Hydrogénases et catalyseurs bioinspirés

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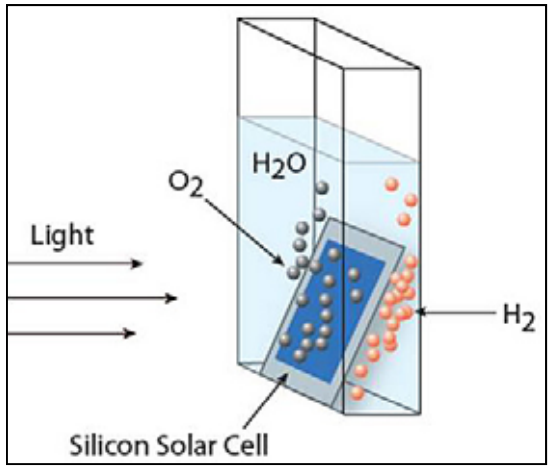
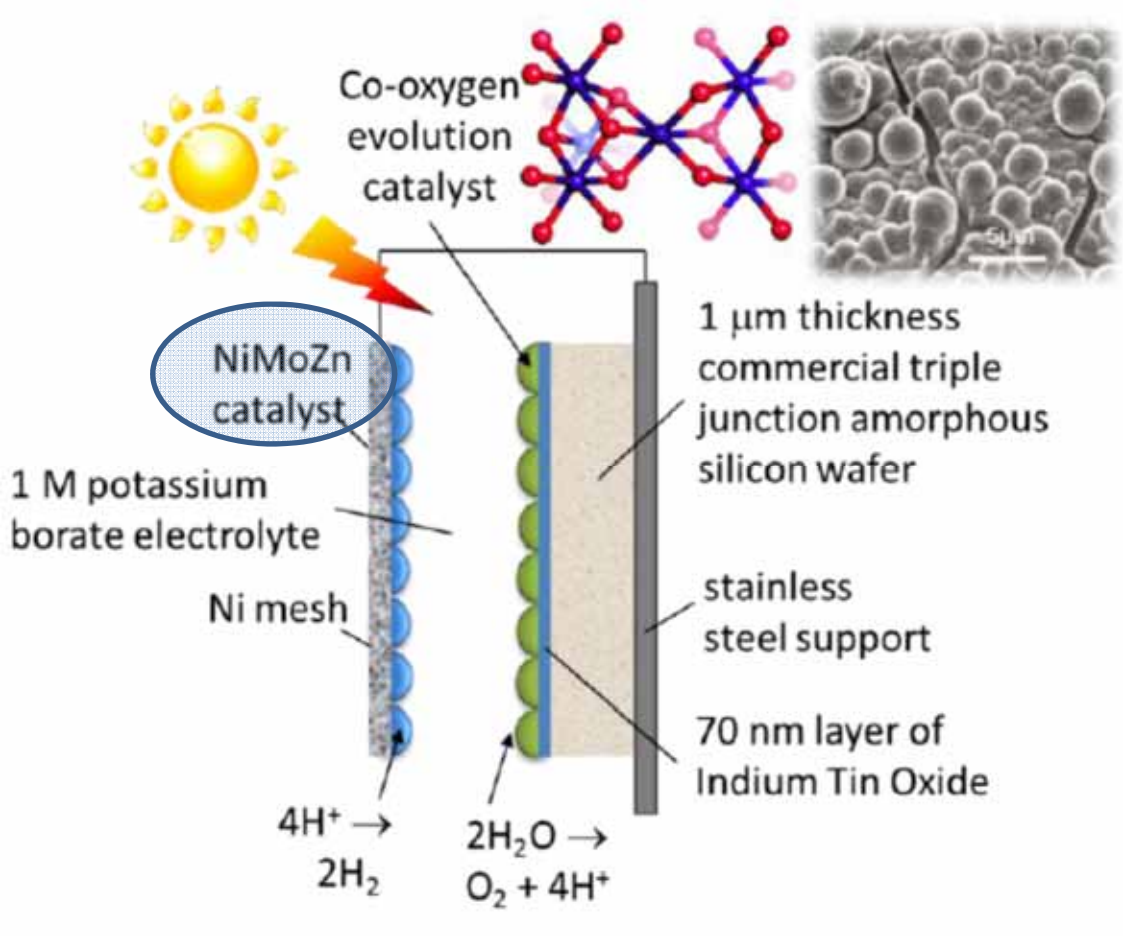
La « feuille artificielle »: H_2 bioinspiré

