J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, January 29, 2025, Prague, Czech Republic

Electrocatalysis as Major Enabling Technology for Decarbonization

Plamen Atanassov

Chemical & Biomolecular Engineering and Materials Science & Engineering
National Fuel Cell Research Center
University of California Irvine, USA

NFCRC
NATIONAL FUEL CELL RESEARCH CENTER
UNIVERSITY OF CALIFORNIA • IRVINE

University of California, Irvine

Home to the National Fuel Cell Research Center

36,000+ students

#9 Public University in the U.S.
— *U.S. News & World Report 2020*

200,000+ Anteater alumni

82 majors — **75** minors

#1 Best College in the U.S.
— *MONEY*

#1 Cool School in the U.S. for sustainability
Top 10 for 10 years
— *Sierra* magazine

Most applied to UC campus for California's aspiring freshmen for a second year in a row

$133 million private donor support in 2018-19

$5 billion annual economic impact in Orange County

UCIRVINE

one of the 10 campuses of the University of California

… and, oh well, the mascot is – Peter, the…

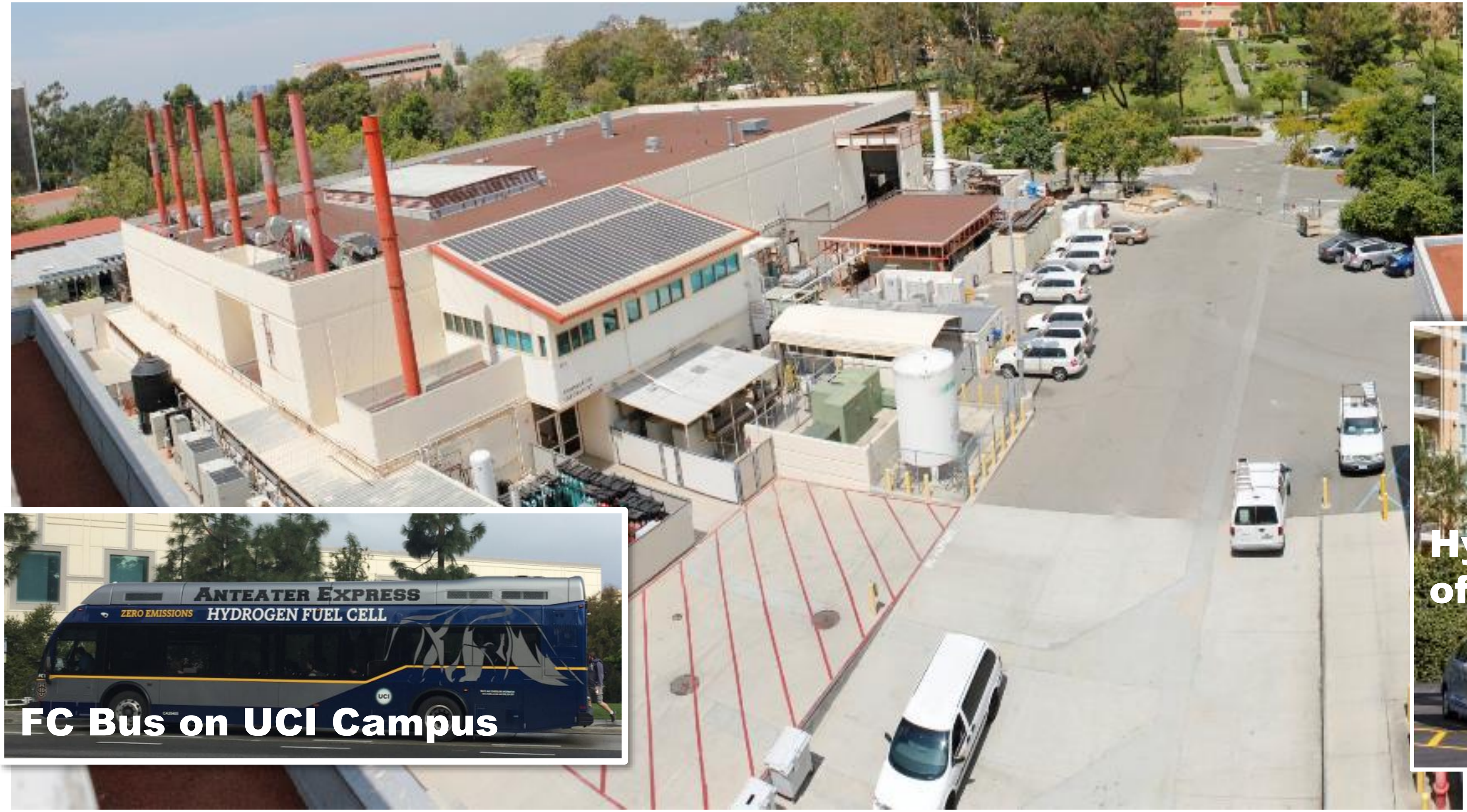
Irvine Clean Energy Institute

Jack Brower – Director CEI

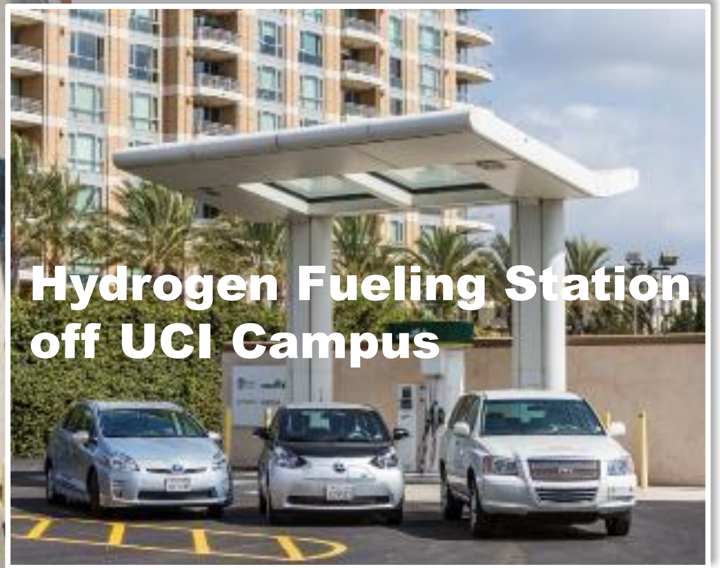
National Fuel Cell Research Center

UCIrvine | University of California

Iryna Zenyuk – Director NFCRC



FC Bus on UCI Campus

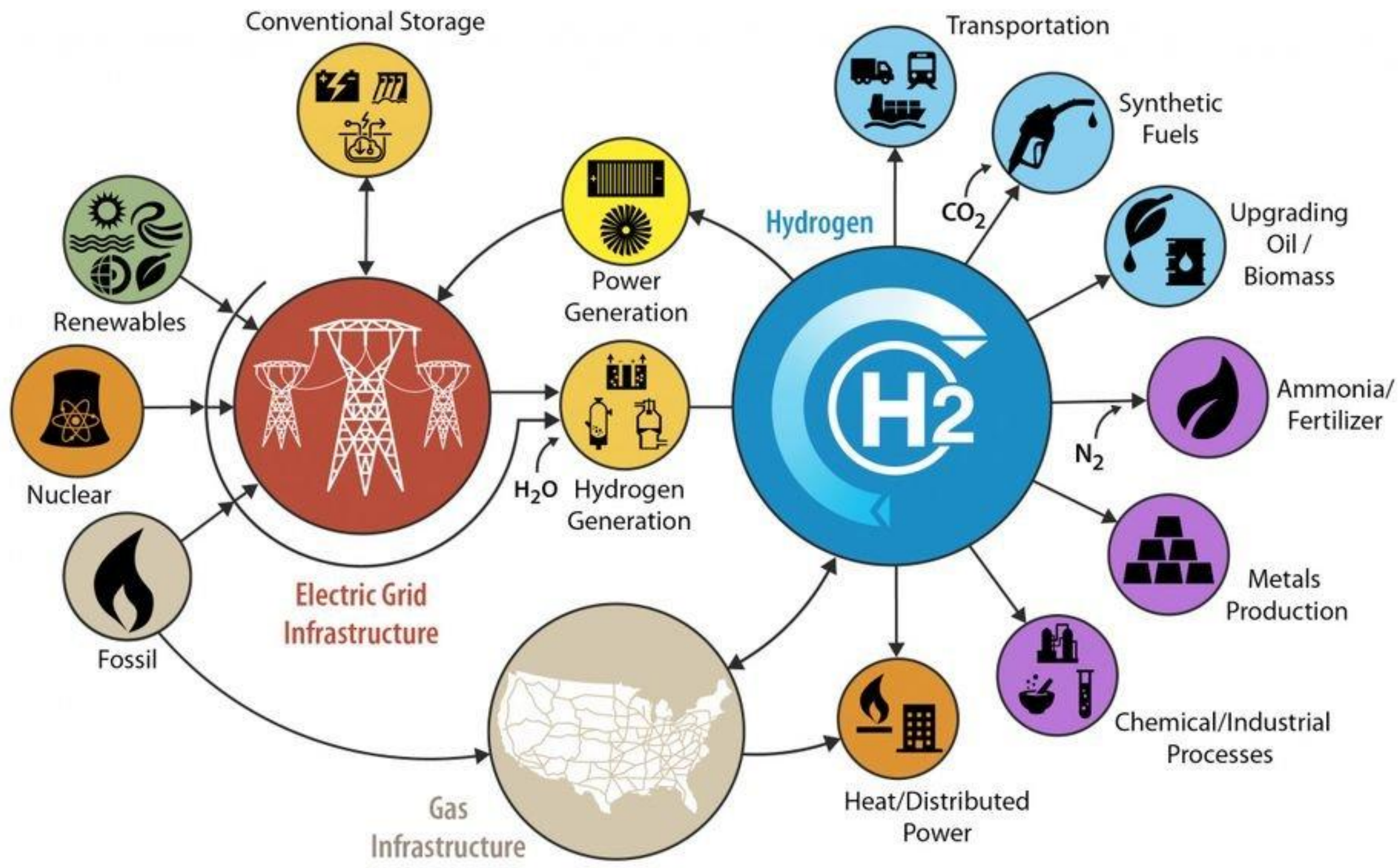


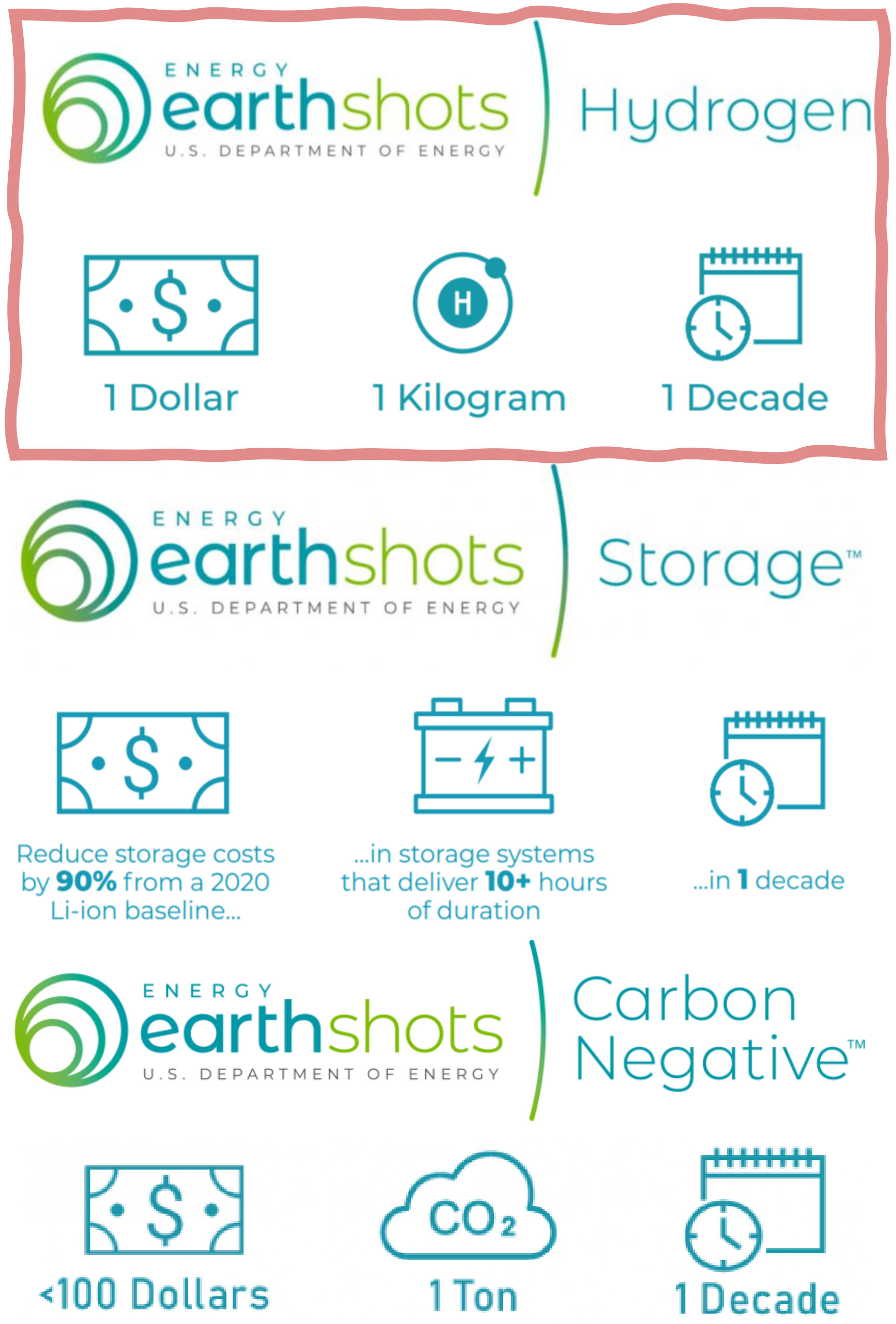
Hydrogen Fueling Station off UCI Campus

UCI

MISSION: to facilitate research, development and deployment of fundamental and applied science for renewable and clean energy technology systems

US DOE H2@Scale and EarthShots





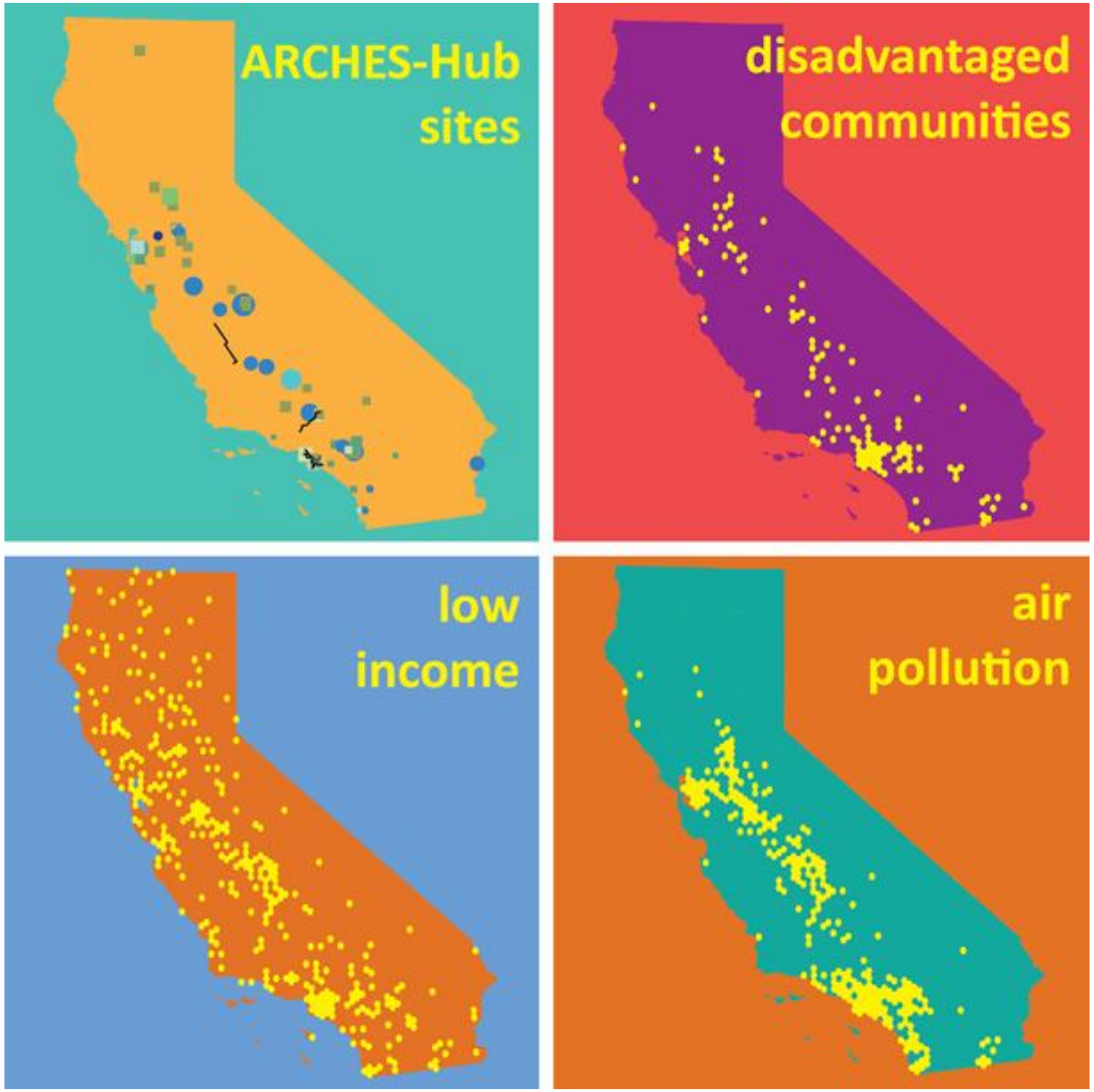
UCI

SELECTED REGIONAL CLEAN HYDROGEN HUBS

ARCHES H2

OCED
Office of Clean Energy Demonstrations

ARCHES Benefits California Communities



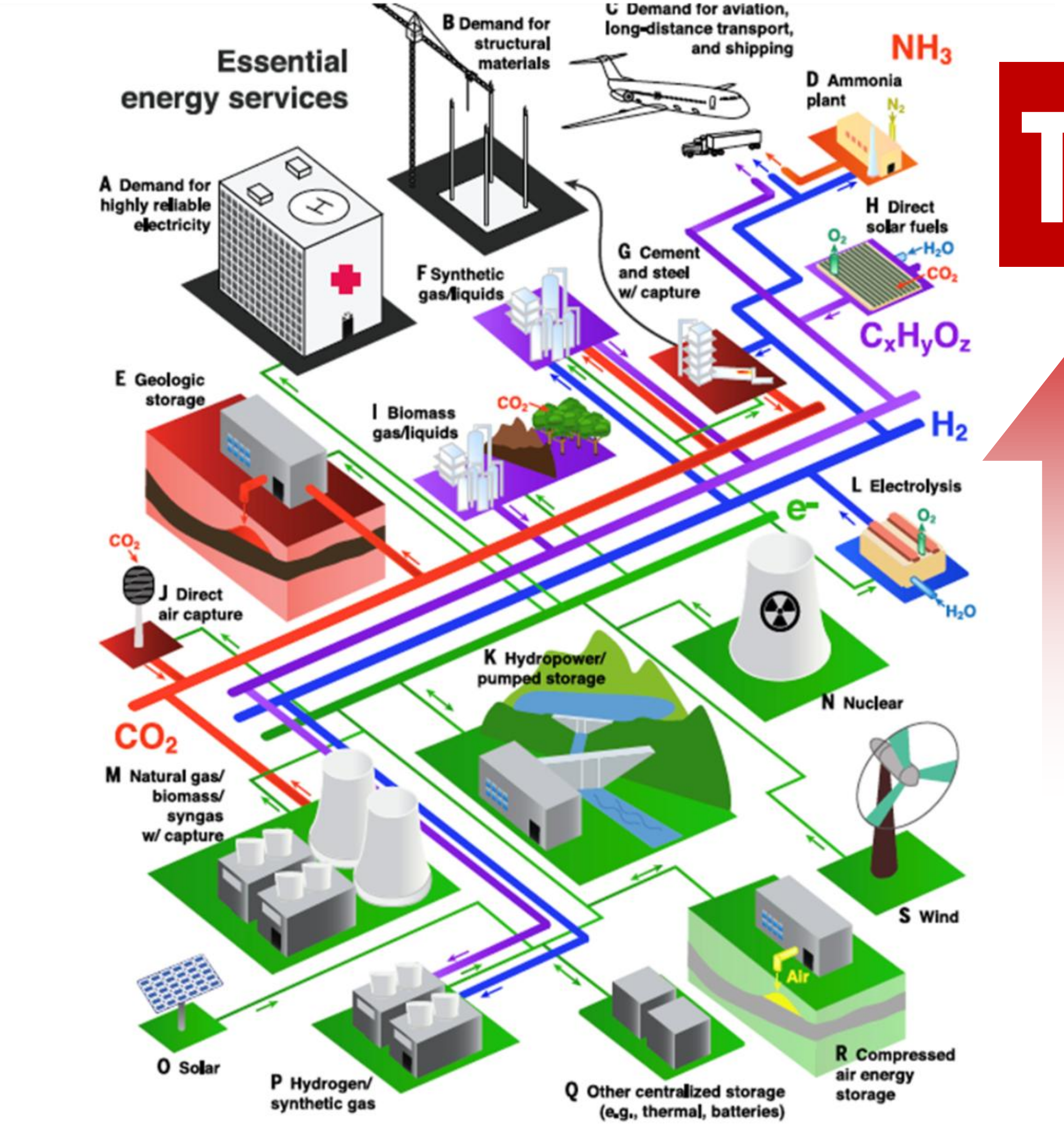
*EJ40 database and CalEnviroScreen

COMMUNITY

▲ $2.95 billion	Economic value of increased health* and associated health costs savings per year
▲ 222,400	Number of jobs created ar
▼ 2,097	Fewer hospitalizations for respiratory & cardiac illness per year
▼ 13,292	Fewer work loss days per year
▼ 6,900	Nitrogen oxide net emissions avoided MTPY
▼ 239	Sulfer dioxide net emissions avoided MTPY
▼ 326 (PM 2.5, 10)	Particulate matter net emissions avoided MTPY
▼ 48	Fewer premature deaths per year
▲ $380 million	Invested in community benefits & workforce development

*Reduced premature death, asthma, cancer risk, missed work days

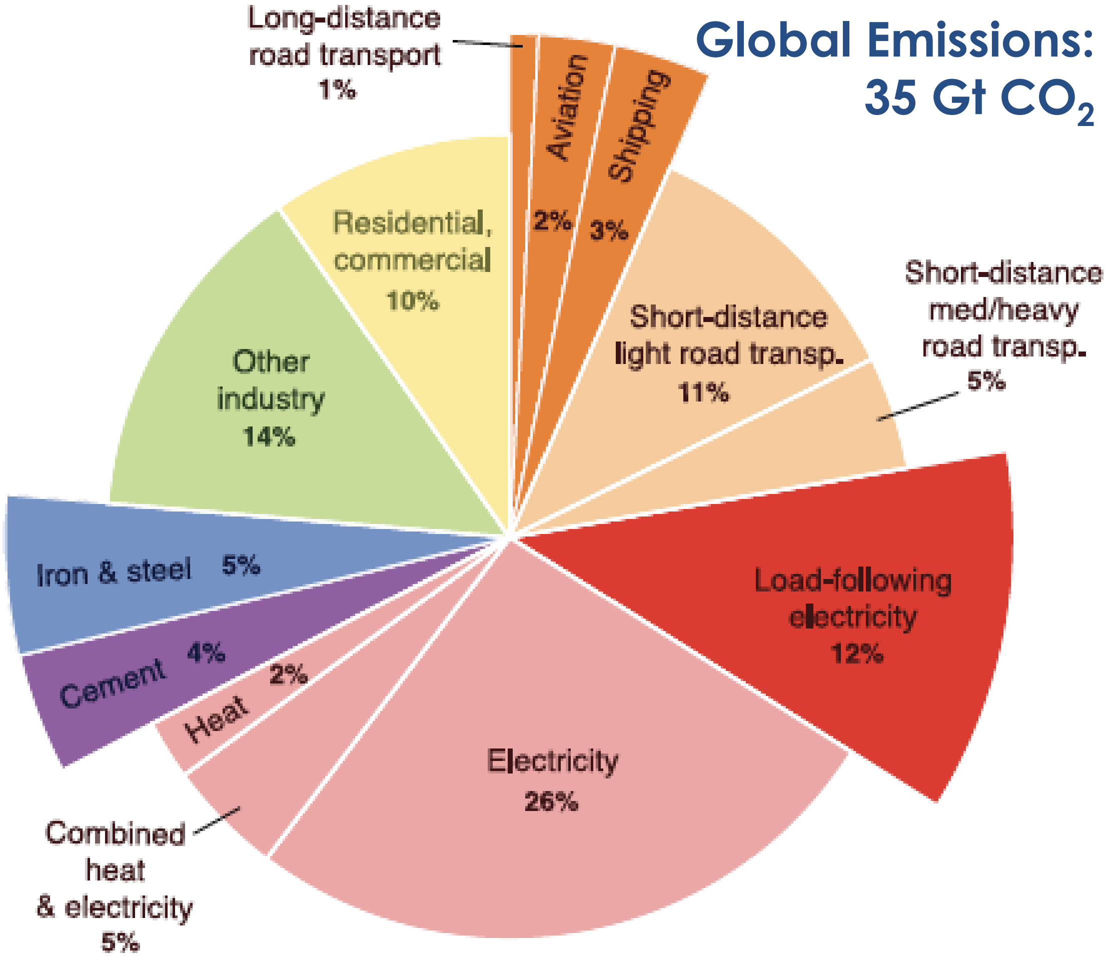
On the Path to Net Zero Emissions



Davis *et al.*, *Science* **360**, eaas9793 (2018) 29 June 2018

TRL

Global Emissions: 35 Gt CO_2

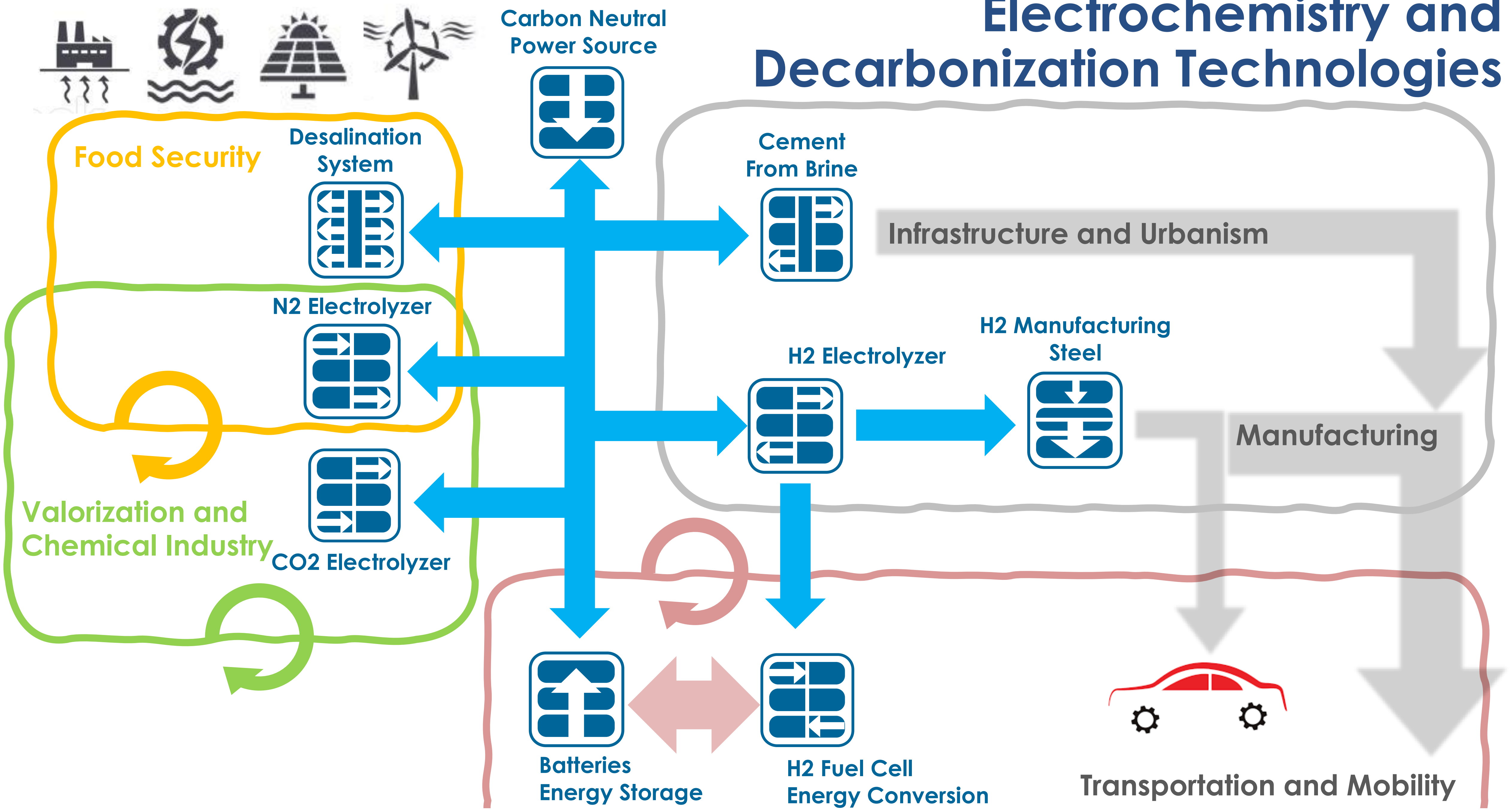


ENERGY

Net-zero emissions energy systems

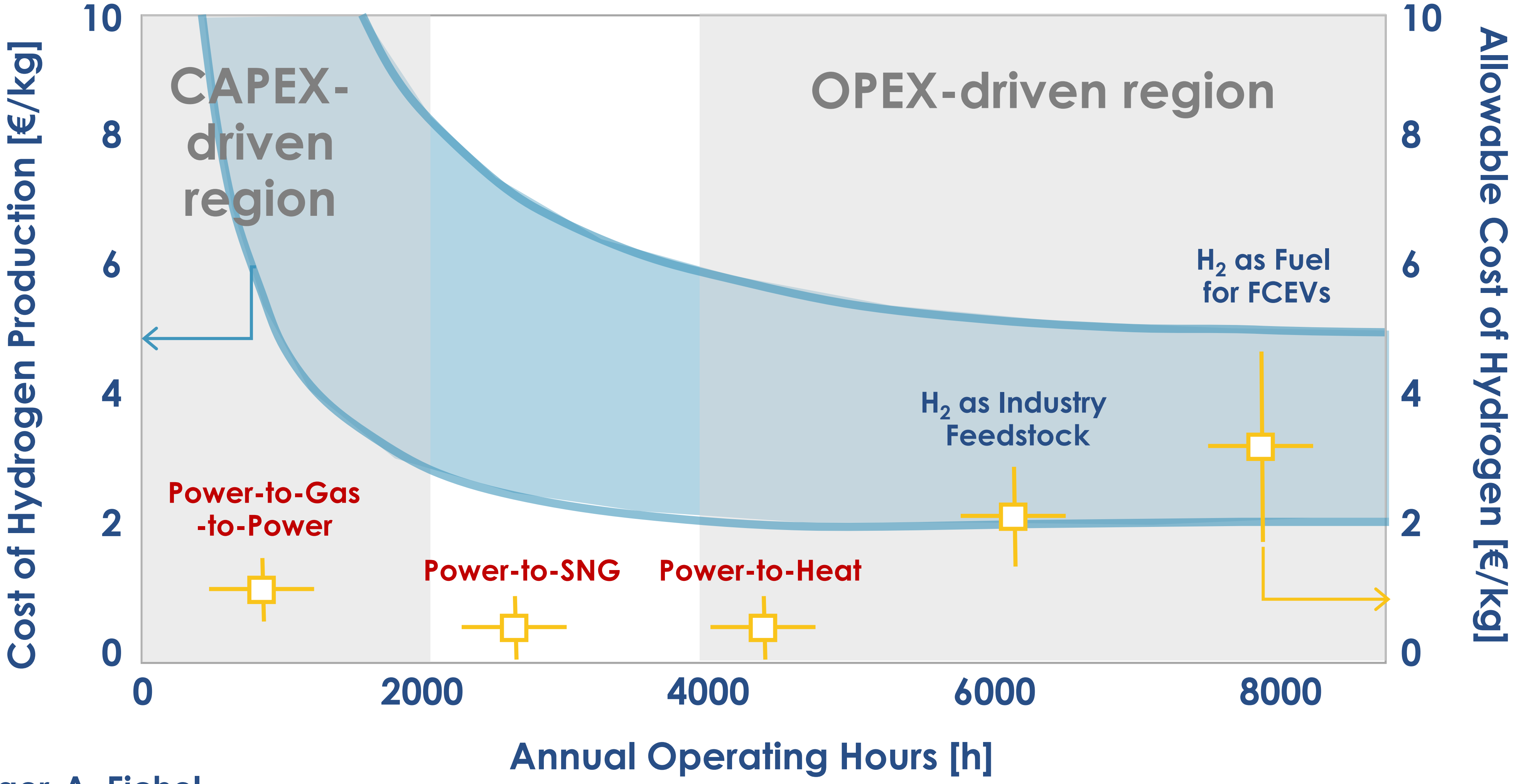
Steven J. Davis[1,2*], Nathan S. Lewis[3*], Matthew Shaner[4], Sonia Aggarwal[5], Doug Arent[6,7], Inês L. Azevedo[8], Sally M. Benson[9,10,11], Thomas Bradley[12], Jack Brouwer[13,14], Yet-Ming Chiang[15], Christopher T. M. Clack[16], Armond Cohen[17], Stephen Doig[18], Jae Edmonds[19], Paul Fennell[20,21], Christopher B. Field[22], Bryan Hannegan[23], Bri-Mathias Hodge[6,24,25], Martin I. Hoffert[26], Eric Ingersoll[27], Paulina Jaramillo[8], Klaus S. Lackner[28], Katharine J. Mach[29], Michael Mastrandrea[4], Joan Ogden[30], Per F. Peterson[31], Daniel L. Sanchez[32], Daniel Sperling[33], Joseph Stagner[34], Jessika E. Trancik[35,36], Chi-Jen Yang[37], Ken Caldeira[32*]

Electrochemistry and Decarbonization Technologies



Hydrogen Economy as a Business

Actual and allowable hydrogen production costs for different end-uses

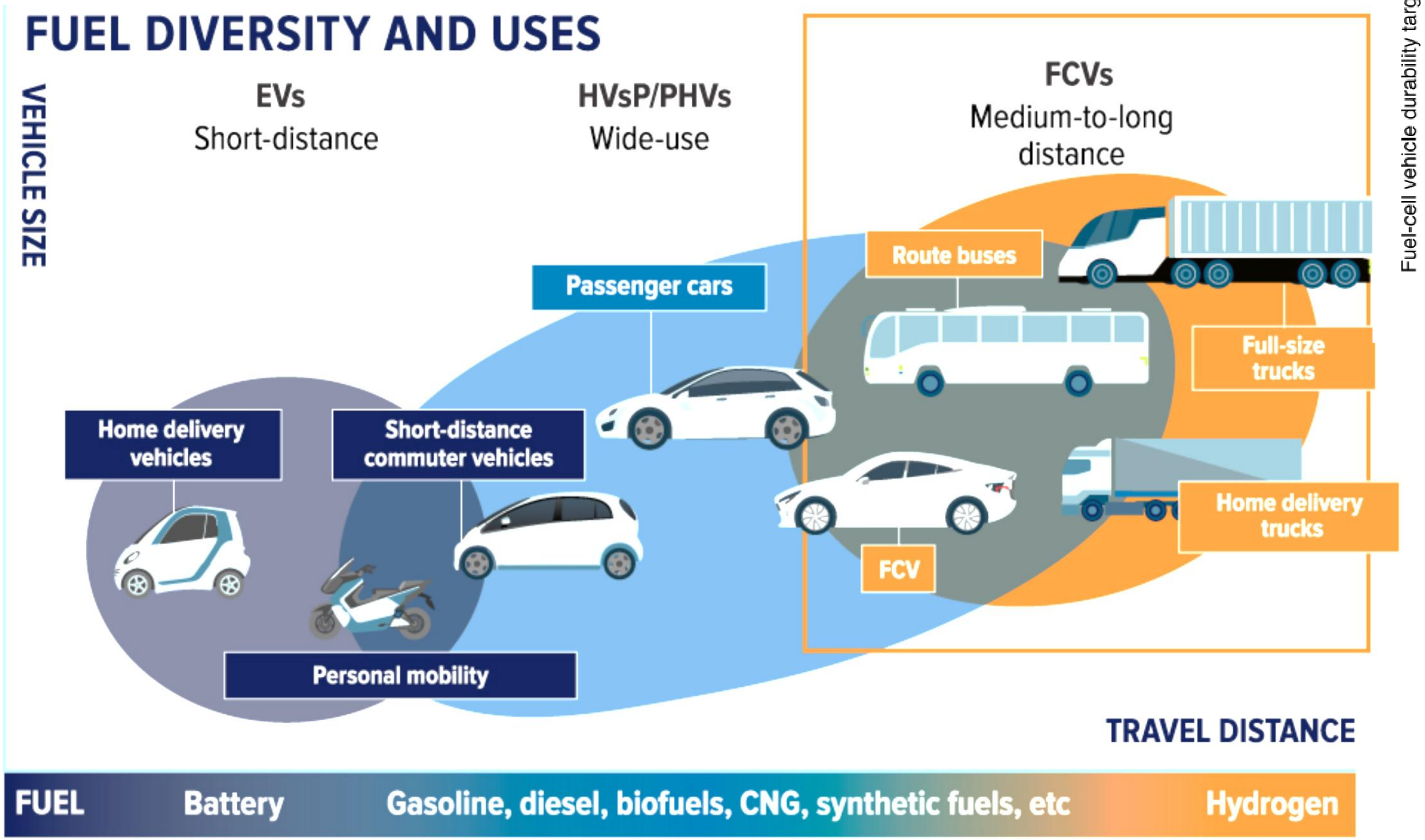


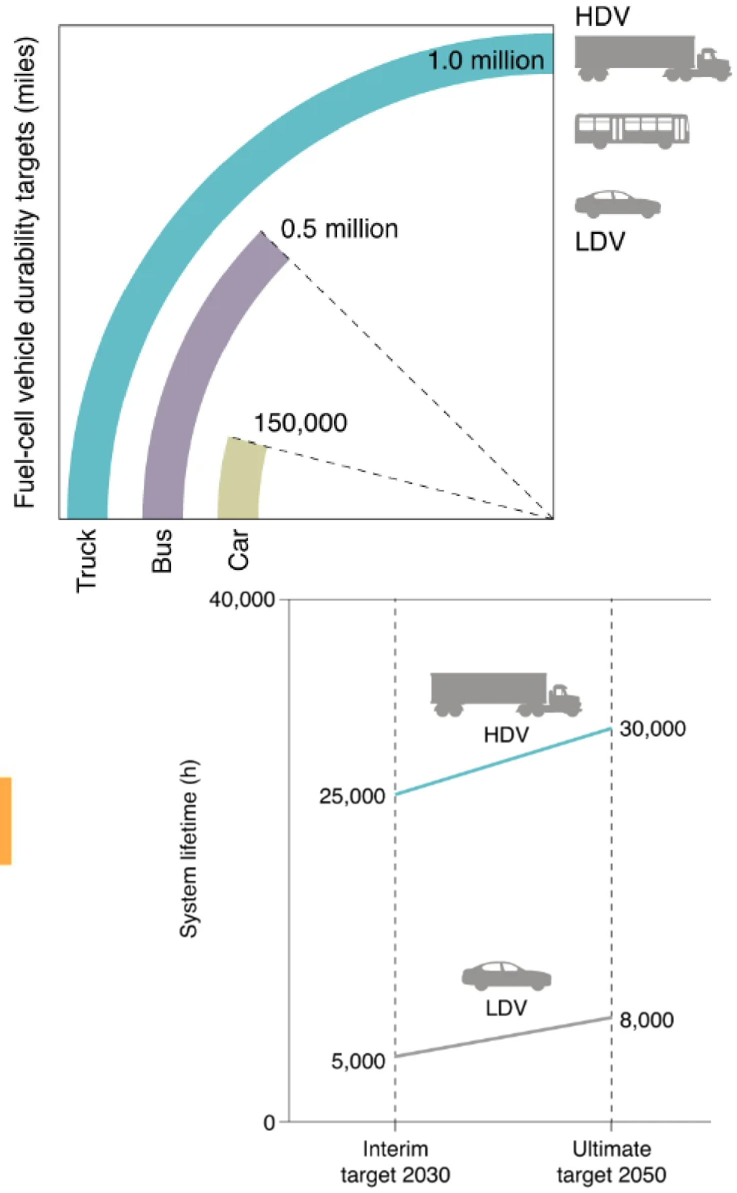
Courtesy: Rüdiger-A. Eichel

DOE Targets Heavy Duty Fuel Cell Trucks

Durability targets are the ultimate challenge for the HDV

MILLION MILE FUEL CELL TRUCK
U.S. DEPARTMENT OF ENERGY

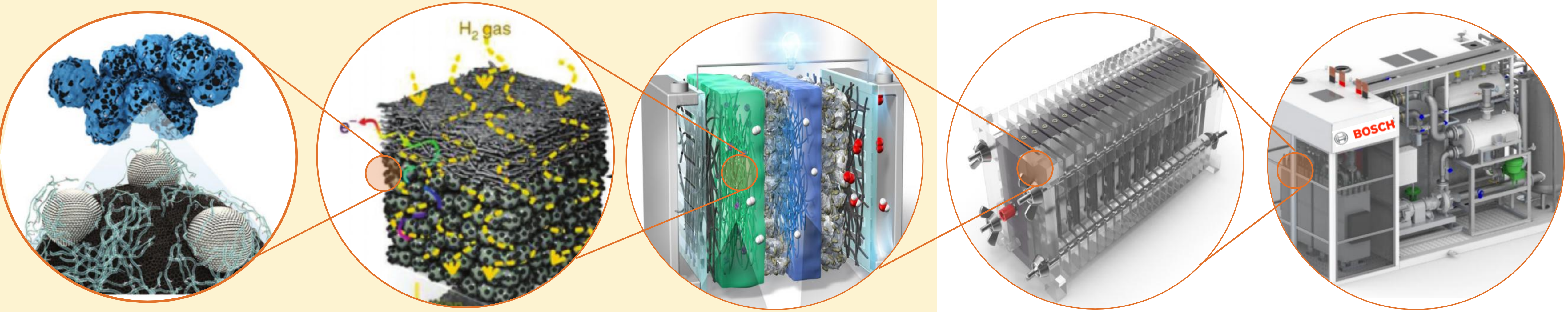




Cullen, D. et al., *Nature Energy* 6 (2021) 462

Big Questions to Solve in Energy Conversion Systems

Electrocatalyst	Catalyst layer	Cell level	Stack	Plant
10 nm	10 µm	1 cm	1 m	10 m



Courtesy: Iryna Zenyuk

Fundamentals

Demonstration projects and system-level studies

- Fundamental science and engineering challenges are from *nm*- scale to *cm*- scale
- Integrated approach is needed
- Complex scale-coupled transport and reaction kinetics problems

