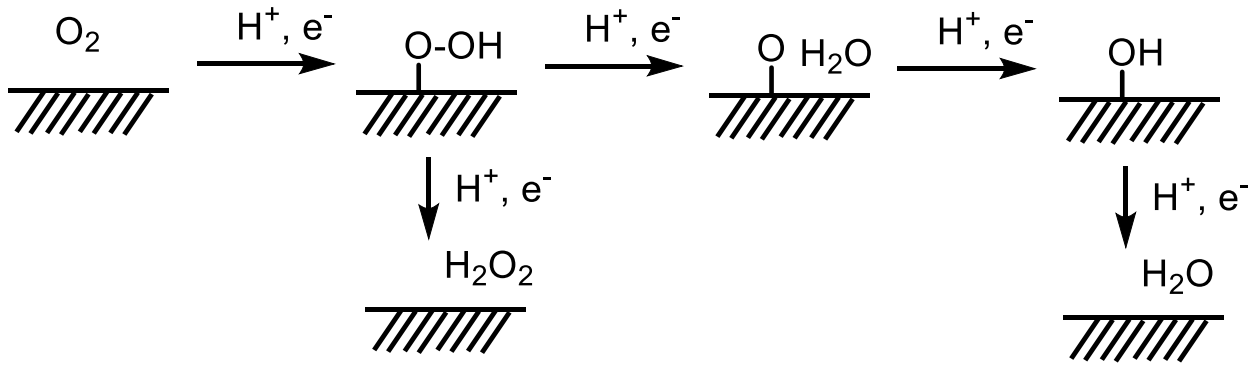






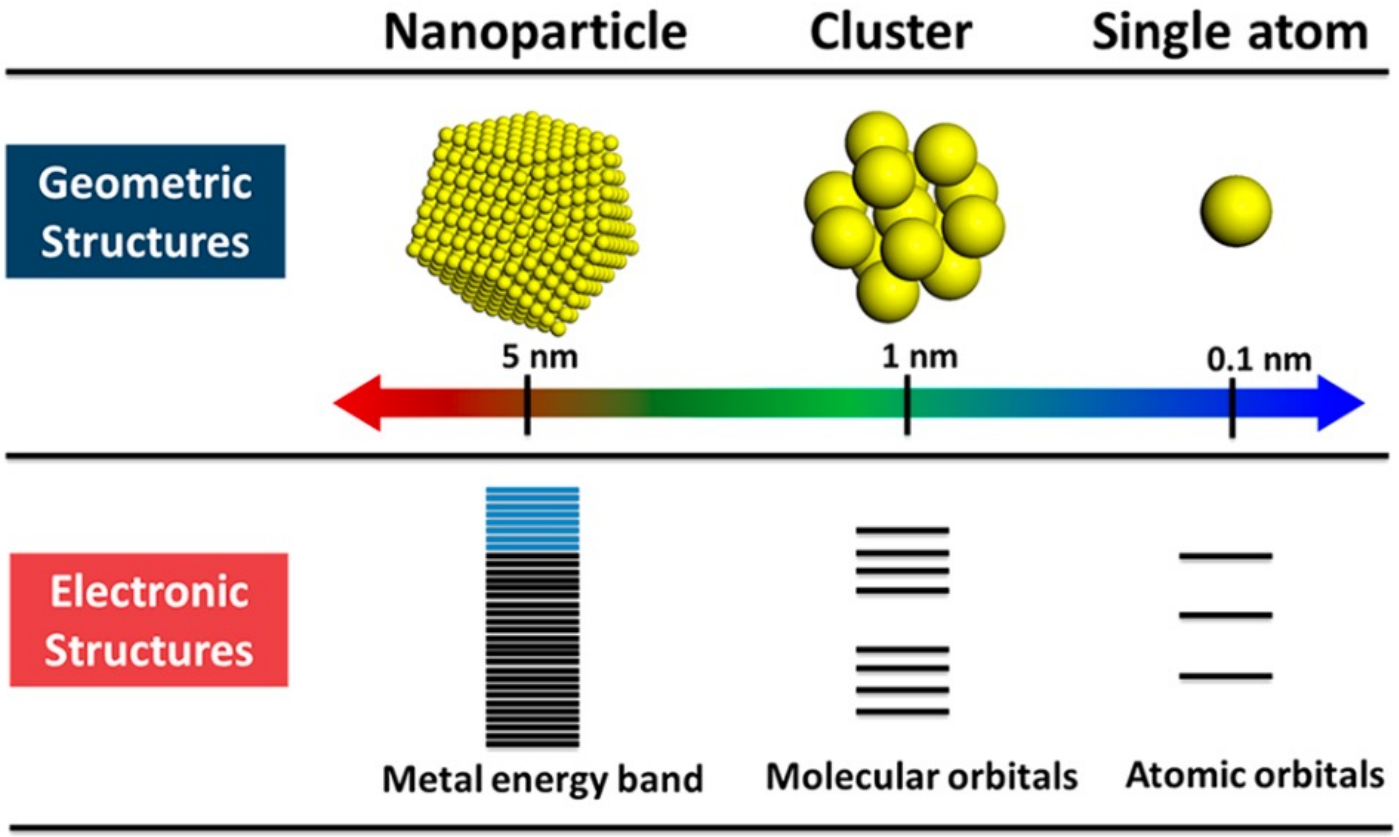


cytochrome c oxidase

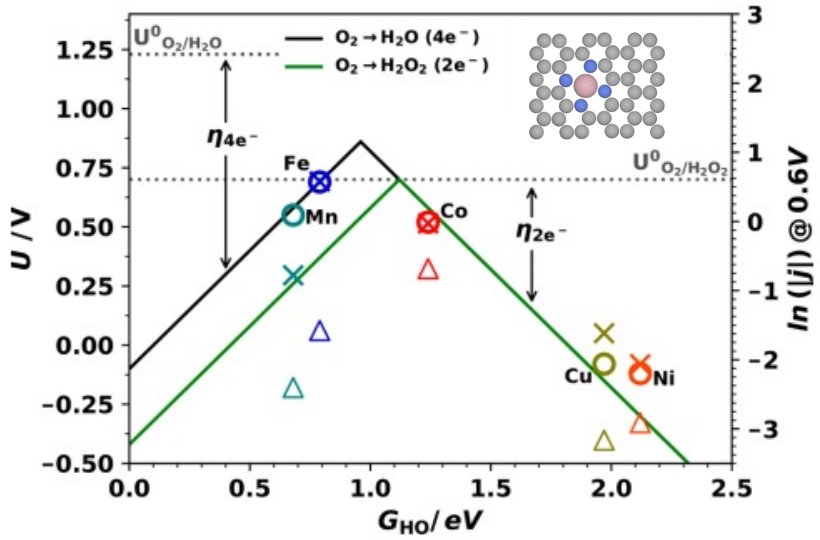


Sun, Silvioli, Sahraie, Ju, Li, Zitolo, Li, Bagger, Arnarson, Wang, Moeller, Bernsmeier, Rossmeisl, Jaouen, Strasser. *J. Am. Chem. Soc.* **2019,** 141, 12372

Platinum-free catalysts: Fe-N-C materials (FeN_4)



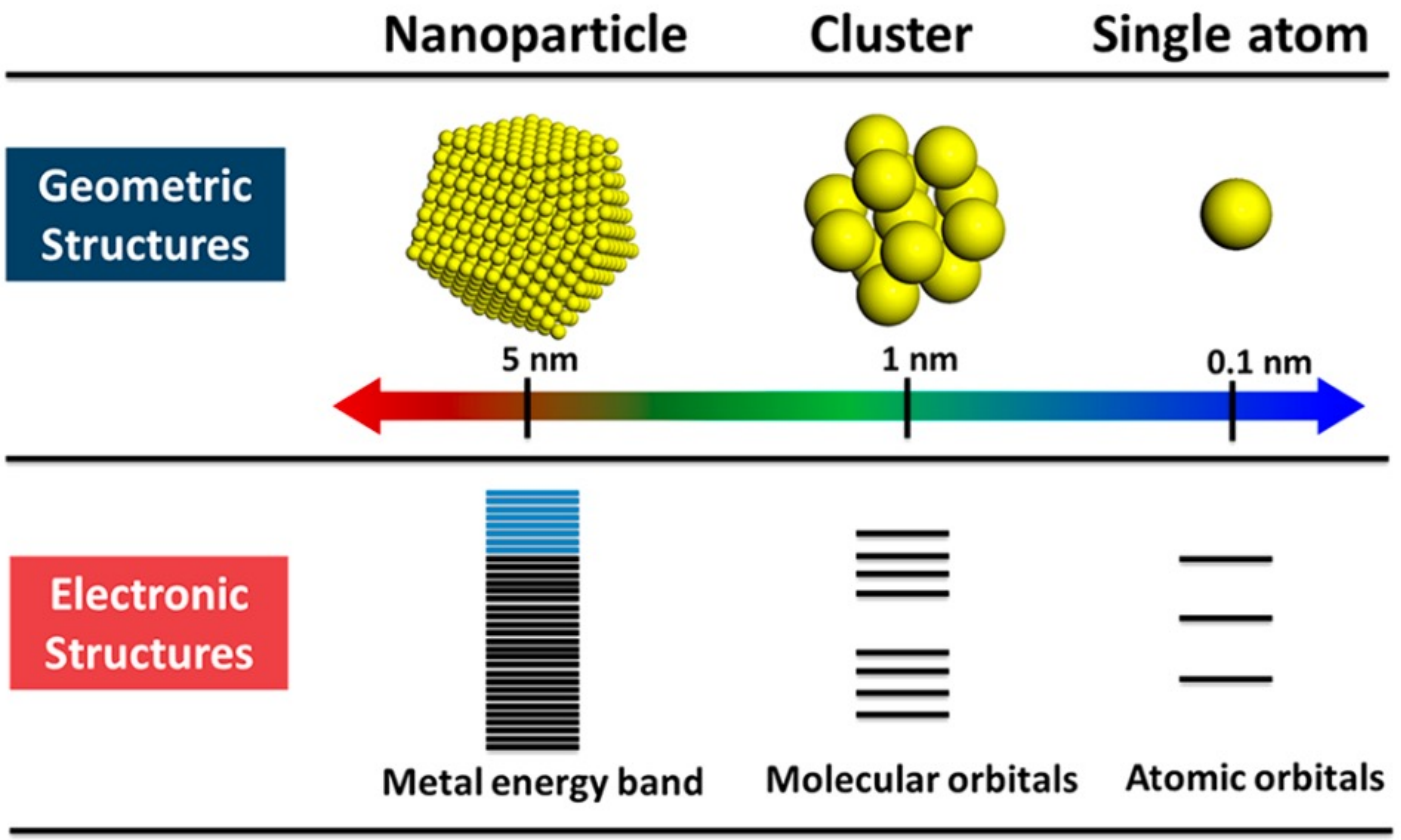
Liu, Corma. *Chem. Rev.* **2018,** 118, 4981-5079



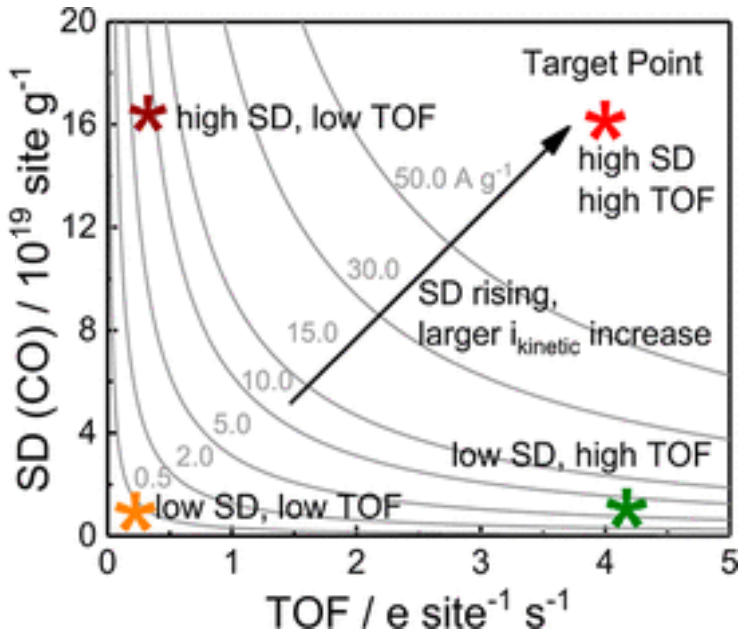
- Active site number (sites g^{-1})
- Intrinsic activity (TOF)
- Active site utilization
- Electronic conductivity