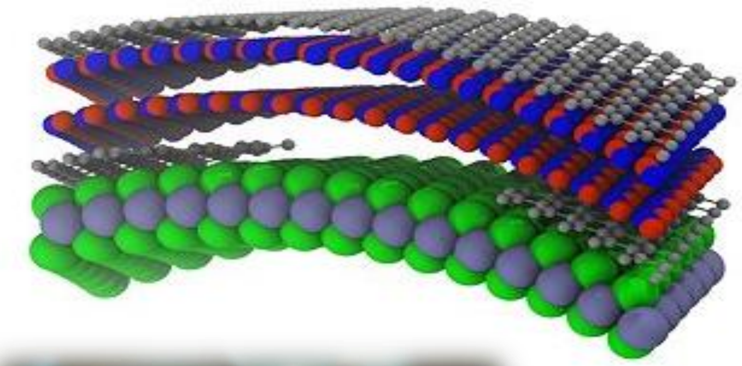
UCI

In collaboration with: Prof. Jack Brouwer, Director of Irvine Clean Energy Institute
Prof. Iryna Zenyuk, Director of National Fuel Cell Research Center and
Prof. Vojislav Stamenkovic, Director of Horiba Institute for Mobility and Connectivity

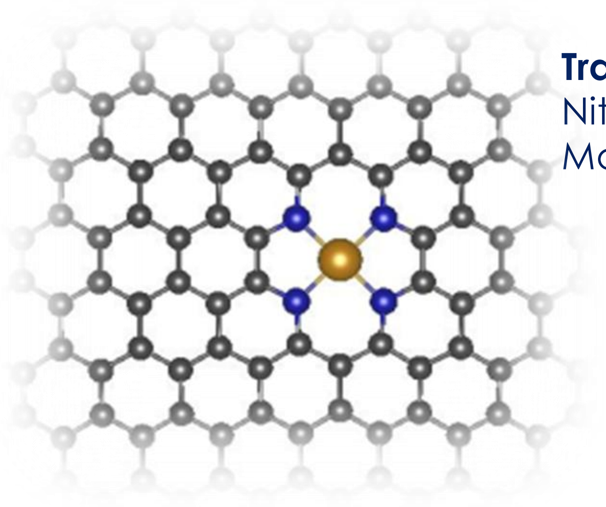
NFCRC

HIMaC^2

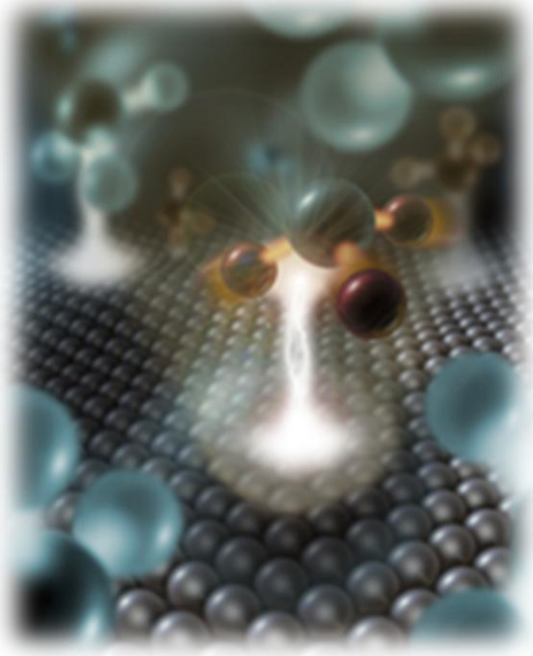
Electrocatalysts Materials Development Programs

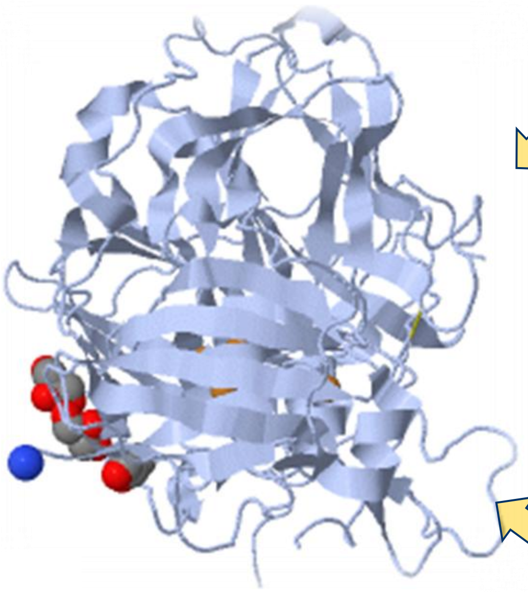


Metal Oxides,
Carbide,
Nitrides,
MXenes,
VdW materials

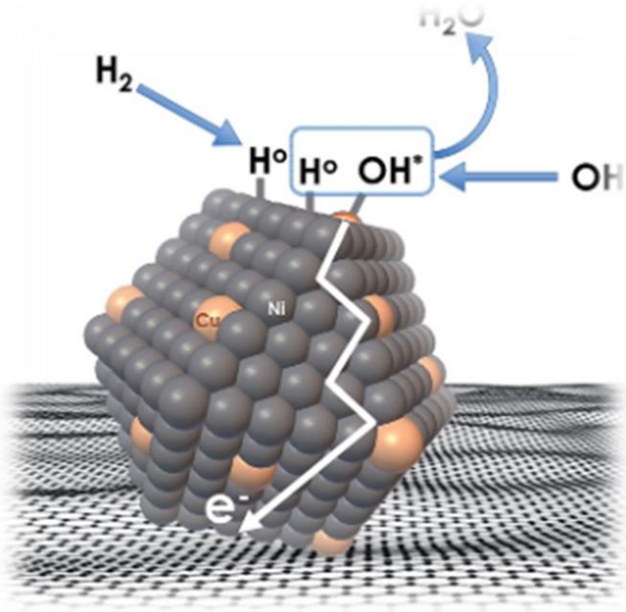


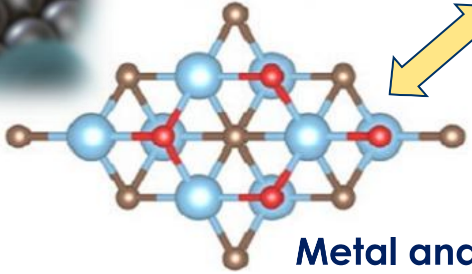
Transition Metal-
Nitrogen-Carbon
Materials





Enzymes and
Redox Proteins





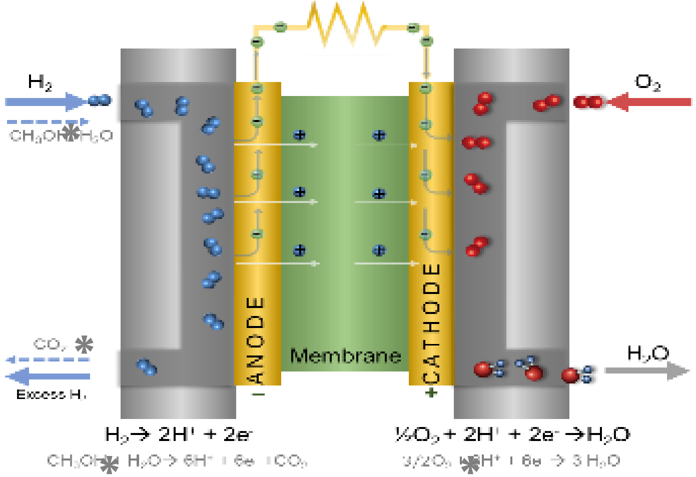
Metal and
metal-containing nano-clusters

Multi-metallic nano-particles

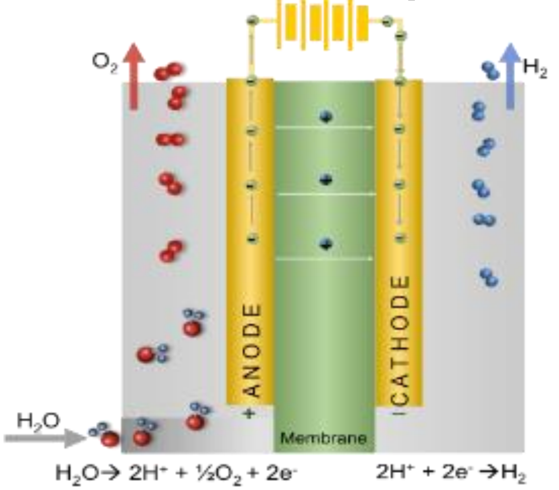
Plamen Atanassov's Group at UCI

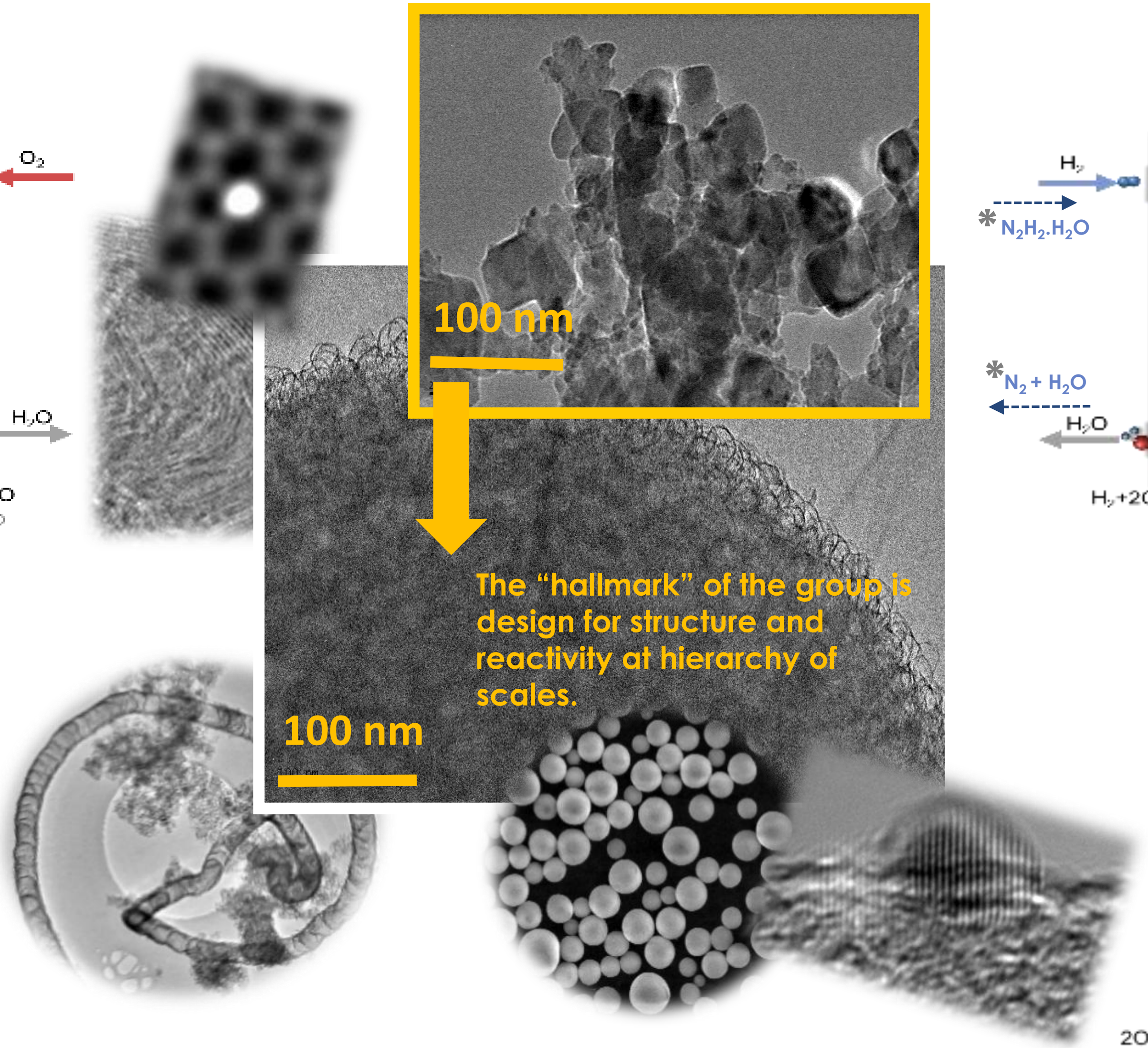
Materials for energy conversion projects address electrocatalyst needs of fuel cells and electrolyzers functioning in both alkaline and acid electrolyte.

PEM FC or DMFC

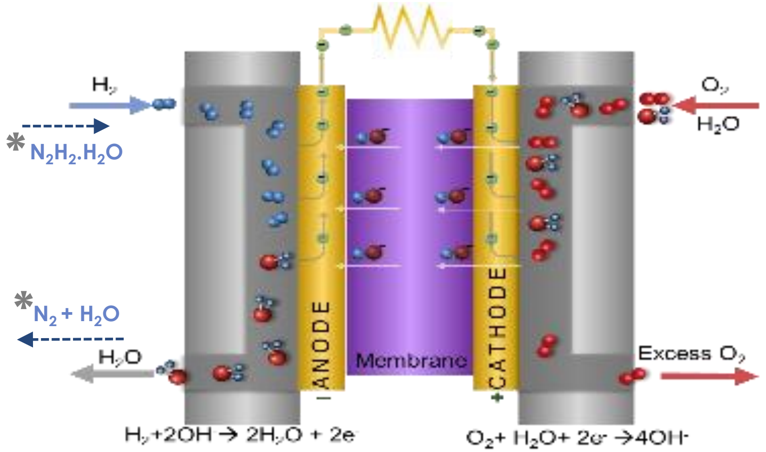


PEM Electrolyzer

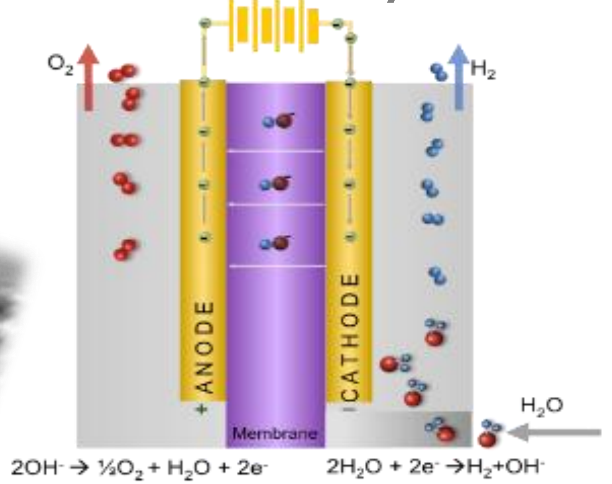




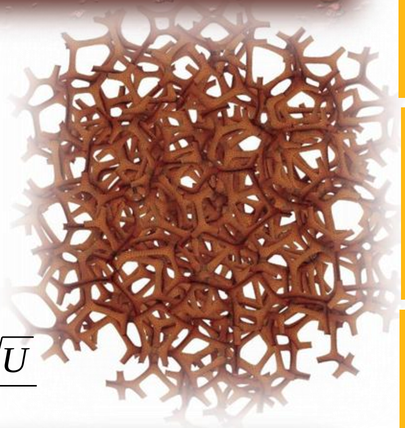
AEM FC or DHFC



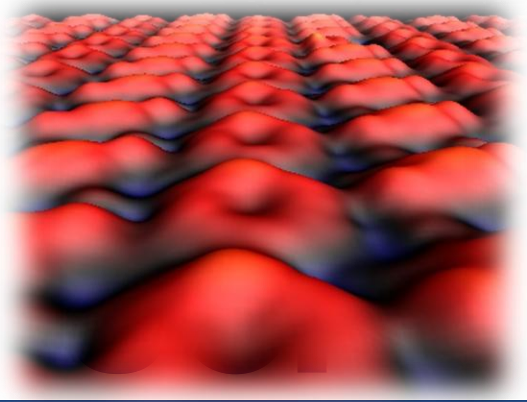
AEM Electrolyzer



Electrocatalysts Design at Hierarchy of Scales



$$\varepsilon = \frac{\tanh\sqrt{U}}{\sqrt{U}}$$



10 μm	Catalysts Layer thickness; design parameters	
1 μm	Macro-pores; agglomerates	Compression Convection
100 nm	Meso-pores; aggregates	Bulk Diffusion Knudsen Diffusion
10 nm	Meso-pores; primary particles	Configurational Diffusion Surface Diffusion
1 nm	Ionomer domains; catalyst particles	Electric Double Layer Effects Tunneling
1 Å	Inner Helmholtz Plane; catalyst surface effects	Chemical Transformation

Enzymatic Catalyst

Metallic Catalyst

Molecular Catalyst

catalysts / support surface/ … biotic/abiotic interface

Catalysts Design Platform: Carbonaceous Materials Pyrolysis

How much we know… how much we can control?

The "lava state":

- kinetics of solid-state reactions
- release of gaseous products/CVD
- quenching and kinetically stabilized moieties

Carbonaceous materials:

- defects and defects engineering
- morphological changes
- energy and entropy of defects formation

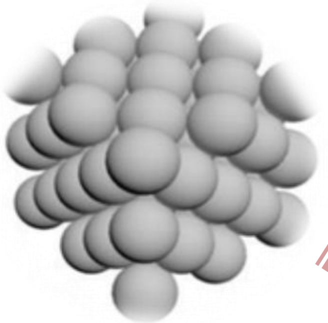
Atomoically dispersed materials:

- List of transition metals in atomically dispersed (liganded) state
- Possibility to introduce multiple metallic sites on one matrix
- Technology to decorate the materials with secondary nano-particles

Photo taken by the author during 2004 Mauna Loa eruption, Hawaii

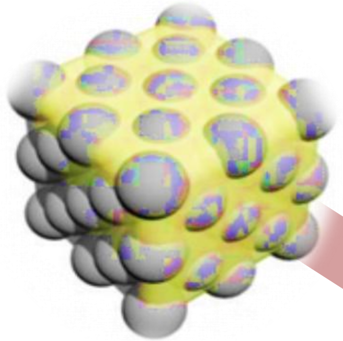
Hard Templated Materials Synthesis:

Sacrificial Support Method (SSM) – we know how to do it, because we have invented quite a bit of it ☺



Template (Sacrificial Support):

- mono-dispersed silica
- mix of mono-dispersed silica particles
- structured silica or other oxide

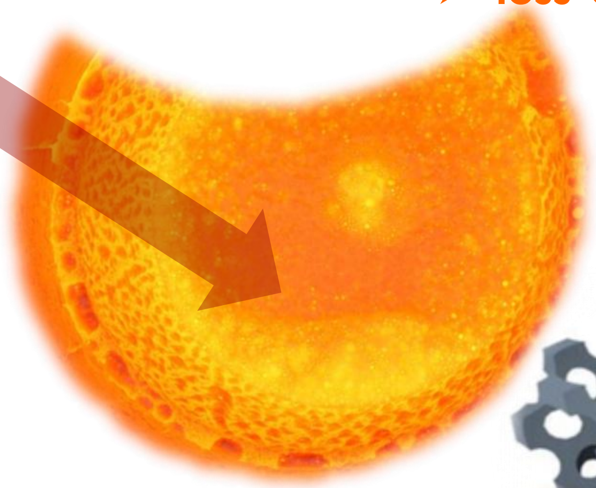


Integration:

- wet impregnation
- dry impregnation
- Mechanochemical
  a.k.a. “ball-milling”

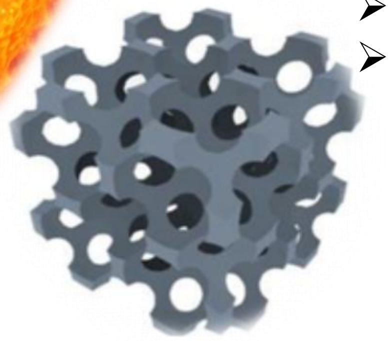
Precursor:

- metal salts for metals and ceramics
- organic molecules for carbons
- less-defined “stuff” ☺



Pyrolysis:

- controlled atmosphere, temperature
- ramping, duration time, quenching
- spray pyrolysis, flame pyrolysis, etc.



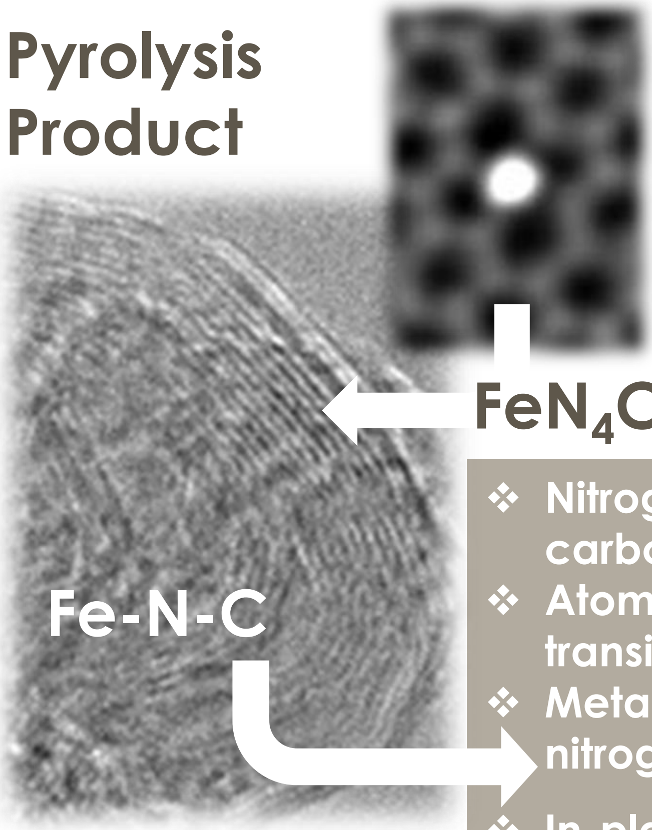
Release:

- leaching the sacrificial support
- using acid or base
- post-processing or re-pyrolysis

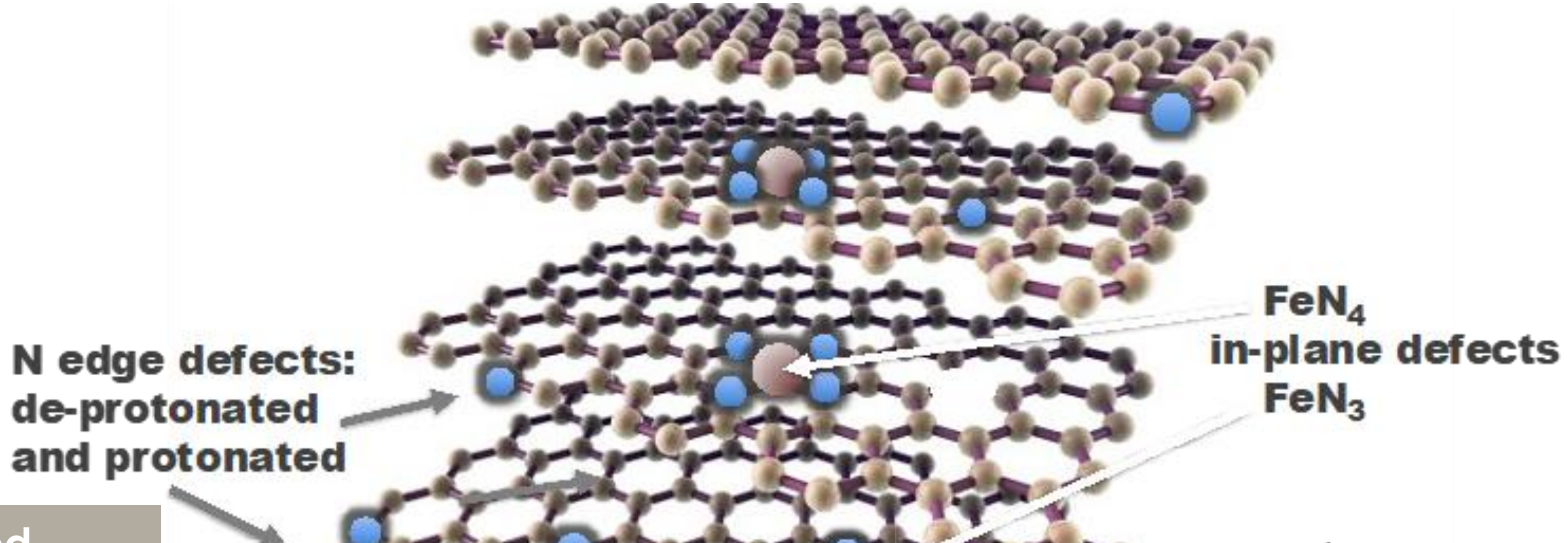
2000-2018

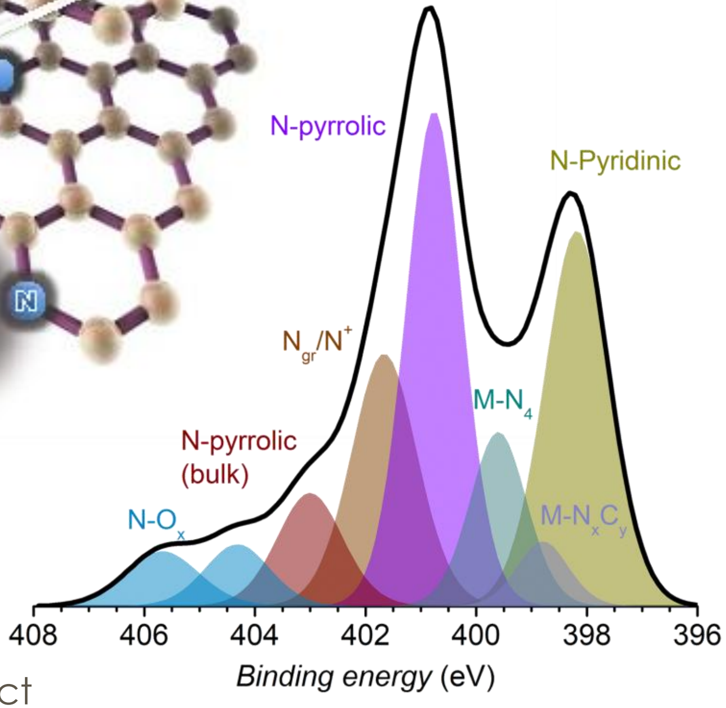
AD-Transition Metal-Nitrogen-Carbon (M-N-C) Catalysts

Pyrolysis Product



- Nitrogen-doped carbon
- Atomically dispersed transition metal ions
- Metal liganded with nitrogen
- In-plane defects
- Edge defects
- Microstructure effects





PAJARITO POWDER

First & only commercially available PGM-free catalyst product

PGM-free M-N-C Catalysts by Pajarito Powder LLC

Technology transfer success story – since 2012

PAJARITO POWDER

NPC-2000 - PGM-free cathode catalyst

- Demonstrated 1.0 kg and beyond
- Customizable formulations

Precious-Metal-Free-Catalysts™, Varipore™ technology

PHC-3000 - Catalyst support for low-PGM catalysts

- High corrosion resistance & dispersion of Pt

Engineered Catalysts Supports™

US Patent 9,728,788 August 8, 2017
US Patent 9,673,456 June 6, 2017
US Patent 9,634,331, April 25, 2017
US Patent 9,570,761, February 14, 2017
US Patent 9,515,323, December 6, 2016
US Patent 9,425,464, August 23, 2016
US Patent 8,252,711, August 28, 2012

US Patent 7,678,728 March 16, 2010
US Patent 8,252,711, August 28, 2009
PCT/US15/30890 May 14, 2015
… and more!

First catalyst product launched February 2014 – 10+ years ago!

Alexey Serov

OAK RIDGE National Laboratory

United States Patent
Olson et al.
(10) Patent No.: US 7,678,728 B2
(45) Date of Patent: Mar. 16, 2010

SELF SUPPORTING STRUCTURALLY ENGINEERED NON-PLATINUM ELECTROCATALYST FOR OXYGEN REDUCTION IN FUEL CELLS

Inventors: Tim Olson, Albuquerque, NM (US); Plamen Atanassov, Albuquerque, NM

United States Patent
Serov et al.
(10) Patent No.: US 9,728,788 B2
(45) Date of Patent: Aug. 8, 2017

MECHANOCHEMICAL SYNTHESIS FOR PREPARATION OF NON-PGM ELECTROCATALYSTS

Applicants: Alexey Serov, Albuquerque, NM (US); Plamen B Atanassov, Santa Fe, NM

B01J 37/08 (2006.01)
B01J 23/745 (2006.01)
(52) U.S. Cl.
CPC *H01M 4/8605* (2013.01); *B01J 23/745* (2013.01); *B01J 37/08* (2013.01); *H01M 4/8652* (2013.01); *H01M 4/9083* (2013.01);

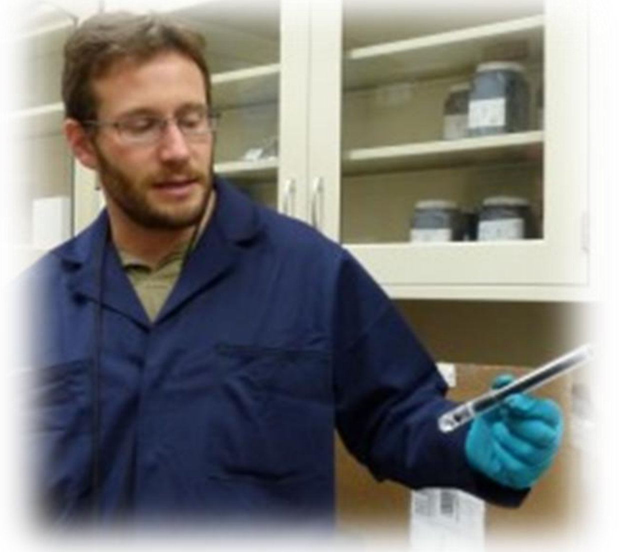
United States Patent
Serov et al.
(10) Patent No.: US 9,515,323 B2
(45) Date of Patent: Dec. 6, 2016

CATHODE CATALYSTS FOR FUEL CELLS

Applicant: STC.UNM, Albuquerque, NM (US)

Inventors: Alexey Serov, Albuquerque, NM (US); Barr Halevi, Albuquerque, NM (US); Kateryna Artyushkova, Albuquerque, NM (US); Plamen B Atanassov, Santa Fe, NM (US)

B01J 37/08 (2006.01)
B01J 23/70 (2006.01)
H01M 8/02 (2016.01)
H01M 8/10 (2016.01)
H01M 4/86 (2006.01)
H01M 4/88 (2006.01)
(52) U.S. Cl.
CPC *H01M 4/90* (2013.01); *B01J 23/70* (2013.01); *B01J 37/08* (2013.01); *H01M*

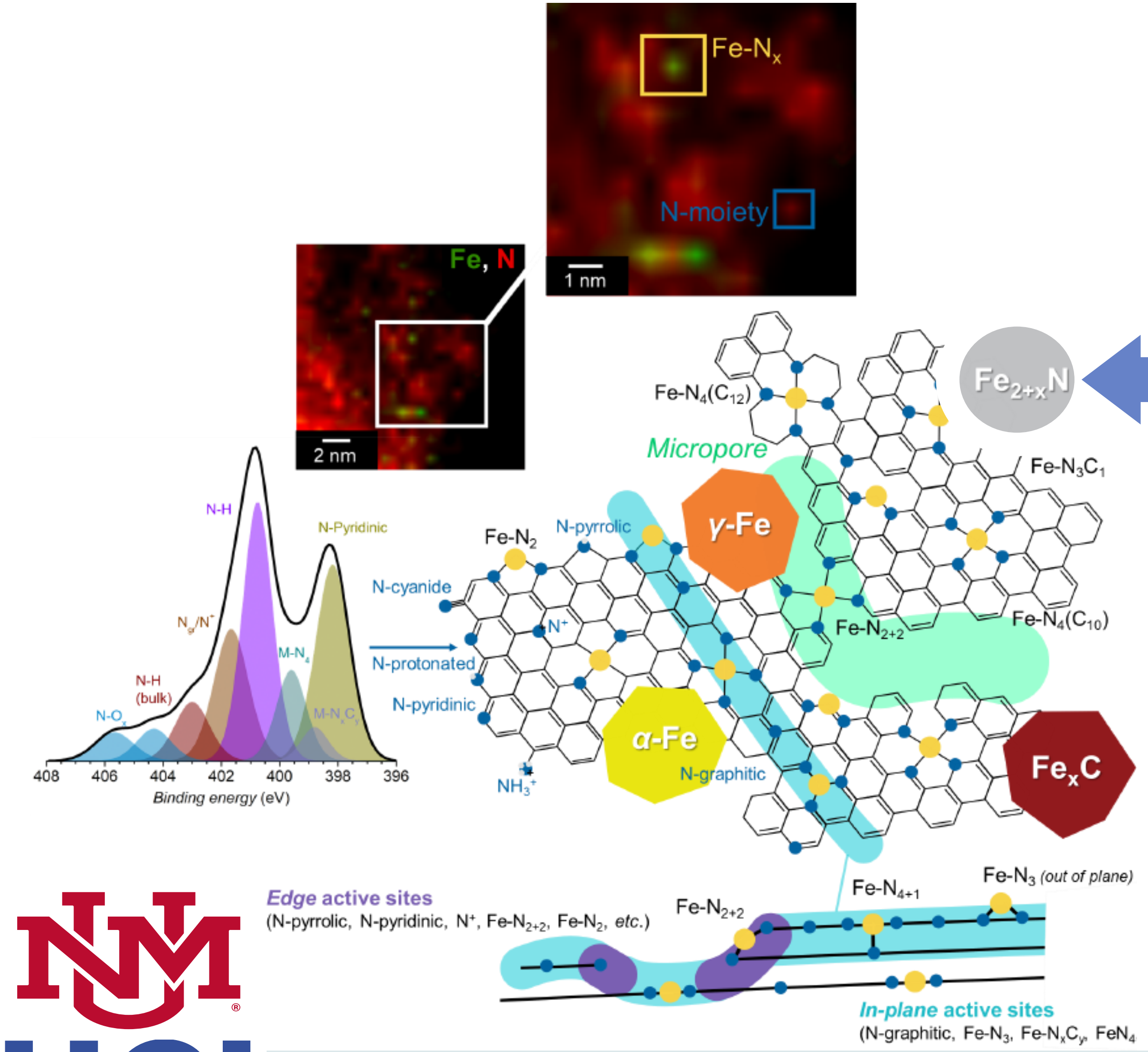


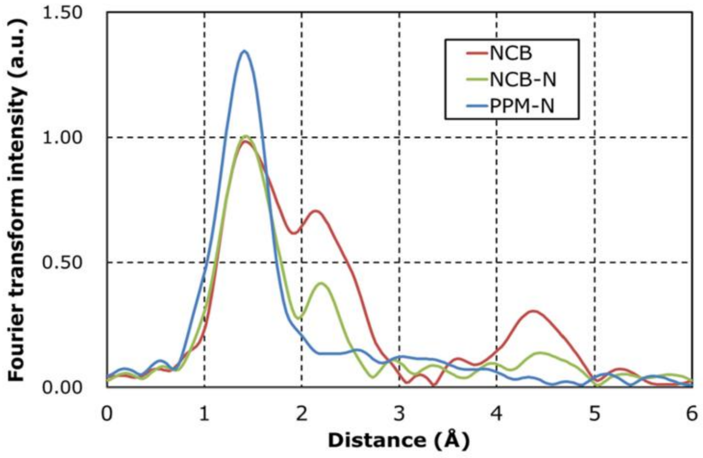
Bar Zulevi

ELECTRIC HYDROGEN

PGM-free Fe-N-C ORR Catalysts

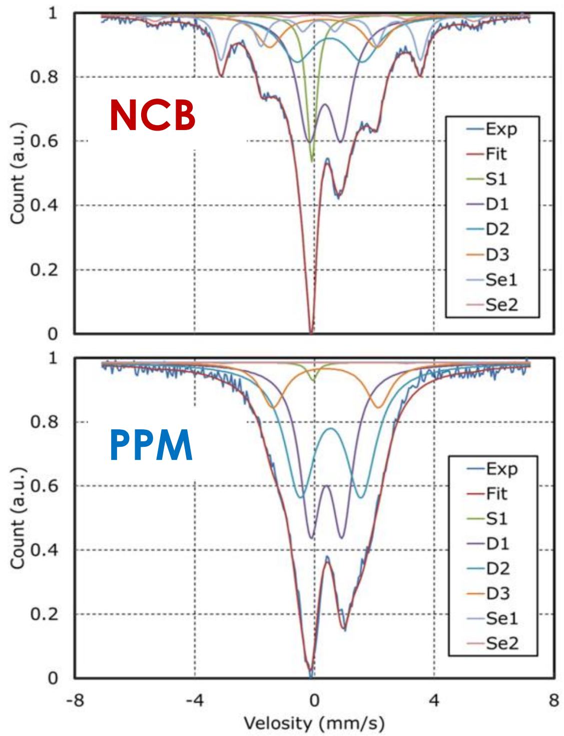
Interplay between structure and morphology





Tristan Asset

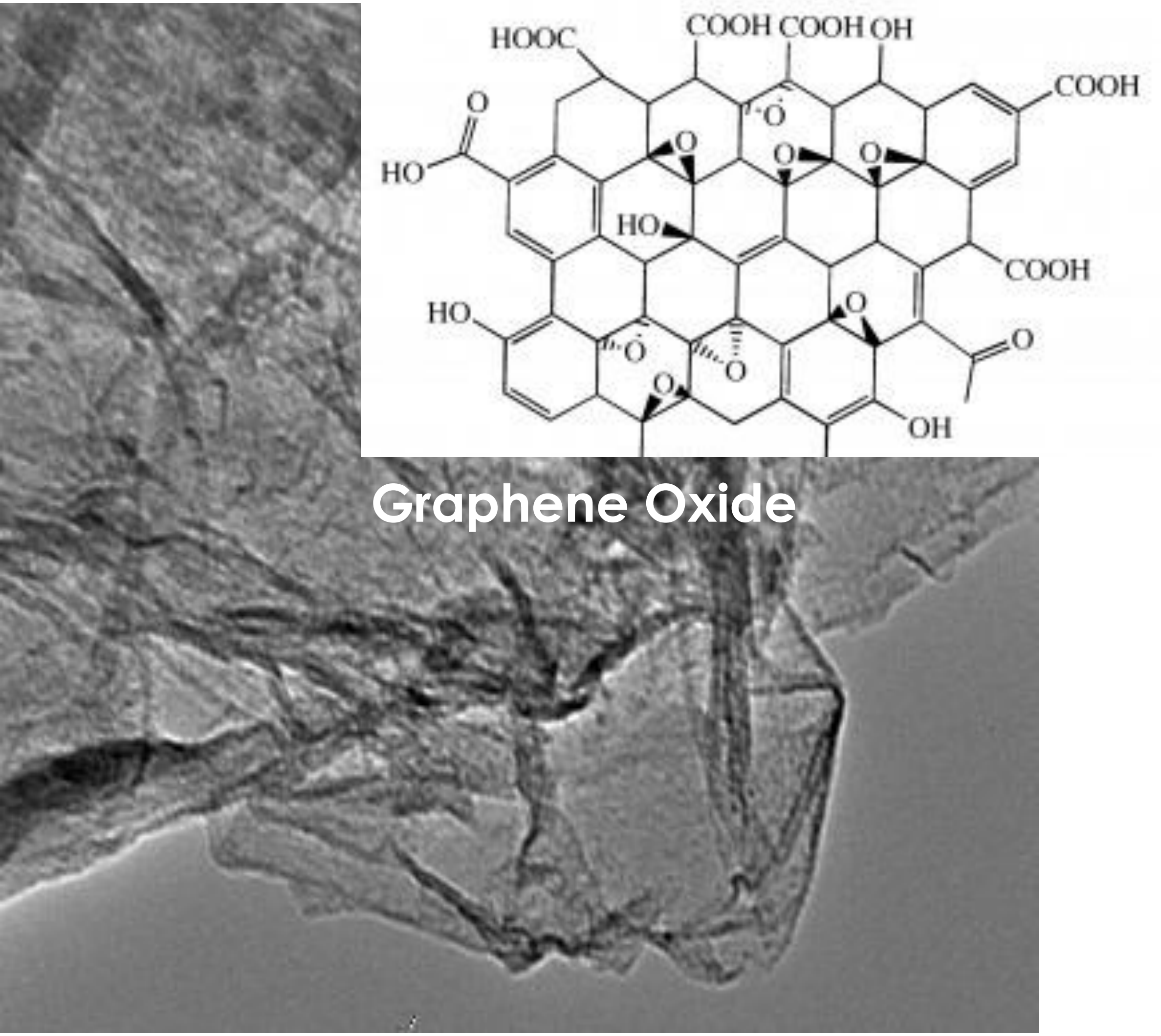
Atomically-dispersed M-C Moieties in Graphene Matrix



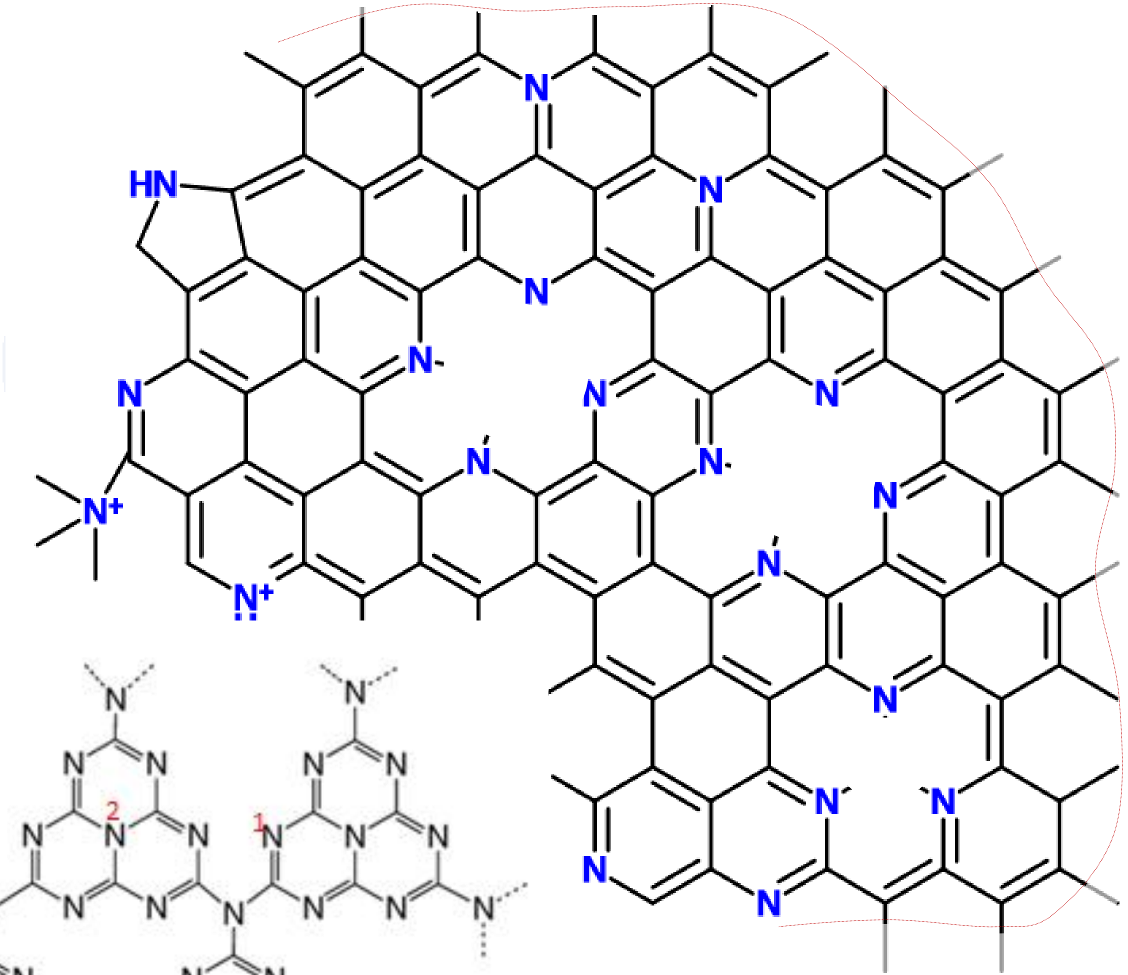
T. Asset and P. Atanassov, Surface Chemistry, Morphology and Reactivity of Iron-Nitrogen-Carbon Catalysts for Oxygen Reduction Reaction, *Joule* 4 (2020) 33-44

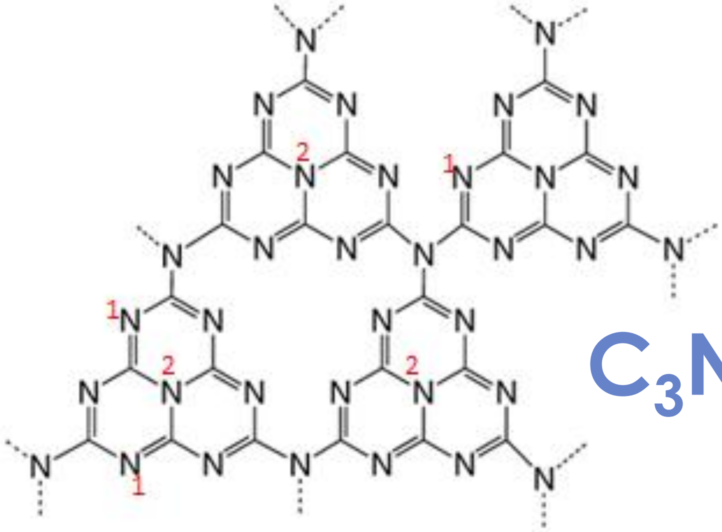
Graphene and N-C Catalysts

"Graphene Oxide" and "Graphene Nitride" ☺



Graphene Nitride!



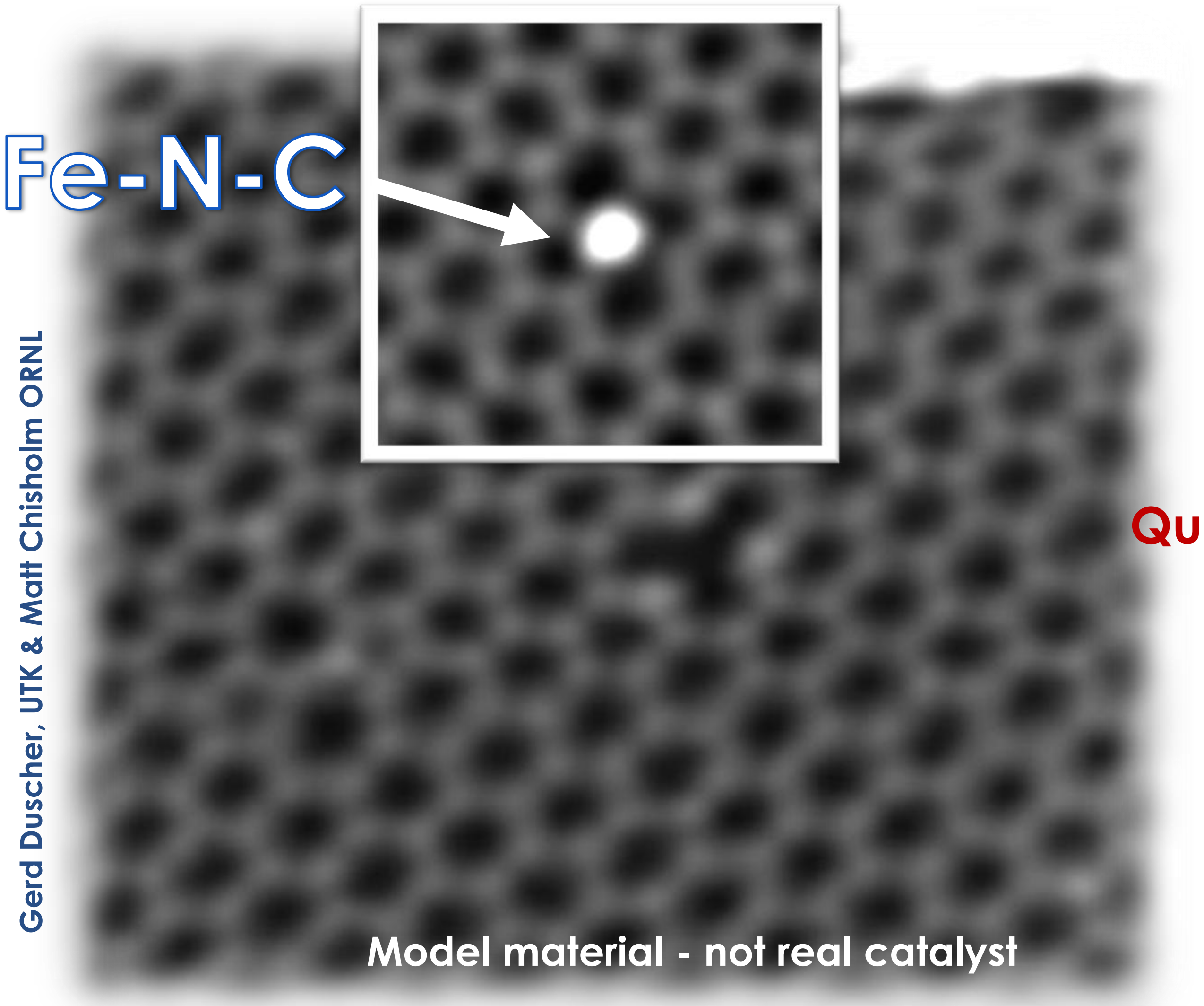


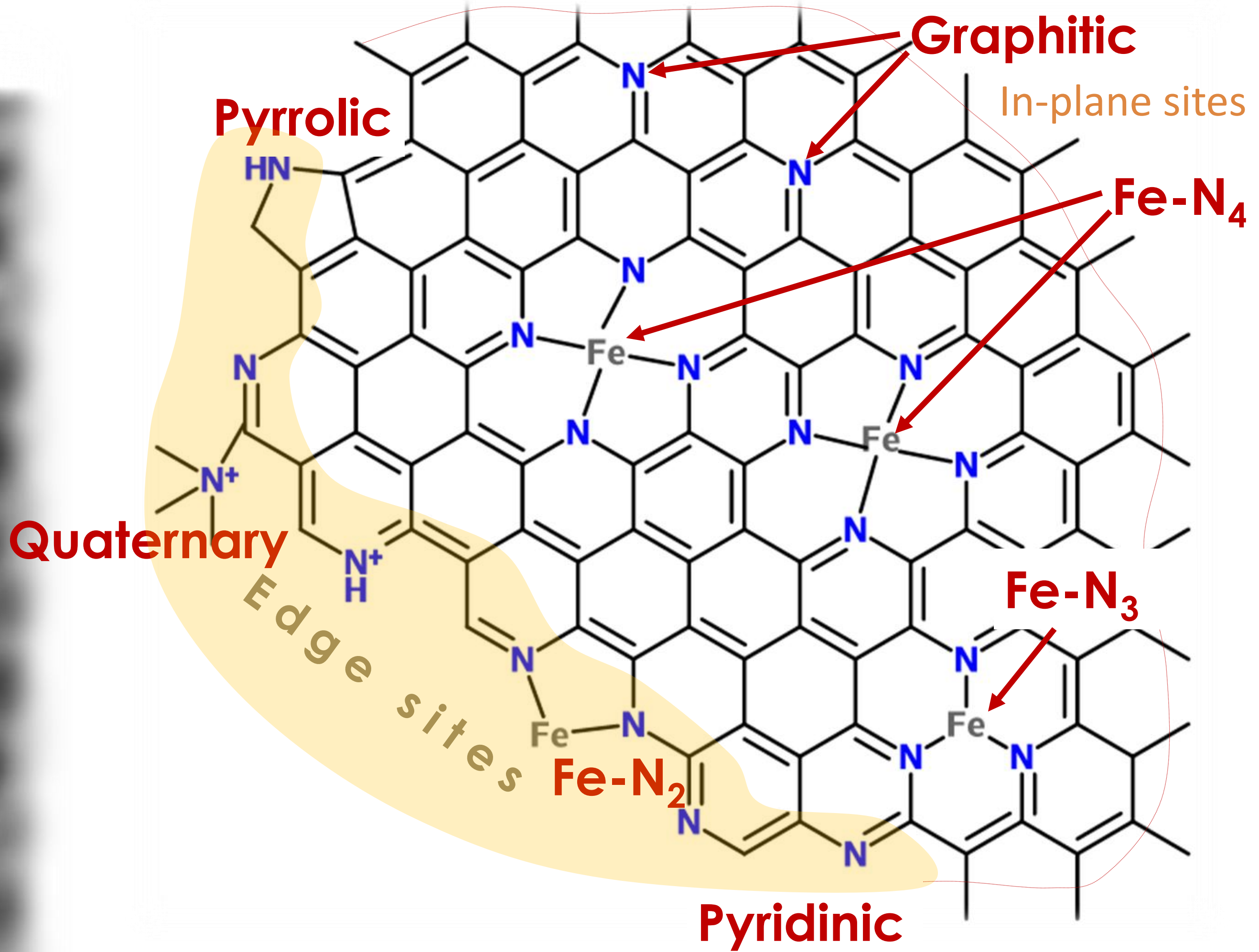
C_3N_4

UCI

Graphene and Fe-N-C Catalysts

Nitrogen-containing and transition metal moieties



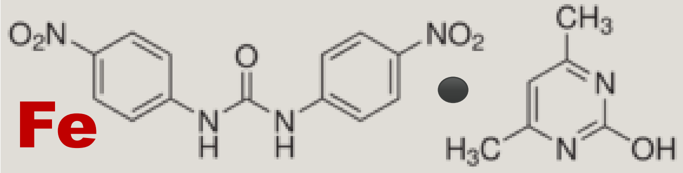


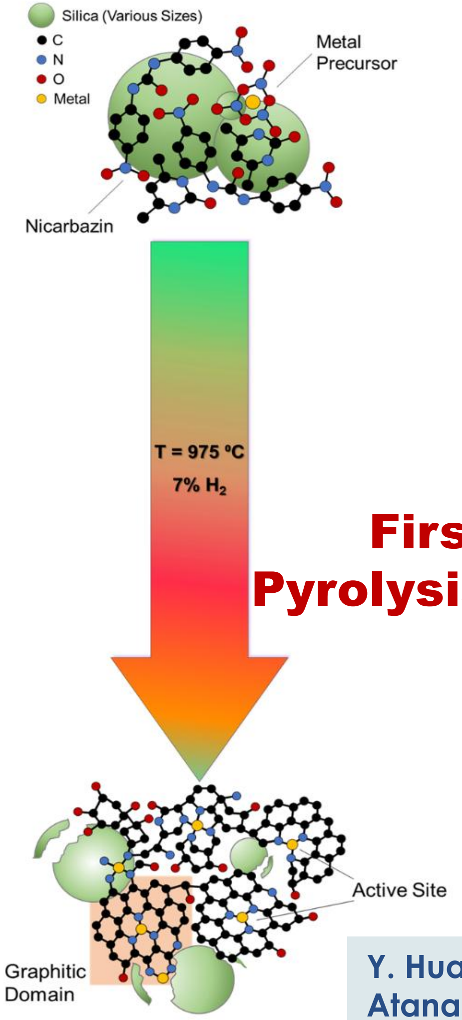
UCI

Understanding the active sites as defect structures in graphene sheet

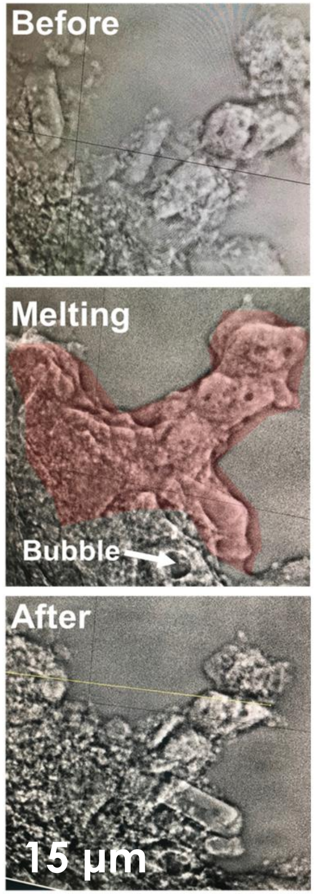
In Situ Pyrolysis of Fe-N-C Catalyst

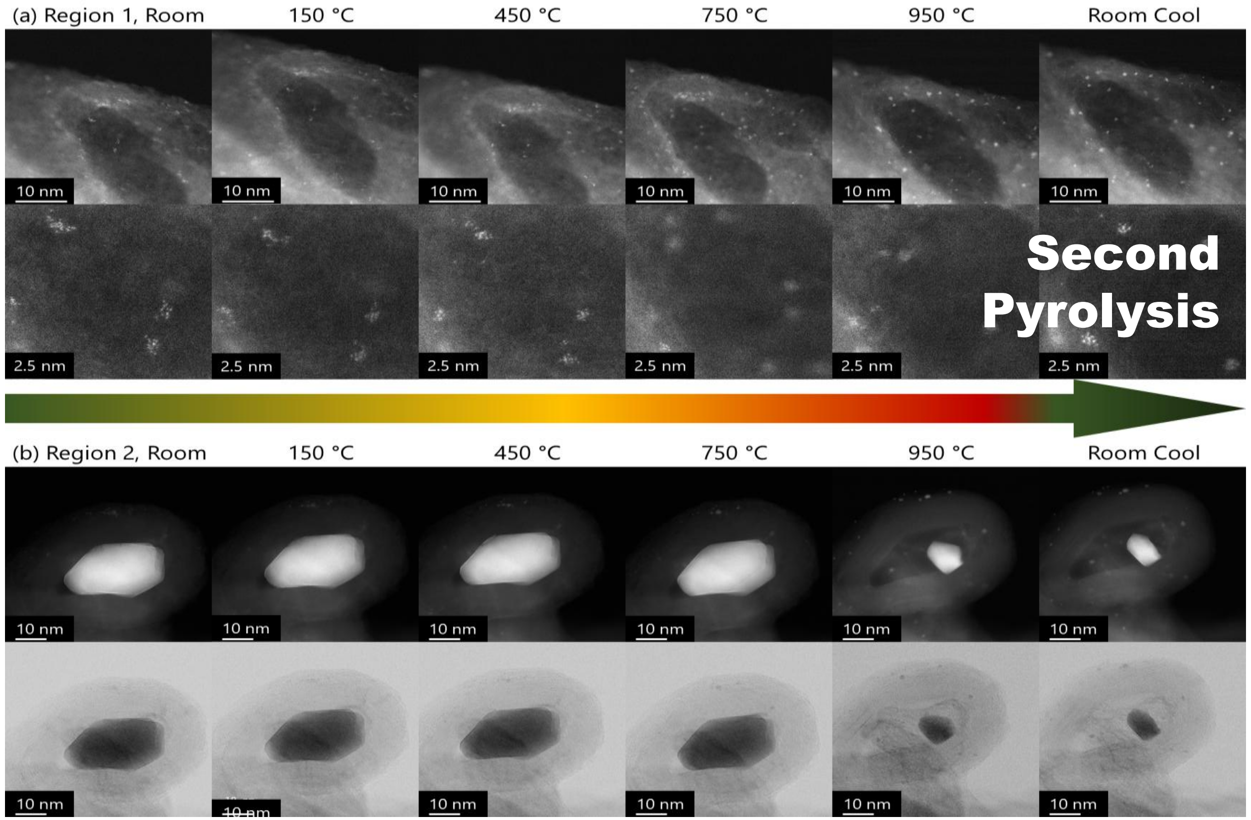
Techniques for in situ and ex situ study of the pyrolysis process





First Pyrolysis





Ying Huang

eurofins | EAG Laboratories

Yechuan Chen

Y. Huang, Y. Chen, M. Xu, T. Asset, P. Tieu, A. Gili, D.S. Kulkarni, V. de Andrade, F. De Carlo, H.S. Barnard, A. Doran, D. Parkinson, X. Pan, P. Atanassov and I.V. Zenyuk, Catalysts by Pyrolysis: Direct Observation of Chemical and Morphological Transformation Leading to Transition Metal-Nitrogen-Carbon Catalysts, *Materials Today*, 47 (2021) 53-68

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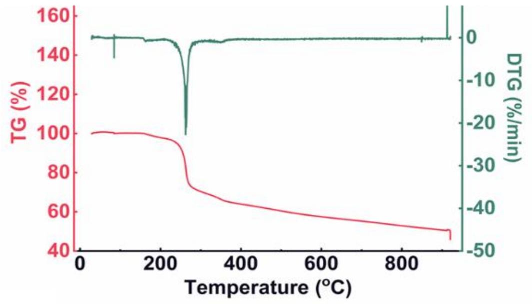
Y. Chen, Y. Huang, M. Xu, T. Asset, X. Yan, K. Artyushkova, M. Kodali, E. Murphy, A. Ly, X. Pan, I.V. Zenyuk and P. Atanassov, Catalysts by pyrolysis: Direct observation of transformations during re-pyrolysis of transition metal-nitrogen-carbon materials leading to state-of-the-art platinum group metal-free electrocatalyst, *Materials Today*, 53 (2022) 58-70

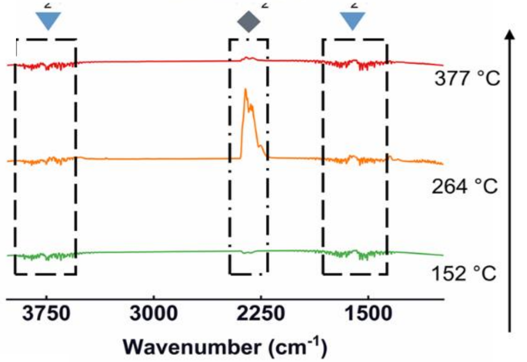
In Situ Pyrolysis by Nano X-ray CT

Material melting and decomposition during pyrolysis

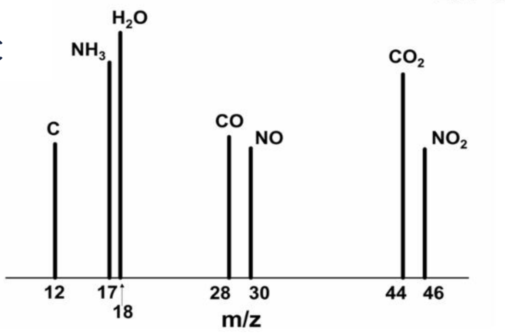
TGA and DTG plots from 180 °C to 880 °C

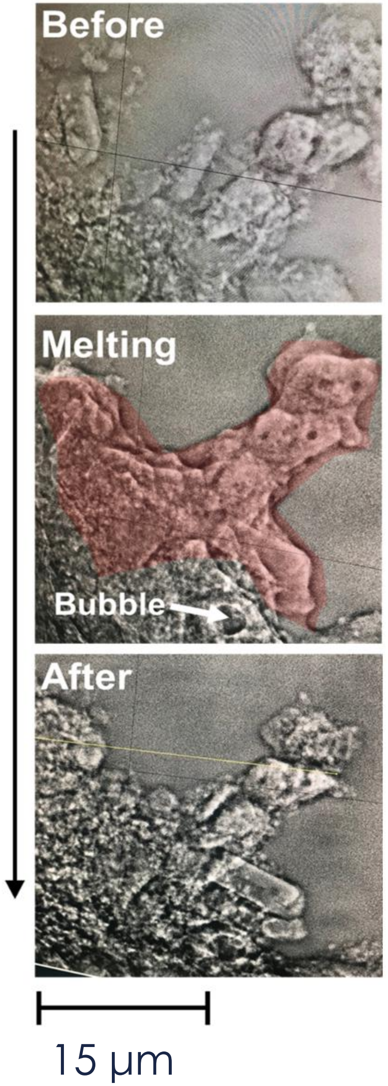


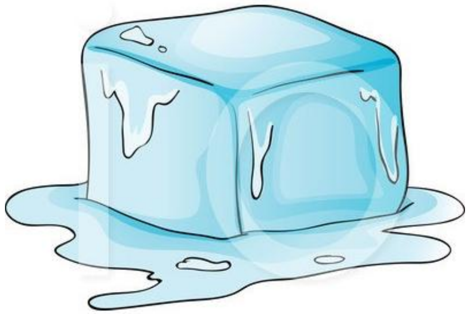
FTIR

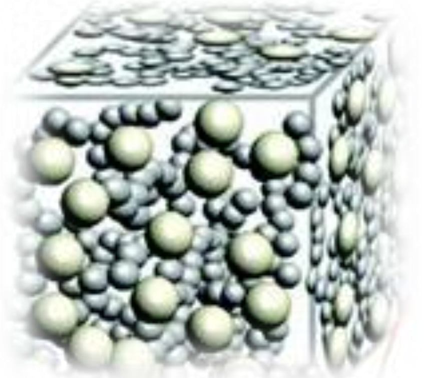


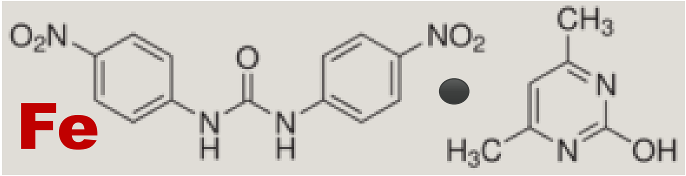
MS
264 °C

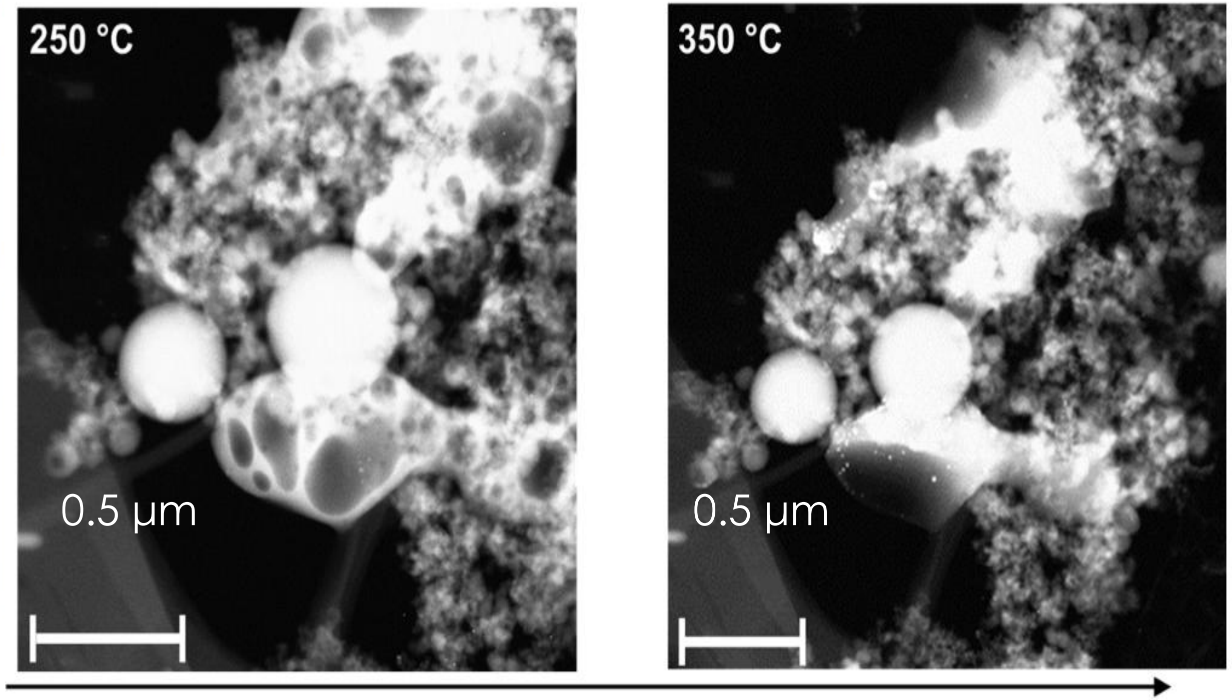












STEM micrographs @ melting stage
***in situ* STEM under ultra-high vacuum**

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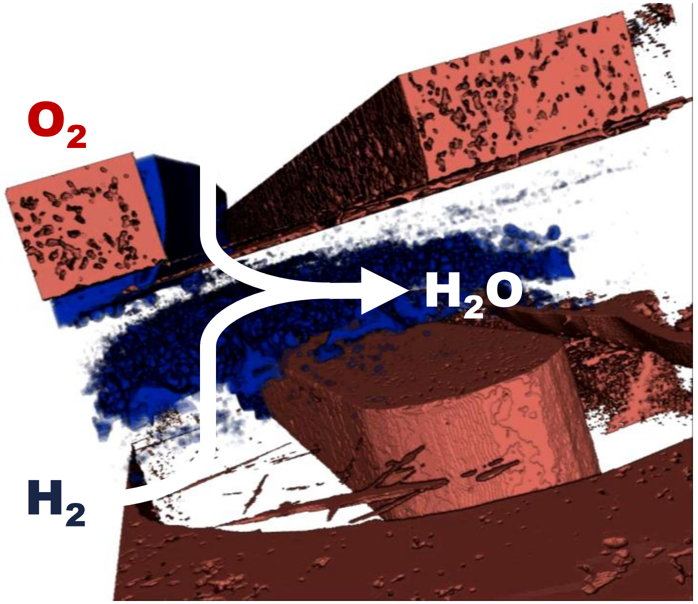
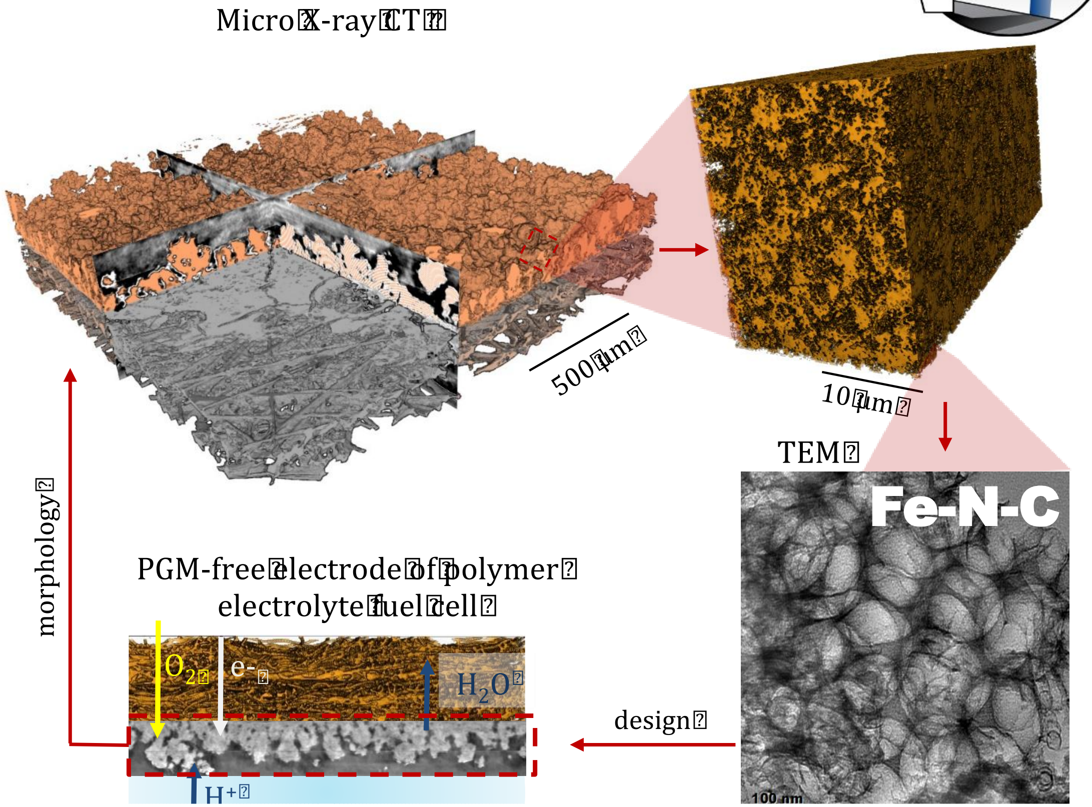
PGM-free M-N-C ORR Catalysts in Single MEA PEMFC

Structure of the catalyst layer and the effect of water management on performance

Prof. Iryna Zenyuk
NFCRC





- Water formation in catalysts layer by Nano-X-ray CT
- Operando observation of water removal by Micro-X-ray CT

A. Serov, A.D. Shum, X. Xiao, K. Artyushkova, I.V. Zenyuk and P. Atanassov, Platinum Group Metal-free Catalyst Design and Electrode Architecture: Insights from Chemical Composition and Morphology on Membrane Electrode Assembly Structure and Function, *Appl. Catalysis B,* 237 (2018) 1139-1147

S.J. Normile, D. Sabarirajan, O. Calzada, V. De Andrade, X. Xiao, P. Mandal, D.Y. Parkinson, A. Serov, P. Atanassov and I.V. Zenyuk, Direct Observations of Liquid Water Formation at Nano- and Micro-scale in Platinum Group Metal-free Electrodes by *Operando* X-ray Computed Tomography, *Materials Today – Energy*, 9 (2018) 187-197

J. Liu, M.R. Talarposhti, T. Asset, D.C. Sabarirajan, D. Parkinson, P. Atanassov and I.V. Zenyuk, Understanding the Role of Interfaces for Water Management in PGM-free Electrodes in PEFC, *ACS Applied Energy Materials*, 2 (2019) 53542-3553

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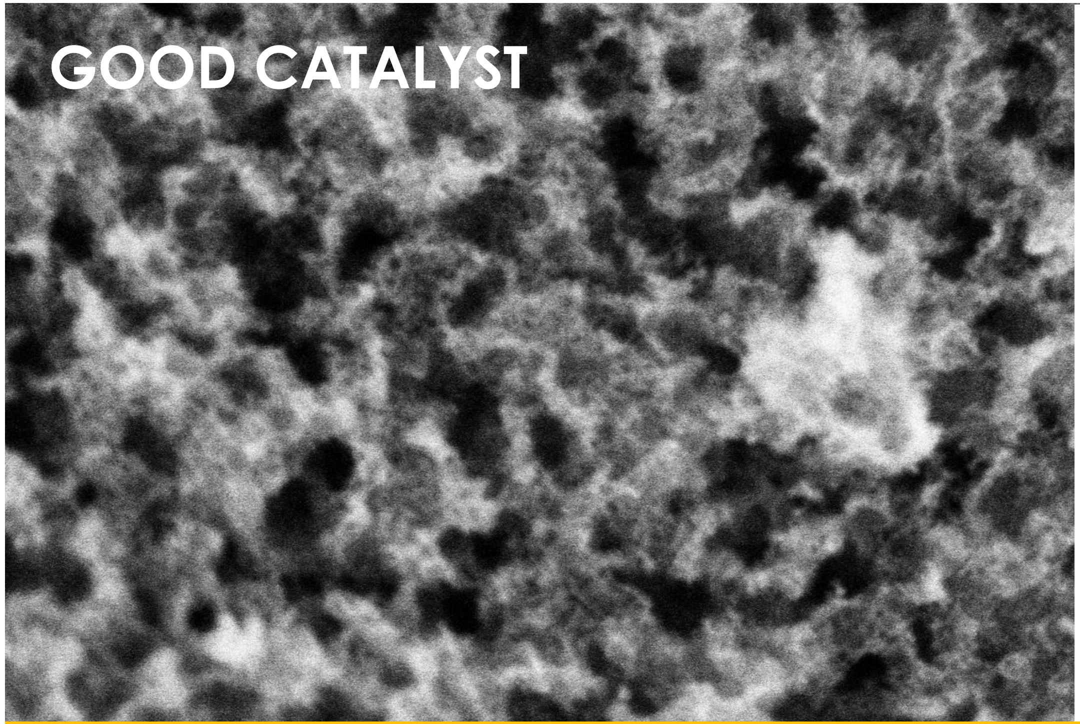
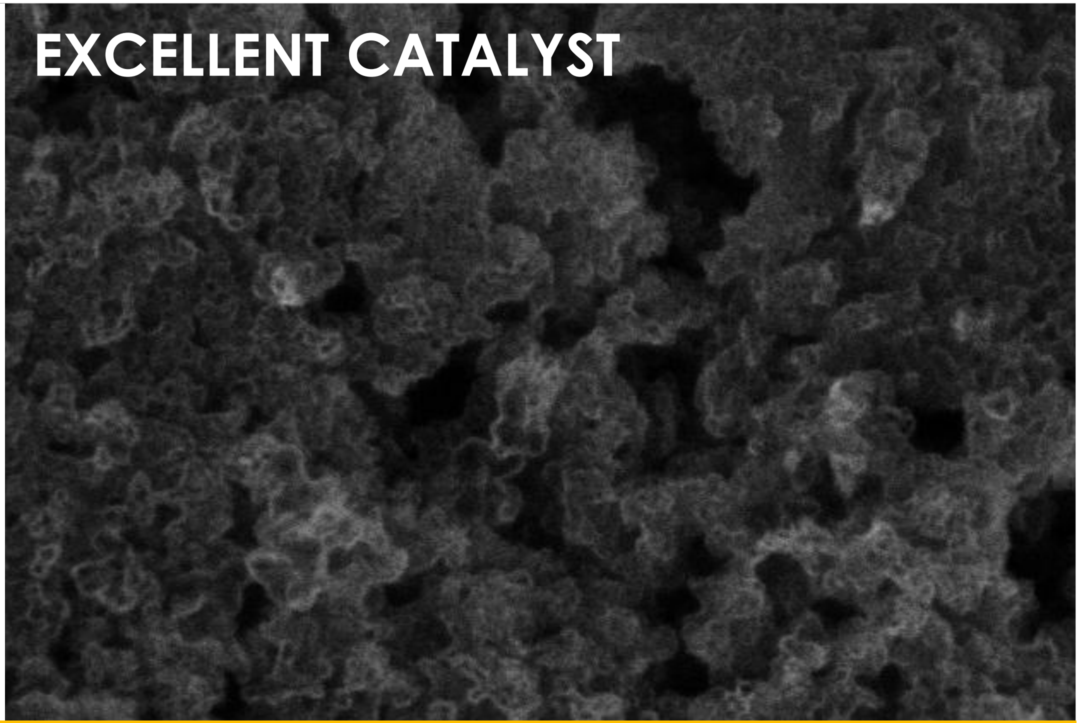
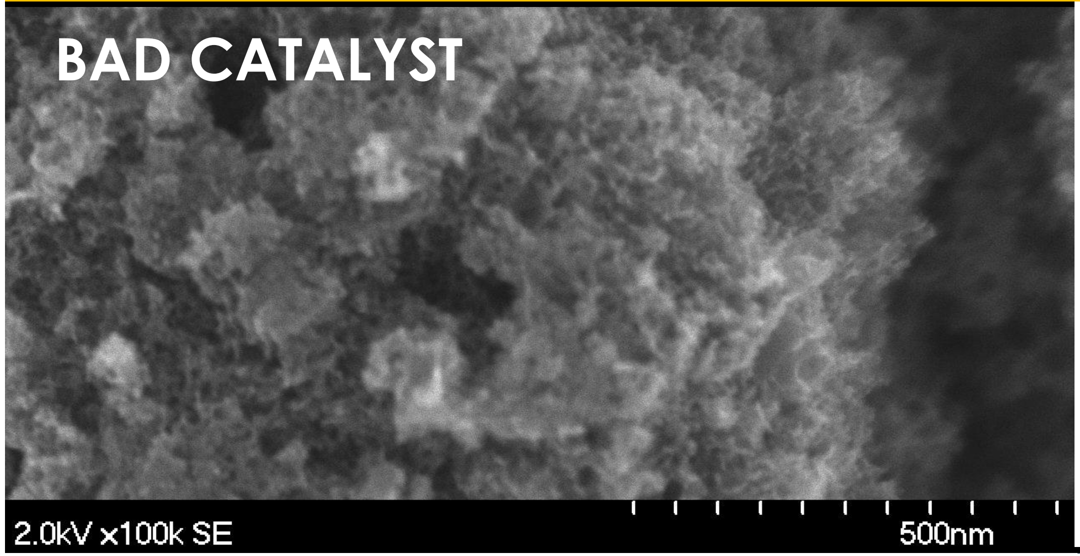
M-N-C Catalysts Morphology

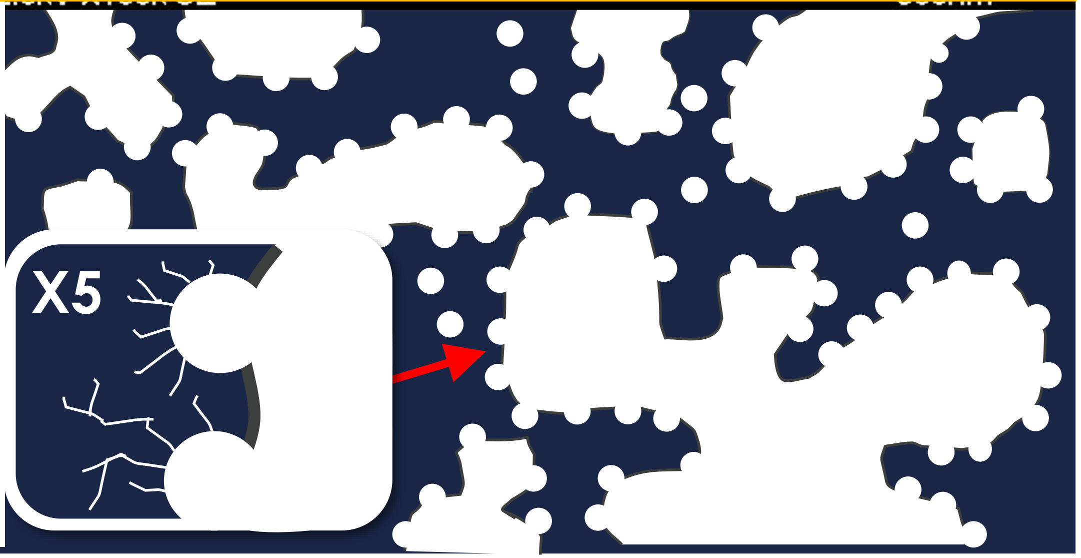
Micro-porosity is disadvantageous/detrimental



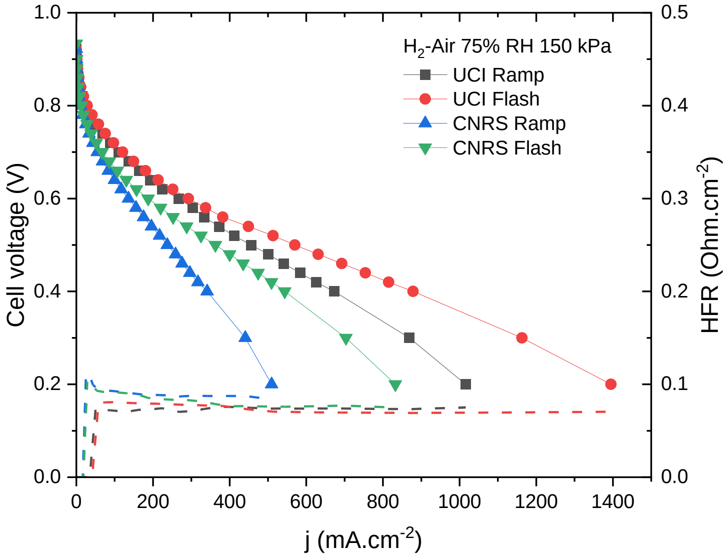


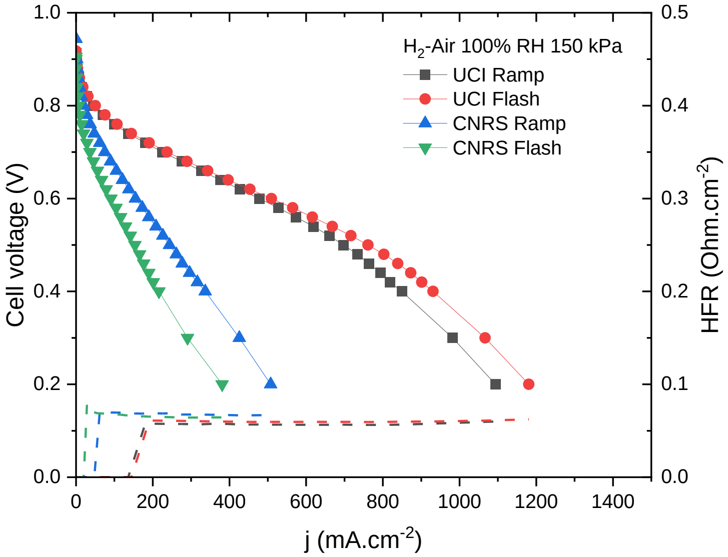
Porosity / PSD in Fe-N-C catalysts is critically important for MEA success

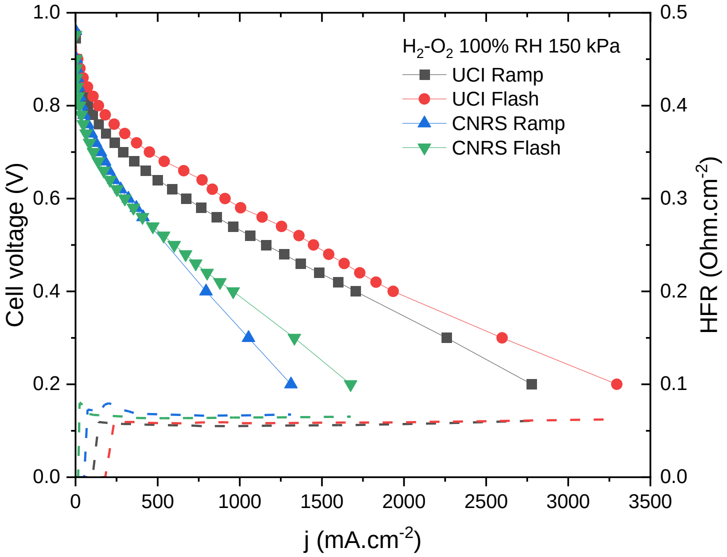




Effects of Catalysts Morphology on MEA Performace







- Fe-N-C PGM-free catalysts derived from different precursor/synthesis methods are distinctly different materials
- Hierarchical porosity is displayed across different classes of materials and result in distinctly different catalysts' behavior specifically in MEA.
- Successful MEA optimization is a task "within the sub-class
- Achieving superior performance with such distinctly different Fe-N-C PGM-free catalysts is often associated with water management.
- This suggests Eley-Rideal-like microkinetic mechanism of ORR in MEA.