Sun, Silvioli, Sahraie, Ju, Li, Zitolo, Li, Bagger, Arnarson, Wang, Moeller, Bernsmeier, Rossmeisl, Jaouen, Strasser. *J. Am. Chem. Soc.* **2019,** 141, 12372

Platinum-free catalysts: Fe-N-C materials (FeN_4)



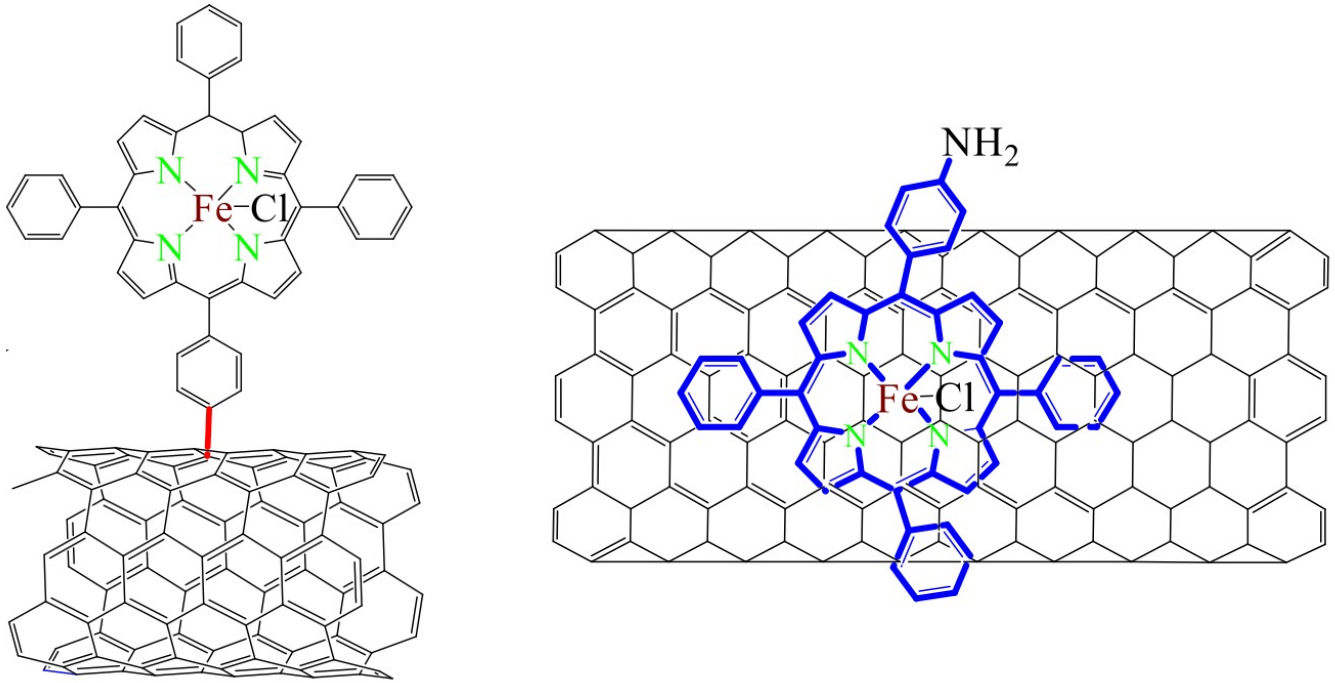
Liu, Corma. *Chem. Rev.* **2018,** 118, 4981-5079



- Active site number (sites g^{-1})
- Intrinsic activity (TOF)
- Active site utilization
- Electronic conductivity

Luo, Wagner, Ju, Primbs, Li, Wang, Kramm, Strasser. *J. Am. Chem. Soc.* **2022**

Platinum-free catalysts: M-N-C materials



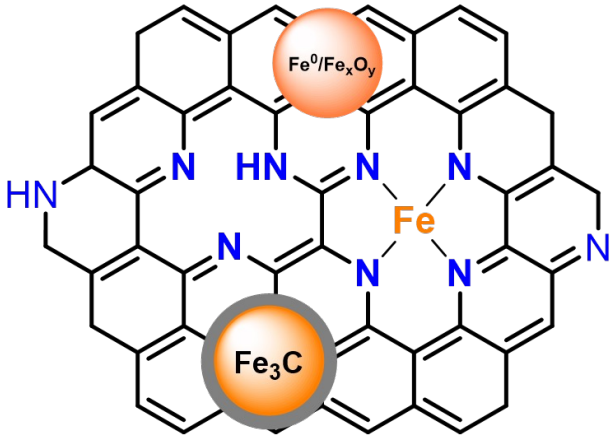
- **Unstable in the acidic media of PEMFC**

Li, Xu, Pedersen, Wang, Zhang, Feng, Luo, Titirici, Jones. Adv. Funct. Mater. 2024, 34, 2311086

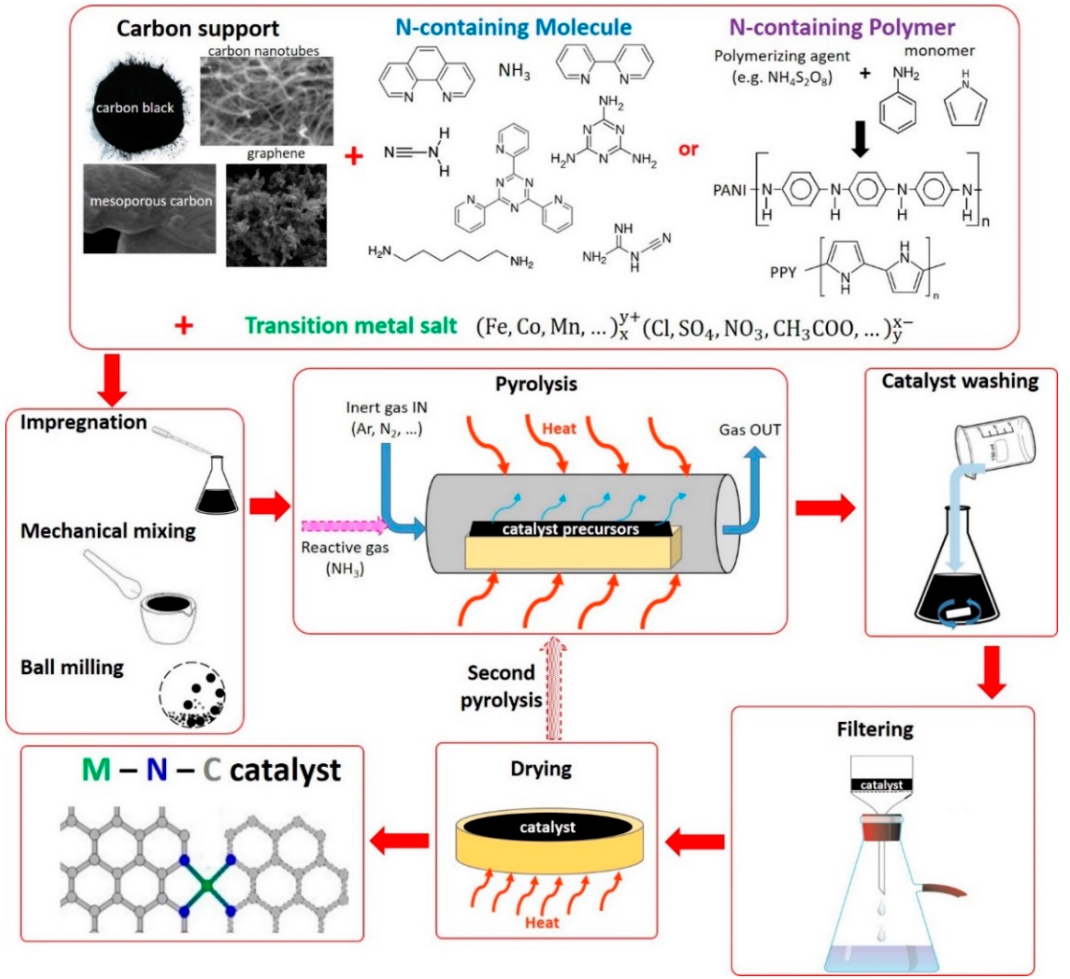
Platinum-free catalysts: M-N-C materials

Fe + N + C

High temperature



- **Unstable**
- **Mix of FeN_x and inactive aggregates**
- **Inaccessible sites**

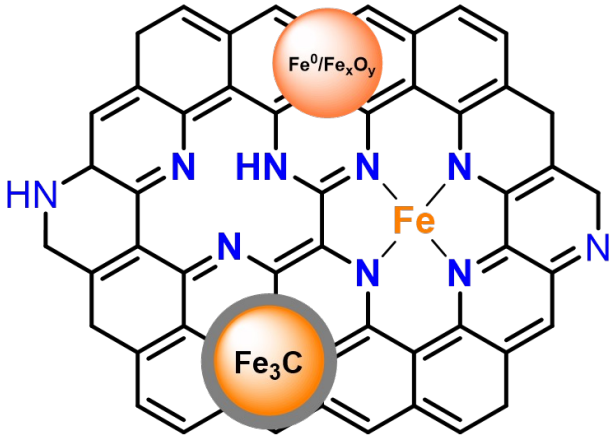


Osmieri, *ChemEngineering* **2019**, *3*(1), 16

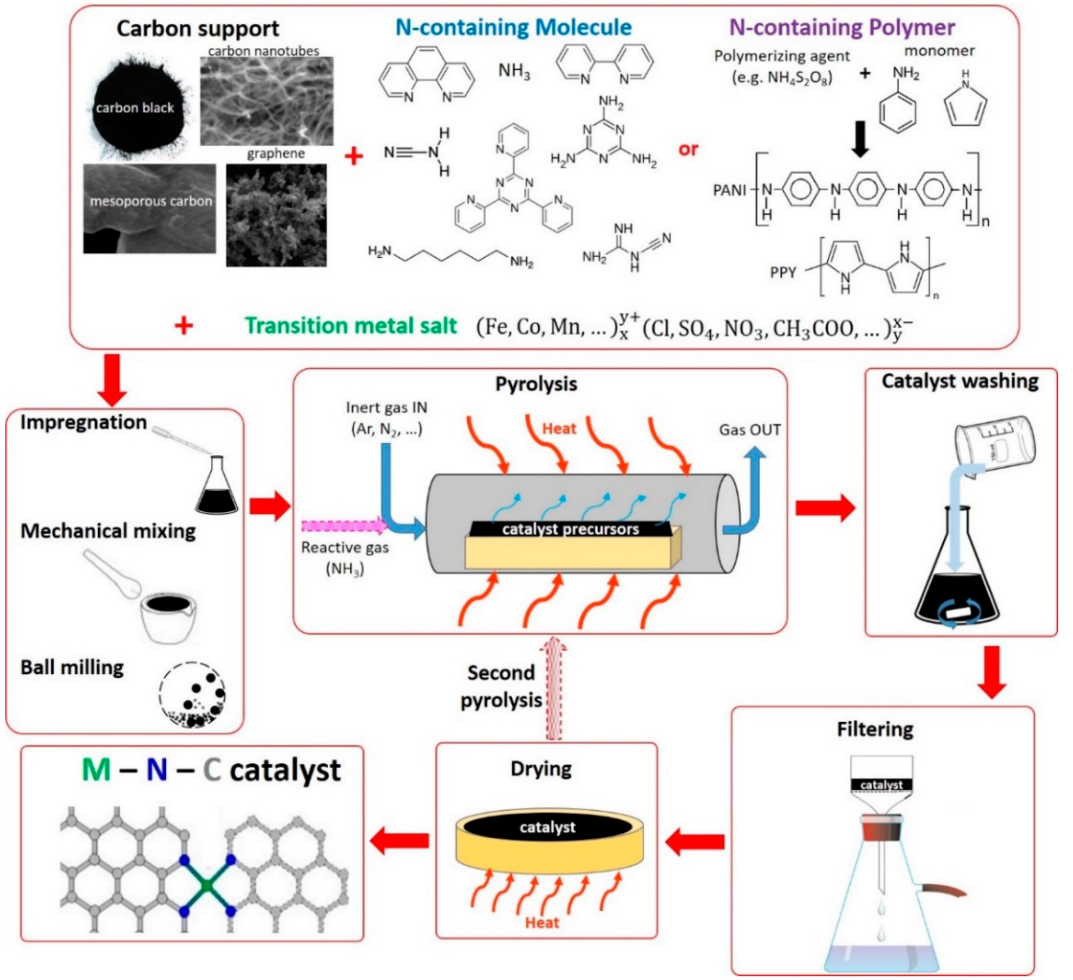
Platinum-free catalysts: M-N-C materials