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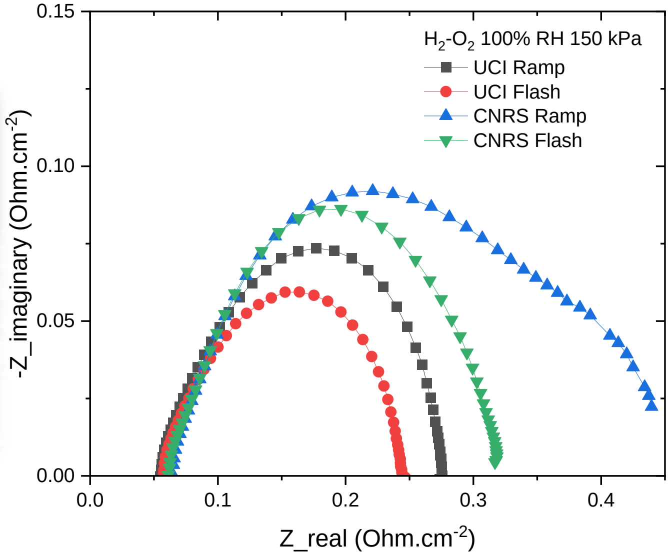
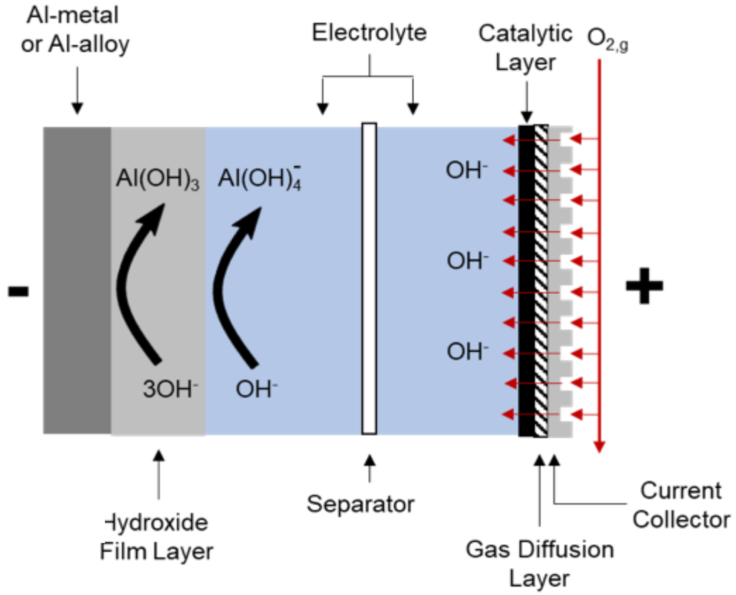
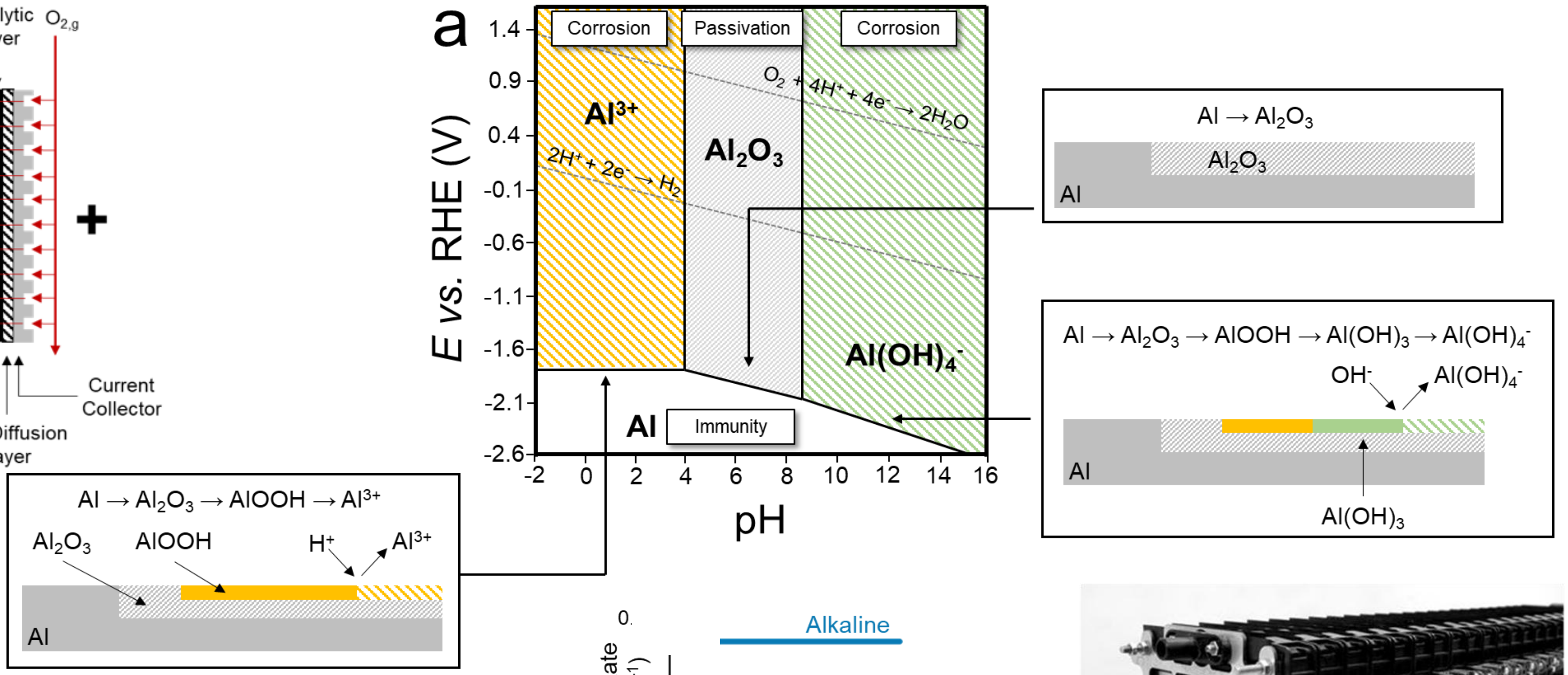
Yuanchao Liu

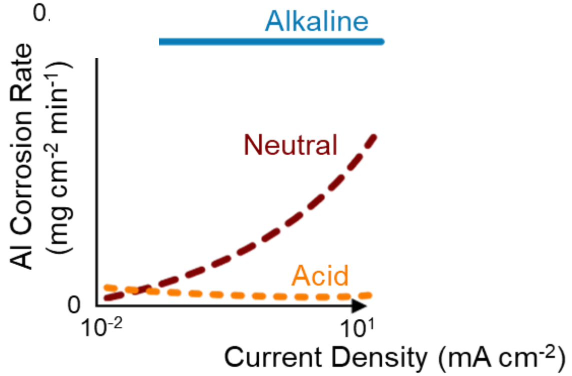
3M



Aluminum-air and Zn-air Batteries







Robert Buckingham

GENERAL ATOMICS

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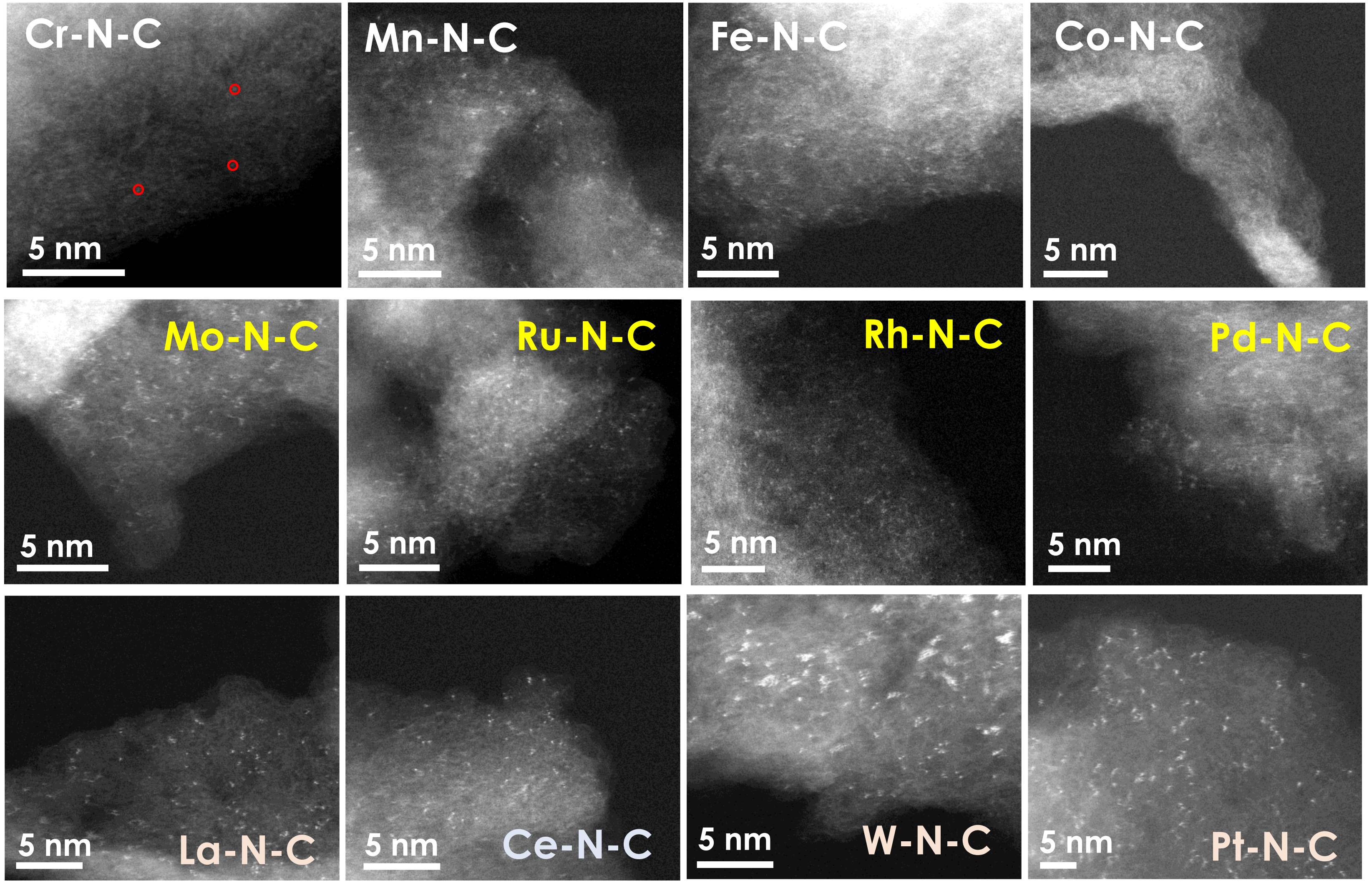
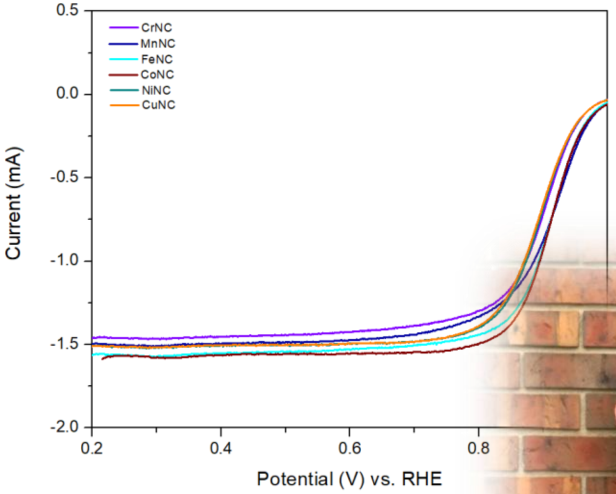
R. Buckingham, T. Asset and P. Atanassov, New Generation of Aluminum-Air Batteries: Critical Advances in Alloys, Electrolytes and Design, *Journal of Power Sources*, (2021), DOI: 10.1016/j.jpowsour.2021.229762

Broad Spectrum of M-N-C Materials



M-N-C ORR Catalysts

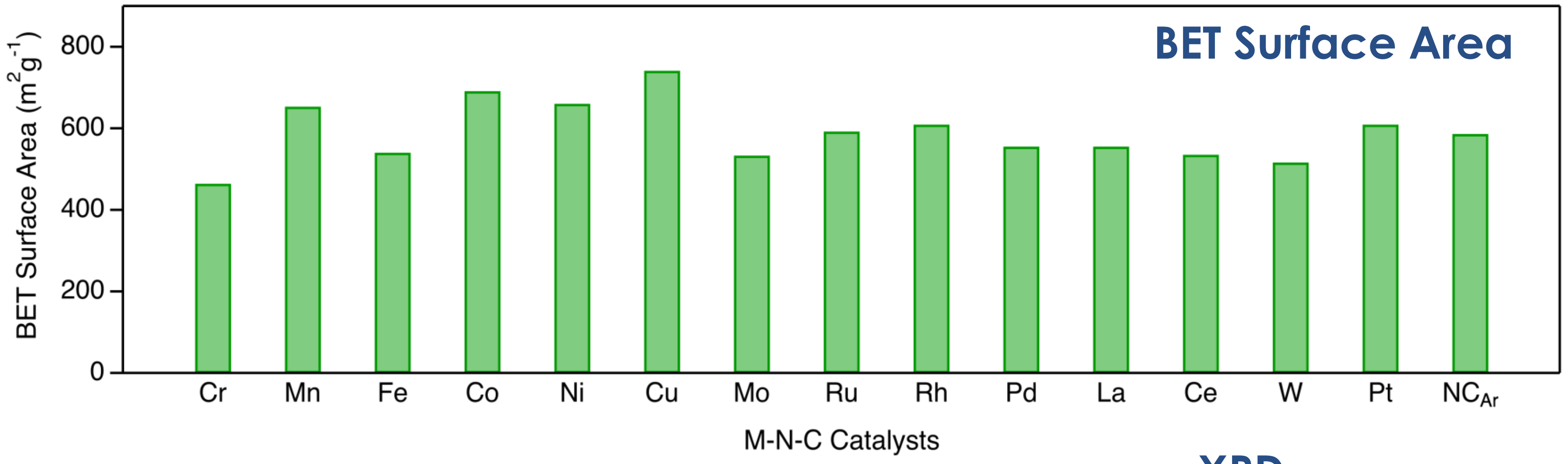


UCI Broad diversity of atomically-dispersed M-N-C materials enables addressing broad spectrum of catalytic reactions

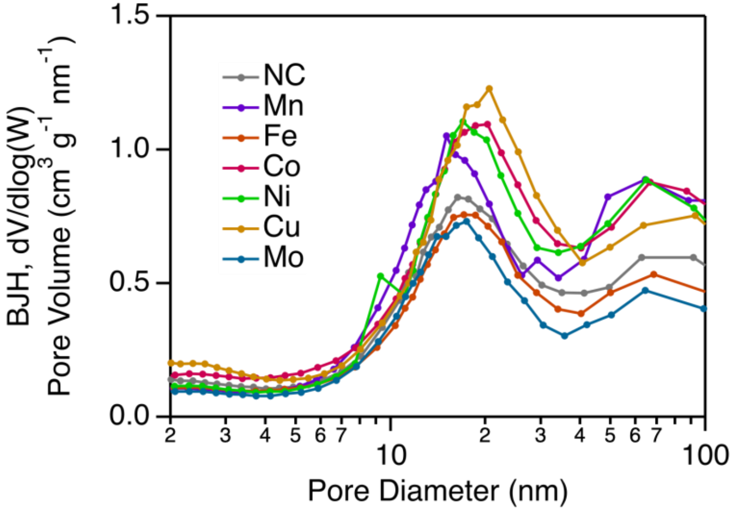
Eamonn Murphy

Los Alamos NATIONAL LABORATORY

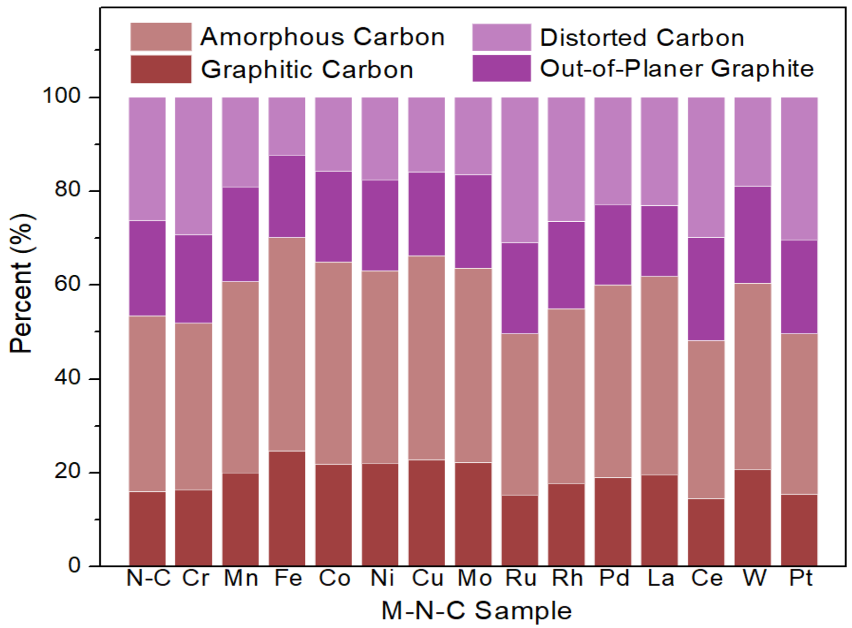
Structure of Atomically Dispersed M-N-C Materials



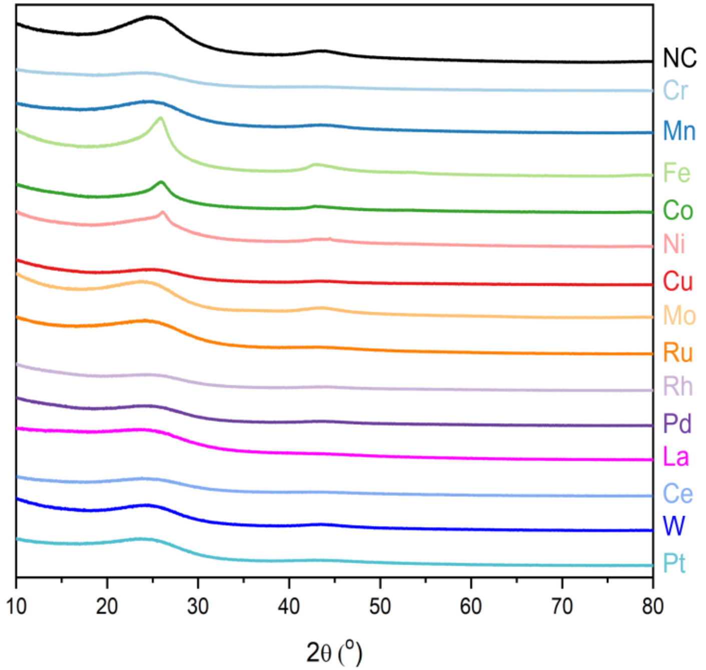
Pore size distribution



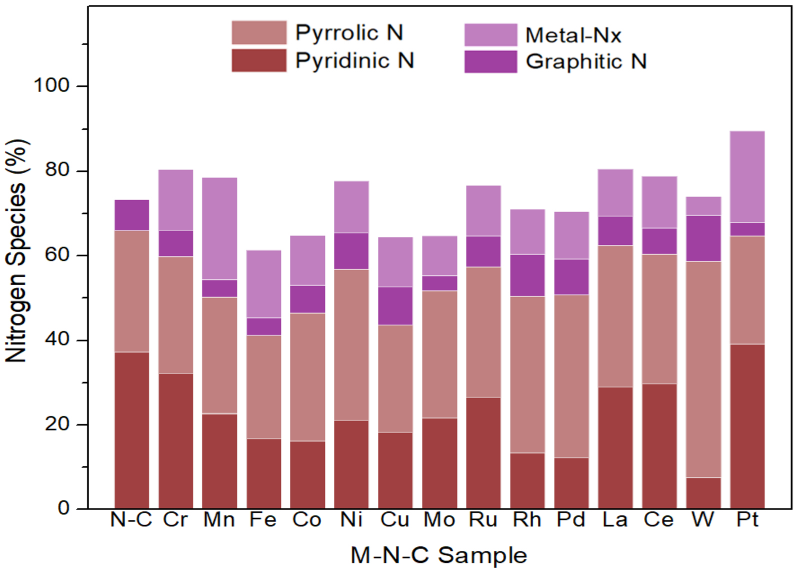
Raman – carbon type content



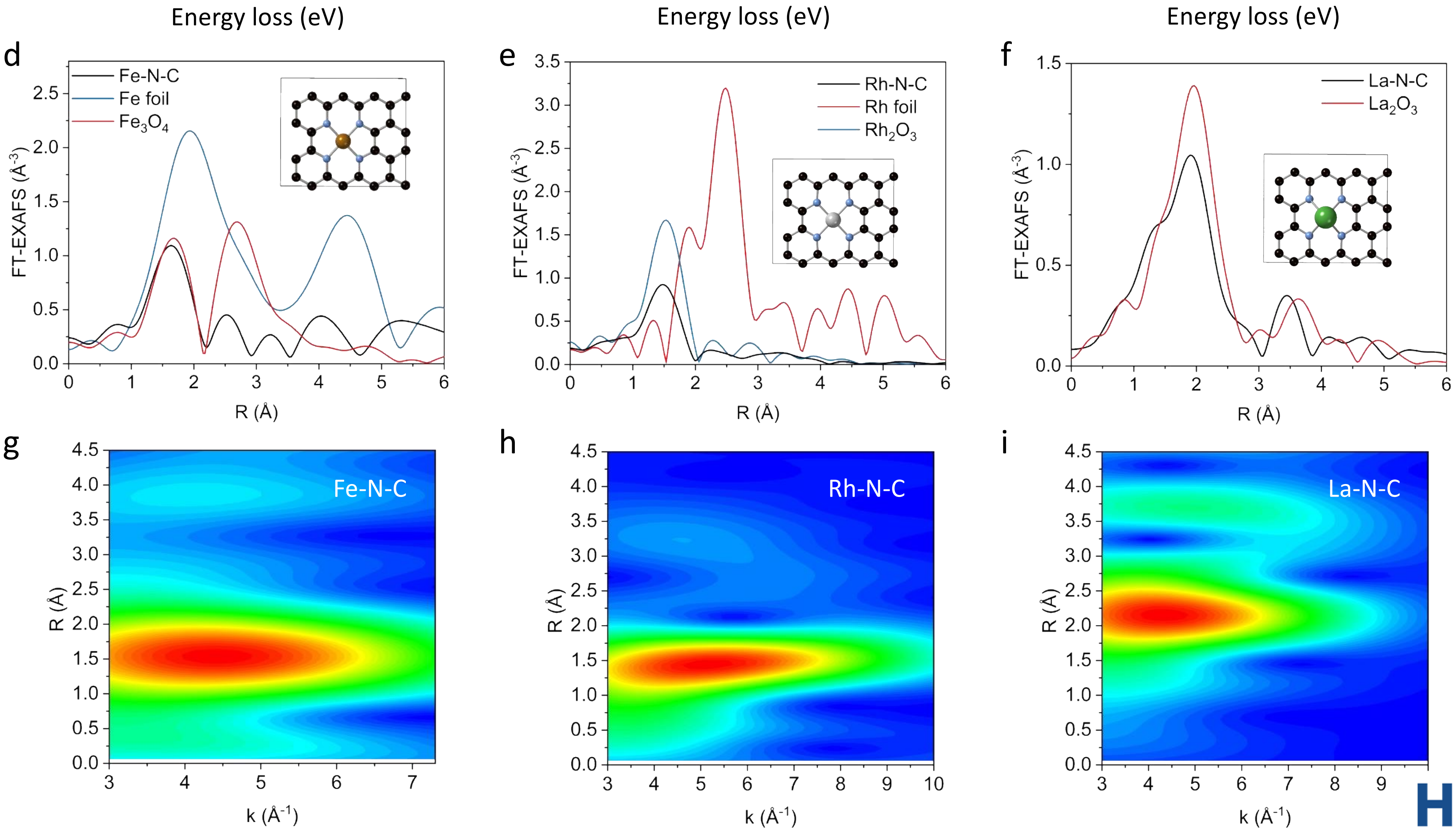
XRD



XPS- nitrogen speciation



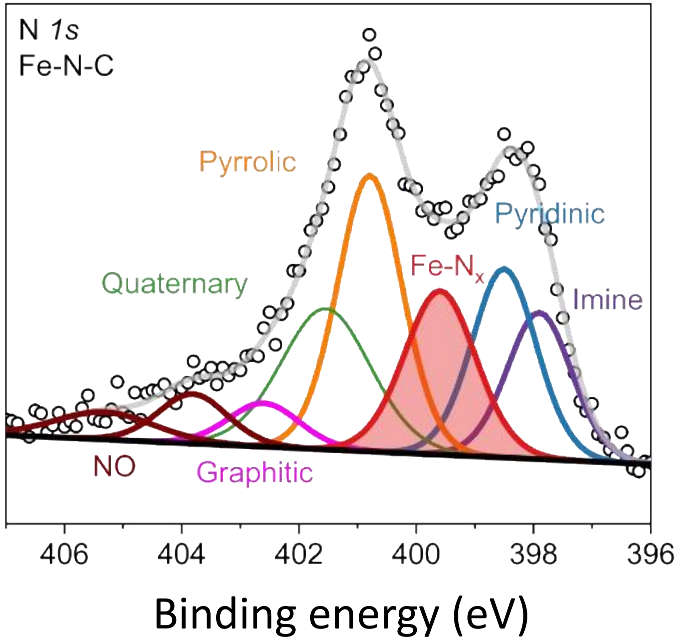
Chemical Structure of M-N-C Materials in the "Library"

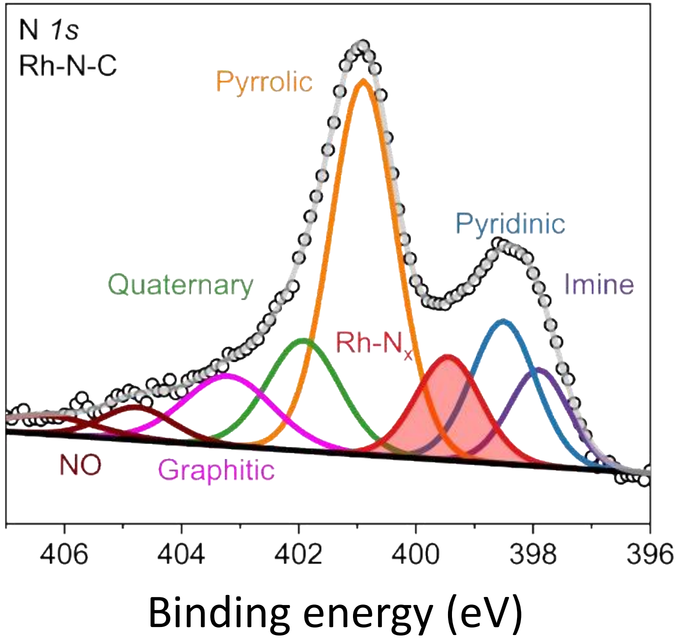


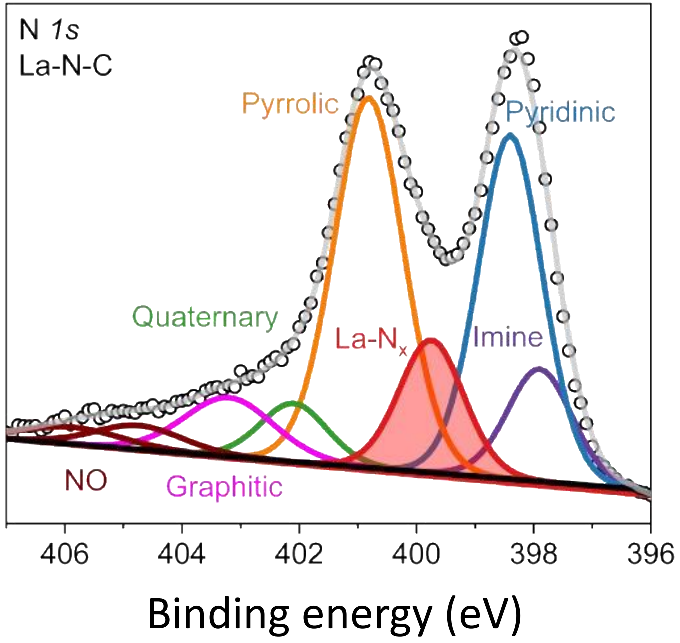
E. Murphy, Y. Liu, I. Matanovic, Y. Huang, A. Ly, S. Guo, W. Zang, X. Yan, A. Martini, J. Timoshenko, B. Roldan Cuenya, I.V. Zenyuk, X. Pan, E.D. Spoerke, and P. Atanassov, Elucidating Electrochemical Nitrate and Nitrite Reduction over Atomically Dispersed Transition Metal Sites, *Nature Communications*, (2023) DOI: 10.1038/s41467-023-40174-4

Surface Composition of M-N-C Materials in the “Library”

Rich surface chemistry of M-N-C by SSM allow targeting multiple reactions: CO_2RR and beyond







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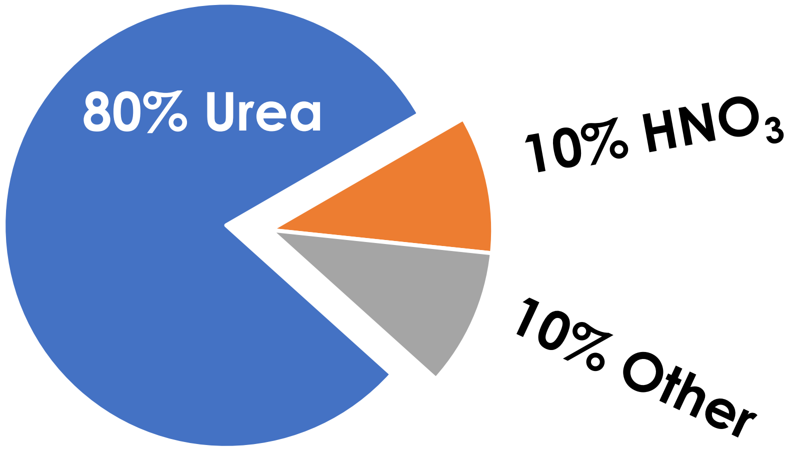
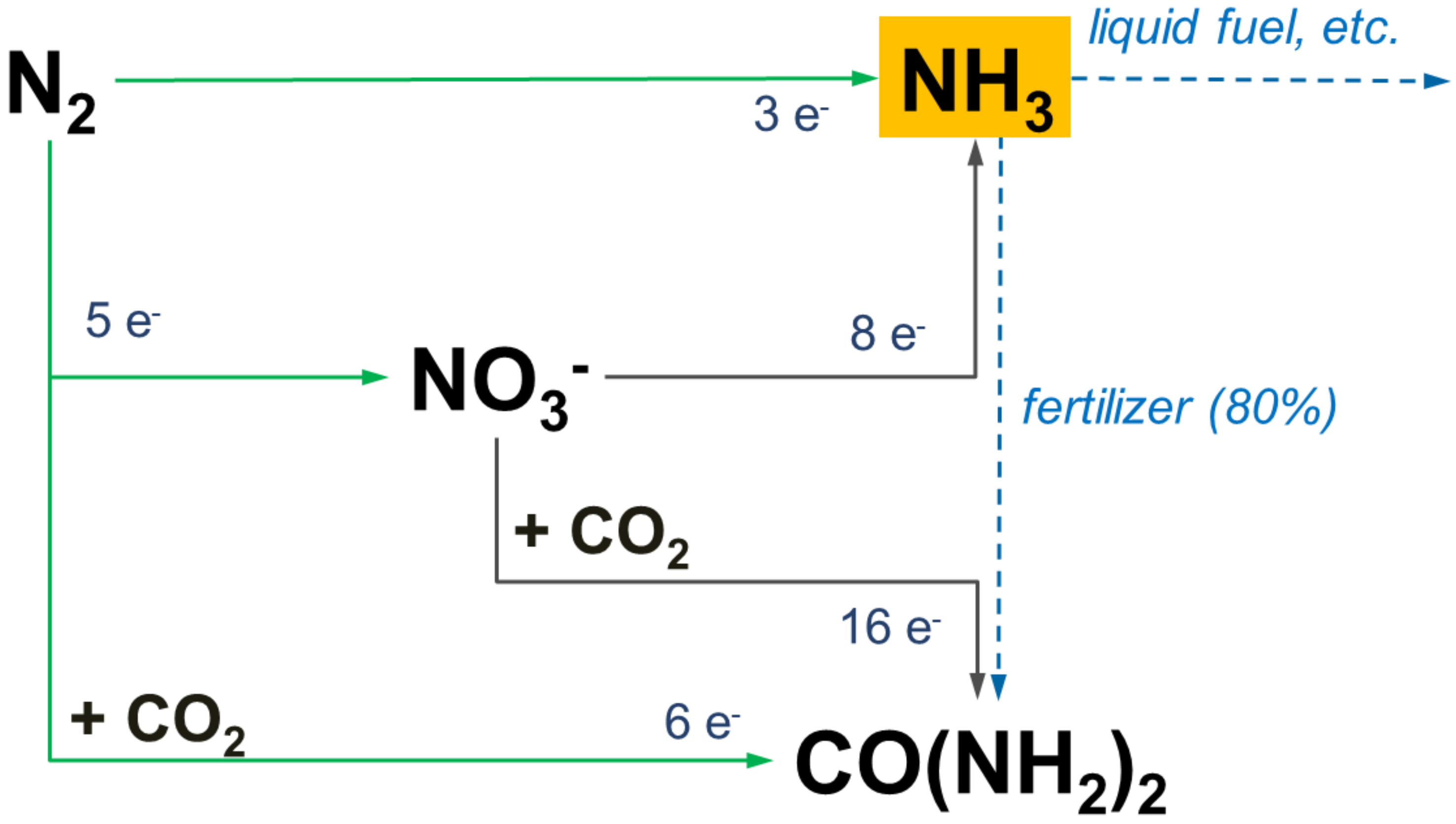
E. Murphy, Y. Liu, I. Matanovic, Y. Huang, A. Ly, S. Guo, W. Zang, X. Yan, A. Martini, J. Timoshenko, B. Roldan Cuenya, I.V. Zenyuk, X. Pan, E.D. Spoerke, and P. Atanassov, Elucidating Electrochemical Nitrate and Nitrite Reduction over Atomically Dispersed Transition Metal Sites, *Nature Communications*, (2023) DOI: 10.1038/s41467-023-40174-4

Electrocatalytic Coupling NO_3^-RR and CO_2RR

Allocation of produced NH_3





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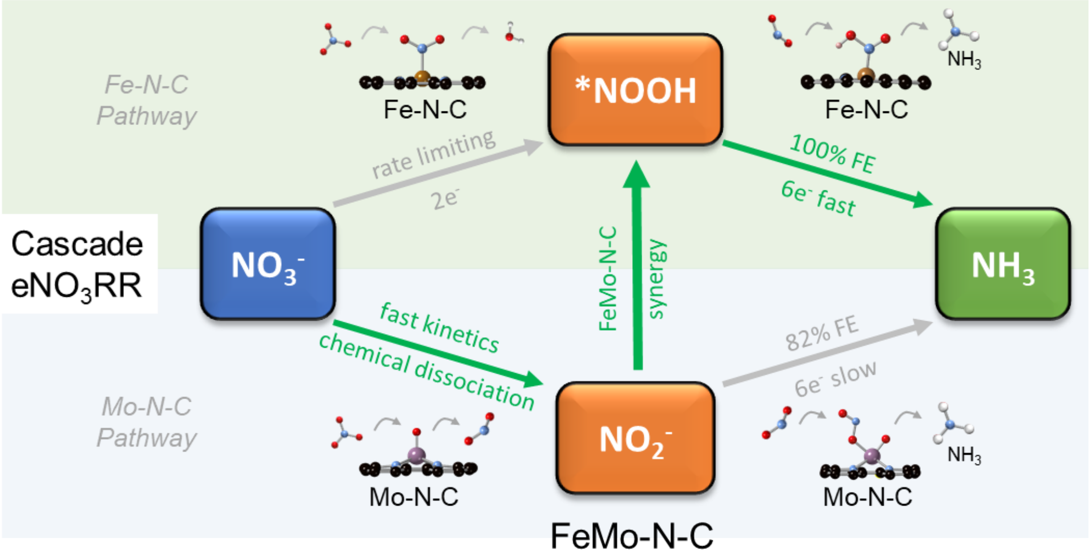
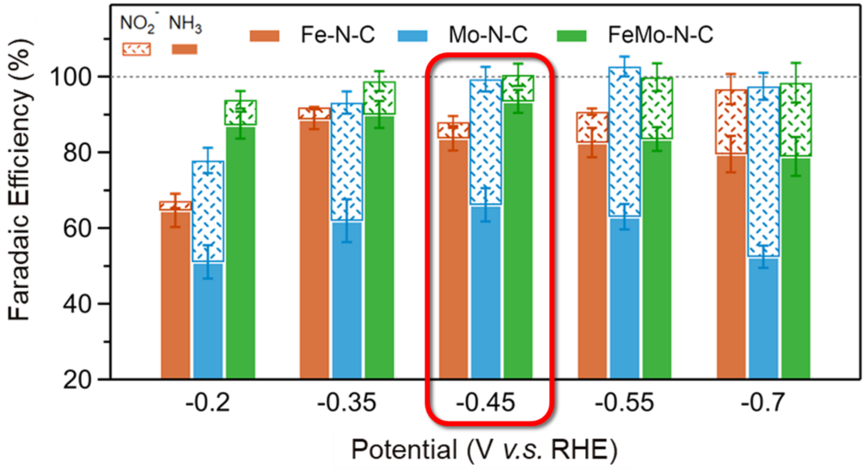
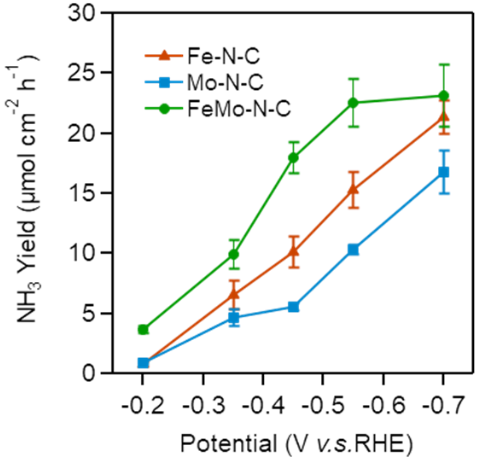
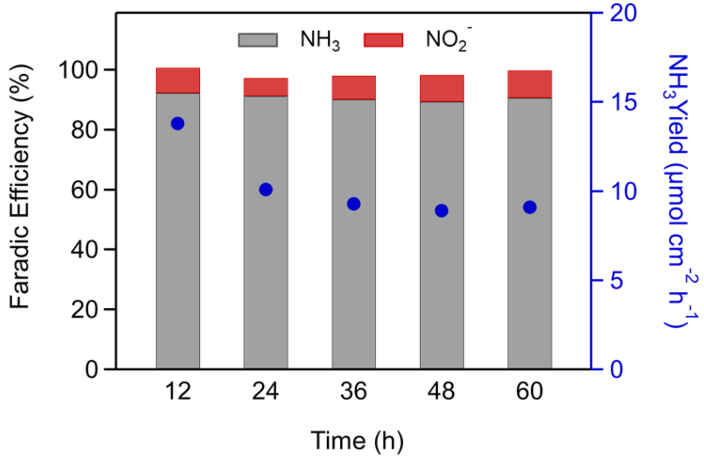
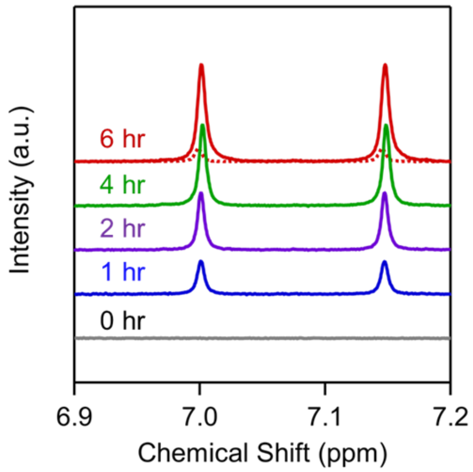
NO_3^- Reduction to Ammonia on M-N-C Materials

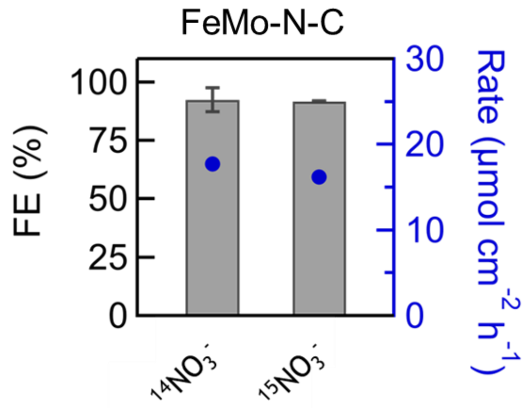












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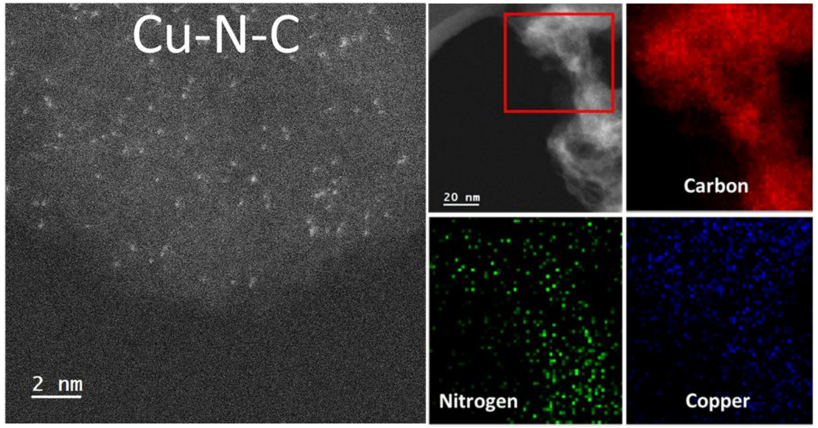
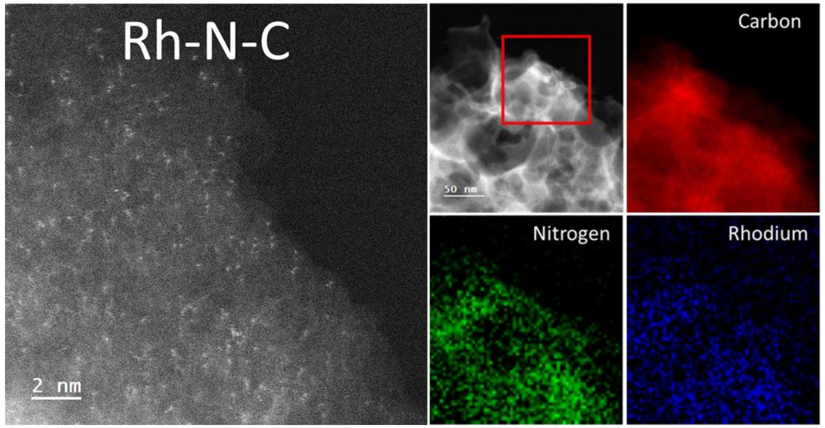
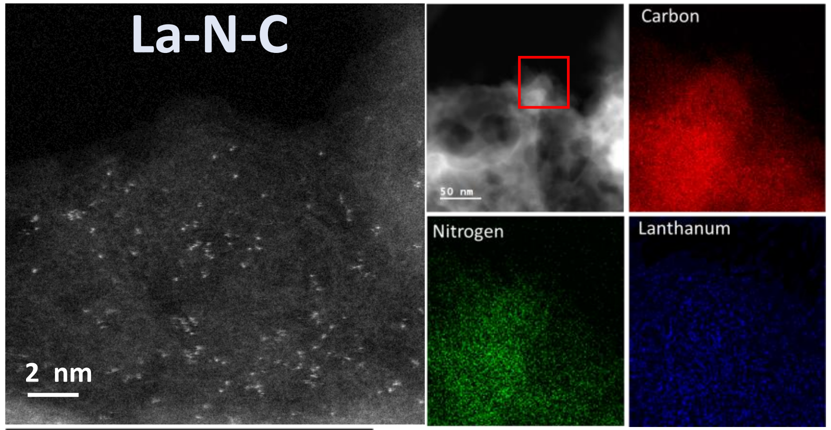
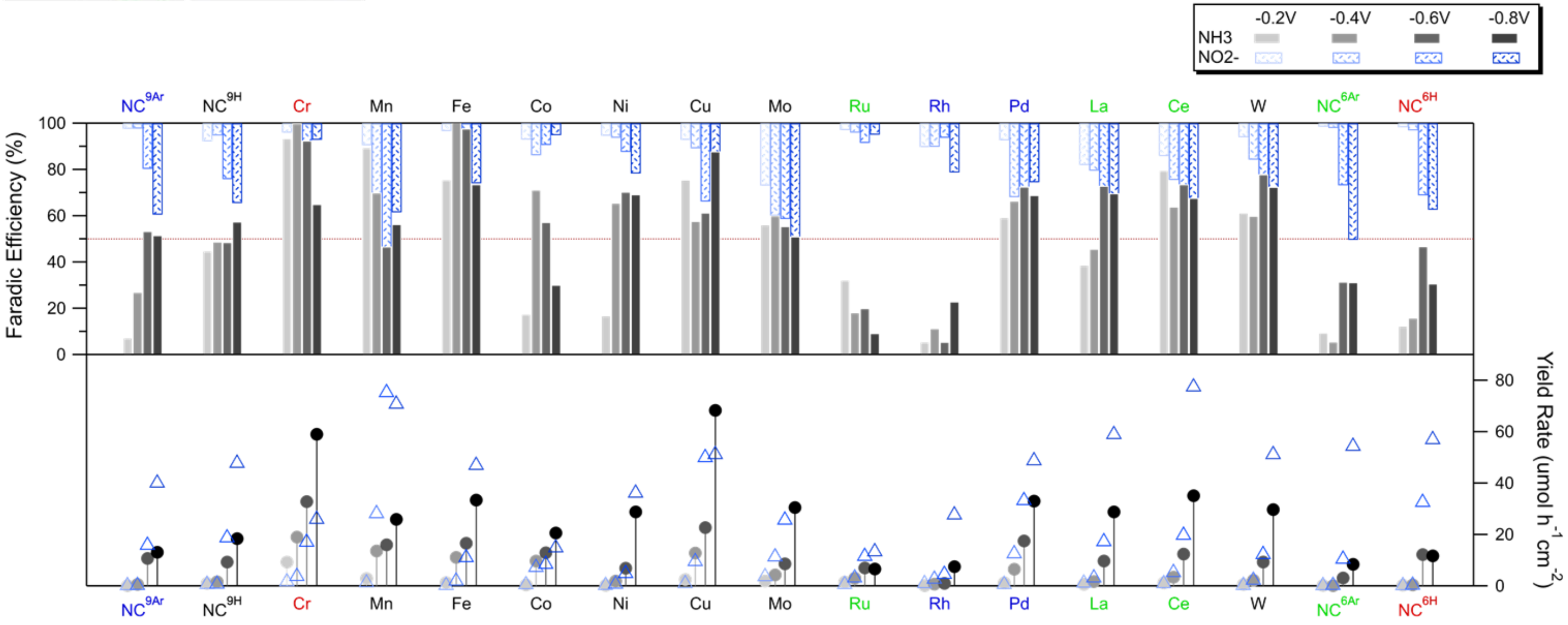
E. Murphy, Y. Liu , I. Matanovic, S. Guo, P. Tieu, Y. Huang, A. Ly, I. Zenyuk, X. Pan, E.D. Spoerke, and P. Atanassov, Nature-Inspired Electro-chemical Nitrate Reduction to Ammonia via a Cascade Mechanism over an Atomically Dispersed Bi-Metallic Fe and Mo Based Catalyst, *ACS Catalysis*, 12 (2022) 6651-6662

NO_3^- Reduction to Ammonia on M-N-C Materials









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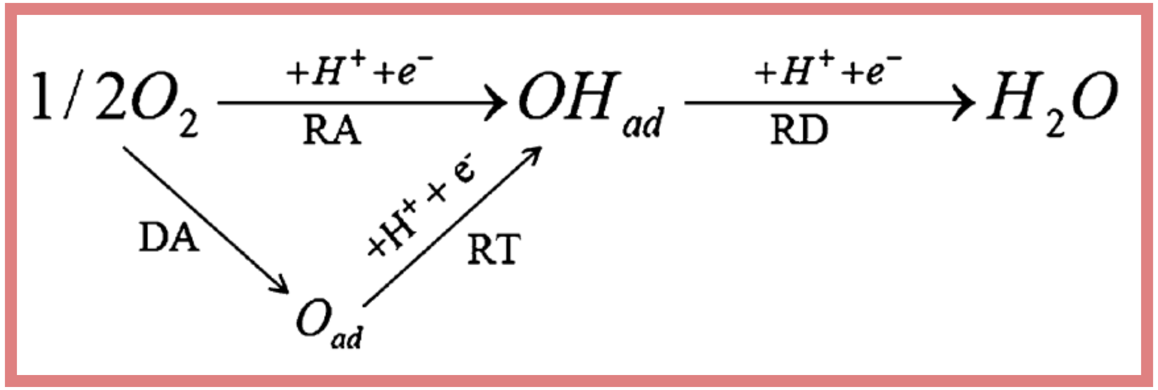
Electrocatalysts Design and Challenges of Selectivity

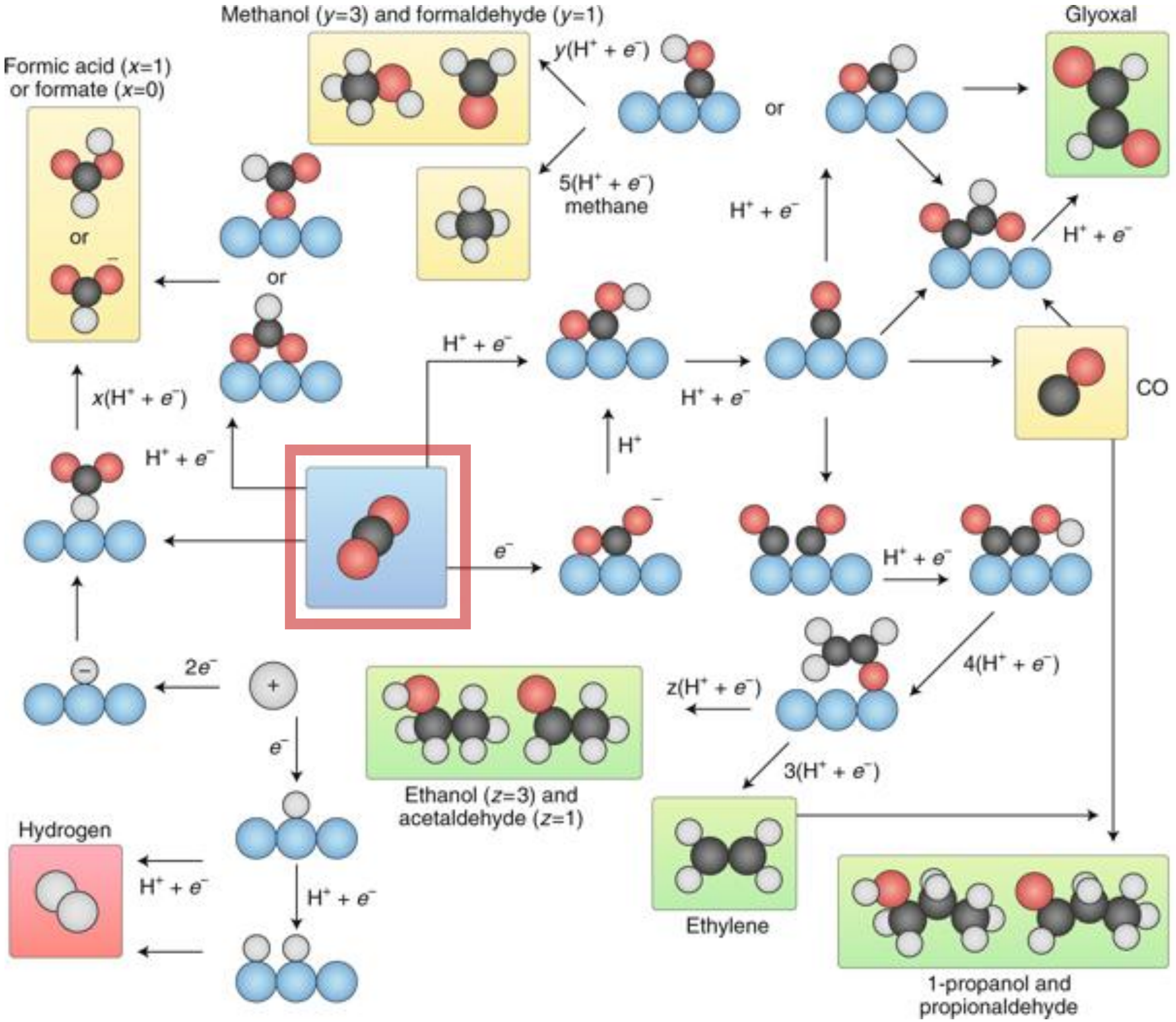
CO_2 Reduction Reactions and Pathways:

- ***Advances***
- ***Challenges***
- ***Opportunities***

How do you move from this:



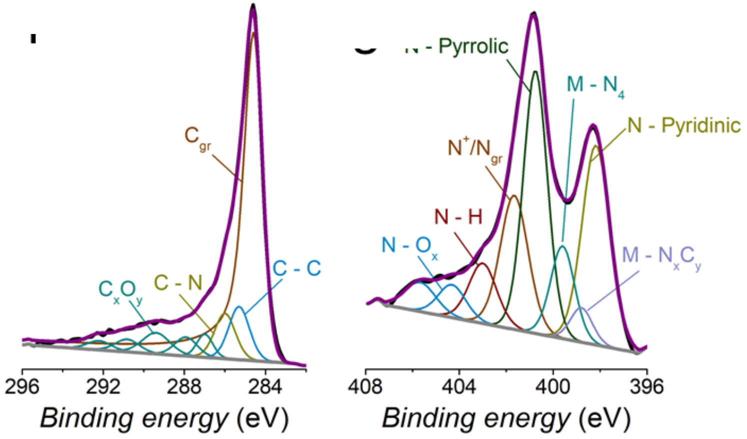
… to something like this:

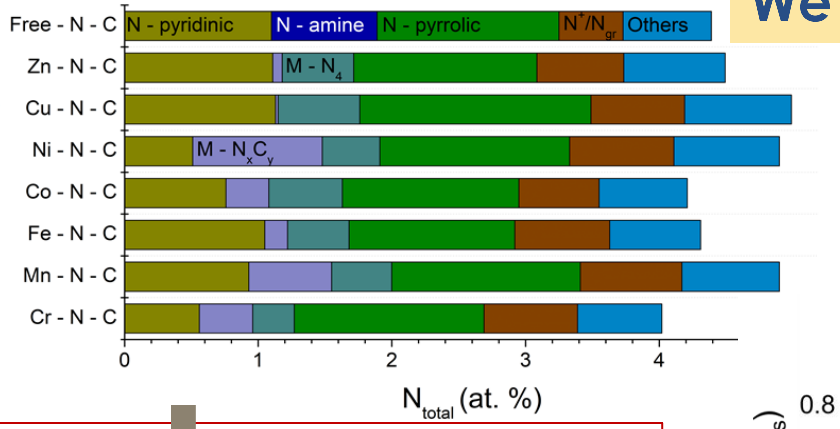


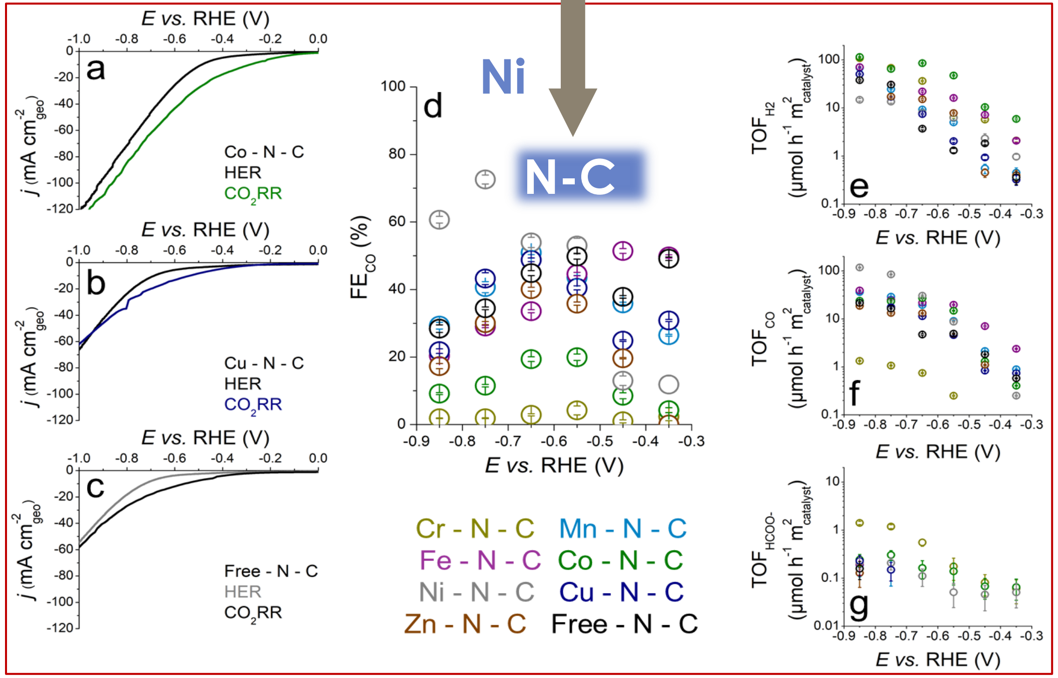
Birdja, et al. *Nature Energy*, 4, 2019, 732–745, DOI: 10.1038/s41560-019-0450-y

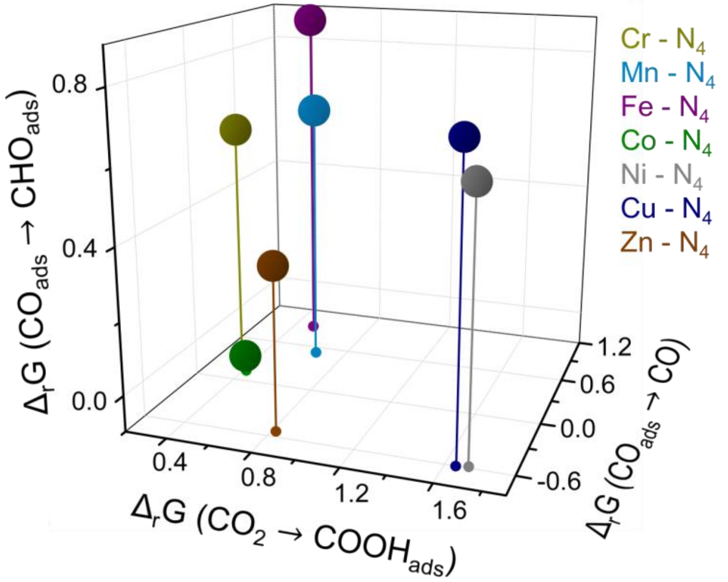
CO_2RR on M-N-C Electrocatalysts: Activity & Selectivity

We deploy our M-N-C by SSM for CO_2RR





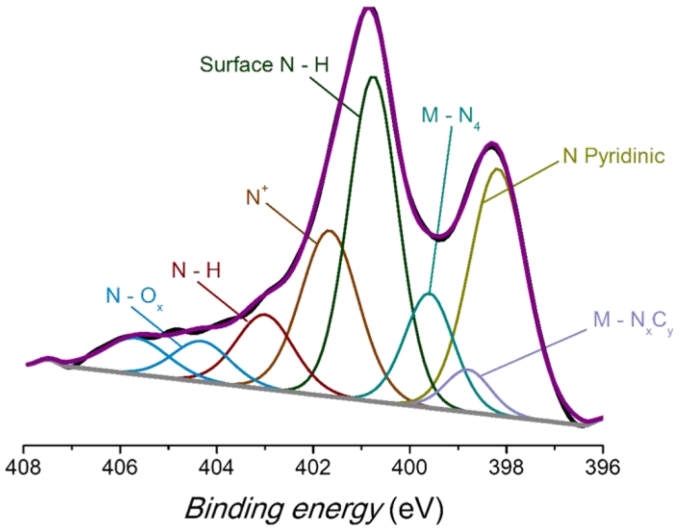




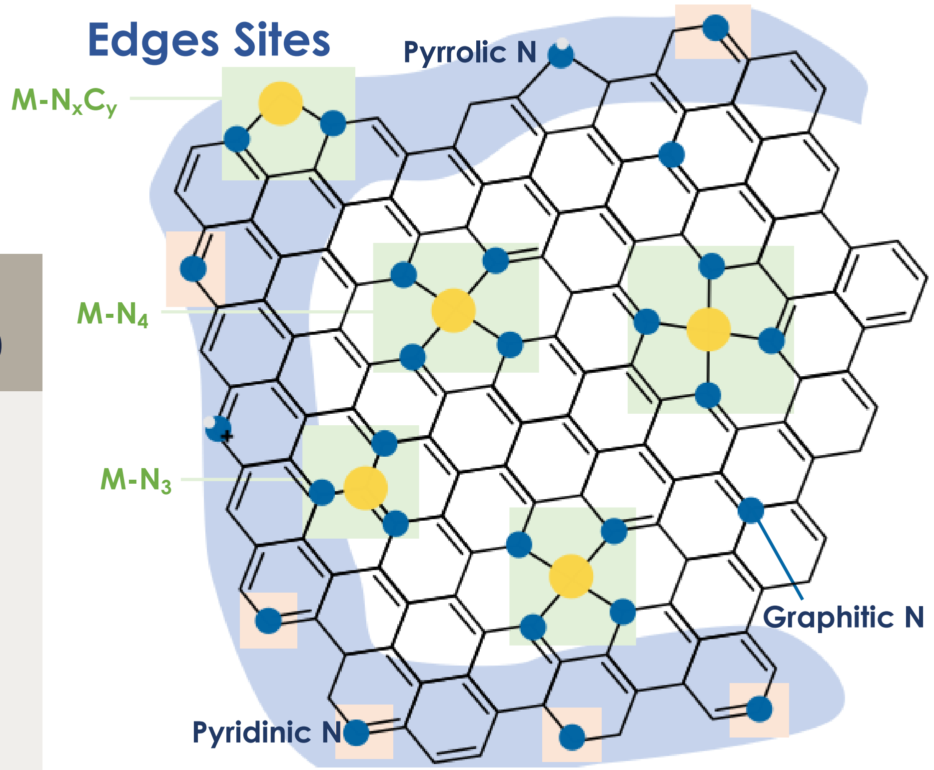
Tristan Asset

T. Asset, S.T. Garcia, S. Herrera, N. Andersen, Y. Chen, E.J. Peterson, I. Matanovic, K. Artyushkova, J. Lee, S.D. Minteer, S. Dai, X. Pan, K. Chavan, S. Calabrese Barton and P. Atanassov, Investigating the Nature of Active Sites for the CO_2 Reduction Reaction on Carbon-based Electrocatalysts, *ACS Catalysis*, 9 (2019) 7668

Properties of M-N-C Electrocatalysts: Surface Chemistry



	N at. %	N Pyridinic (%)	$N_4N_xC_y$ (%)
Cr-N-C	4.0	13.9	17.6
Mn-N-C	4.9	19.0	21.8
Fe-N-C	4.3	24.3	14.5
Co-N-C	4.2	18.2	20.3
Ni-N-C	4.9	10.4	28.7
Cu -N-C	5.0	22.6	12.6
Zn -N-C	4.5	24.7	13.5
Me-free N-C	4.4	25.2	0.0



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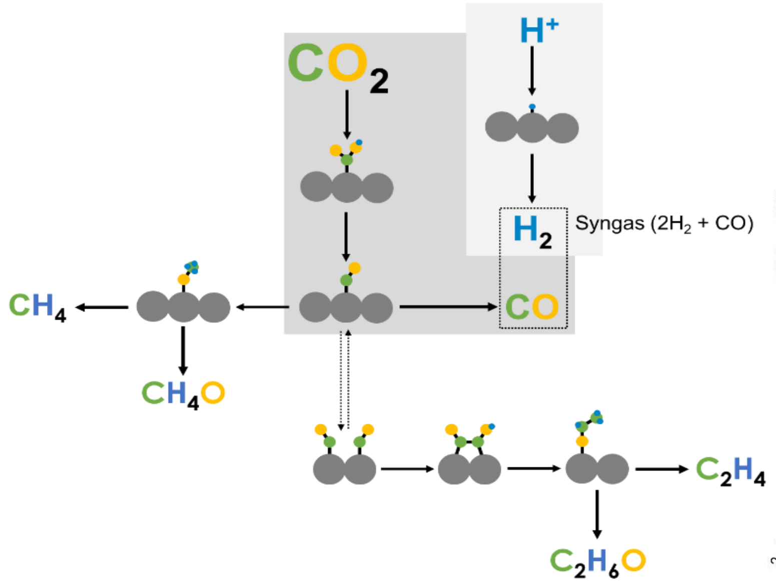
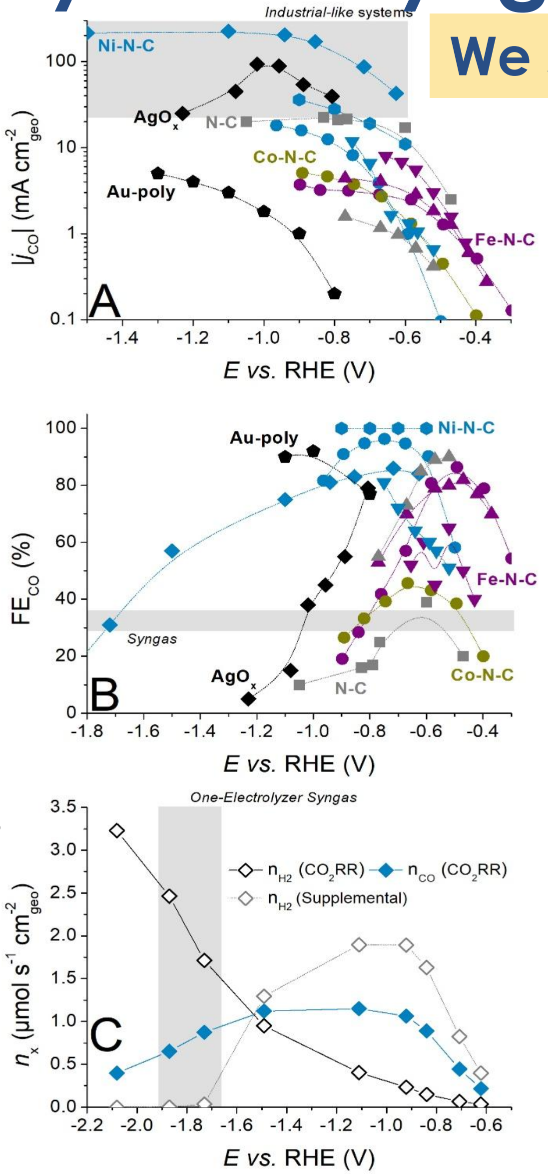
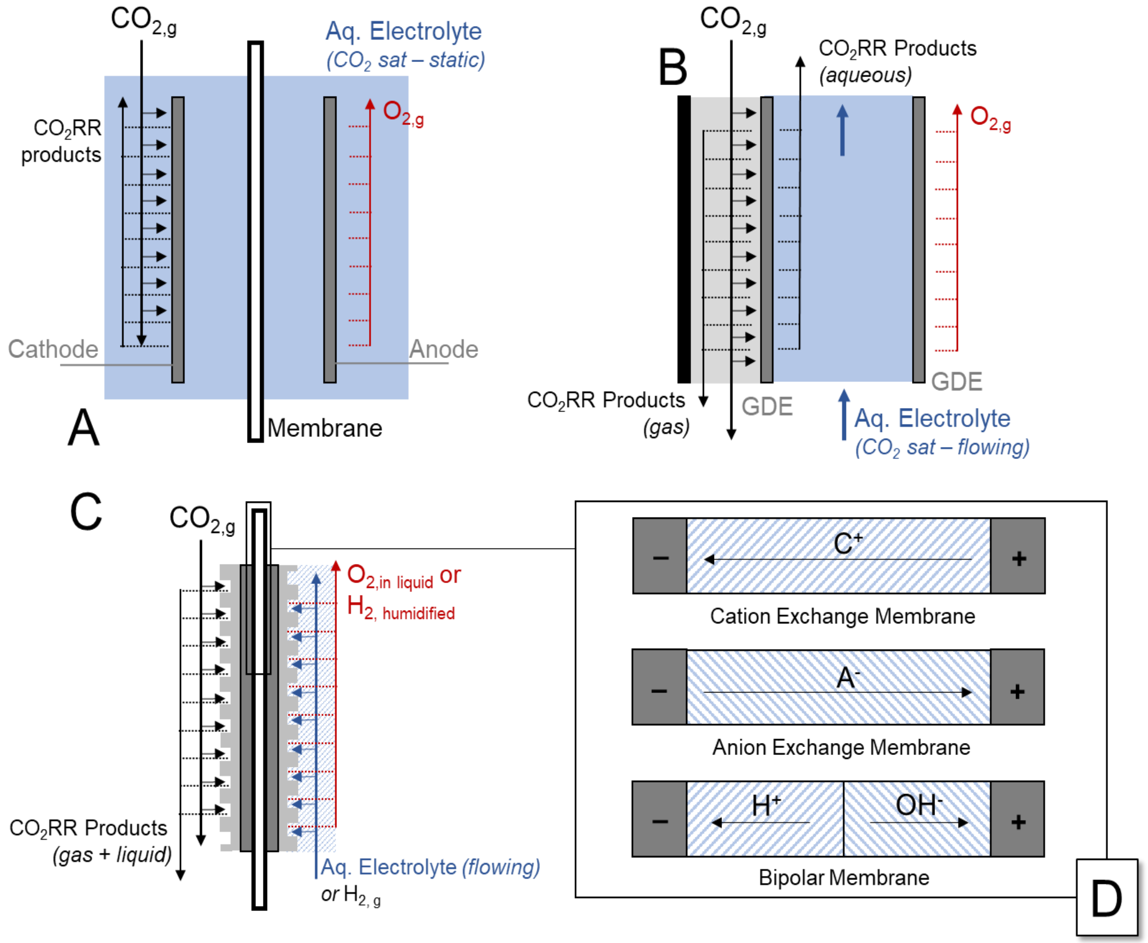
ALS
ADVANCED LIGHT SOURCE

M-N-C CO_2RR Catalysts for Syngas Generation

We start by doing what we know how to do best ☺







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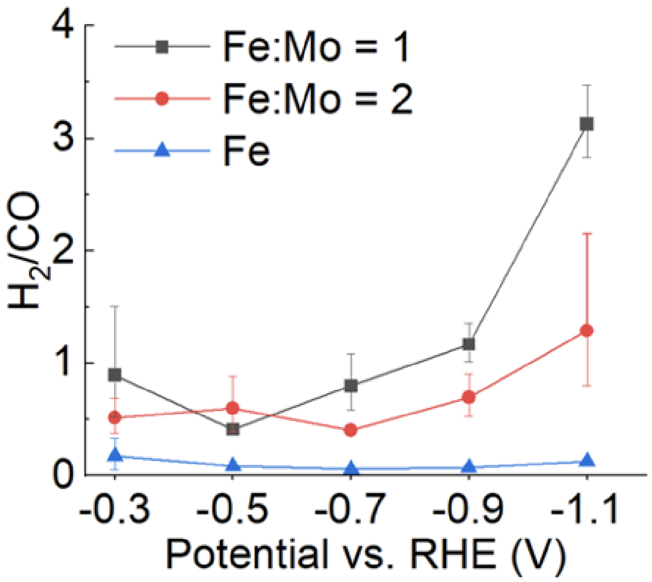
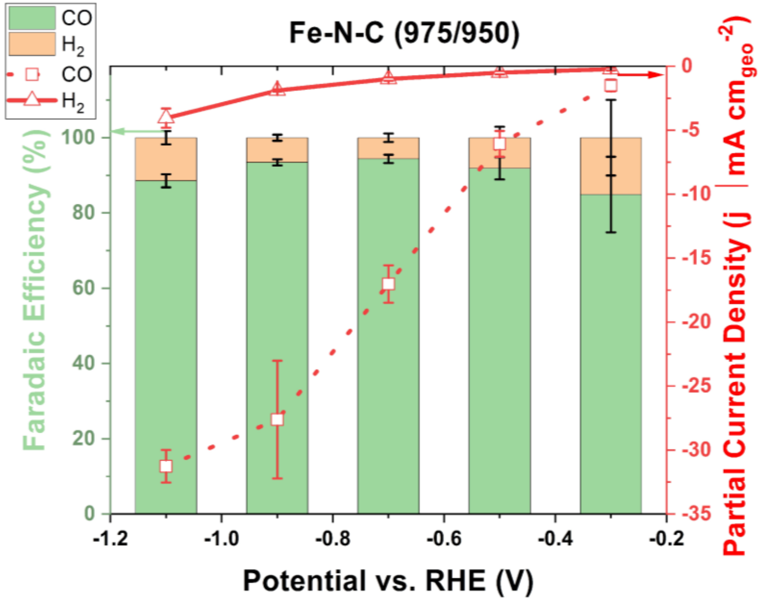
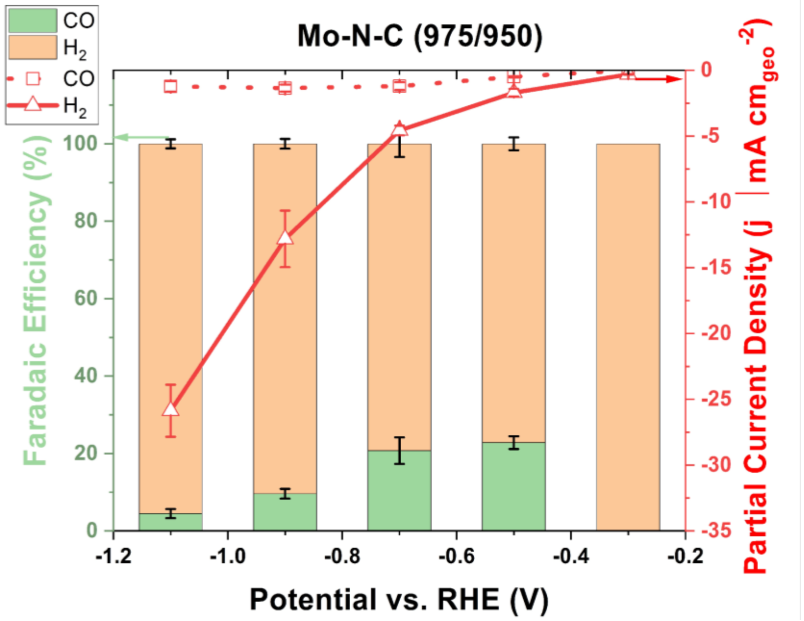
L. Delafontaine, T. Asset and P. Atanassov, Metal-Nitrogen-Carbon Electrocatalysts for CO_2 Reduction Towards Syngas Generation, *ChemSusChem*, 13 (2020) 1688-1698

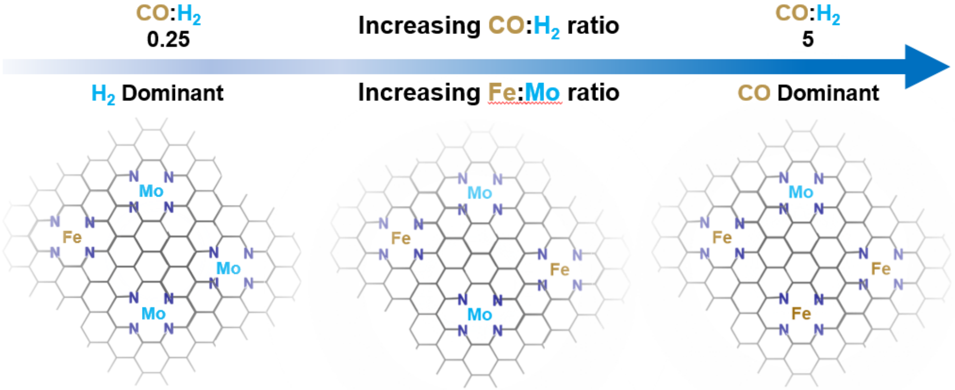
M-N-C CO2RR Catalysts for Syngas Generation





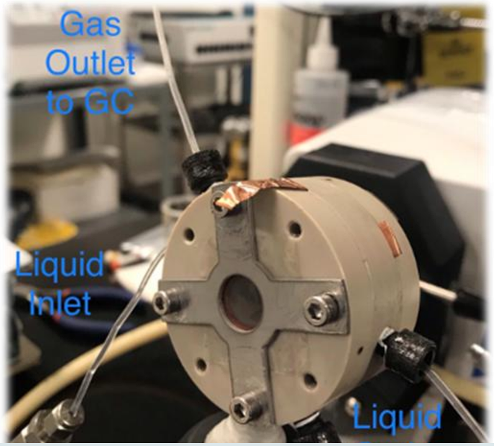


Tailoring Syngas Composition Through Fe-N_x & Mo-N_x sites



Fe-N-C high CO_2RR
Mo-N-C high HER activity

Laurent Delafontaine



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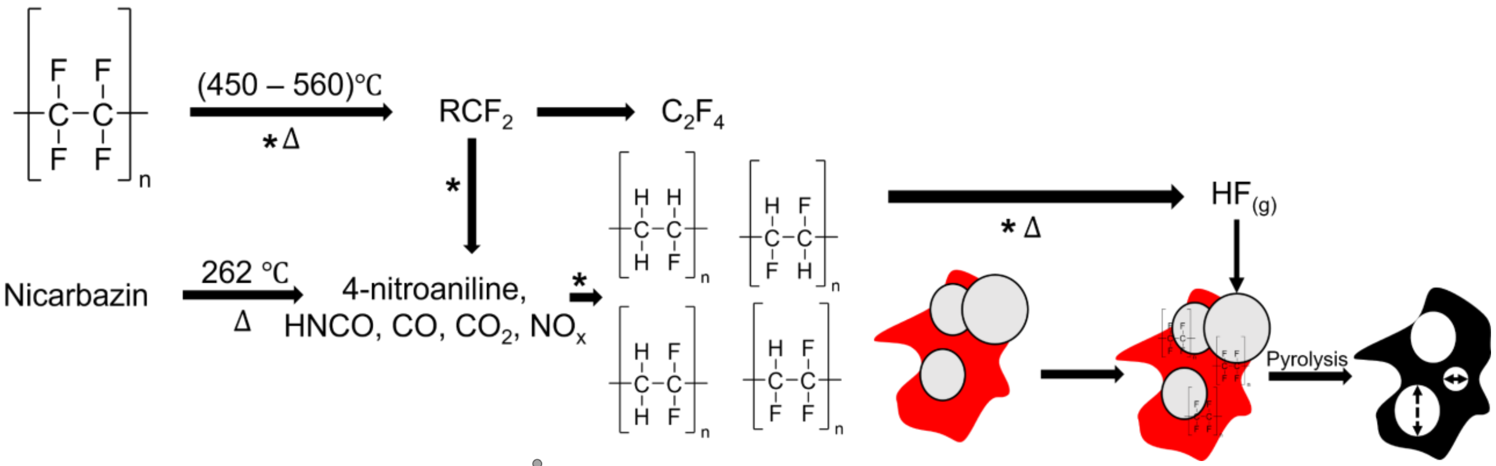
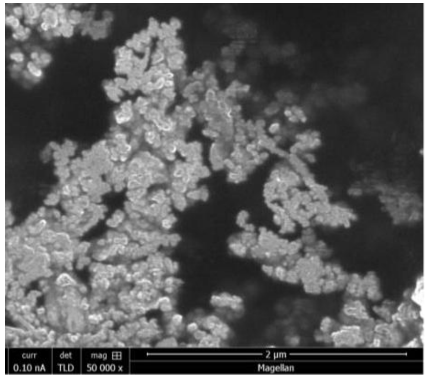
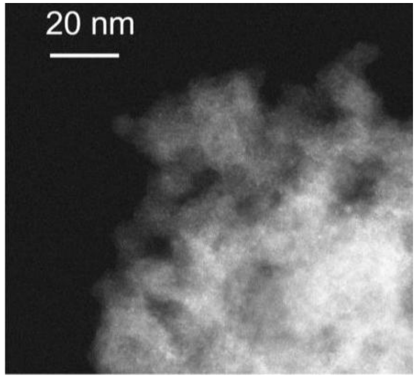
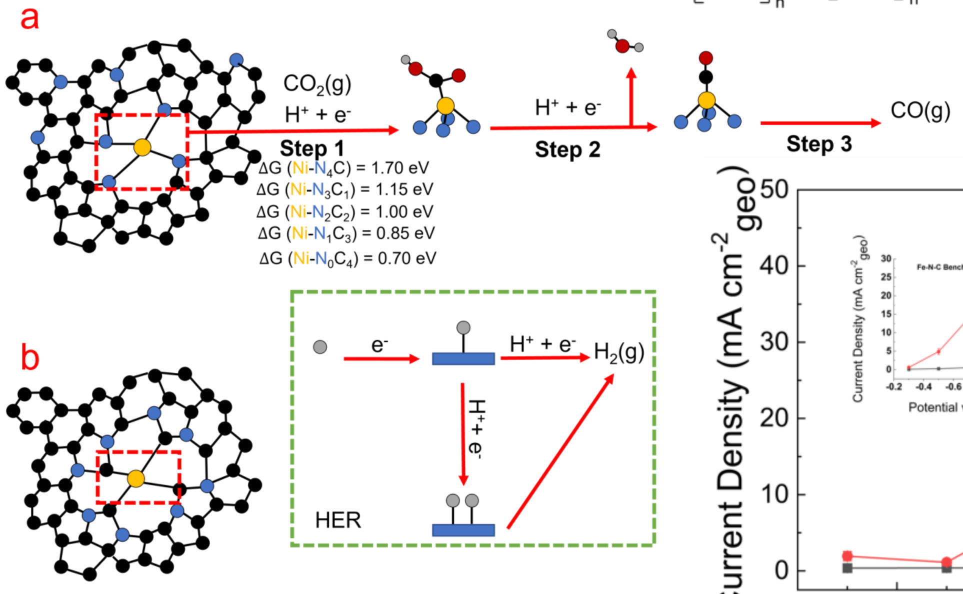
L. Delafontaine, E. Murphy, S. Guo, T. Asset, Y. Liu, X. Pan and P. Atanassov, Synergistic Electrocatalytic Syngas Production from Carbon Dioxide by Bi-metallic Atomically Dispersed Catalysts, *ChemSusChem*, 2022, in press

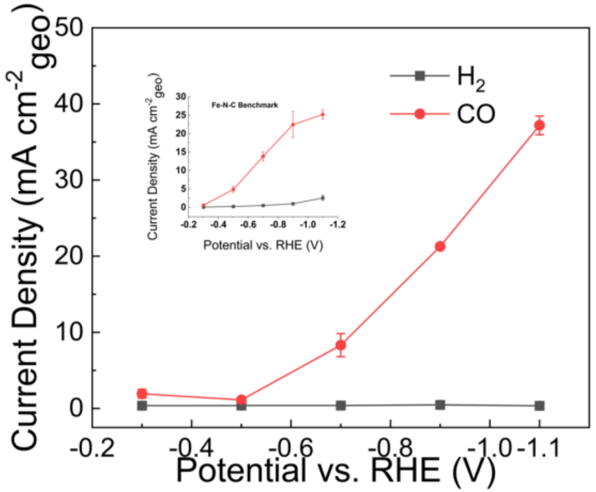
M-N-C Catalysts for CO_2RR: "One-Pot Synthesis"