Fe + N + C

High temperature



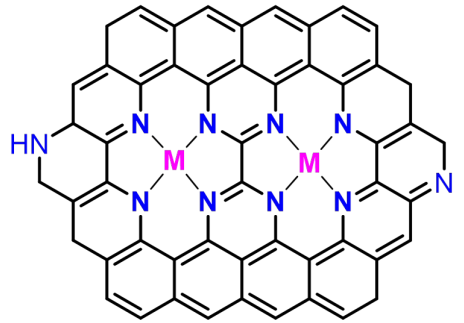
- **Unstable**
- **Mix of FeN_x and inactive aggregates**
- **Inaccessible sites**



Osmieri, *ChemEngineering* **2019**, *3*(1), 16

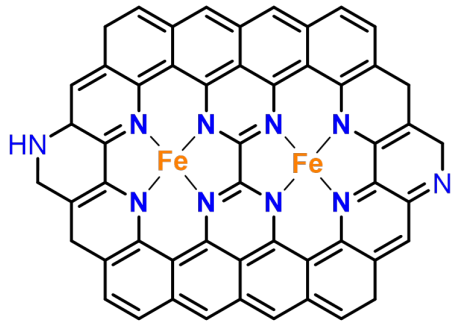
M + N + C

(M = Zn^{2+}, Mg^{2+})



Low temperature

Fe

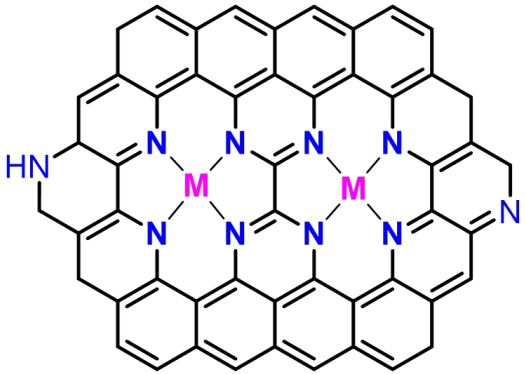


- **Active site template**
- **High FeN_x density**

Decoupled synthesis of M-N-C materials

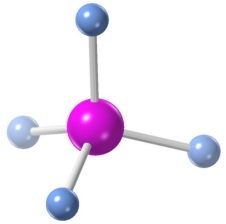
M + N + C

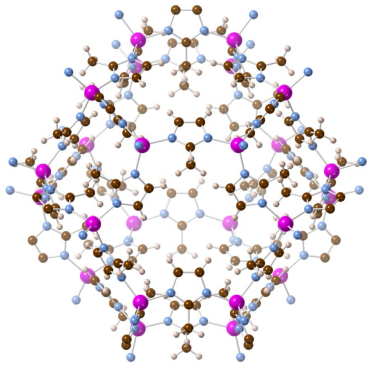
(M = Zn^{2+}, Mg^{2+})



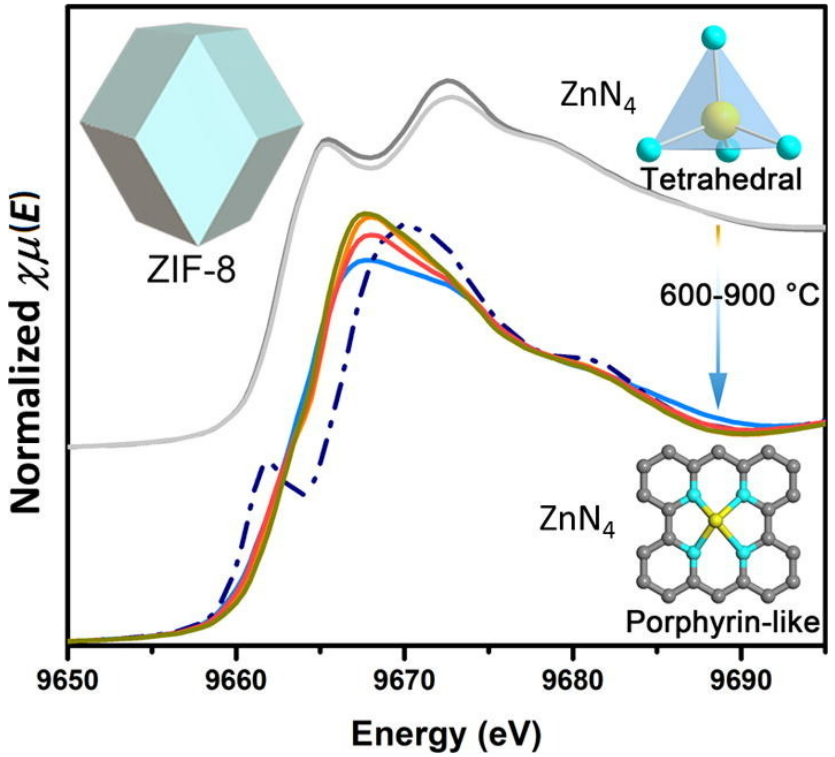
Zeolitic Imidazole Framework-8 (ZIF-8)

Zn-N_4



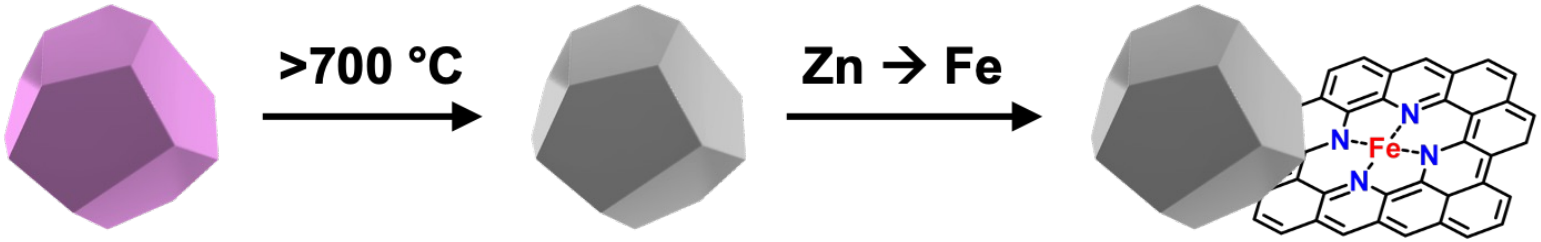


Yaghi. *PNAS* **2006**
Chen. *Angew. Chem. Int. Ed.* **2006**



Waterhouse. *Sci. Bull.* **2020**

ZIF-8 → Zn-NC → Fe-NC

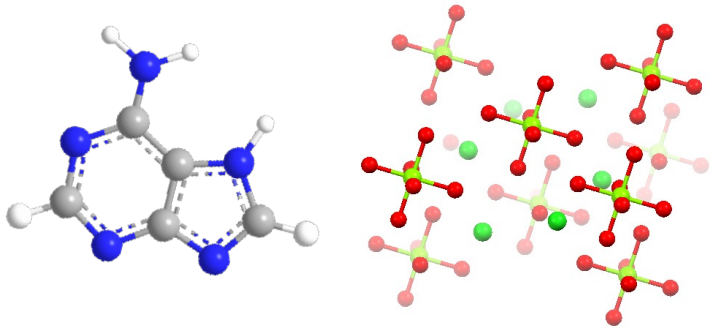


Jiao, …Jaouen, Myers. *Nat. Mater.* **2021**
Mehmood, Gong,…Kucernak. *Nat Catal.* **2022**
Castells-Gil, Zhu, Itskou, Wolpert, Hunter, Tidey, Pedersen, Solvay, Tyrell, Petit, Barrio. **2025** *In preparation*