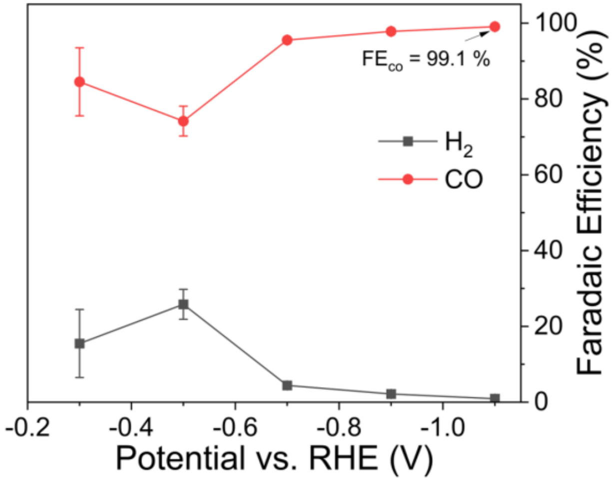


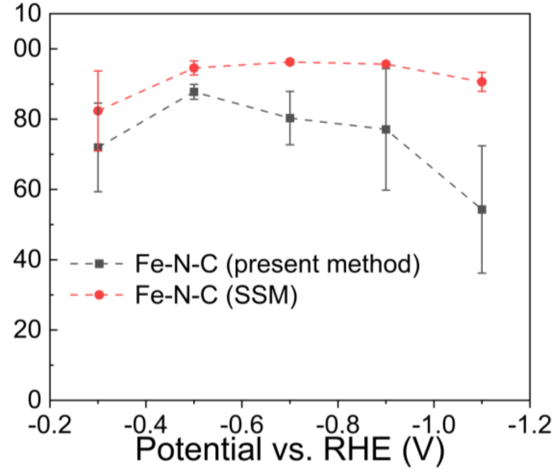












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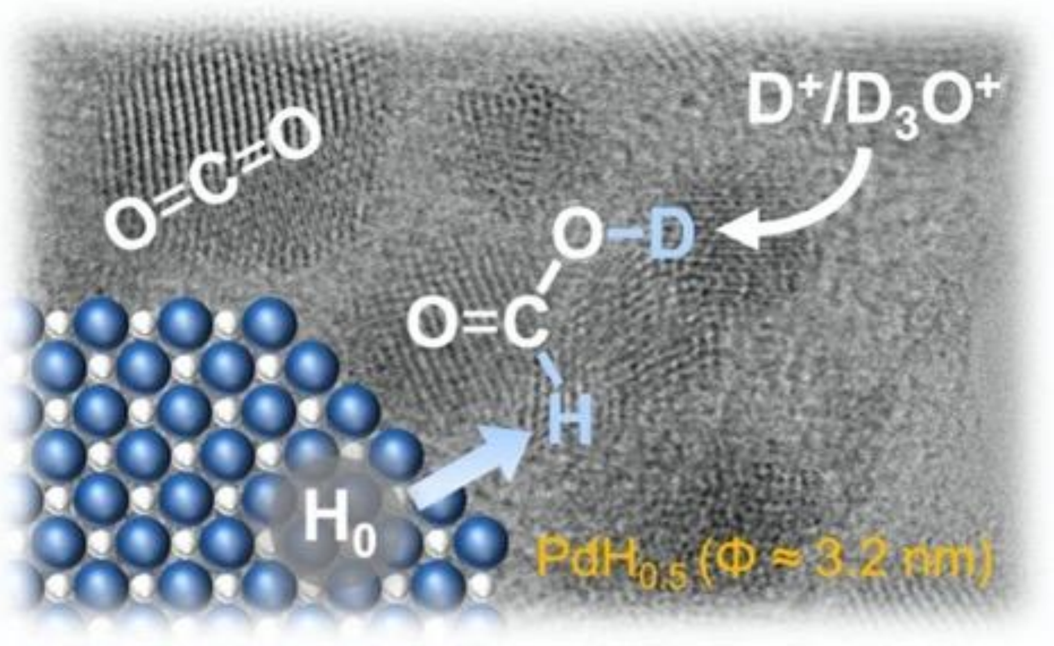
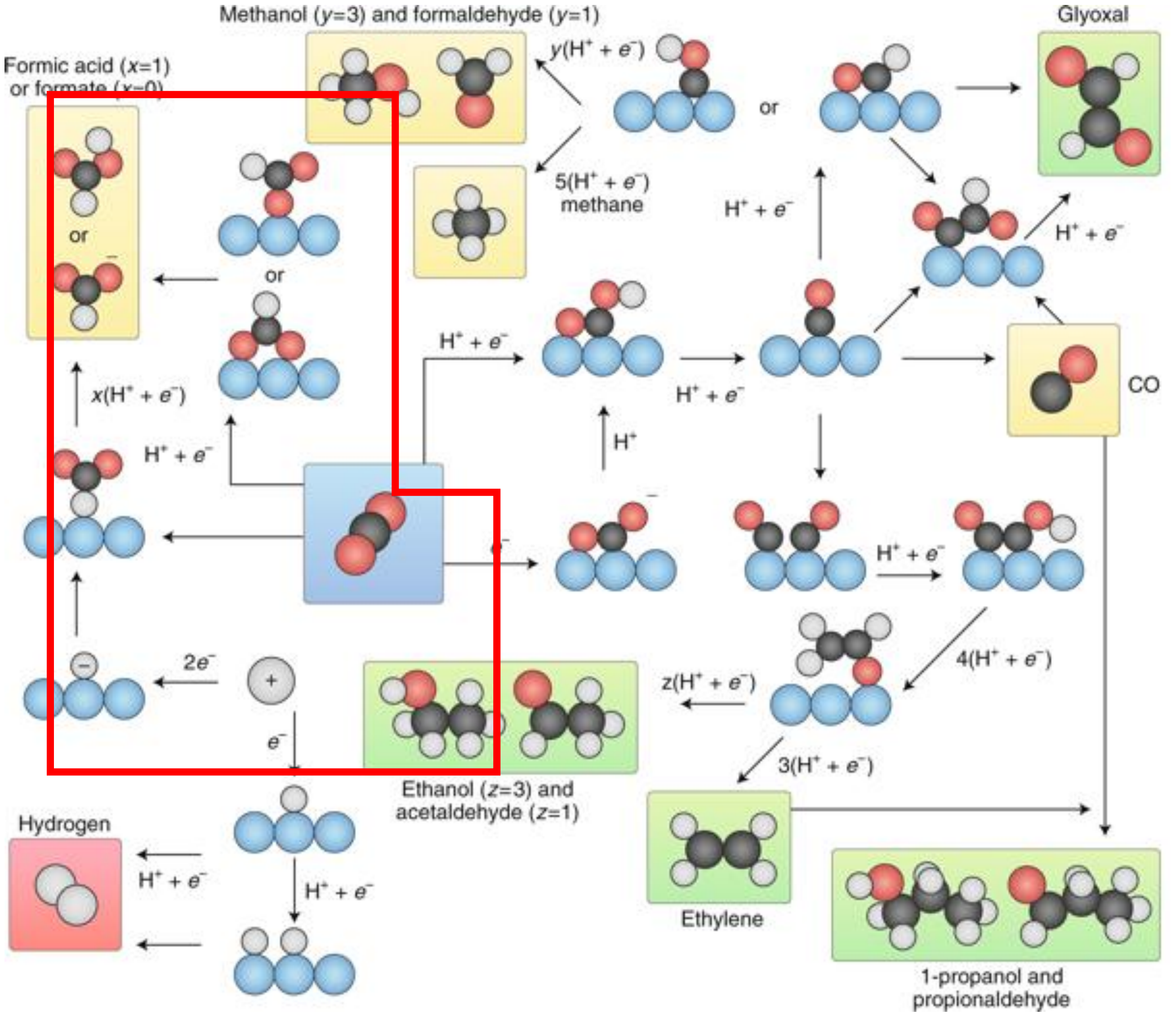
L. Delafontaine, A. Cosenza, E. Murphy, Y. Liu, J. Chen, B. Sun and P. Atanassov, Metal-Nitrogen-Carbon Catalysts by Dynamic Template Removal for Highly Efficient and Selective Electroreduction of CO_2, *ACS Applied Energy Materials*, 6 (2023) 678-691

Palladium Hydride for Electrocatalytic Synthesis of Formate

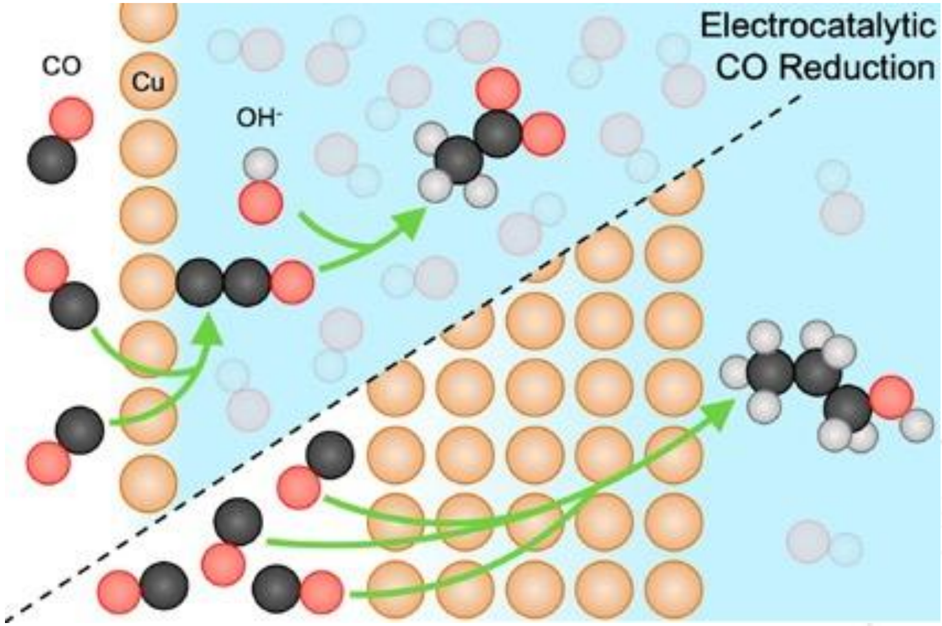


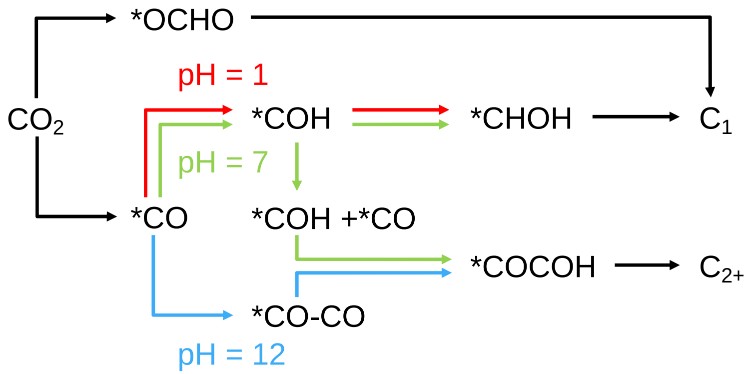


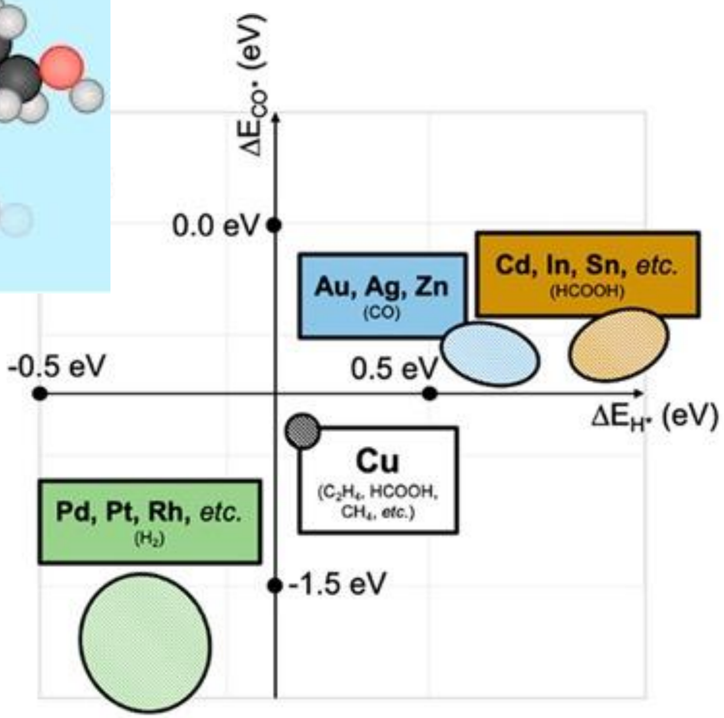
Shengyuan Guo

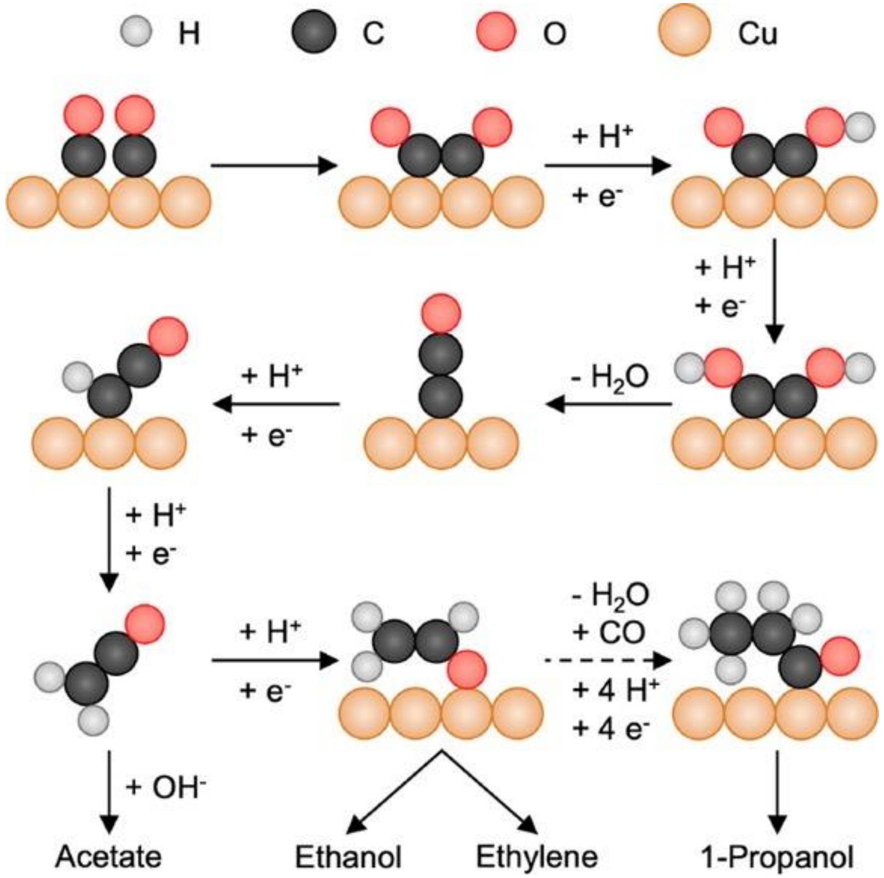
S. Guo, Y. Liu, E. Murphy, A. Ly, M. Xu, I. Matanovic, X. Pan and P. Atanassov, Robust Palladium Hydride Catalyst for Electrocatalytic Formate Formation with High CO Tolerance, *Applied Catalysis B – Environmental*, 316 (2022) 121659

Electroreduction of CO towards Acetate and 1-Propanol









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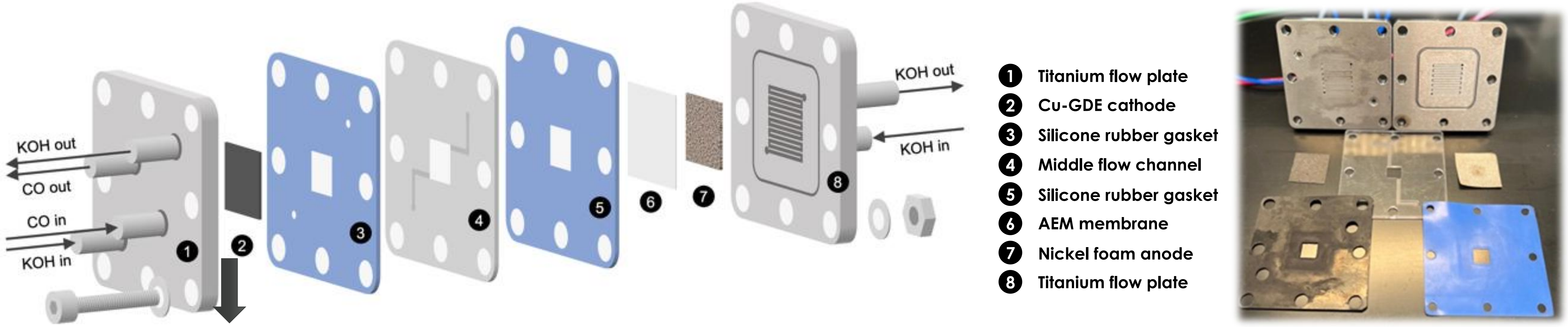
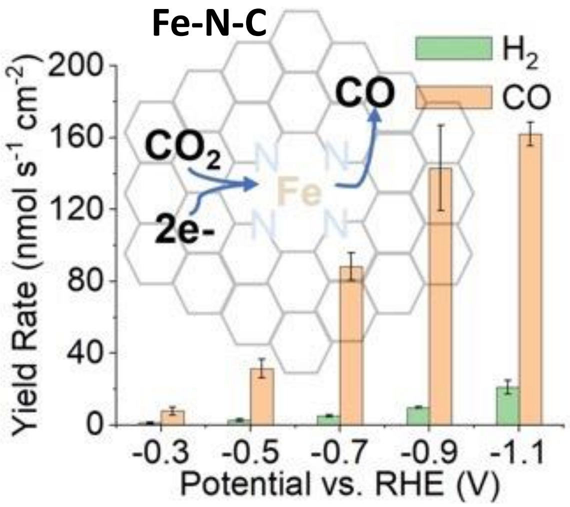
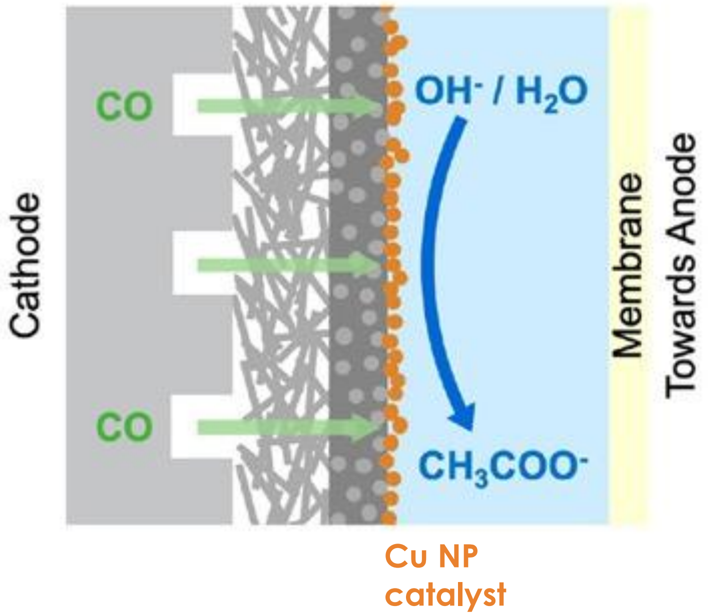
S. Guo, Y. Liu, Y. Huang, H. Wang, E. Murphy, L. Delafontaine, J. Chen, I. Zenyuk and P. Atanassov,
Promoting Electrolysis of Carbon Monoxide towards Acetate and 1-Oropanol in Flow Electrolyzer. *ACS Energy Letters*, 8 (2023) 935-942

CO2 Electrolysis towards Acetate and 1-propanol







- Gas diffusion electrode enhances the gas transfer to catalysts
- CO improves the formation of C-C bond, while prevents carbonate generation
- CO can be produced from CO_2 reduction with high selective catalysts such as Fe-N-C

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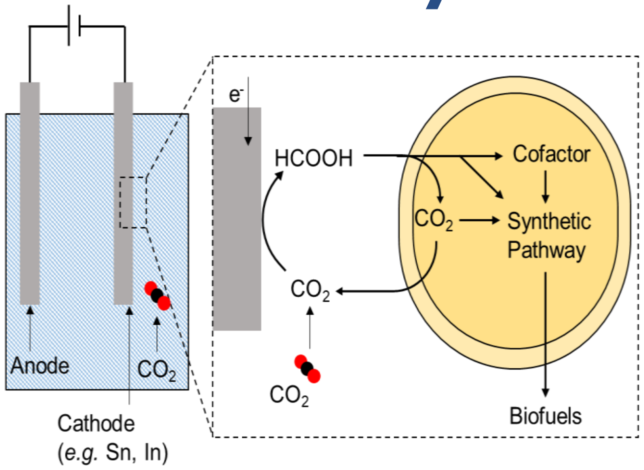
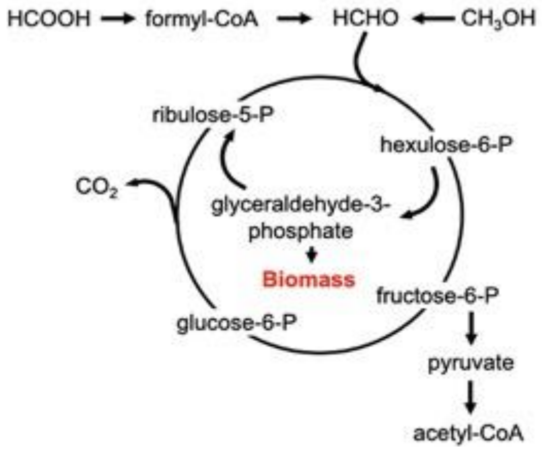
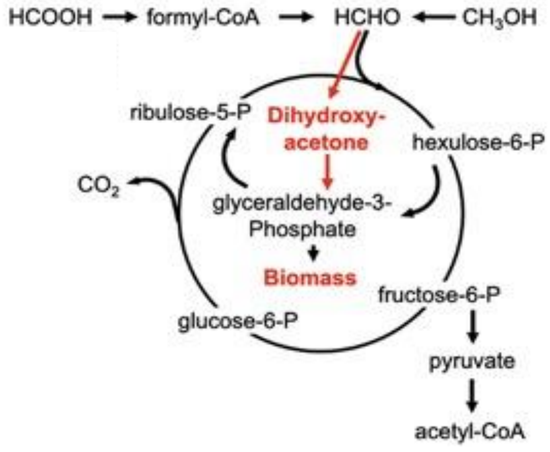
CO_2 Electrocatalysis and Biocatalysts: Products Valorization

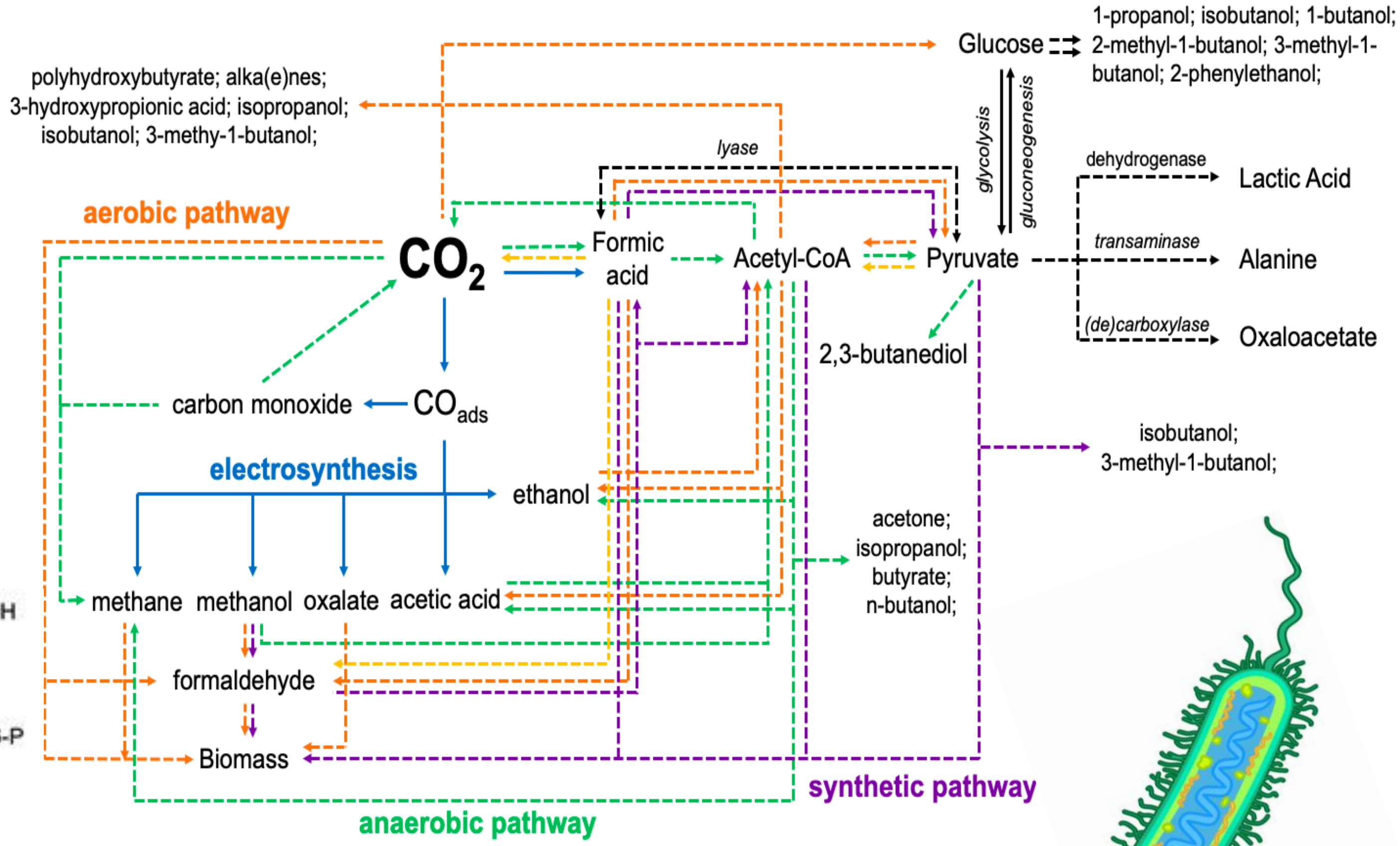


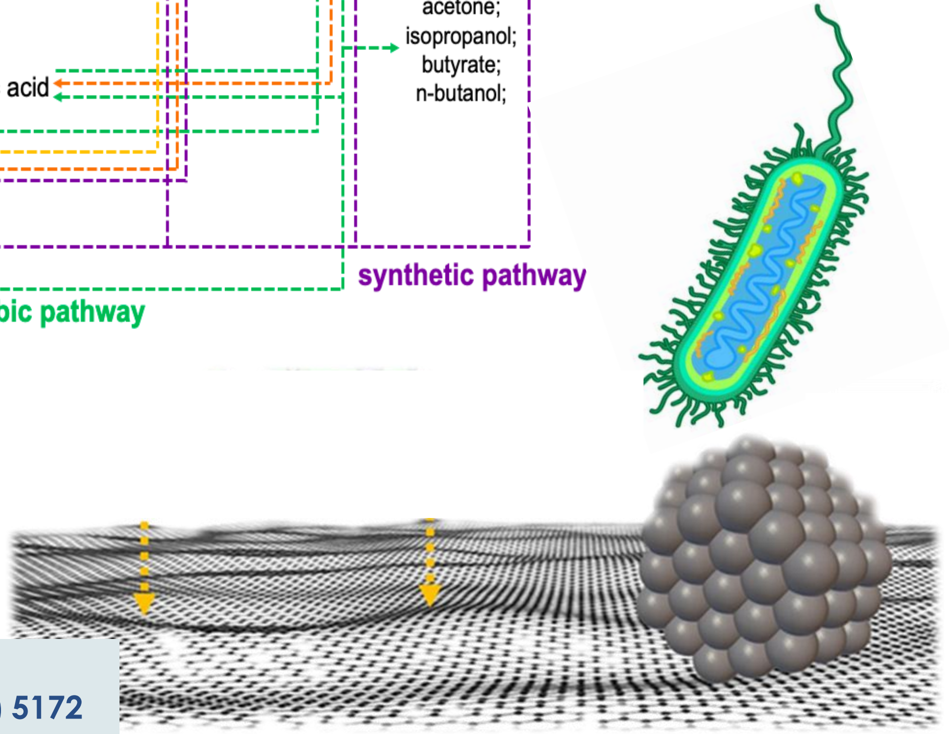
Ribulose Monophosphate (RuMP) cycle



Dihydroxyacetone (DHA) cycle







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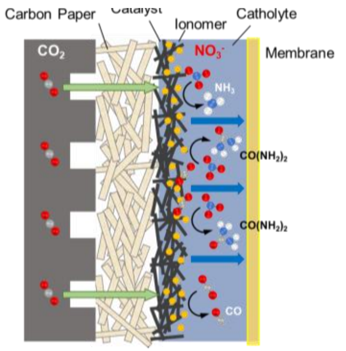
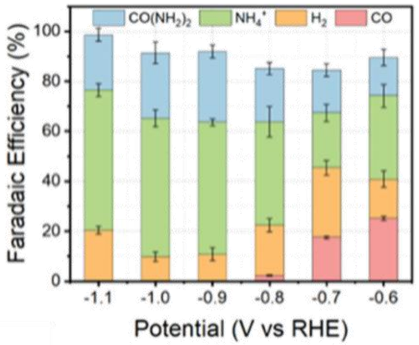
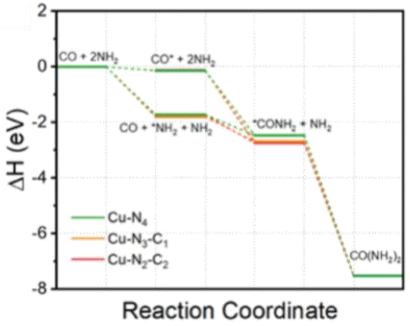
S. Guo, T. Asset, P. Atanassov, Catalytic Hybrid Electrocatalytic/Biocatalytic Cascades for Carbon Dioxide Reduction &Valorization, *ACS Catalysis*, 11 (2021) 5172

Electroreduction to Ammonia and Urea

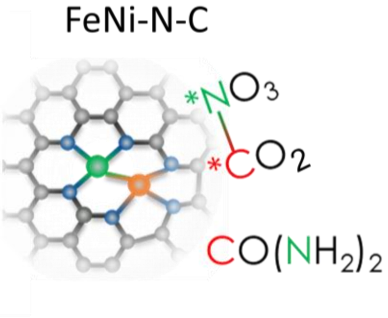
Leverett, J. *et al.*, *Adv. Energy Mater.* 12 (2022)
DOI: 10.1002/aenm.202201500.

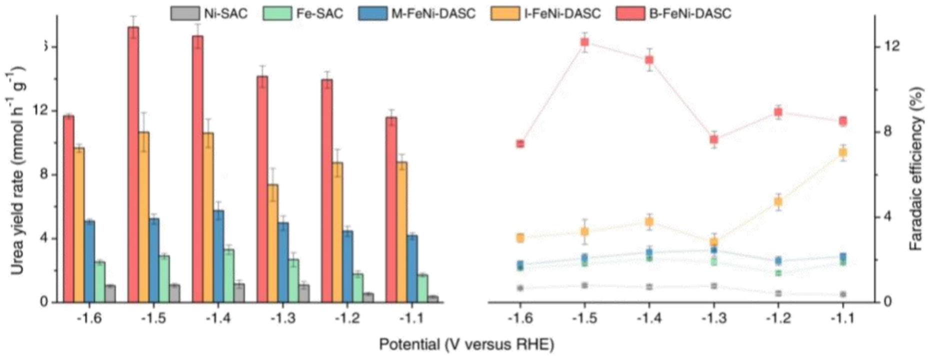


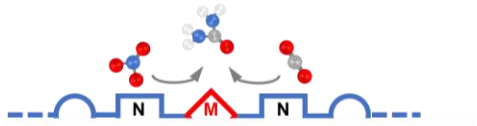




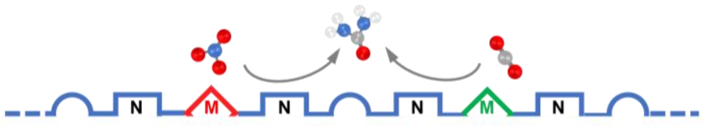
Zhang, X. *et al.*, *Nat. Commun.* 13 (2022)1–9
DOI: 10.1038/s41467-022-33066-6



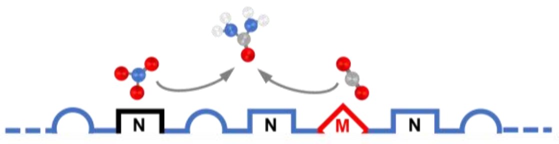




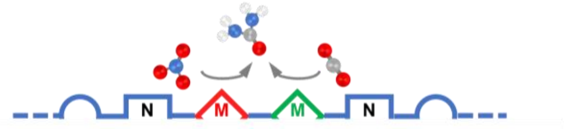
Mono-metallic multi-adsorption/cascade



Independent bi-metallic cascade



Nitrogen site and metal site co-catalysis/cascade



Diatomic catalyst with simultaneous activation

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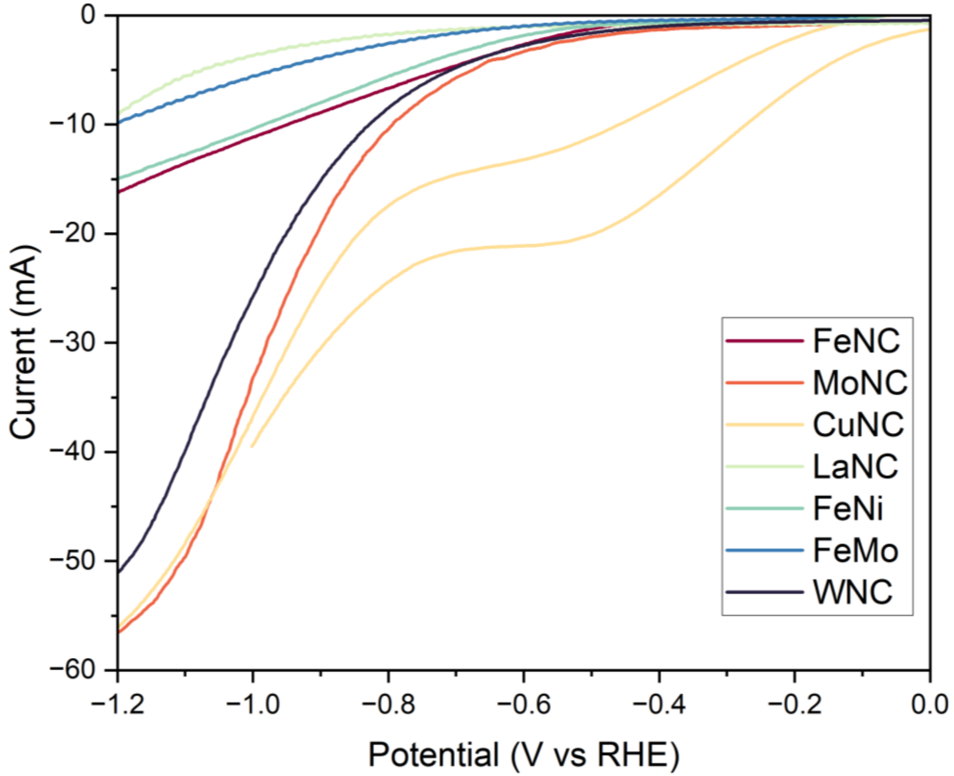
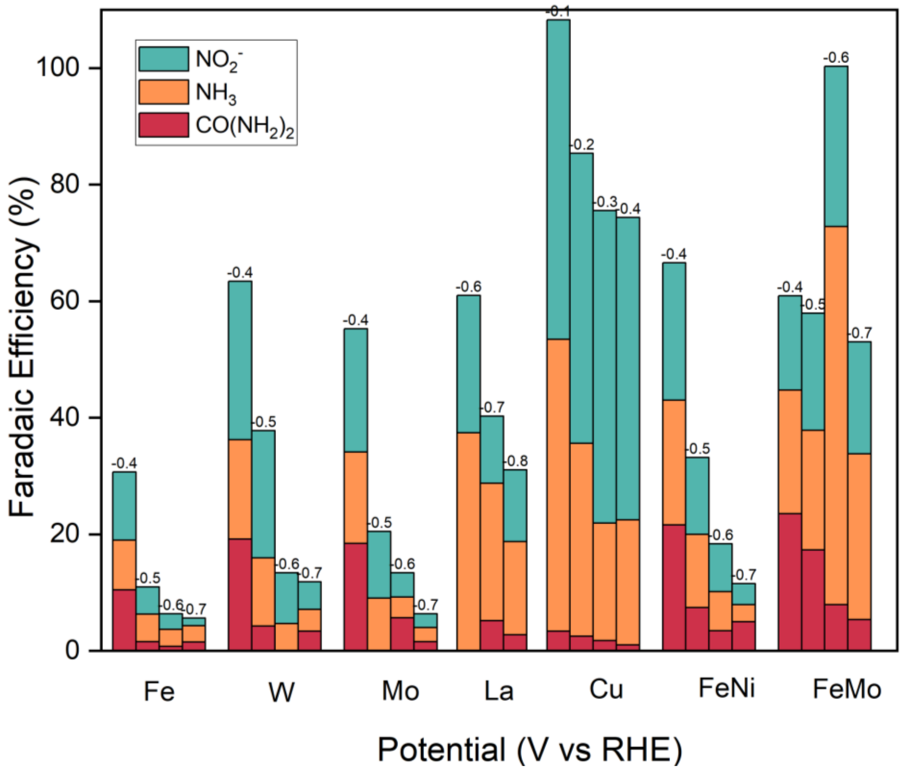
E. Murphy, Y. Liu, Yuanchao; B. Sun, Y.H. Chen, S. Guo and P. Atanassov, Atomically Dispersed Metal-Nitrogen-Carbon Catalysts for Electrochemical Nitrogen Transformations to Ammonia and Beyond, *ACS Catalysis*, 14 (2024) 9797-9781 DOI: 10.1021/acscatal.4c02717

Co-reduction of CO_2 and NO_3^- to Urea on M-N-C Materials

LSV in 0.2M $KHCO_3$ and 0.05M KNO_3



NO_3^- and CO_2 Co-reduction In H-cell



Yu-Han Chen

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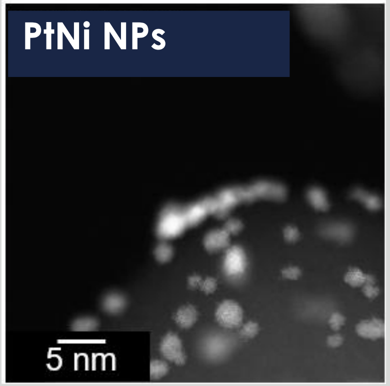
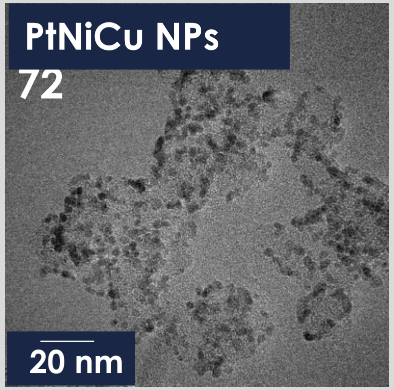
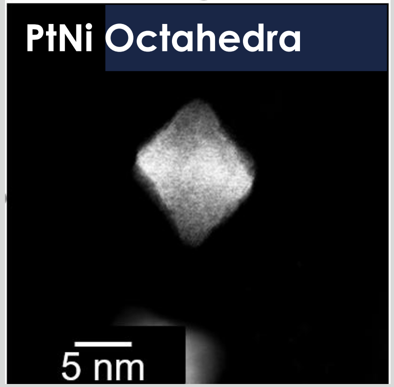
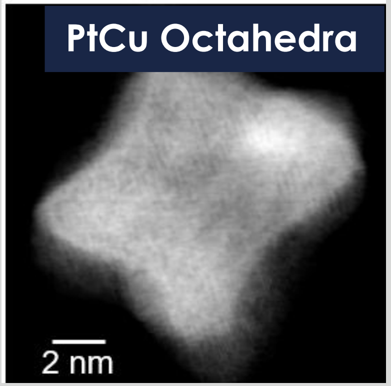
- Fe-Mo-N-C shows the best selectivity towards urea production amongst the library.
- Fe-N_x and Mo-N_x shows synergy of NO_3RR activation and hydrogenation of $*NO_2^-$.