High FeN_x density in microporous N-doped carbon

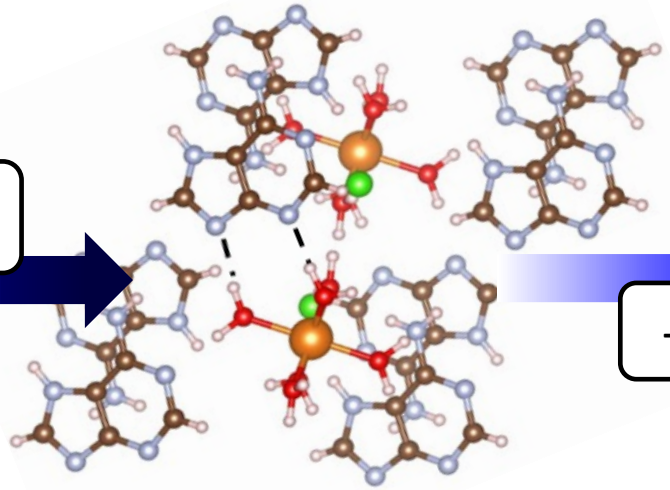
Decoupled synthesis of M-N-C materials

$MgCl_2.6H_2O$ *template*

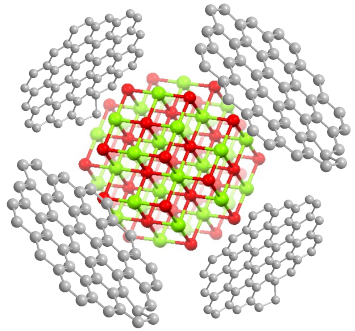


Self-assembly

m.p. 117 C

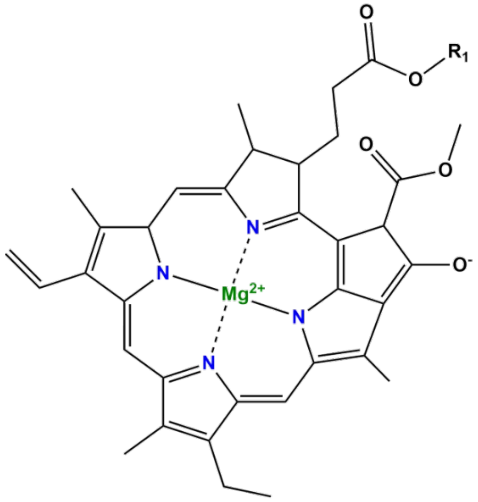


- H_2O

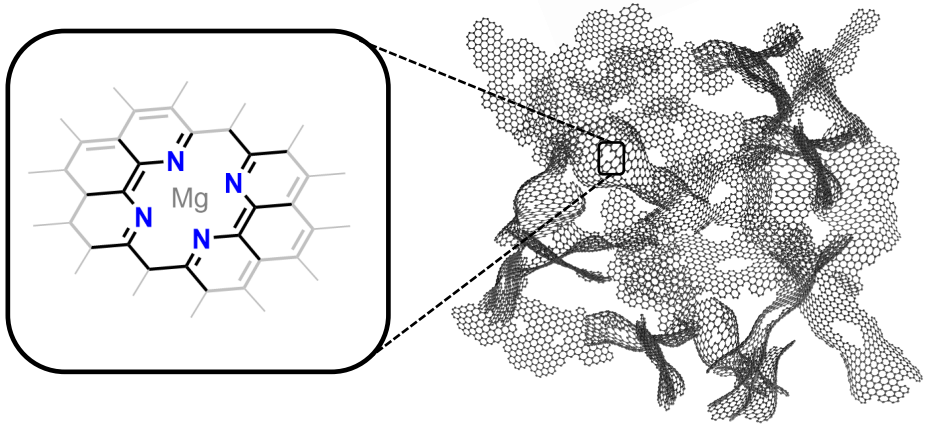


MgO

Acid wash



Chlorophyll a

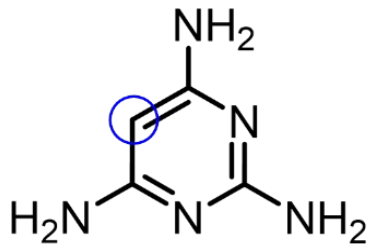


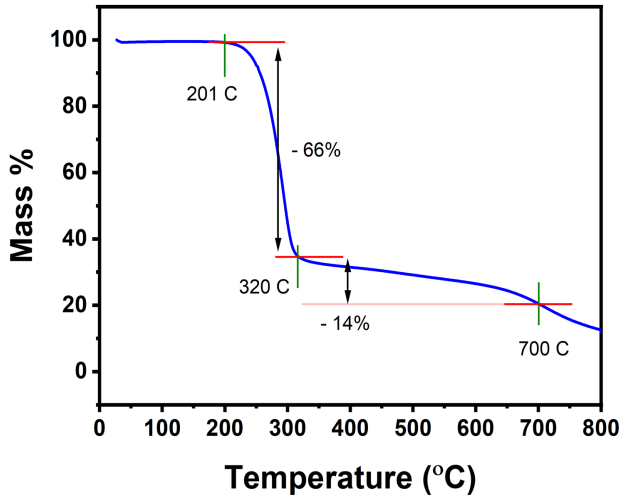
MgN_x sites in mesoporous N-doped carbon

Fellinger. *Mater. Horiz.* **2017,** 4, 493-501

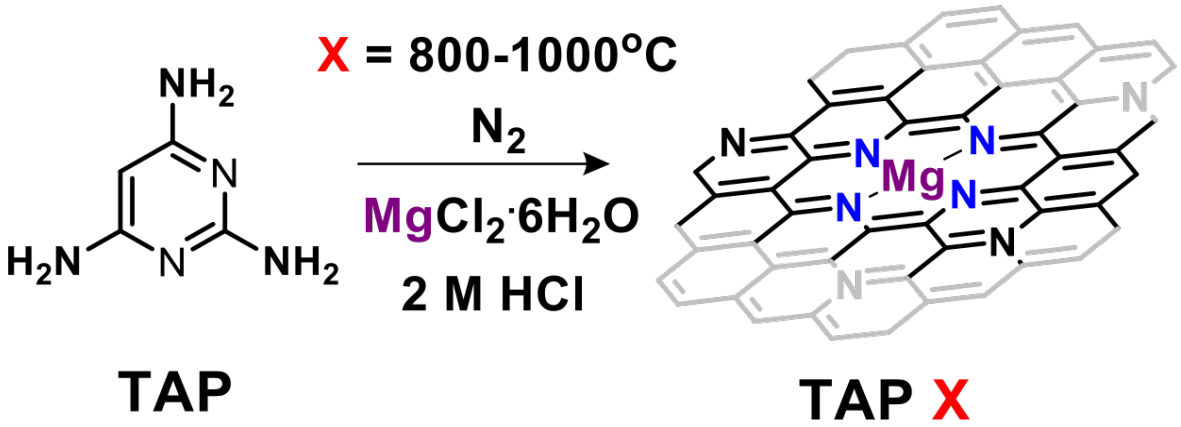
Decoupled synthesis of M-N-C materials

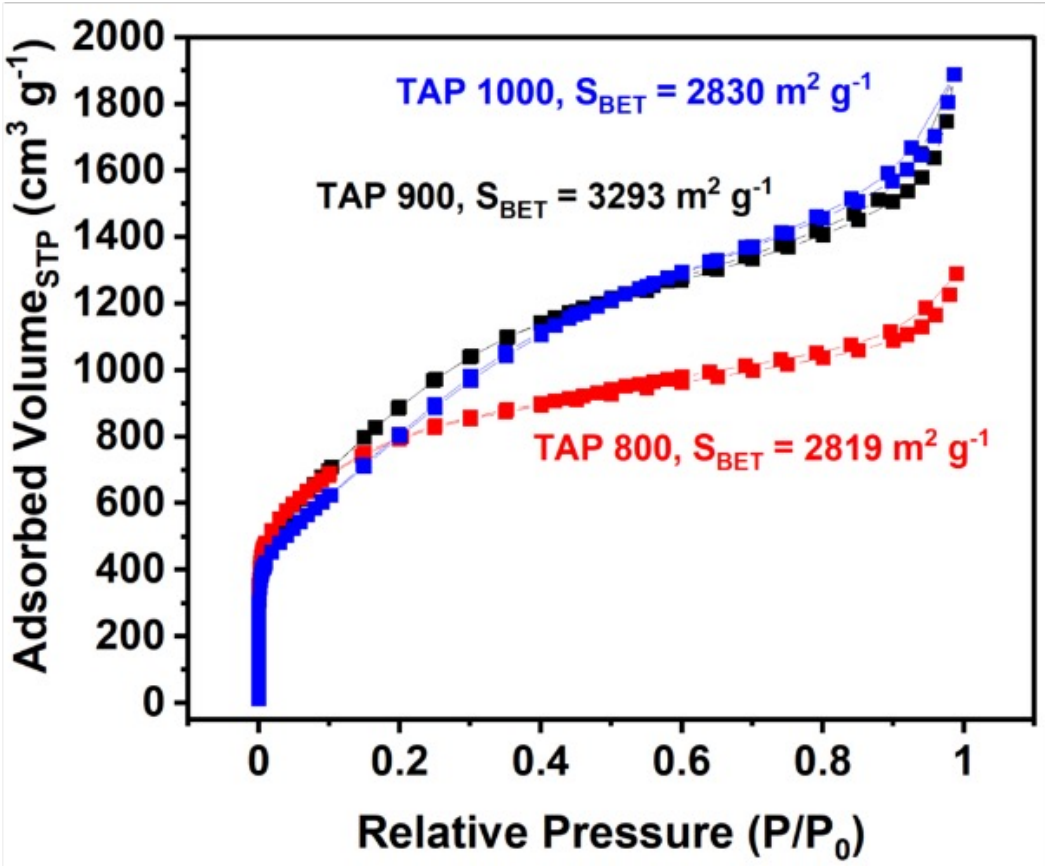
2,4,6-Triaminopyrimidine (TAP)





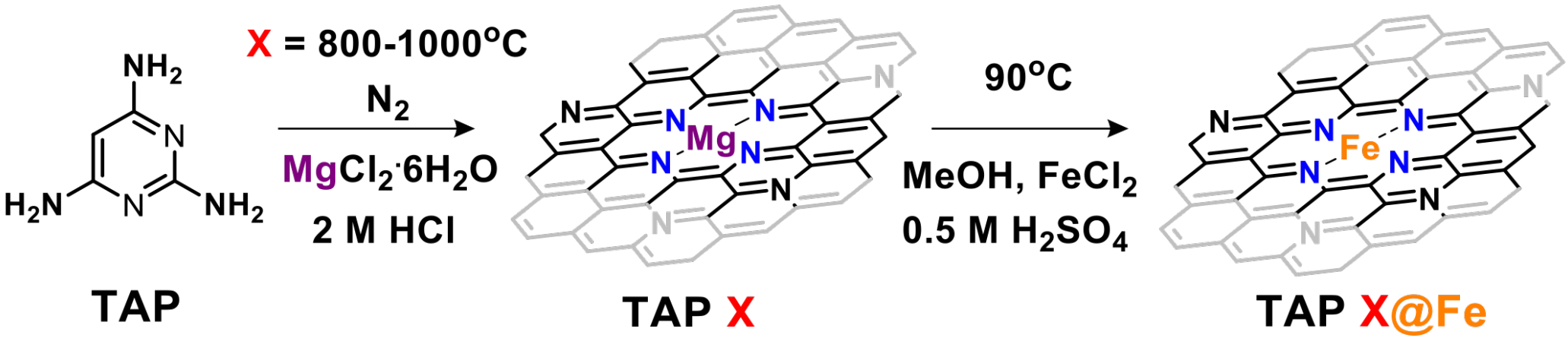
- mp 235 °C
- Formation of N-doped carbon – 700-1000 °C

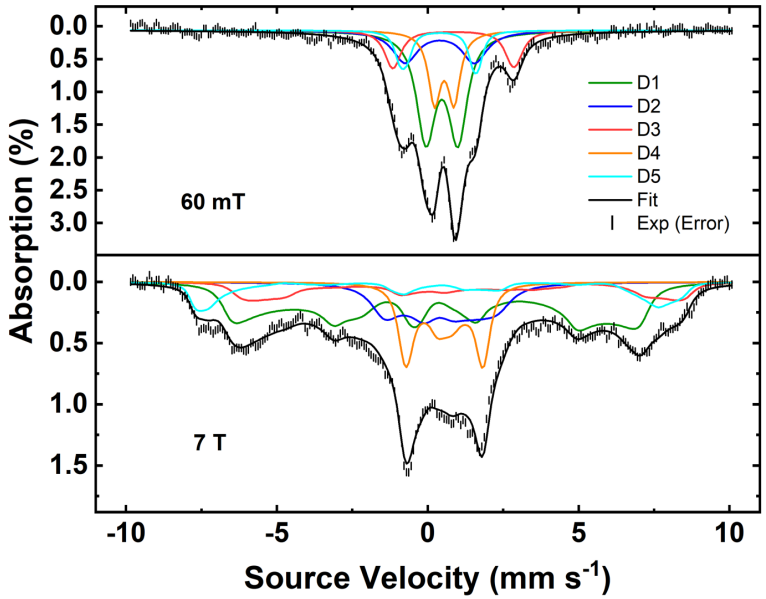


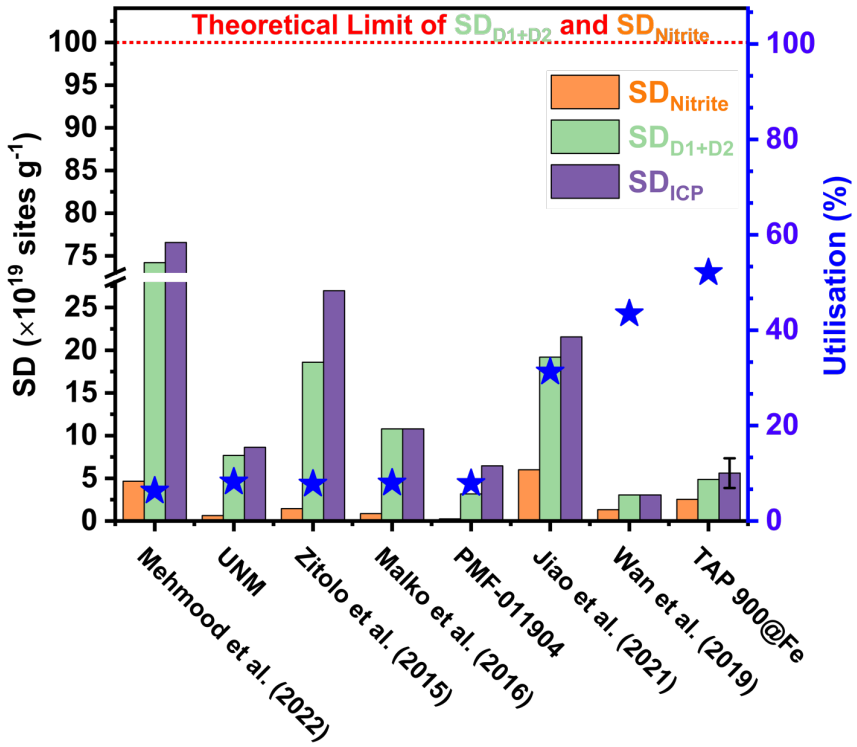


Barrio, Pedersen, Sarma, Bagger, Gong, Favero, Zhao, Garcia-Serres, Li, Zhang, Jaouen, Maillard, Kucernak, Stephens, Titirici. *Adv. Mater.* **2023,** 35, 2211022