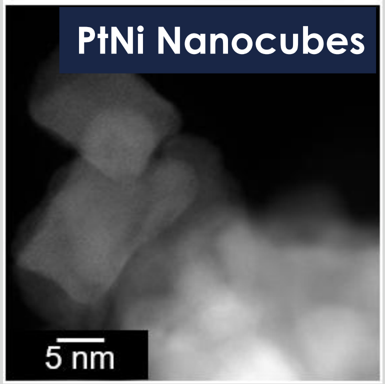
Advanced Nanostructured Pt Catalysts for FC Durability

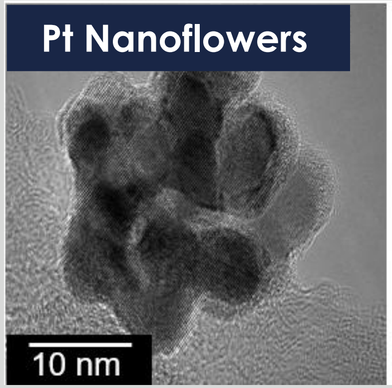


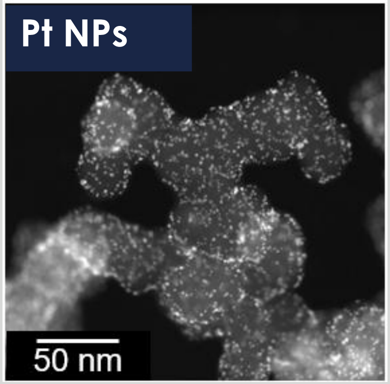


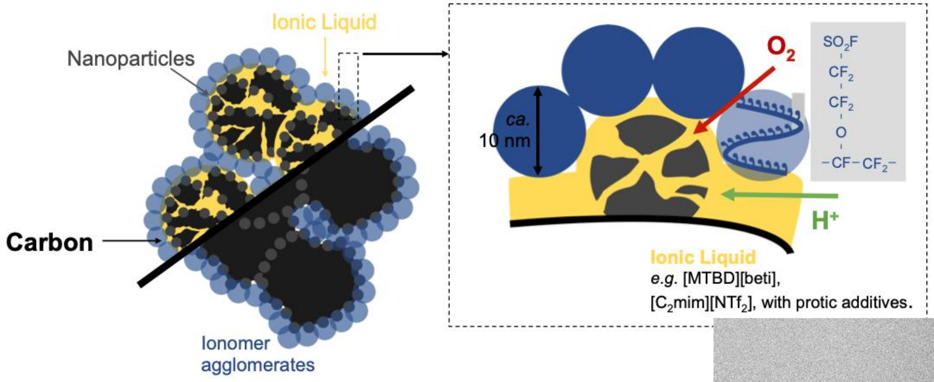


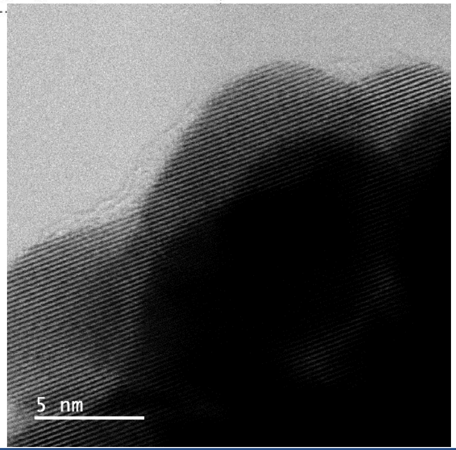


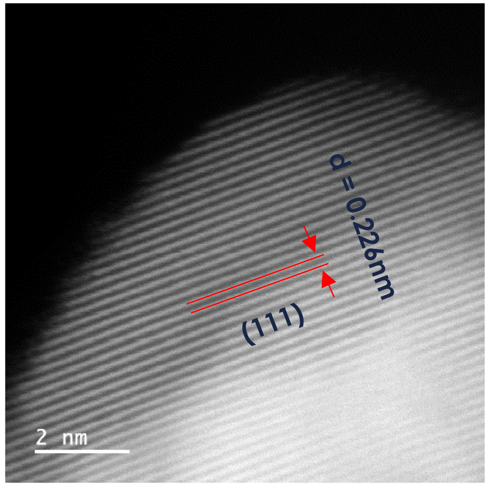


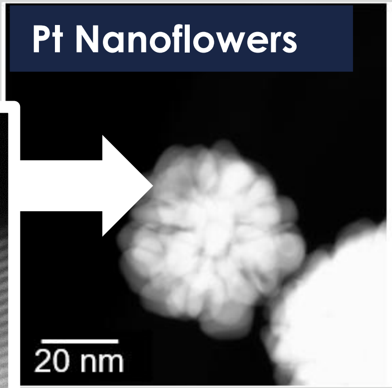












A. Ly, T. Asset and P. Atanassov Integrating Nanostructured Pt-based Electrocatalysts in Proton Exchange Membrane Fuel Cells, *Journal of Power Sources*, 478 (2020) 228516

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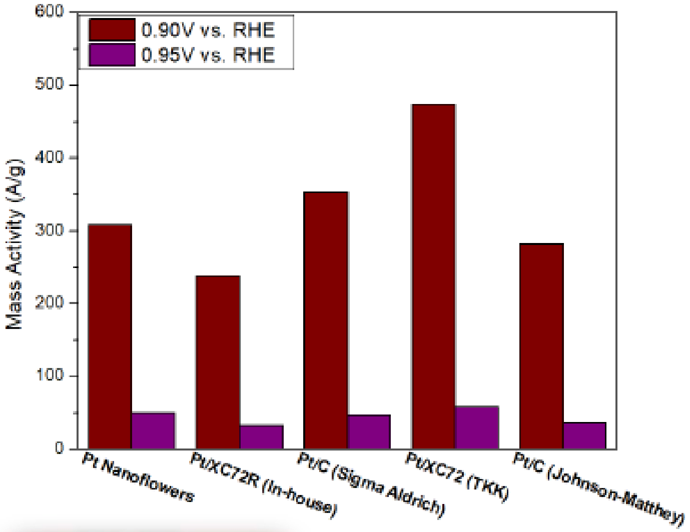
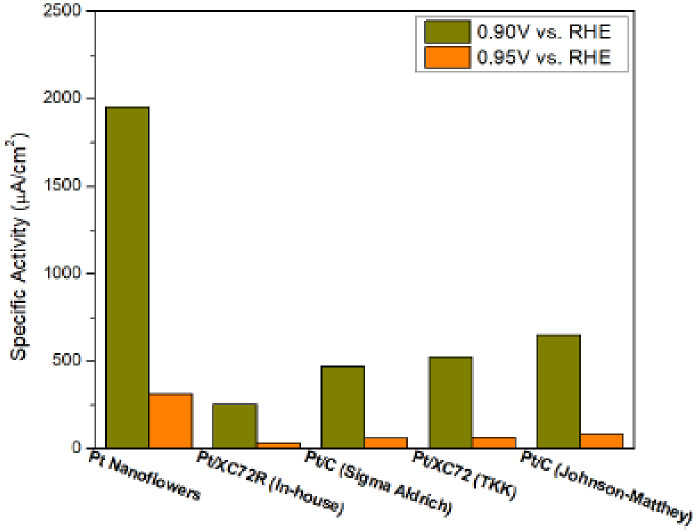
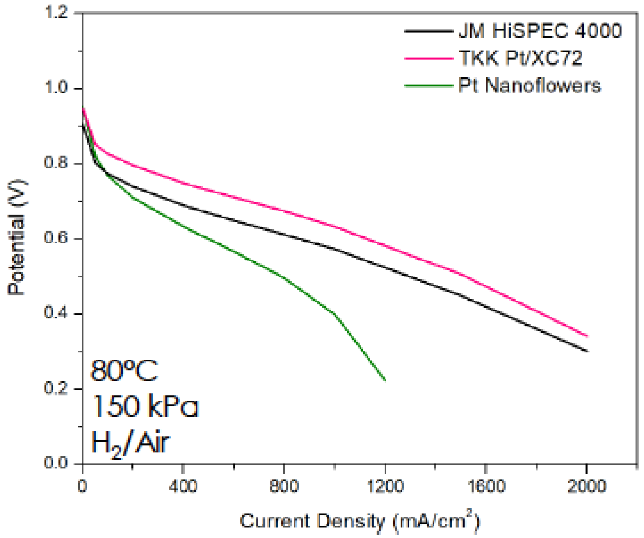
U.S. DEPARTMENT OF ENERGY

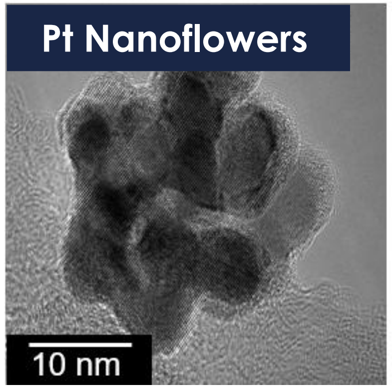
MILLION MILE FUEL CELL TRUCK

Advanced Nanostructured Pt Catalysts for FC Durability

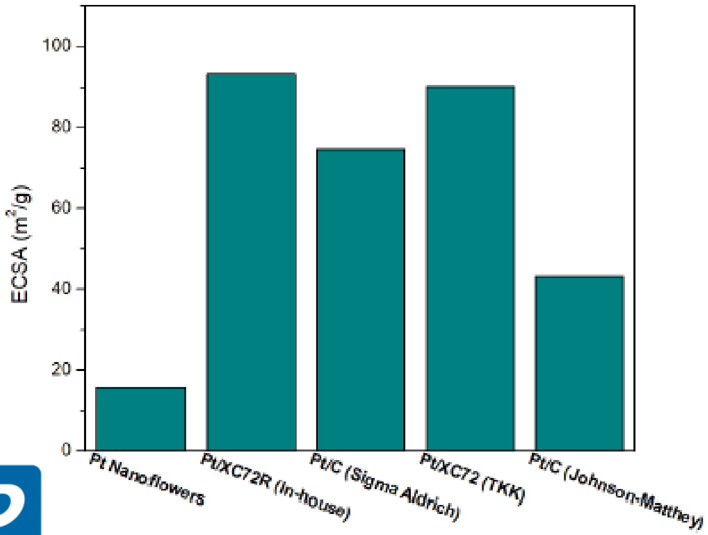


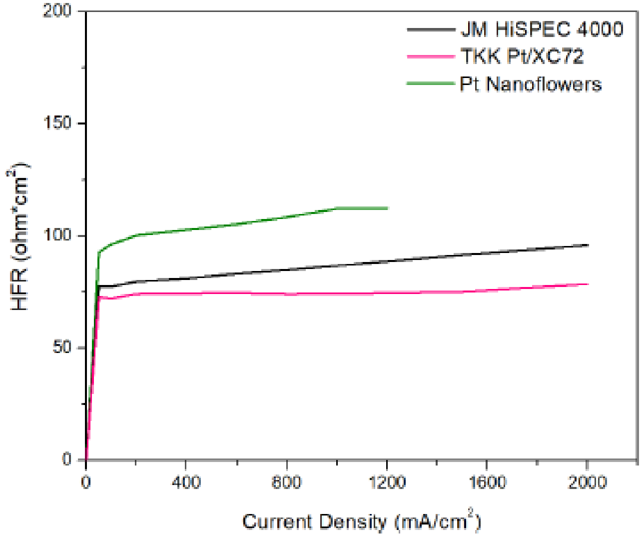


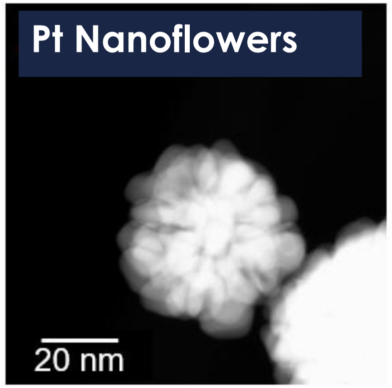


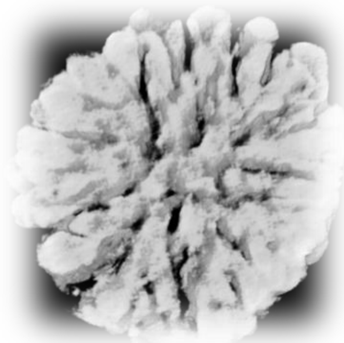


Alvin Ly









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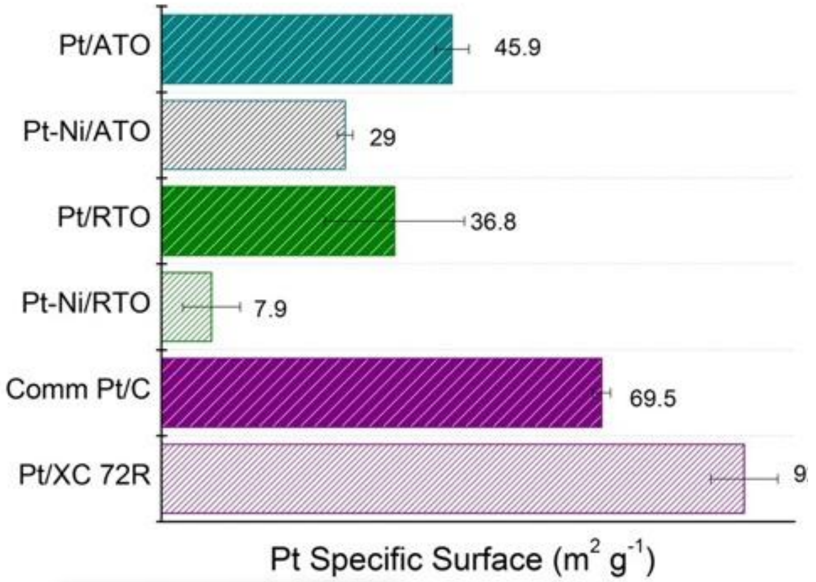
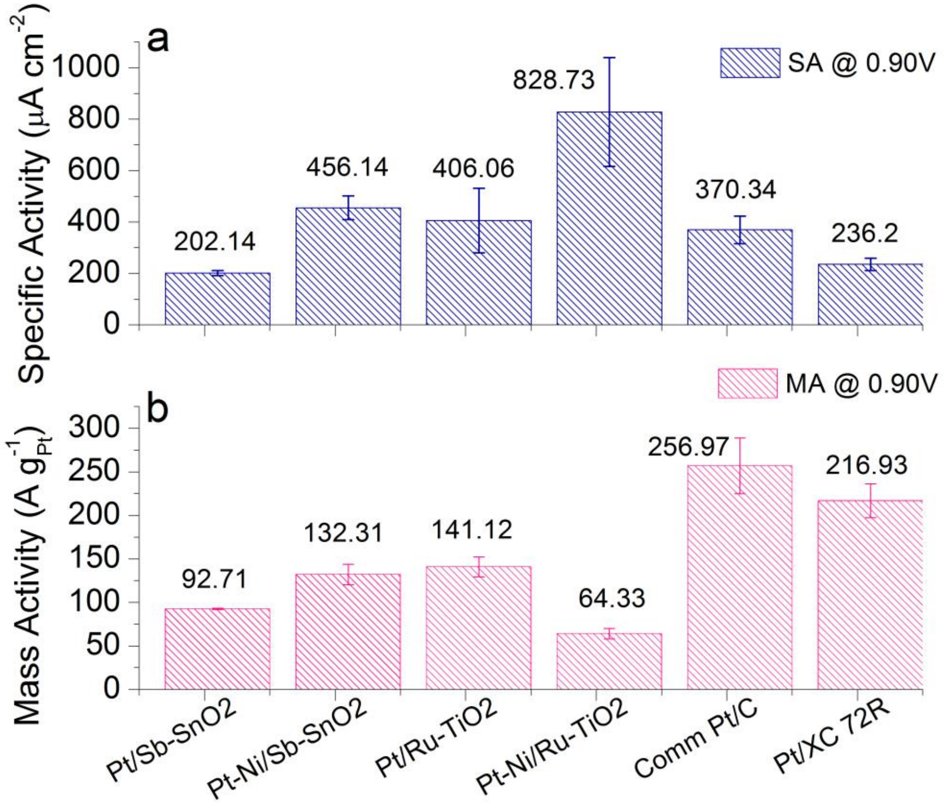
A. Ly, T. Asset, E. Murphy, K. Khedekar, Y. Huang, L. Xing, M. Xu, H. Wang, R. Chattot, X. Pan, I. Zenyuk and P. Atanassov, Design of Platinum Nanoflowers Catalysts Positive Exhibiting Near-ideal Local Coordination in a Complex Shape, *Electrochimica Acta* (2023) DOI: 10.1016/j.electacta.2023.143282

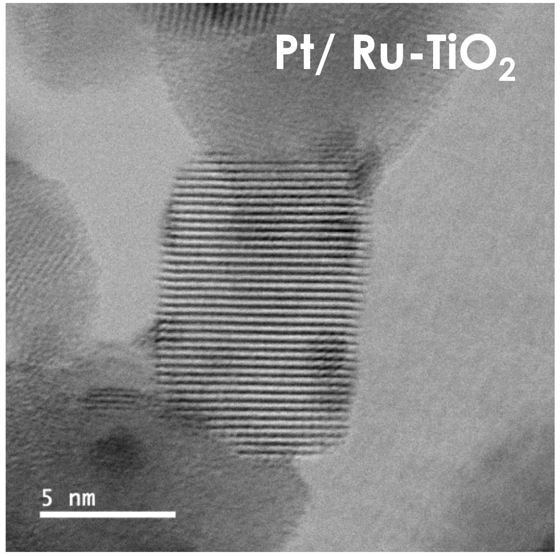
Pt/Conductive Oxides Library and Performance

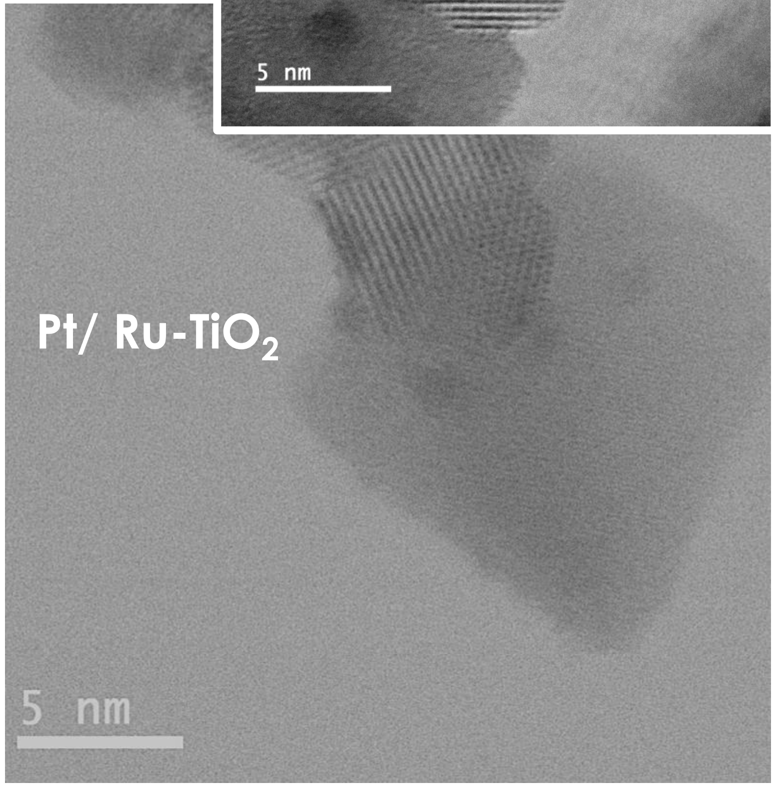
Pt Specific Surface Area



Specific Activity and Mass Activity







Mounika Kodali

DE NORA

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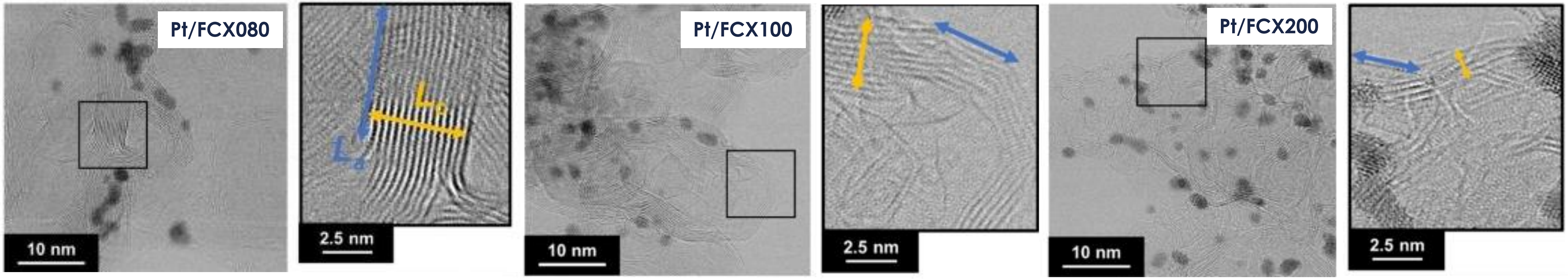
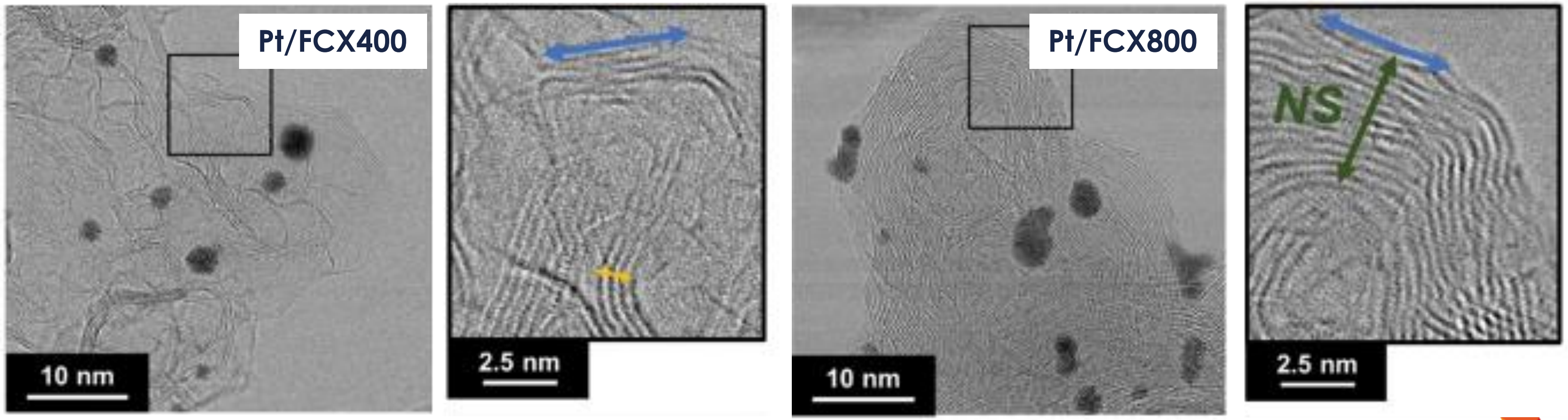
C. He, A. Ells, S. Sankarasubramanian, J. Parrondo, C. Gumeci, M. Kodali, I. Matanovic, A.K. Yadav, K. Bhattacharyya, N. Dale, P. Atanassov and V.K. Ramani, Self-anchored Platinum Decorated on Antimony-doped-Tin Oxide is a Durable Oxygen Reduction Electrocatalyst, *ACS Catalysis*, 11 (2021) 7006-7017

Morphological Variability of Novel Carbon Supports



Morteza Rezaei Talarposhti

twelve



CABOT

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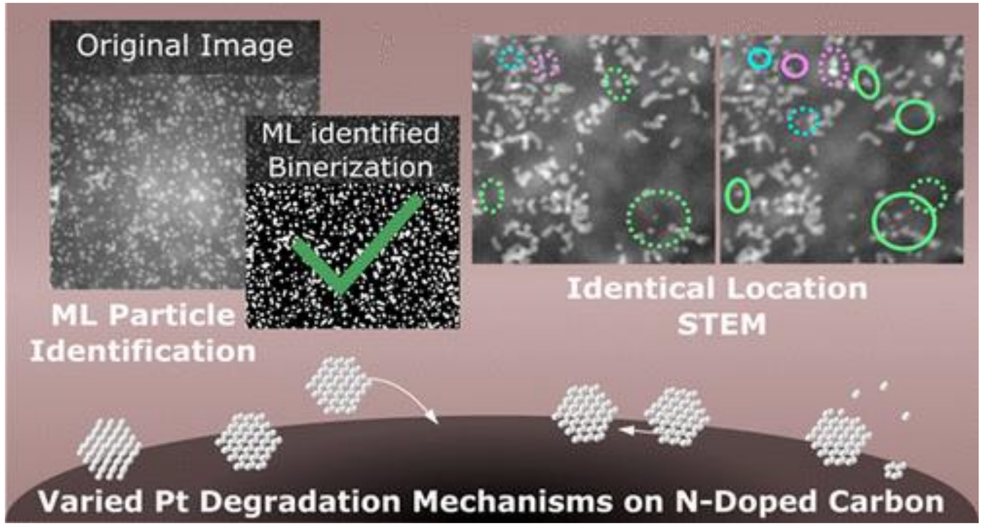
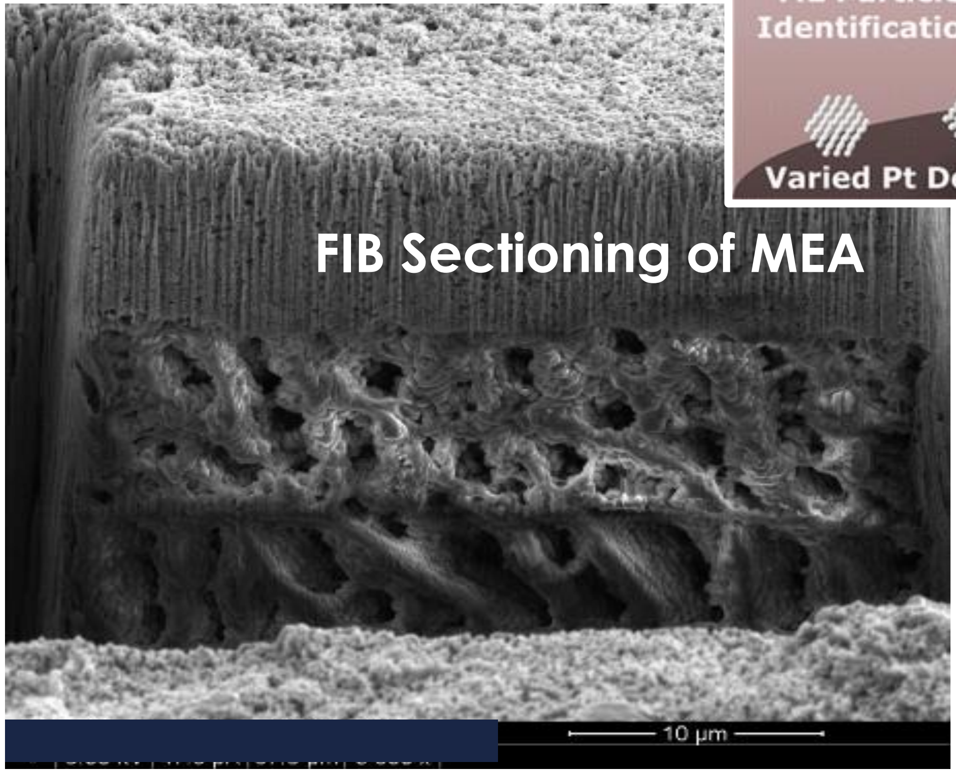
M. Rezaei Talarposhti, T. Asset, S. T. Garcia, Y. Chen, S. Herrera, S. Dai, E. J. Peterson, K. Artyushkova, I. Zenyuk and P. Atanassov, Kinetic Isotope Effect as a Tool To Investigate the Oxygen Reduction Reaction on Pt-based Electrocatalysts – Part II: Effect of Platinum Dispersion, *ChemPhysChem* 2020, *21*, 1331.

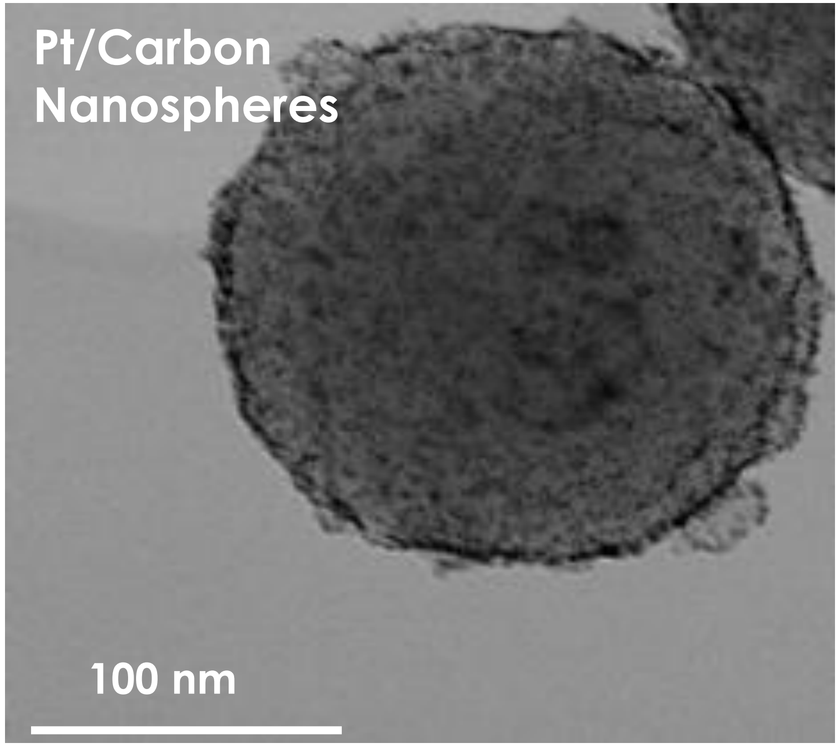
Advanced Carbon Catalysts' Supports

BOSCH





Hanson Wang

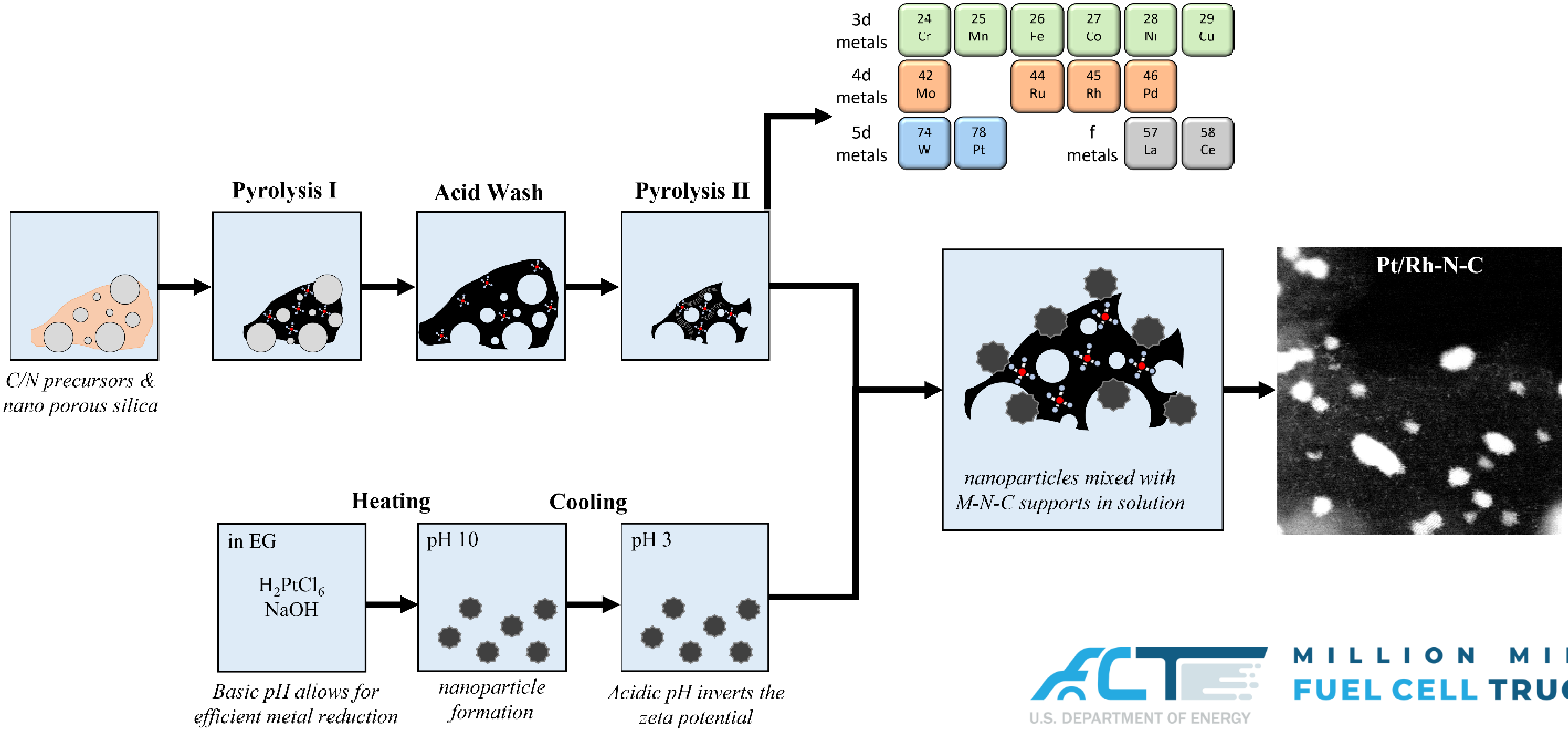


MITSUBISHI CHEMICAL

UCI

M. Fitzgerald, H. Wang, A. Ly, J. Foster, M. Sorrells, T. Asset, P. Atanassov, and S. Pylypenko, Probing Catalyst-Support Interactions: Effect of Nitrogen Defects on Pt Nanoparticle Dispersion and Stability Through Electron Microscopy Paired with Machine Learning Image Processing, *ACS Applied Nano Materials*, 6 (2023) 5313-5324

M-N-C Materials as Designer Supports for the PGM Catalysts



MILLION MILE FUEL CELL TRUCK

U.S. DEPARTMENT OF ENERGY

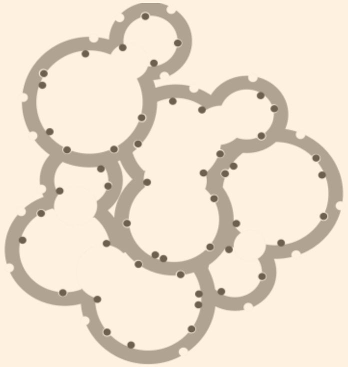
UCI

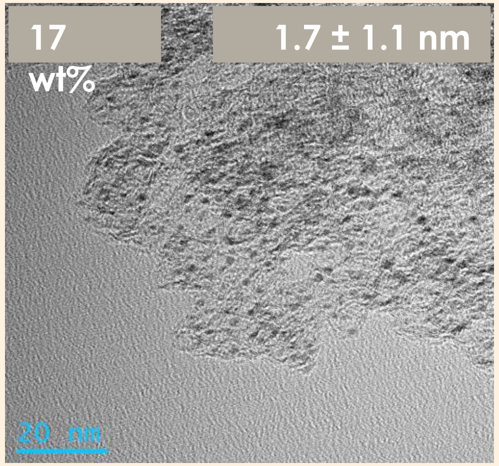
A. Ly, E. Murphy, H. Wang, Y. Huang, G. Ferro, S, Guo, T. Asset, Y. Liu, I. Zenyuk, P. Atanassov, Electrochemical Trends of a Hybrid Platinum and Metal-Nitrogen-Carbon Catalyst Library for the Oxygen Reduction Reaction, *EES – Catalysis*, 2 (2024) 624 DOI: 10.1039/d3ey00235g

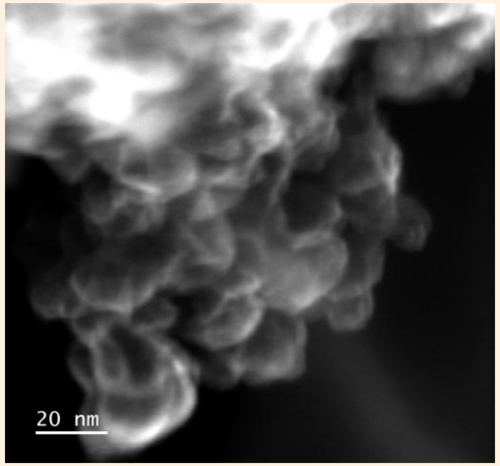
Designer Platinum Catalyst/Conductive Carbon Supports

Pt/FCX®A IN and Pt/FCX®B IN have very similar physical characteristics

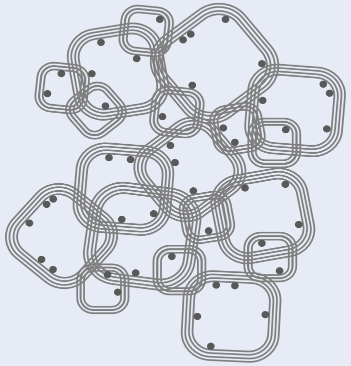
Pt/FCX® IN
A

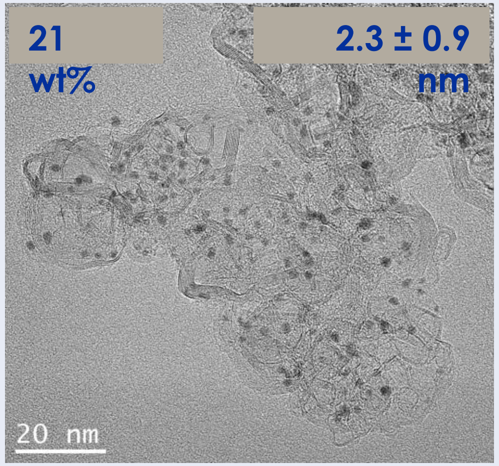


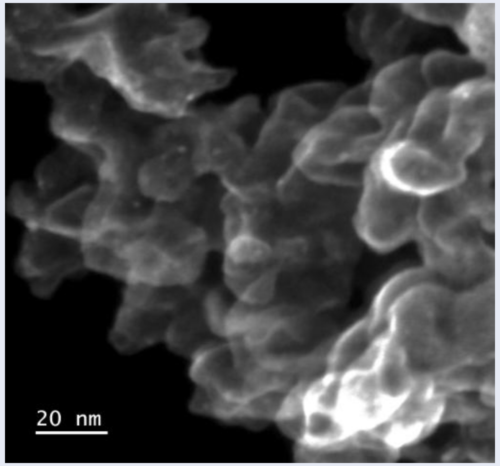




Pt/FCX®B IN







Gio Ferro

UCI
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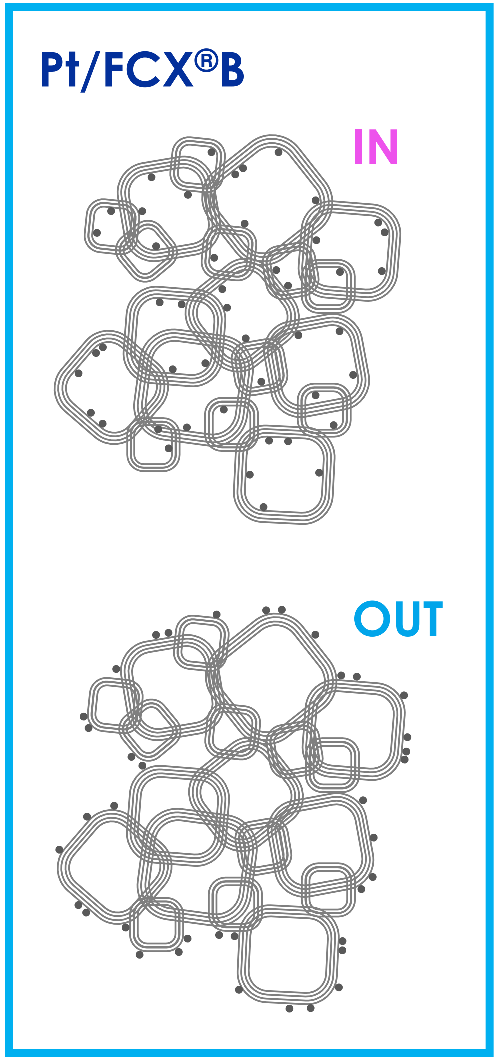
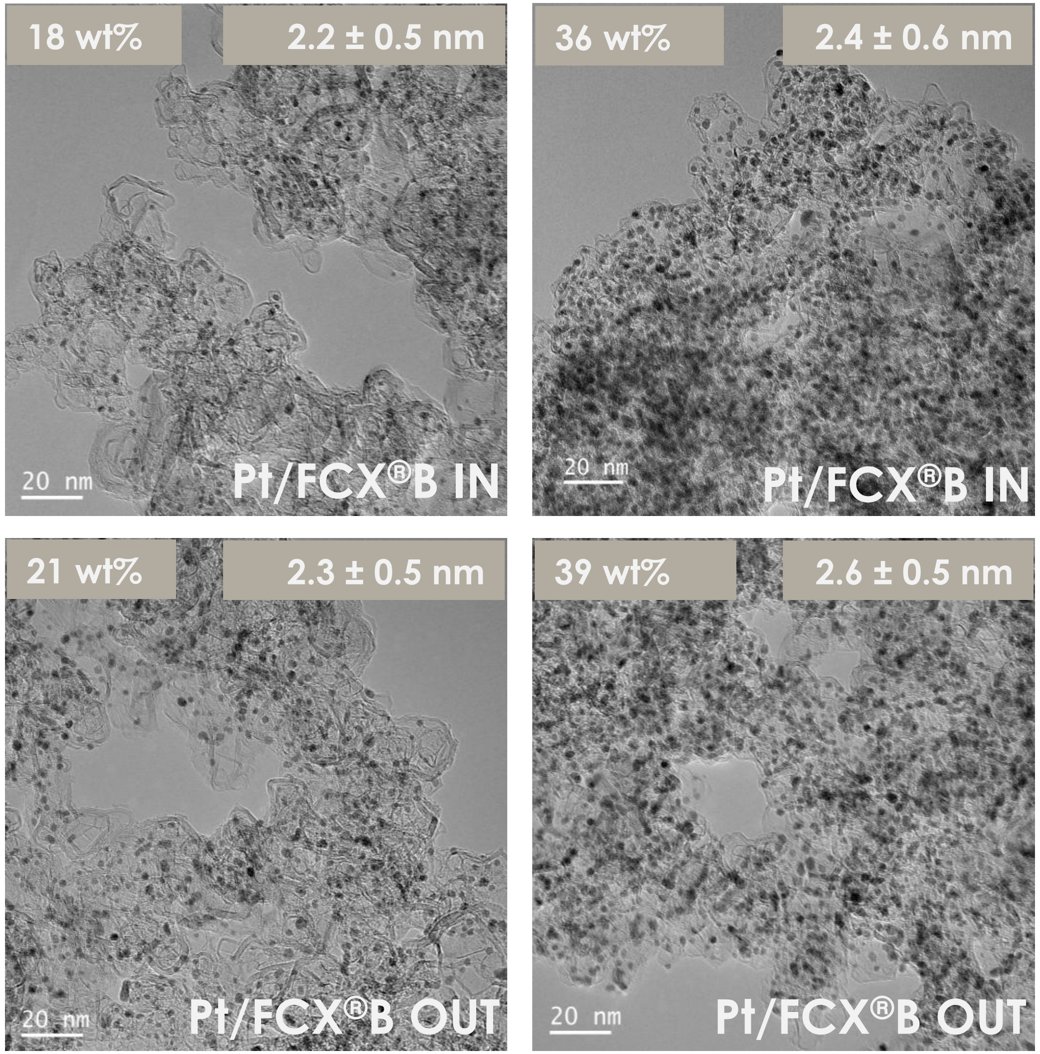
MILLION MILE
FUEL CELL TRUCK

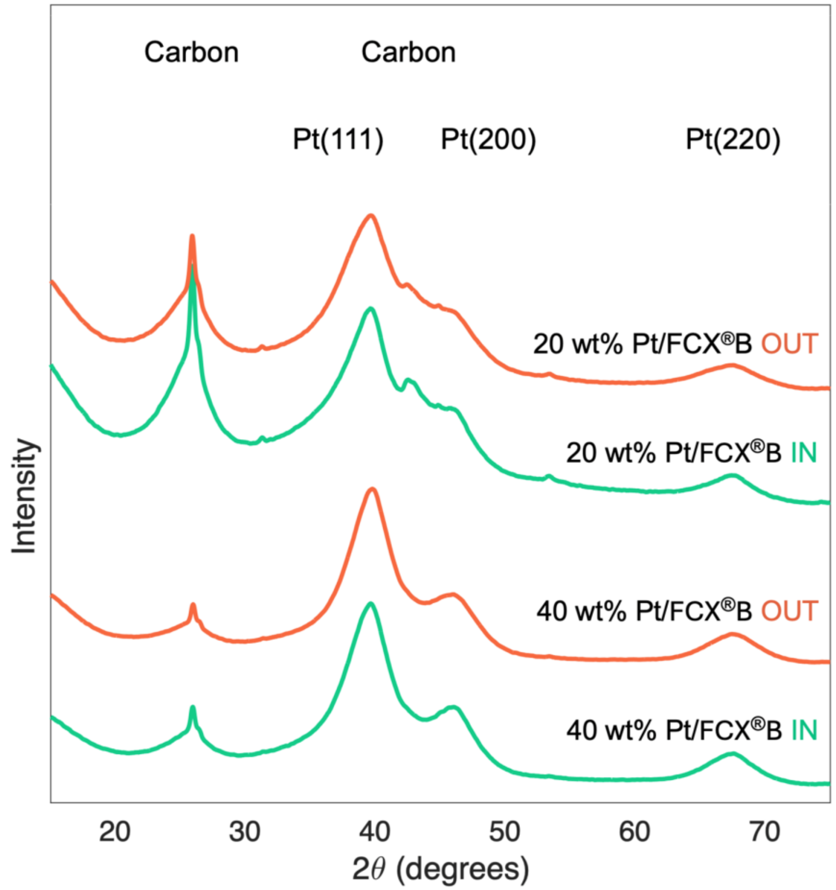
CABOT
BOSCH

Optimizing Catalysts Structure for Comparability

Optimized 20% wt. and 40% wt. Pt/FCX®B IN and Pt/FCX®B OUT with close/identical Pt crystallinity







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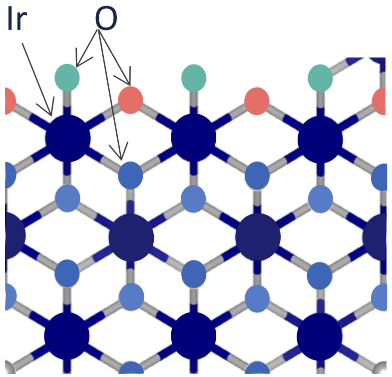
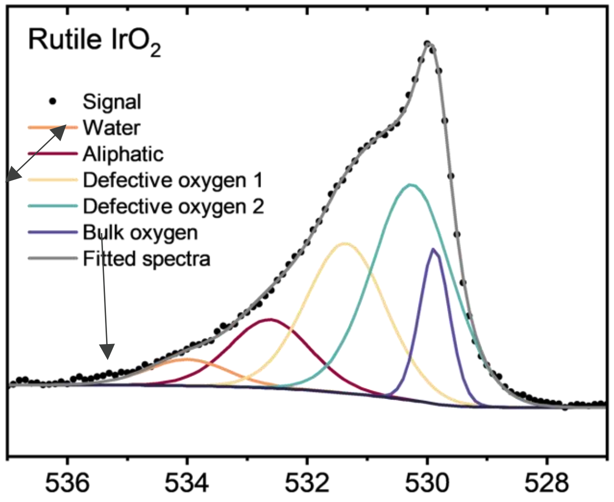
CABOT
BOSCH

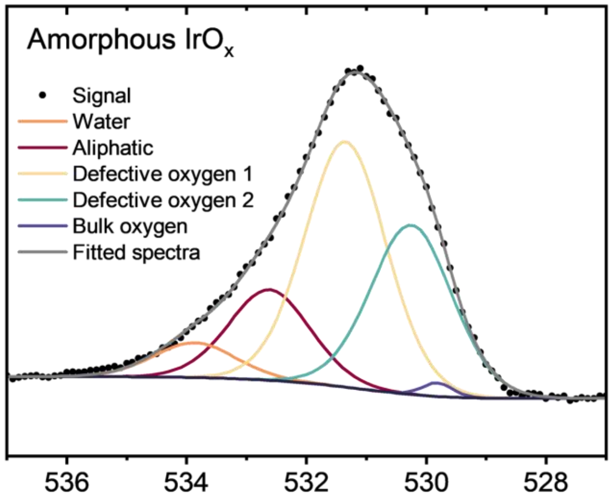
XPS Method of Evaluation IrO_x Catalysts via O1s SF-Structure

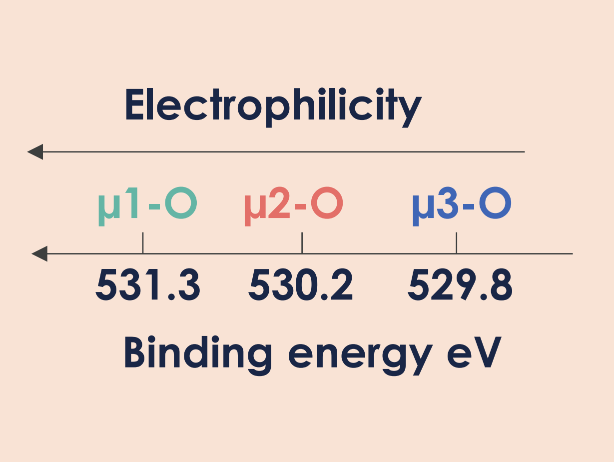


Edge of the IrO_2 crystal

Camille Roiron

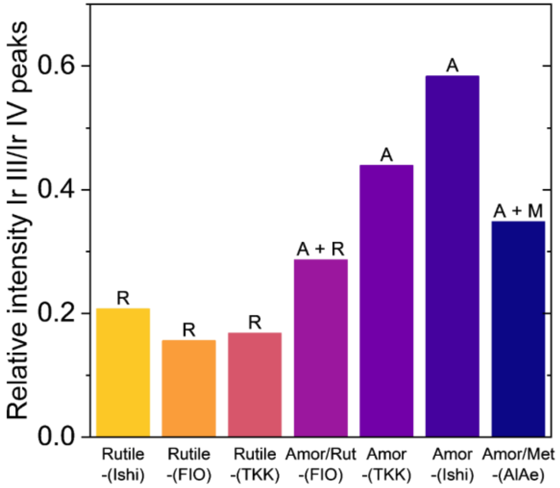


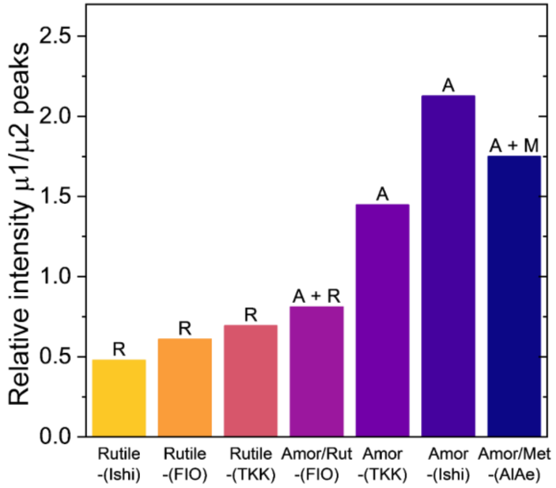




Model can be applied for both amorphous and crystalline IrO_x

Designation of the species by their assumed binding with Ir





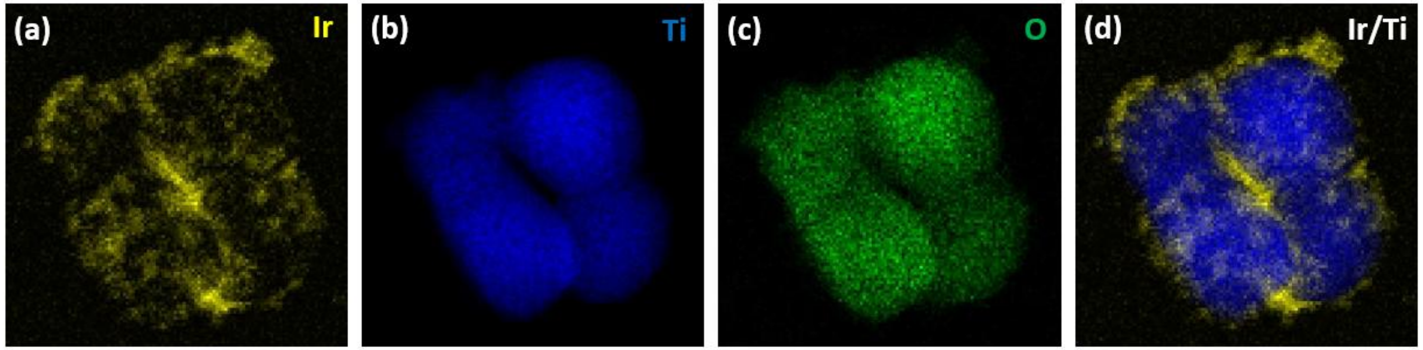
- Surface defectivity of the iridium oxide does not translate directly into electrochemical parameter.
- Different composition depending if we look at extreme surface, sub-surface or bulk

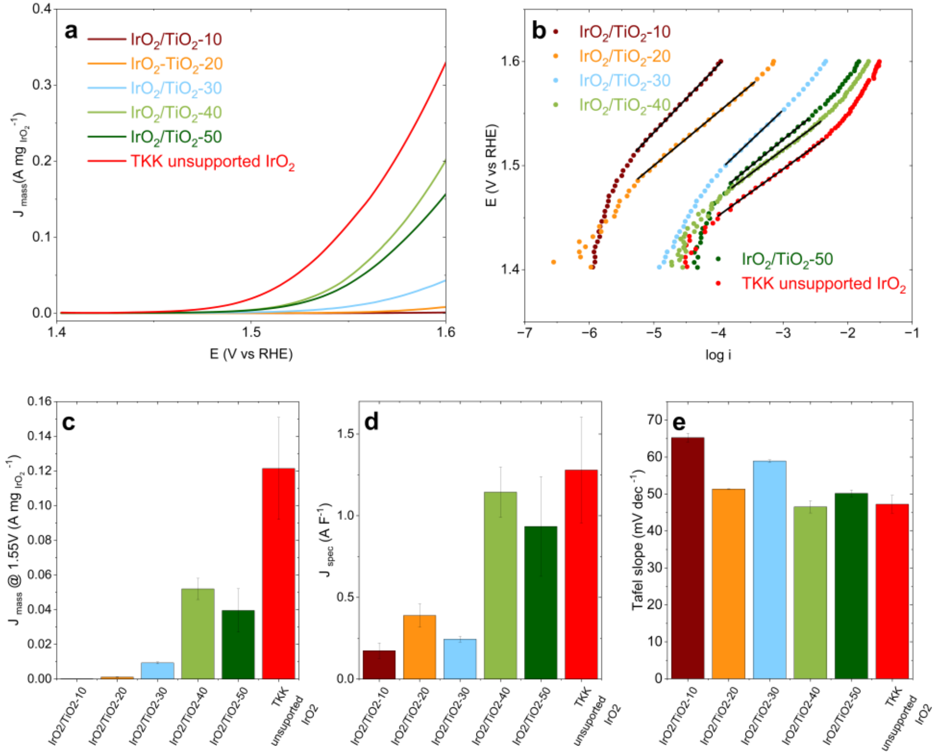
UCI

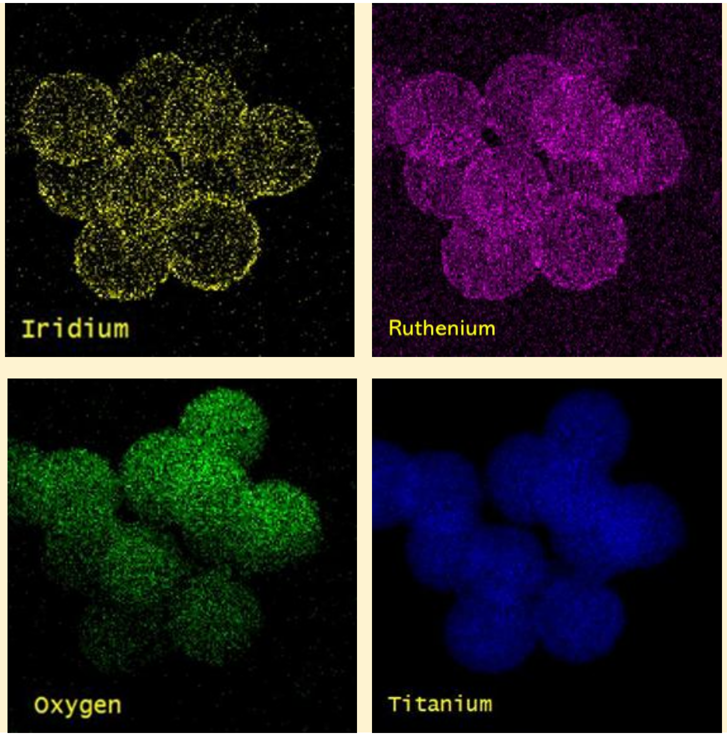
C. Roiron, C. Wang, I.V. Zenyuk and P. Atanassov, Oxygen 1s X-ray Photoelectron Spectra of Amorphous and Crystalline Iridium Oxides as a Key Descriptor of catalyst surface, *J. Physical Chemistry Letters*, (2024) DOI: 10.1021/acs.jpclett.4c02616

IrO_x/TiO_2 Electrocatalysts for Oxygen Evolution Reaction

IrOx supported on commercially available anatase TiO_2







IrOx on synthetic rutile TiO_2

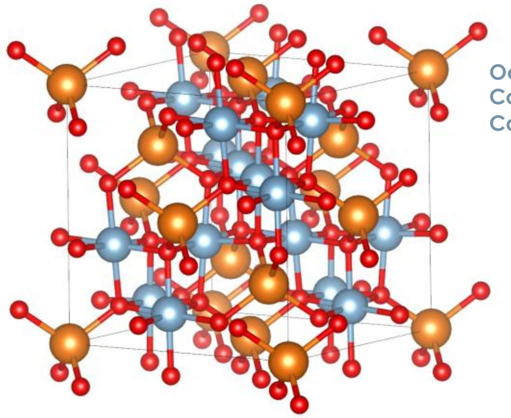
Shabnam Zargarian

UCSD

UCI

S. Zargarian, C. Roiron, G. Ferro and P. Atanassov, Iridium Oxide Network on Non-Conductive TiO2 Support as a Catalyst for Oxygen Evolution, *ChemElectroChem*, (2025) DOI: 10.1002/celc.202400625

PGM-free Electrocatalysts for Oxygen Evolution Reaction



Octahedrally Coordinated Metal Cation (M^{3+})

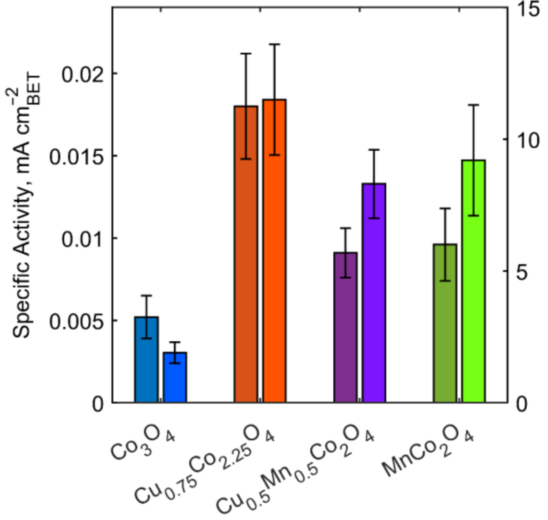
Tetrahedrally Coordinated Metal Cation (M^{2+})

Christopher Liu

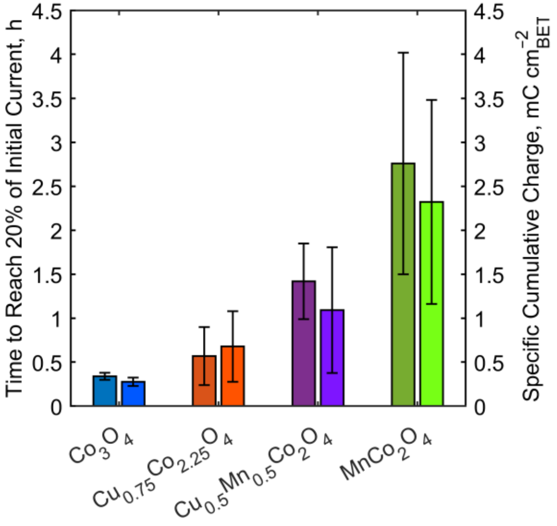
NSF GRFP

UCI

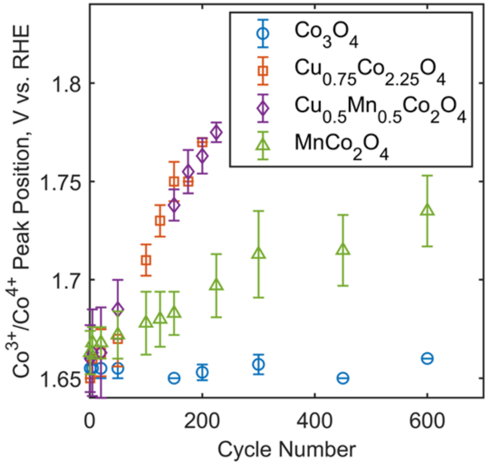
Activity



Current Retention, Potential Cycling



Peak Position Shifts, Potential Cycling

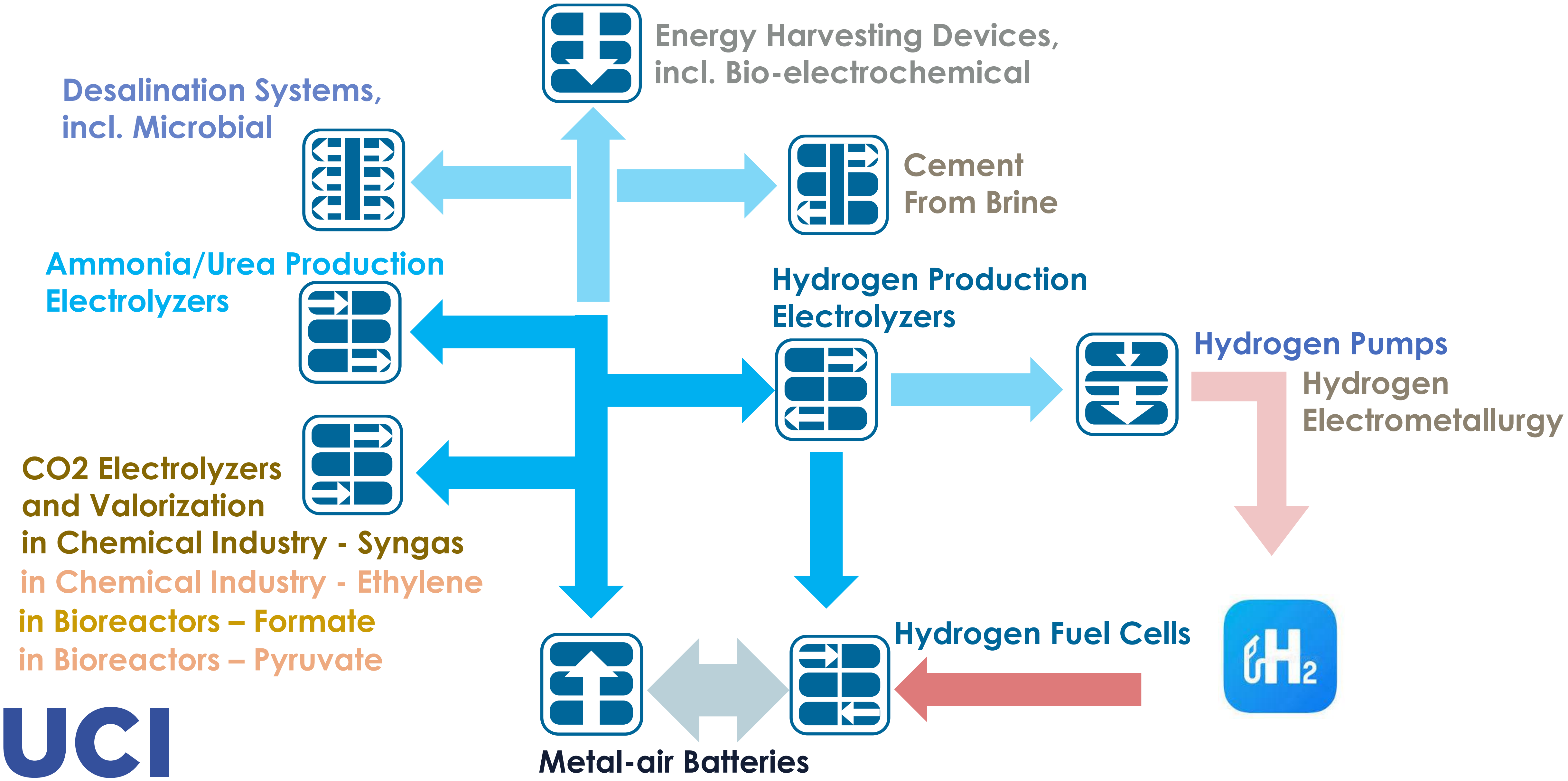


- Cu and Mn were incorporated into Co oxide spinels for comparison of activity, stability, and durability
- $Cu_{0.75}Co_{2.25}O_4$: highest initial activity, lowest stability and potential alternation durability
- $MnCo_2O_4$: highest potential alteration durability and, for the multi-metallic oxides, best potential hold stability and lowest Co^{3+}/Co^{4+} peak shift rate
- Co_3O_4: lowest initial activity, highest potential hold stability, and almost no Co^{3+}/Co^{4+} shift rate

MAX-PLANCK-GESELLSCHAFT
Fritz-Haber-Institut

HZB BESSY II Light Source

Electrocatalysts' Role in Decarbonization Technologies



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Outlook on the Role of Electrocatalysis for Decarbonization

New Materials Focus:

- Critical need to overcome the dependance on PGM metals at least by thrifting for the next decade
- Materials design at hierarchical scale with an emphasis on control of the interfaces
- Addressing materials stability under operating conditions and its effect on durability of devices
- Materials synthesis strategies that provide scaleup and save costs while proving ultimate control
- Integration technologies for device fabrication with high thruput and market orientation

Device Focus:

- Nish markets are growing and overlapping
- Critical need for medium duration storage
- Dynamic operation is highly desirable
- Minimal startup/shut down losses

System Focus:

- Integration with batteries into hybrid systems
- Power electronics solutions for durability
- Modular approach for flexibility
- Deployment at scale

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Alessio Cosenza
Thirawit Sornusuchat
Vivek Devalla
Loki Chen
Florian Chabot
Daniele Moraschini
Camille Roiron
Giovanni Ferro
Yu-Han Chen
Chris Liu

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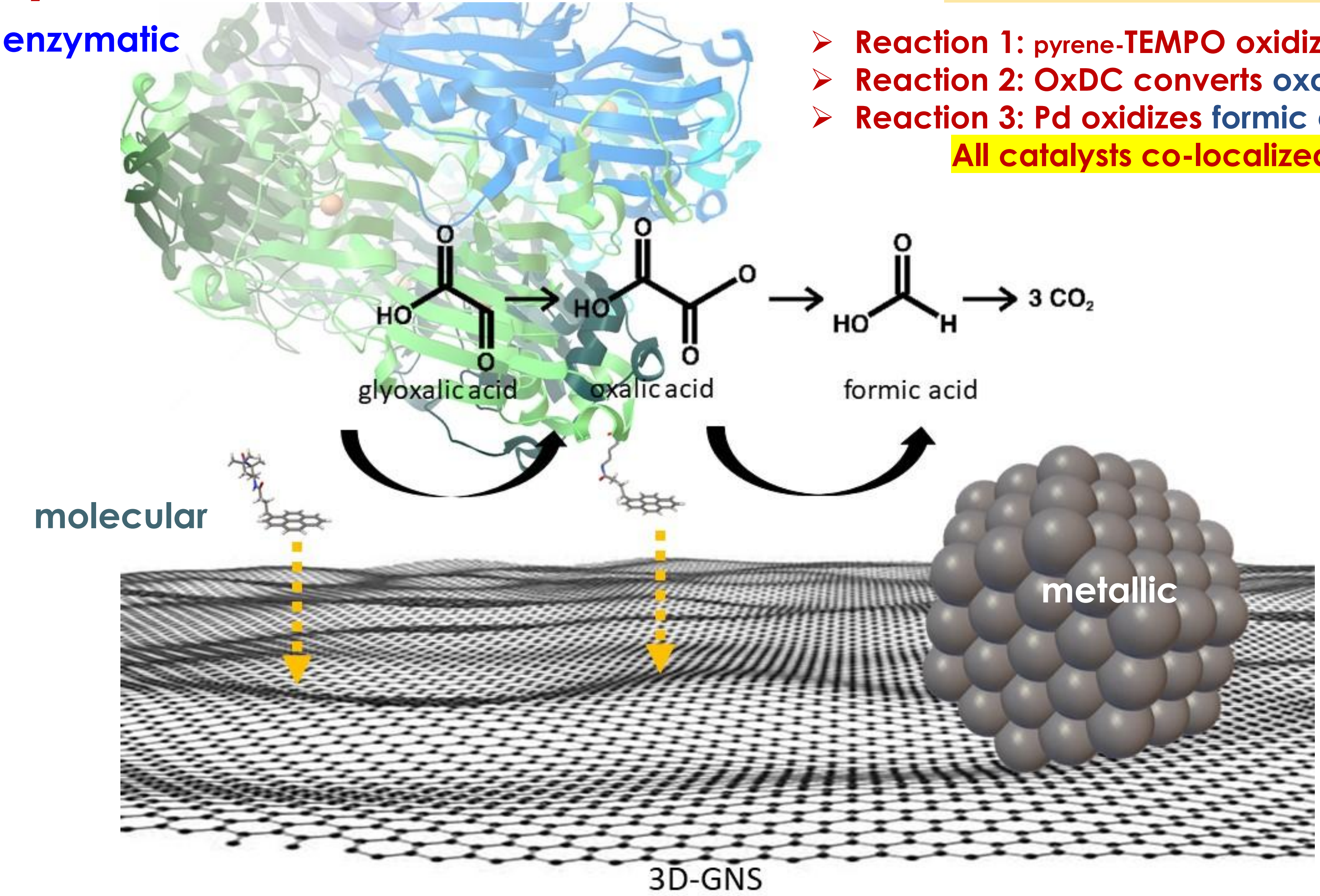
Synthetic Multimodal Cascade: hybrid molecular-enzymatic-inorganic system

- Reaction 1: pyrene-TEMPO oxidizes glyoxalic acid to oxalic acid
- Reaction 2: OxDC converts oxalic acid to formic acid
- Reaction 3: Pd oxidizes formic acid to CO_2

All catalysts co-localized on the same support

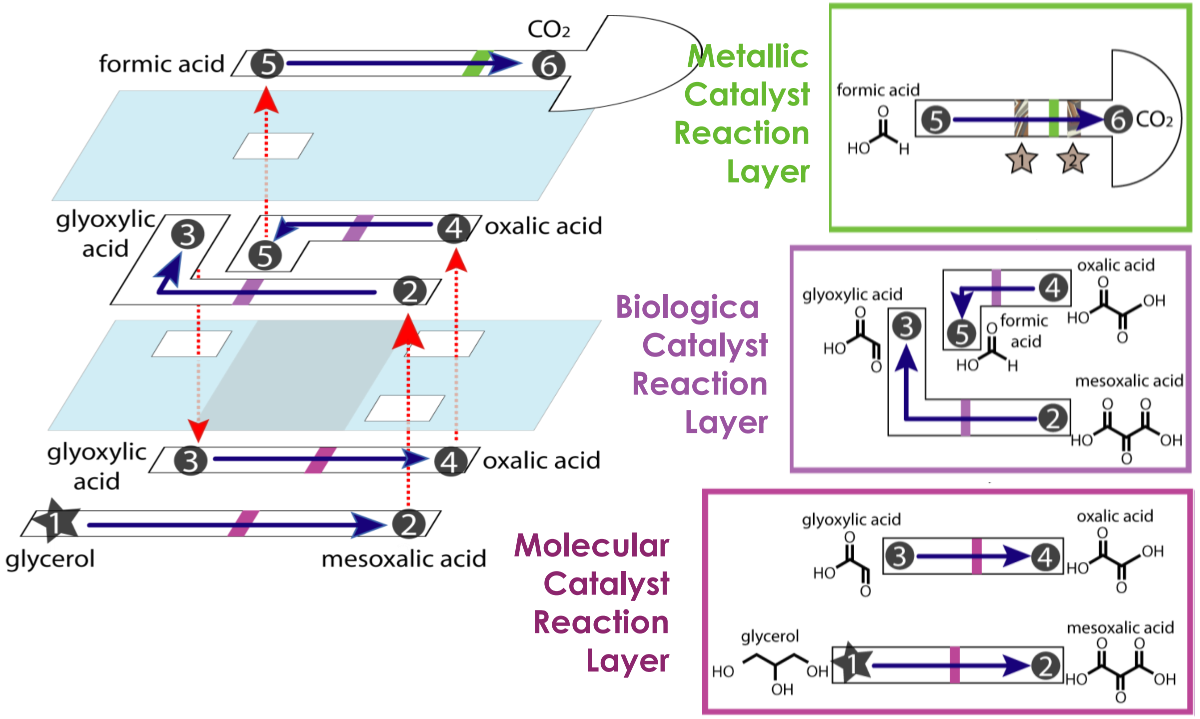


DOD-ARO MURI to University of Utah : W911NF1410263 - Shelley Minteer, PI *Bio-inspired Design of Adaptive Catalysts Cascades*, 2014-2020

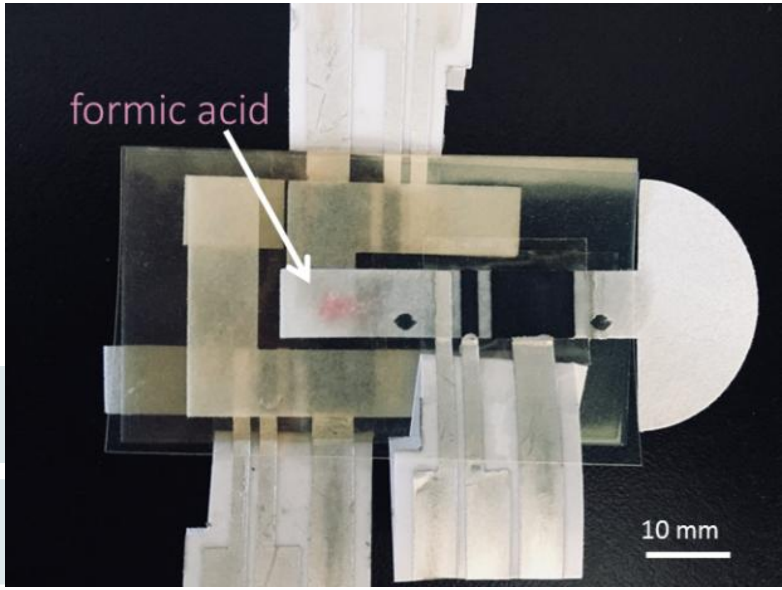
Glycerol to CO_2 Cascade Oxidation in a Singular Device:

paper microfluidics-based spectro-electrochemical platform

S. Abdellaoui, M. Seow Chavez, I. Matanović, A.R. Stephens, P. Atanassov and S.D. Minteer, Hybrid Molecular/Enzymatic Catalytic Cascade for Complete Electro-oxidation of Glycerol Using a Promiscuous NAD-dependent Formate Dehydrogenase from *Candida boidinii*, *Chemical Communications*, 53 (2017) 5368-5371



- the OxDC layer was sandwiched between two plastic films to prevent the OxDC from getting dry and denaturing
- the size of the platform was small (7.5 cm x 8 cm) to fit under the Raman microscope comfortably
- SERS detection zones were located in positions where they are all accessible to the Raman laser



N. Andersen, K. Artyushkova, I. Matanović, D. Hickey, S. Minteer and P. Atanassov, Spectro-Electrochemical Microfluidic Platform for Monitoring Multi-step Cascade Reactions, *ChemElectroChem*, 6 (2019) 246-251

N.I. Andersen, M. Seow Chavez, K. Artyushkova, I. Matanović, D.P. Hickey, S. Abdelloui, S.D. Minteer, and P. Atanassov, Modular Microfluidic Paper-based Devices for Electrocatalysis, *ChemElectroChem*, 6 (2019) 2448–2455

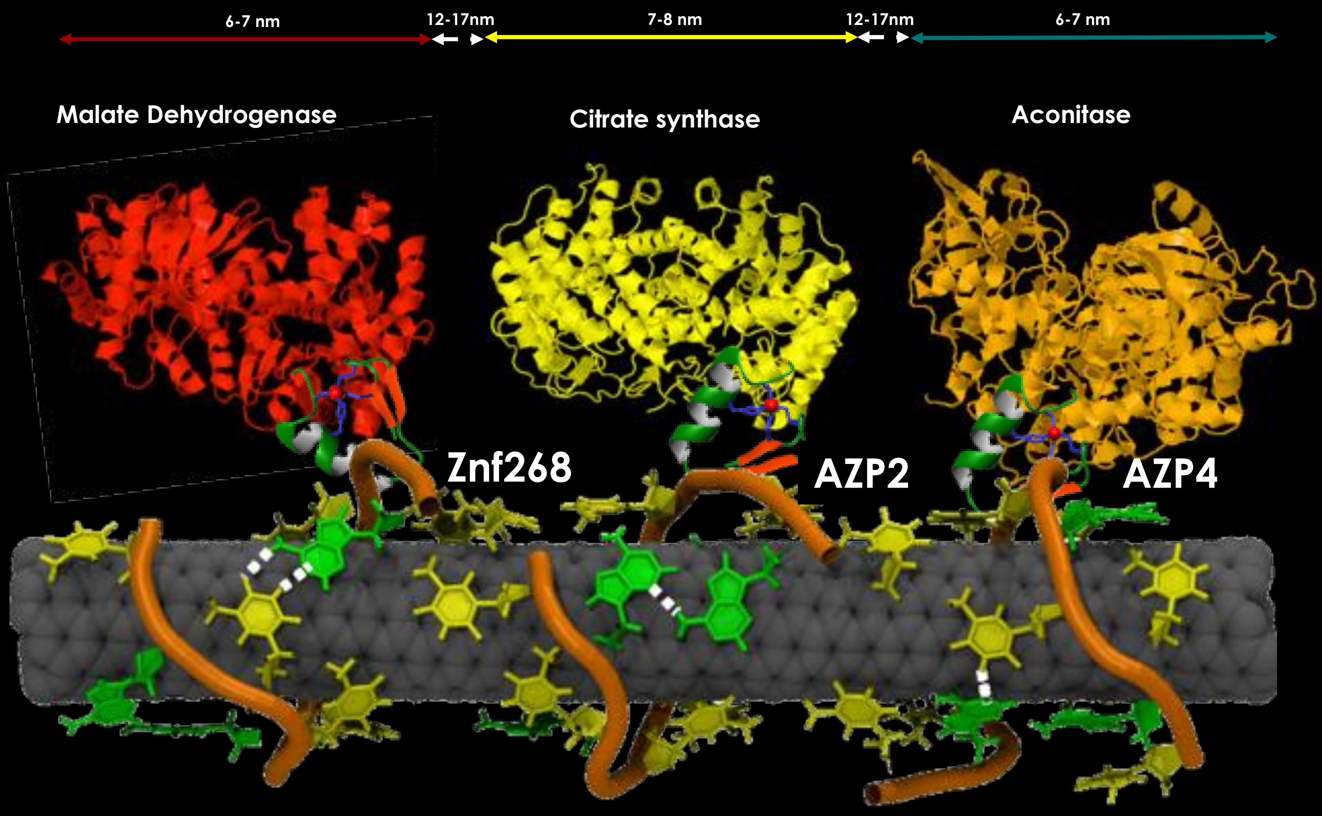
DOD-ARO MURI to University of Utah : W911NF1410263 - Shelley Minteer, PI *Bio-inspired Design of Adaptive Catalysts Cascades*, 2014-2020

Complex Enzyme/Nanomaterials Adducts :

multiple enzymes in channeling formation on DNA-CNT scaffolds

G. R. Szilvay, S. Brocato, D. Ivnitski, C. Li, P. DeLa Iglesia, C. Lau, E. Chi, M. Werner-Washburne, S. Banta, and P. Atanassov, Engineering of a Redox Protein for DNA-Directed Assembly, *Chem. Comm.*, 47 (2011), 7464 - 7466

I. Wheeldon, S. Banta, M. Sigman, P. Atanassov, S. Calabrese Barton, and S. Minteer, Substrate Channeling as a New Approach to Cascade Reactions, *Nature Chemistry*, 8 (2016) 299–309



50 – 80 nm long DNA scaffold

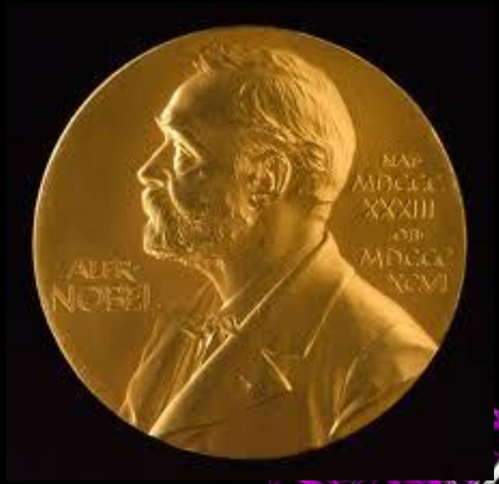
L. Xia, K. Nguyen, Y. Holade, H. Han, K. Dooley, P. Atanassov, S. Banta and S. Minteer, Improving the Performance of Methanol Biofuel Cells Utilizing an Enzyme Cascade Bioanode with DNA Bridged Substrate Channeling, *ACS Energy Letters*, 2 (2017) 1435-1438

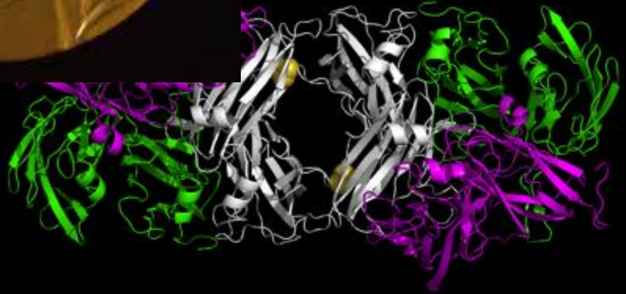
DOD-ARO MURI to University of Utah : W911NF1410263 - Shelley Minteer, PI *Bio-inspired Design of Adaptive Catalysts Cascades*, 2014-2020

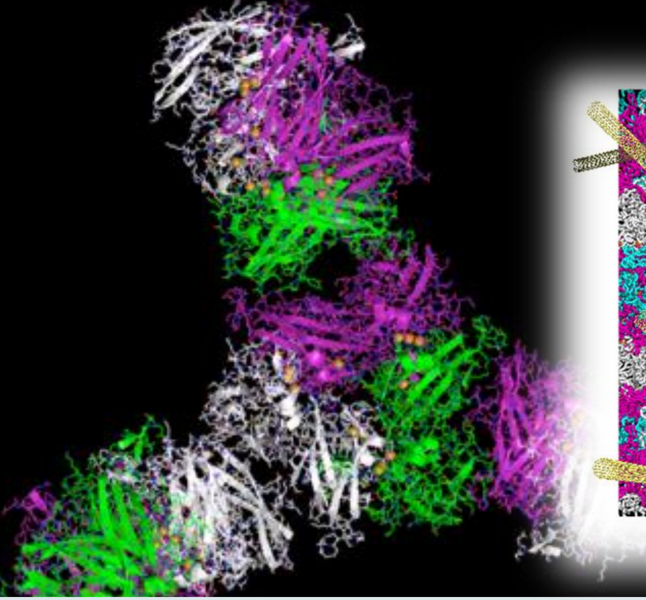
David Baker (one-half of the prize)

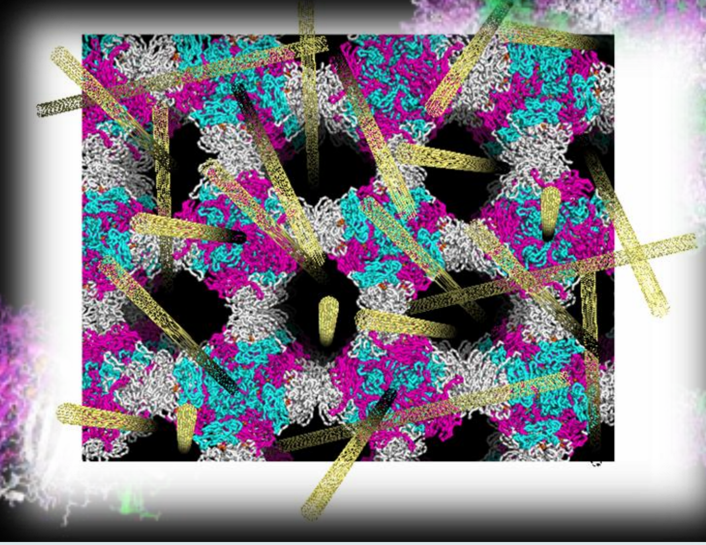
University of Washington, Seattle and Howard Hughes Medical Institute, USA

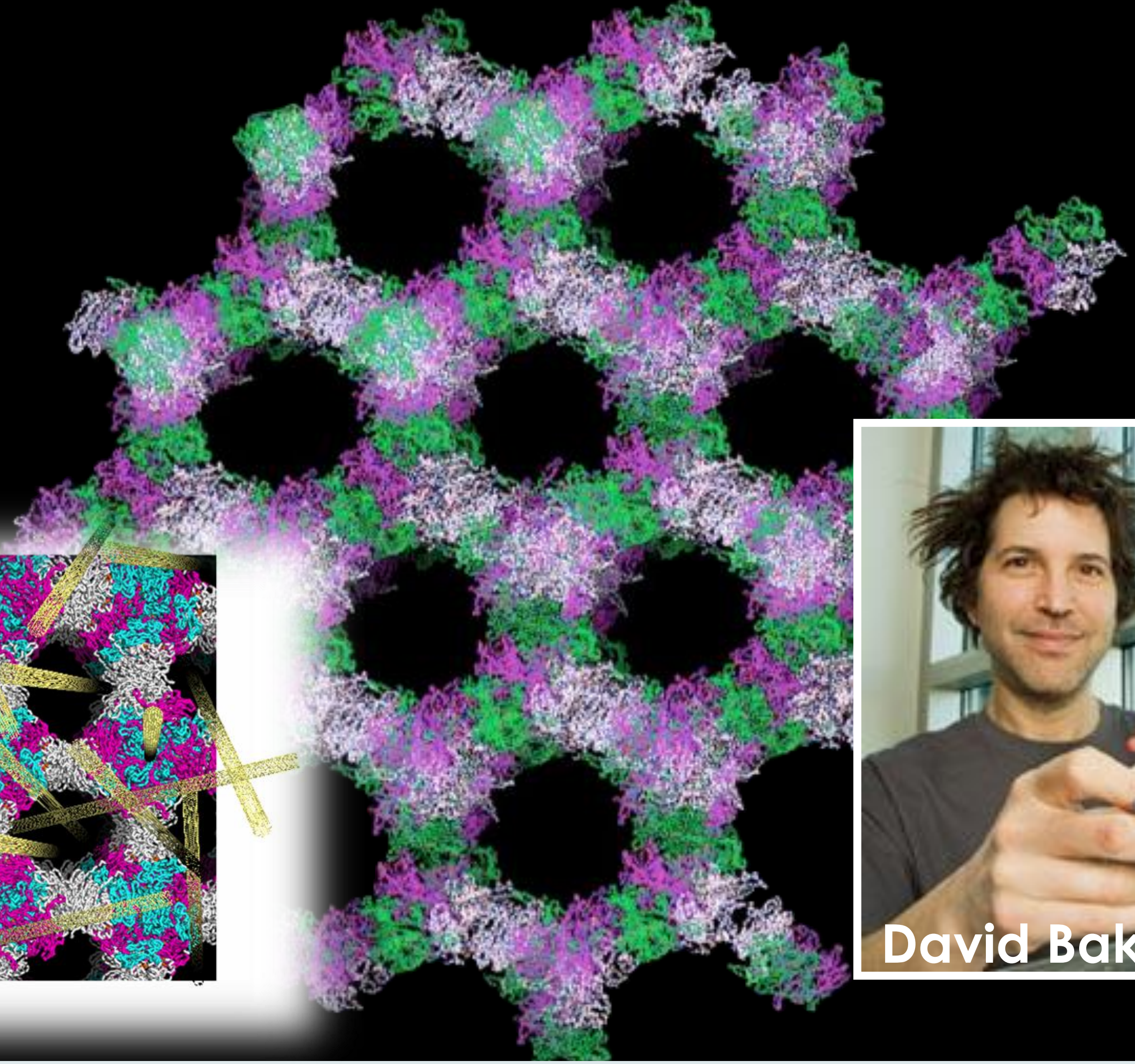
“for computational protein design”

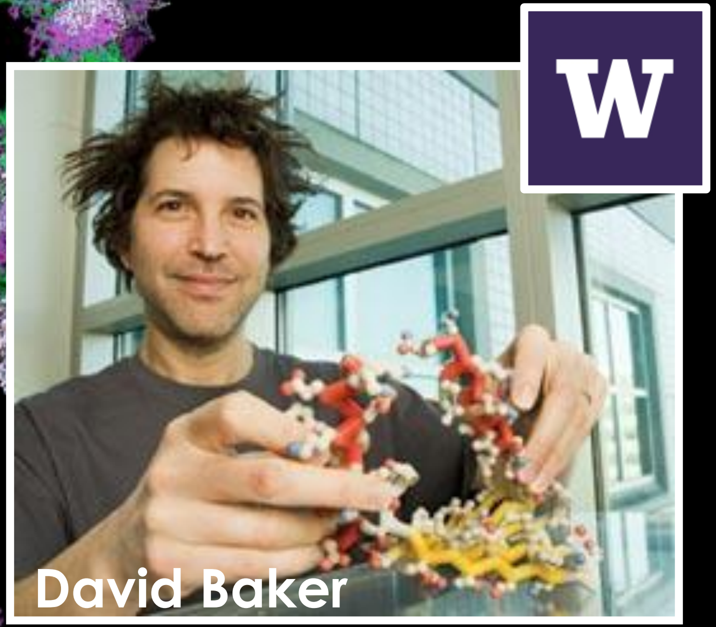












K. Garcia, S. Babanova, W. Sheffler, M. Hans, D. Baker, P. Atanassov and S. Banta, Designed Protein Aggregates Entrapping Carbon Nanotubes for Bioelectrochemical Oxygen Reduction, *Biotechnology & Bioengineering,* 113 (2016) 2321

Global Human Development Index and Power/Energy Use

Challenges:

- Creating a National and reginal sustainable policy of development and growth
- Building National energy independence strategy
- Achieving resilience of power delivery with respect to geopolitical and environmental catastrophic events