Decoupled synthesis of M-N-C materials





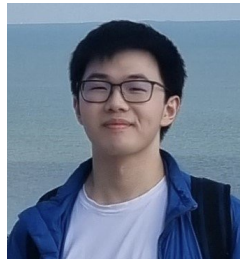


Prof. Frederic Jaouen,
Dr. Ricardo Garcia

Fe(III) high spin (HS) D1 (41%) $\delta = 0.47$ mm s^{-1}, $\Delta EQ = 1.05$ mm s^{-1}

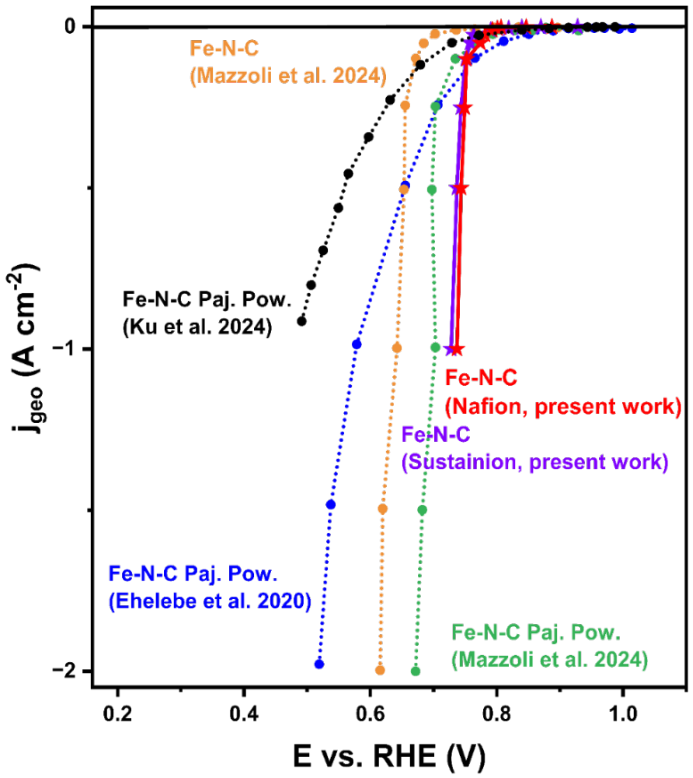
Barrio, Pedersen, Sarma, Bagger, Gong, Favero, Zhao, Garcia-Serres, Li, Zhang, Jaouen, Maillard, Kucernak, Stephens, Titirici. *Adv. Mater.* **2023,** 35, 2211022

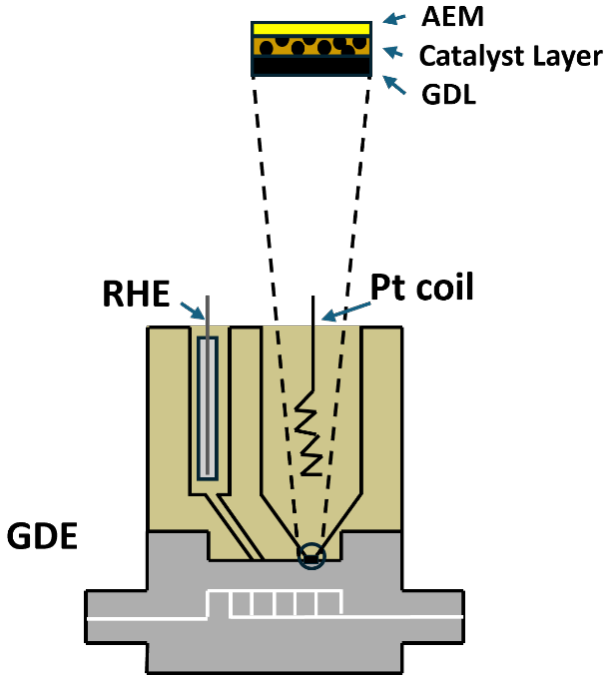
Oxygen reduction electrochemical testing: The gas diffusion electrode

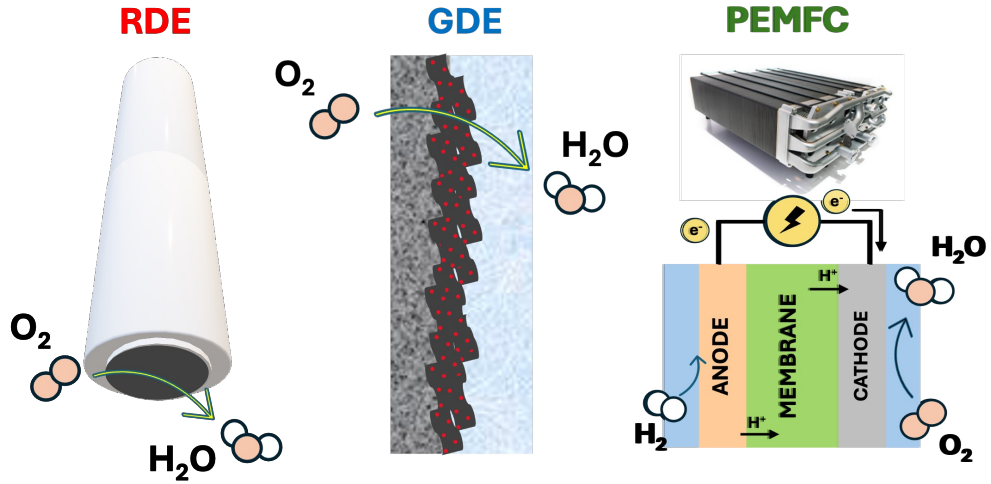


Jinjie Zhu

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \; E^0 \; [V \; vs \; RHE] = 1.23$$







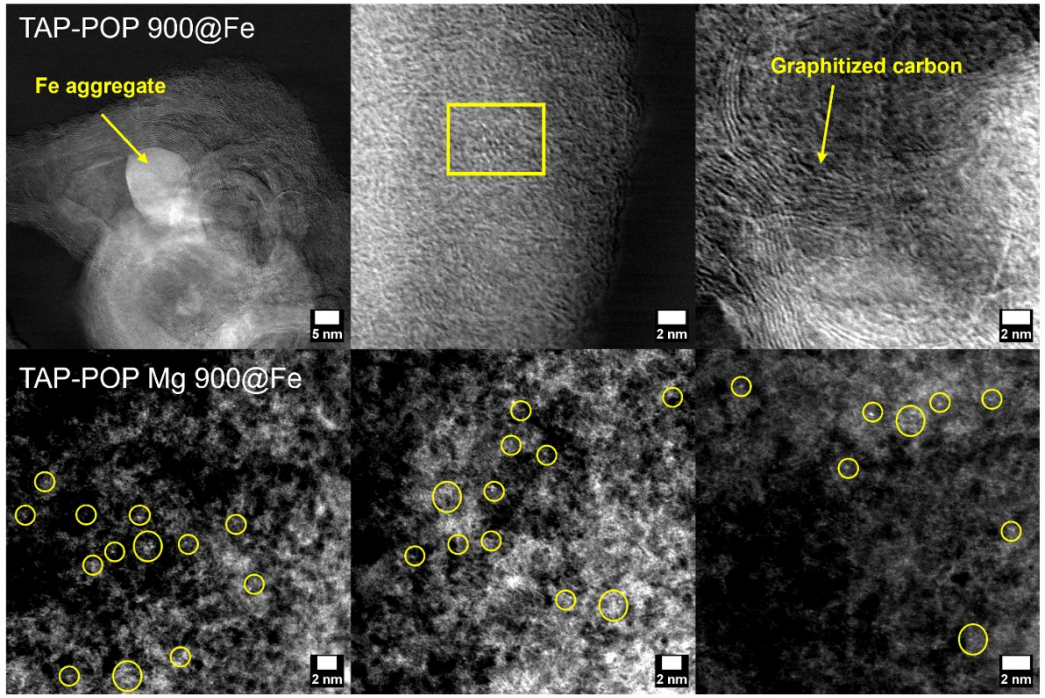
- Catalyst coated on a gas diffusion layer
- Simpler than fuel cells
- Insights on catalyst layer design
- Emulates fuel testing conditions

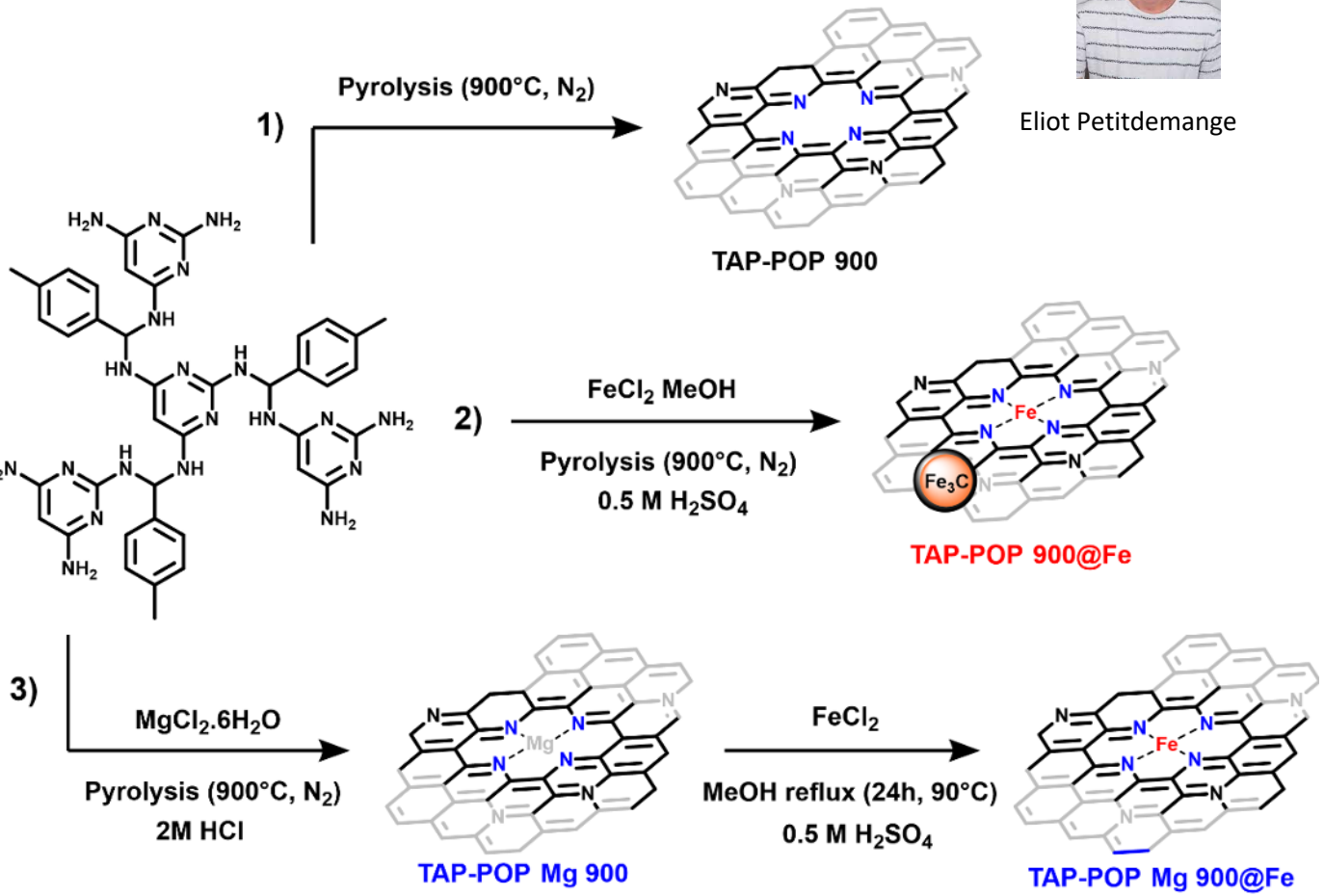
0.737 V vs RHE at 1 A cm^{-2} 1M KOH

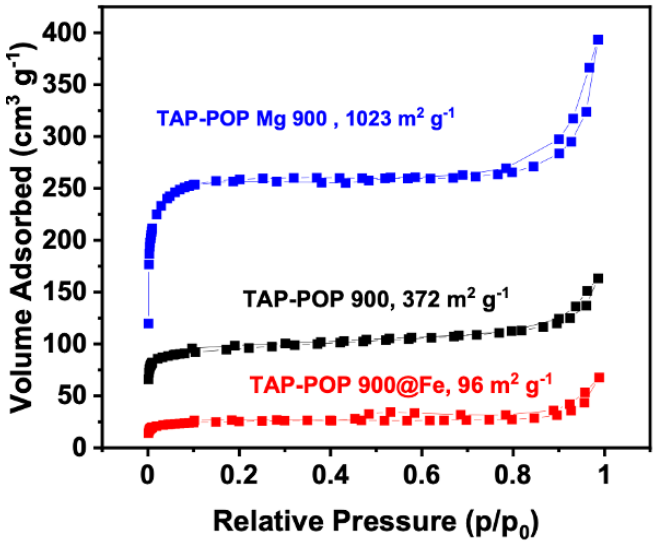
Zhu, Pedersen, Kellner, Hunter, Barrio. *Comm. Chem.* **2025**

Porous organic polymers

Eliot Petitdemange



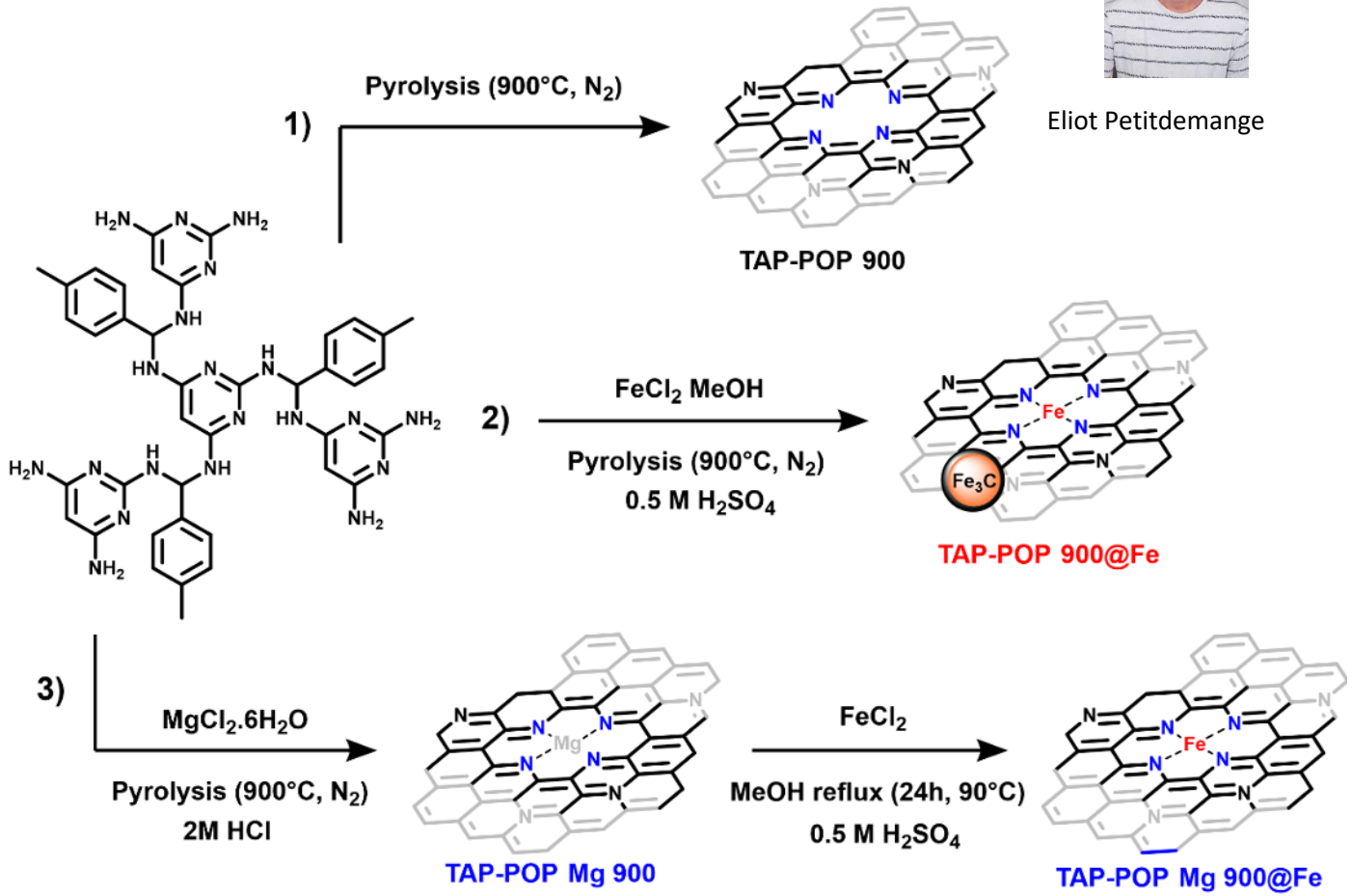


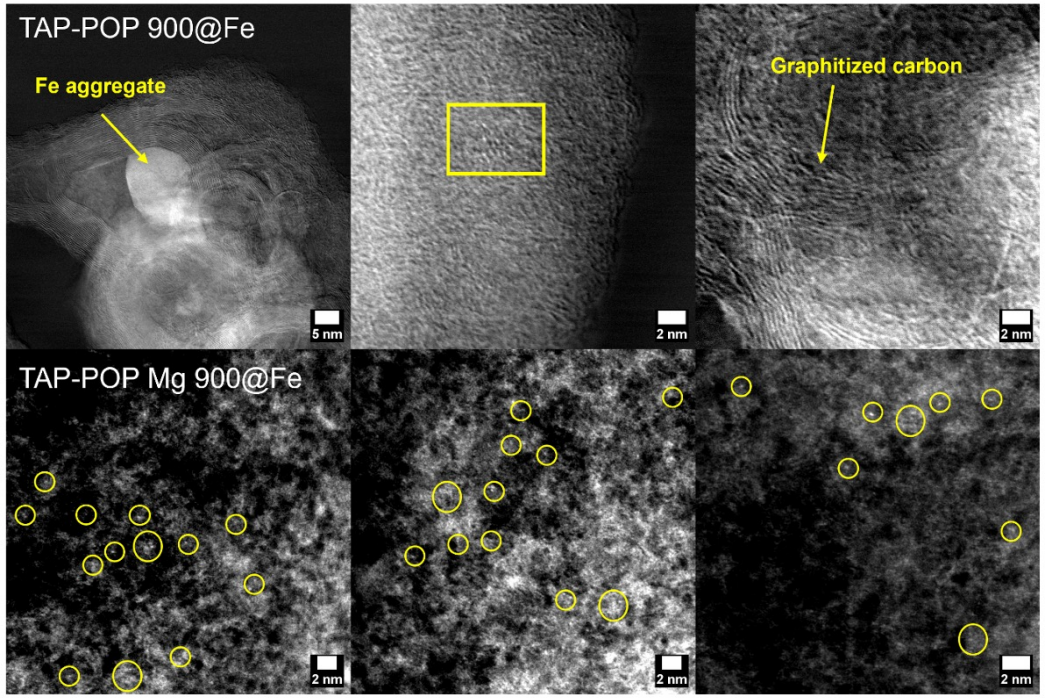


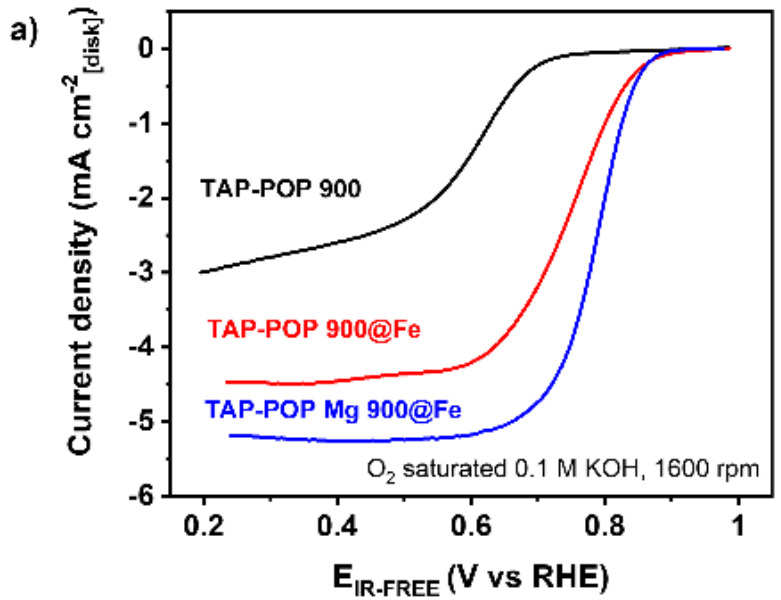
Petitdemange, Zhu, Pedersen, Parker, Balaghi, Favero, Martínez, Haigh, Titirici, Fischer, Barrio. **2025**, *In preparation*

Porous organic polymers

Eliot Petitdemange

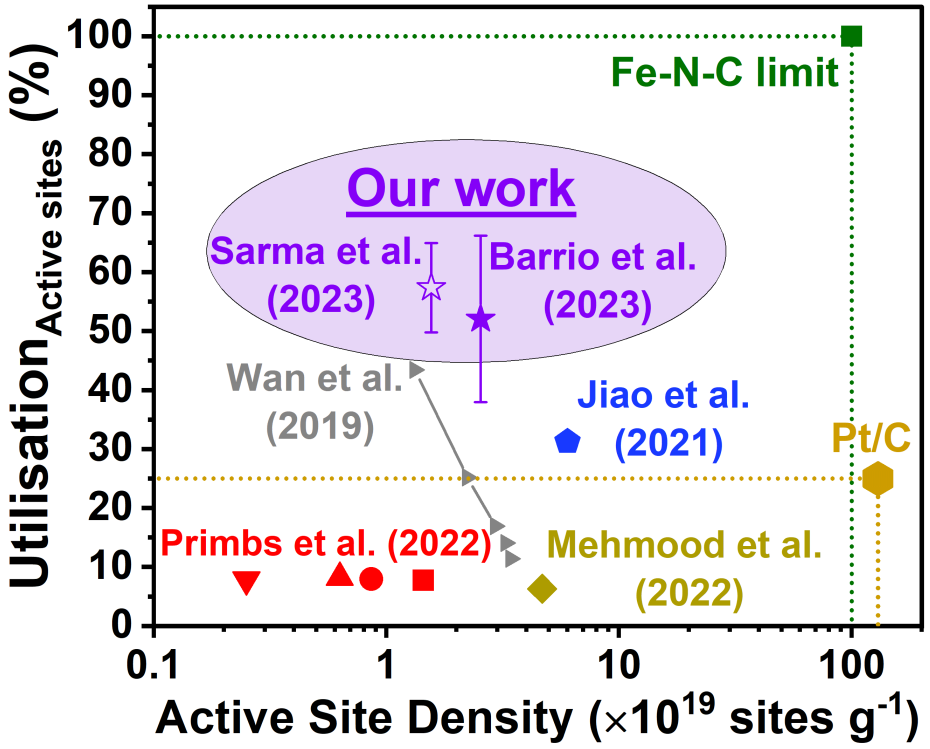


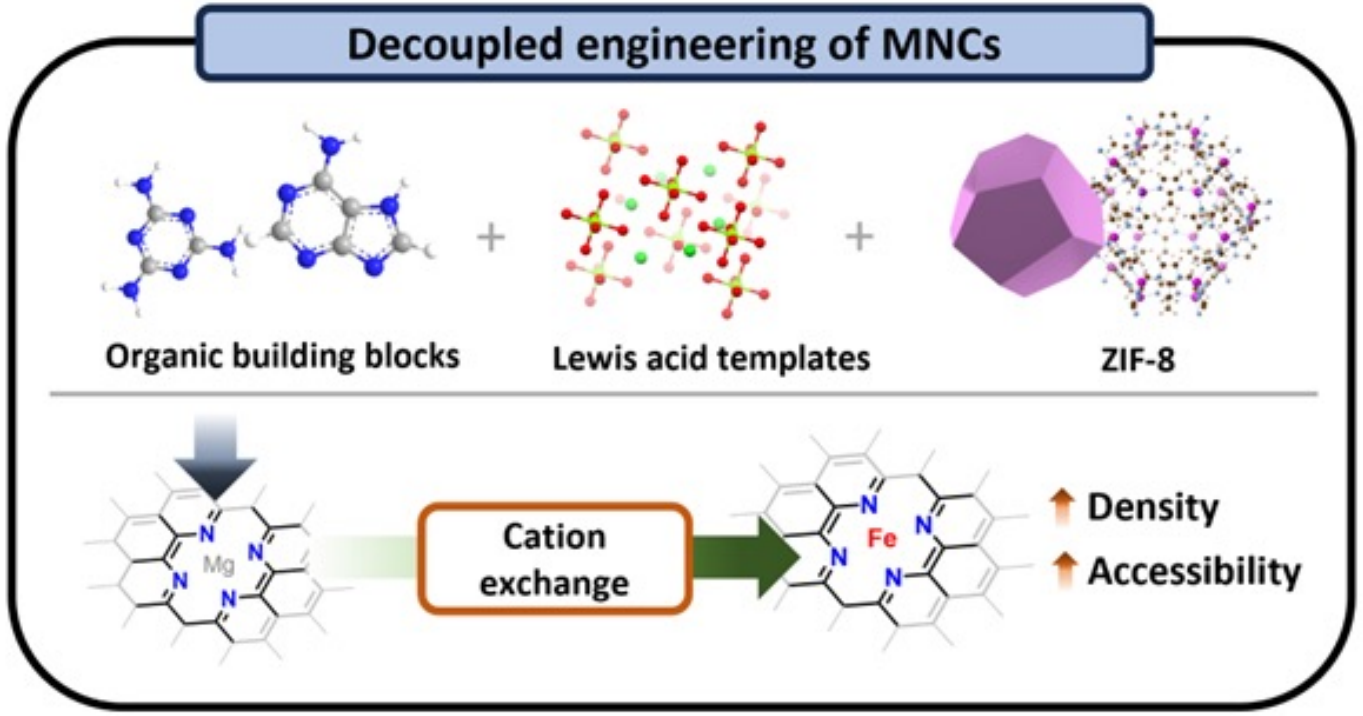




Petitdemange, Zhu, Pedersen, Parker, Balaghi, Favero, Martínez, Haigh, Titirici, Fischer, Barrio. **2025**, *In preparation*

Towards high site density and utilization

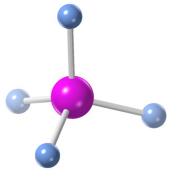


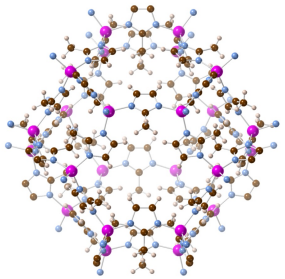


Towards high site density and utilization

Dr. Angus Pedersen

Zn-N_4

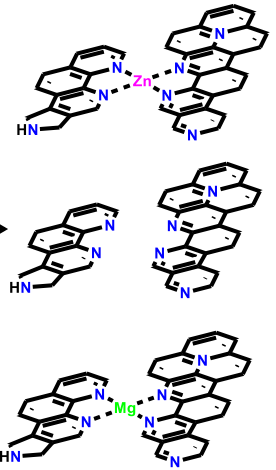




+ $MgCl_2 \cdot 6H_2O$

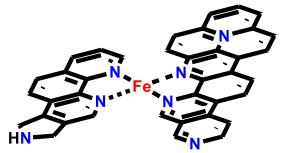
Pyrolysis

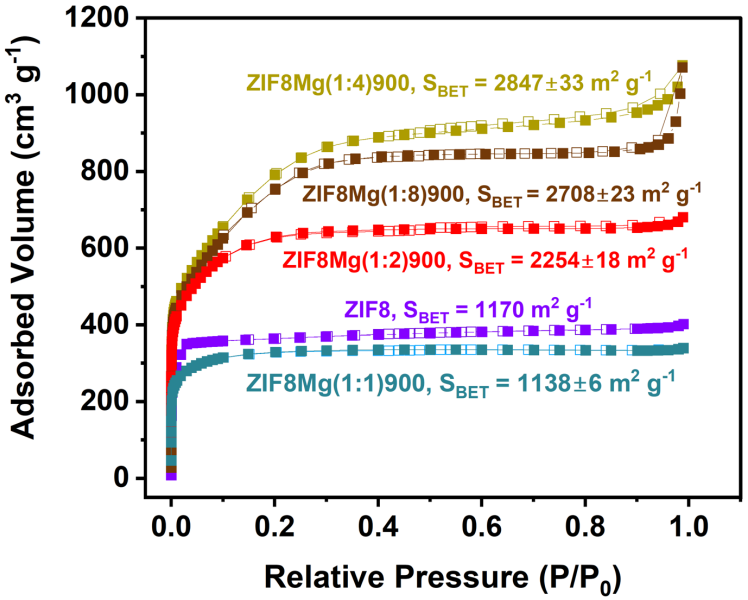
900°C, 1 h, N_2, Wash 2 M HCl

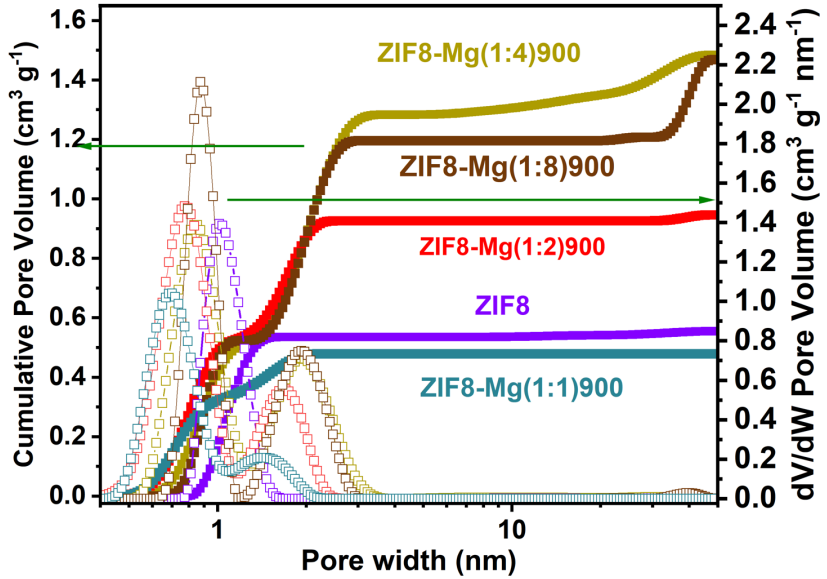


Fe loading

Wash 0.5 M H_2SO_4





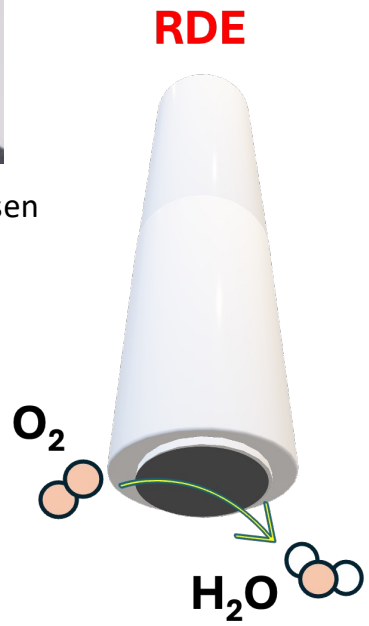


- >2800 m^2 g^{-1} at ZIF:Mg 1:4
- High mesopore volume when Mg is employed

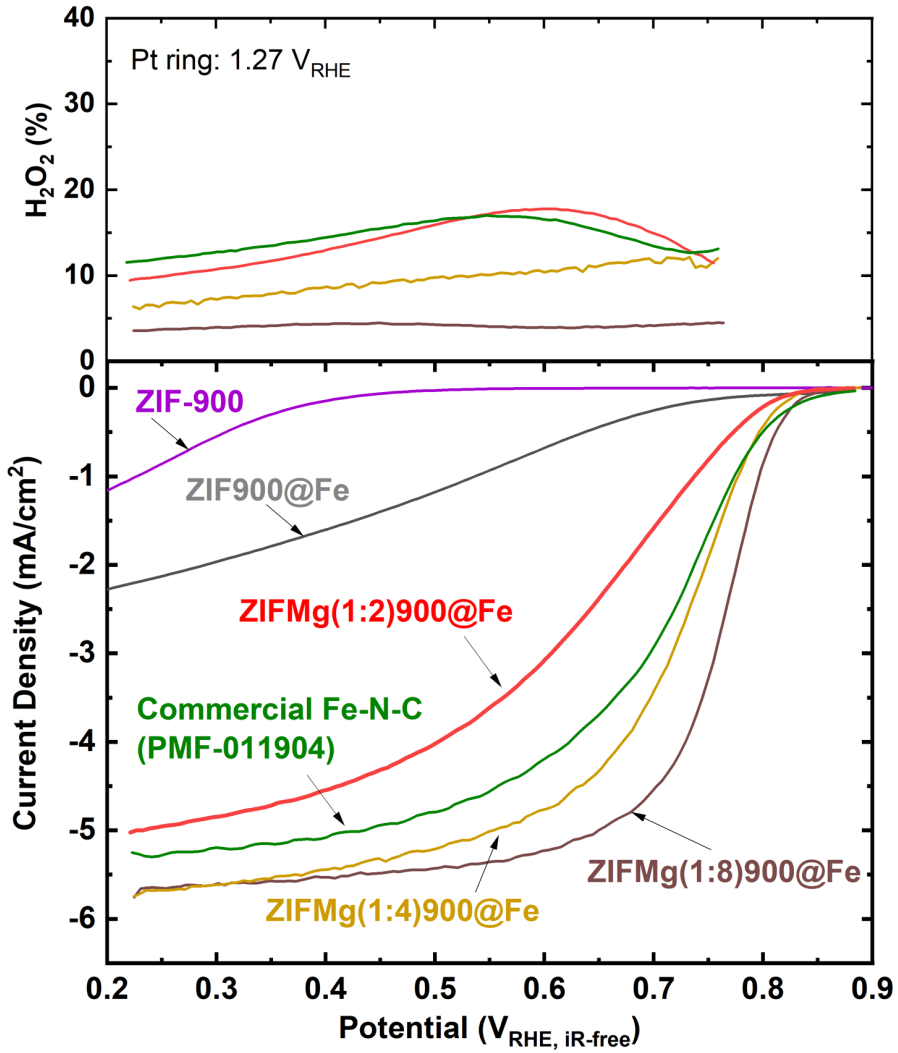
Pedersen, Zhu, Stephens, Barrio, Titirici. *In preparation*

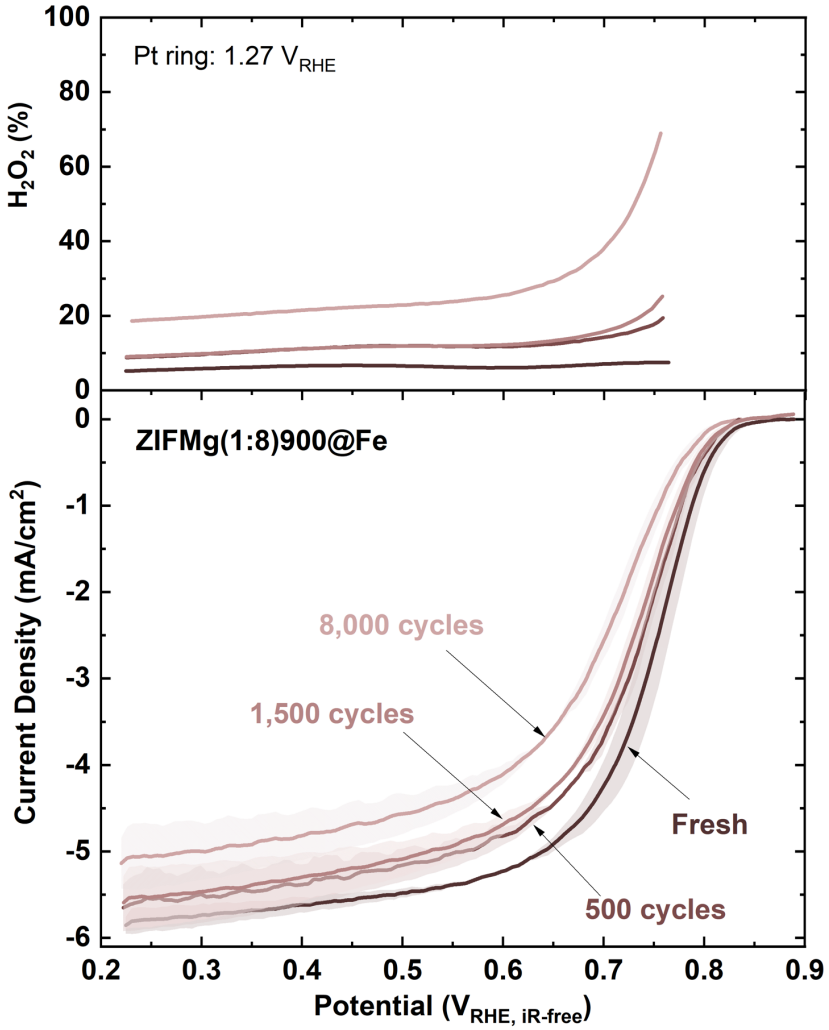
ZIF-derived materials

Dr. Angus Pedersen



- 0.1 M $HClO_4$,
- 0.26 $mg_{Fe\text{-}N\text{-}C}$ cm^{-2}
- 0.9-0.20 V_{RHE}, O_2-N_2, 10 mV s^{-1}.
- Working: 5 mm glassy carbon
- Counter: Graphite rod.
- Reference: Ag/AgCl (calibrated vs RHE)



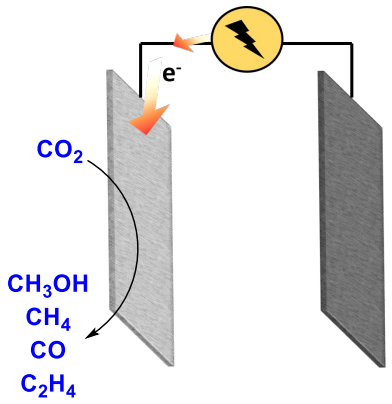


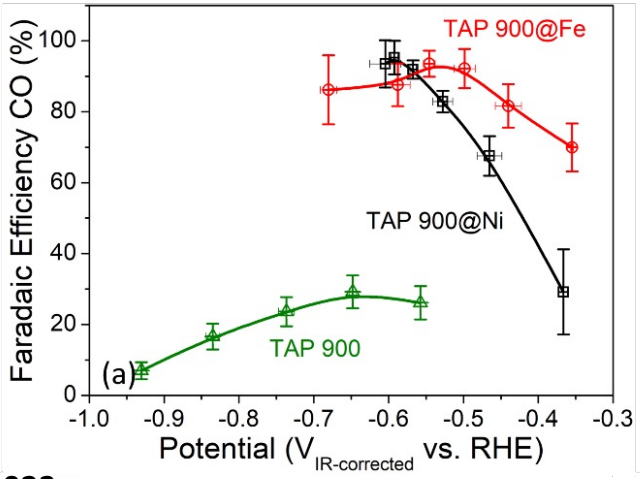
Pedersen, Zhu, Stephens, Barrio, Titirici. *In preparation*

Applications of M-N-C materials beyond ORR

CO_2 reduction

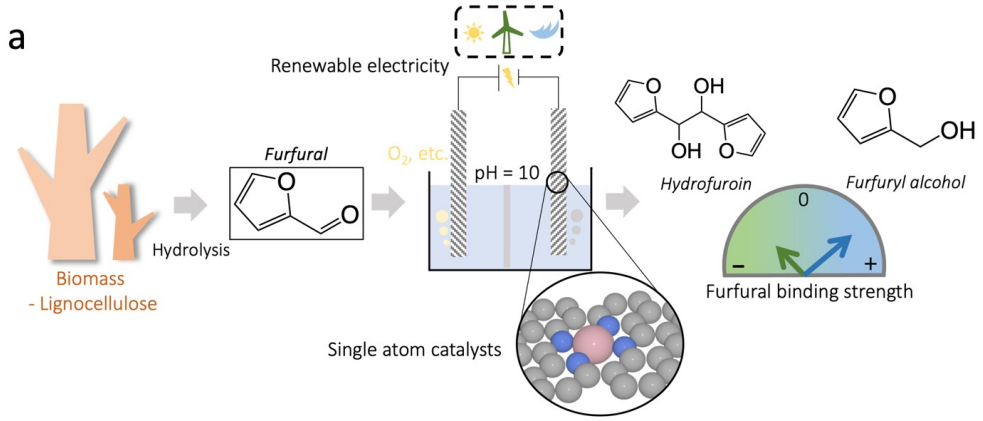
$$CO_2 + 2H_2O + 2e^- \rightarrow CO + 2OH^-$$





Adv. Funct. Mater. **2023,** *E. Acta* **2023**

Furfural coupling Co, Cr, Ni, Fe

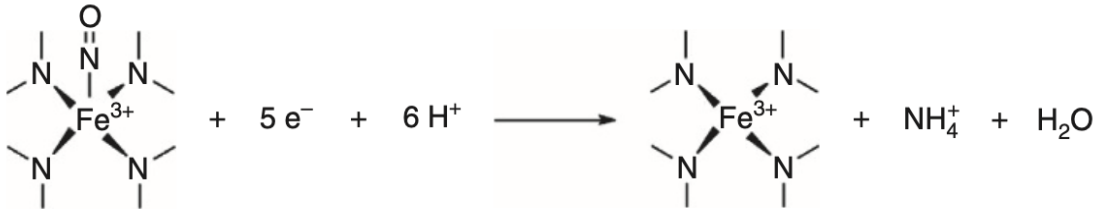


Energy Environ Sci. **2023,** *J. Phys. Chem. C* **2025**

Prof. Georg Kastlunger

Ammonia production via nitrate reduction

Co, Cr, Ni, Fe, Cu

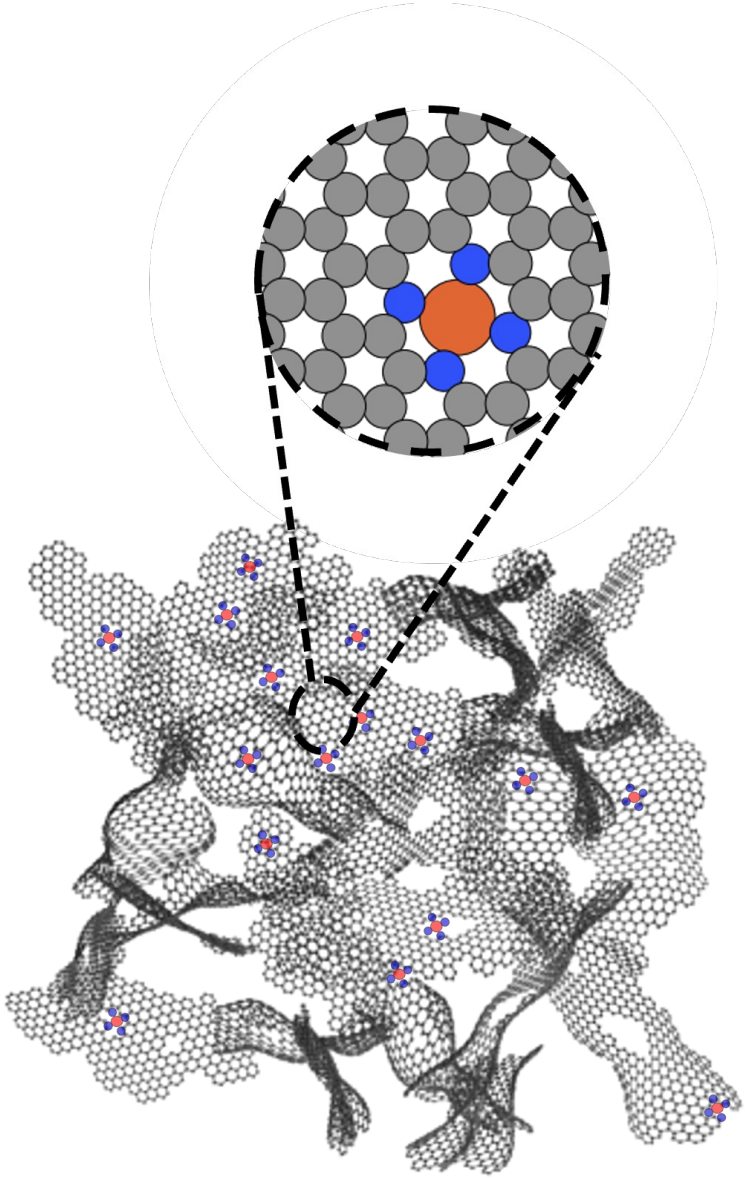


Chemrxiv. **2025**

Prof. Raphael Nagao

Take home message

- FeN_x catalysts can replace Pt in hydrogen fuel cells
- Lewis acid-mediated decoupled synthesis of M-N-C allows the selective formation of accessible single site catalysts
- Microporous materials are a suitable template



Imperial - TUM JADS

Imperial College Research Fellowships

@JesBarrio_

j.barrio-hermida@imperial.ac.uk

Current and previous group members

Jinjie Zhu
Elisa Solvay
Lorenzo Mazzoli
Nattaphon Hongrutai
Eliot Petitdemange
Kari Adourian
Dr. Sara Jerez
Helena Pérez del Pulgar
Craig Burdis
Dr. Silvia Escudero
Jasmine Wang

ICL Collaborators

Dr. Andreas Kafizas
Prof. Ifan Stephens
Dr. Salvador Eslava
Prof. Anthony Kucernak
Prof. Camille Petit
Prof. Magda Titirici

External Collaborators

Dr. Alexander Bagger
Prof. Raphael Nagao
Prof. Frederic Mailliard
Prof. Serhiy Cherevko
Dr. Lior Elbaz
Prof. Sarah Haigh
Prof. Rubén D. Costa
Prof. Félix Zamora
Prof. Menny Shalom
Dr. Javier Castells
Dr. Ignacio Martínez Ruiz
Dr. Miguel Rivero Crespo
Prof. Jiayin Yuan
Prof. Frederic Jaouen