D. NOCERA, Harvard



Solar-to-H_2 = 4.7 %
(PV 7%)
1.5 mA.cm^{-2}
pH neutre

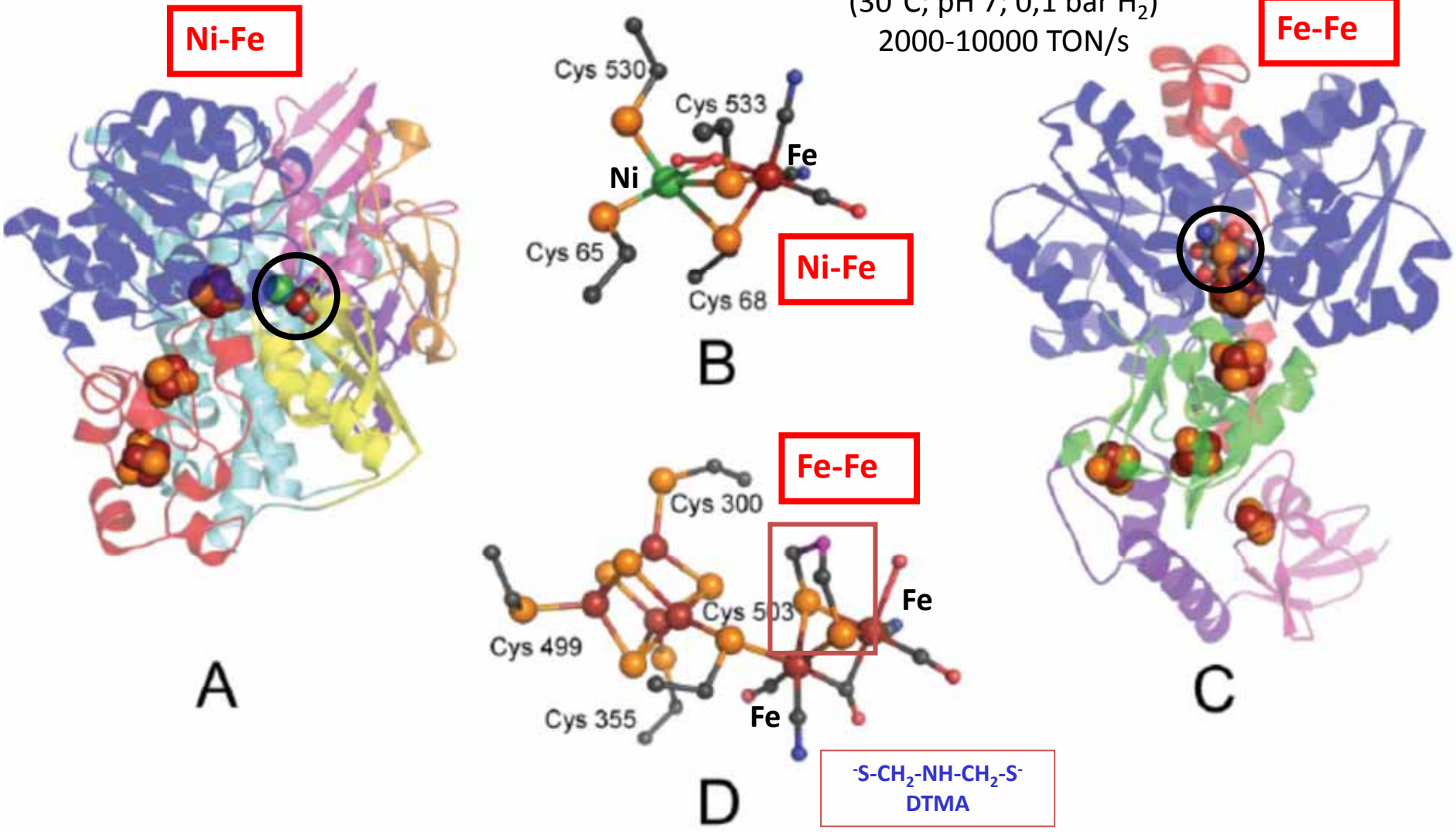


D. Nocera. *Science*, 2011, 334, 645.

Hydrogénases

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

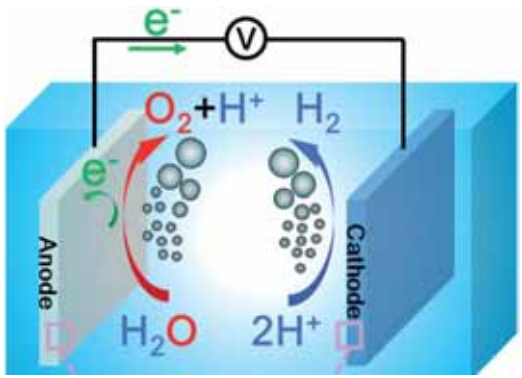
E = -400 mV vs SHE
(30°C; pH 7; 0,1 bar H_2)
2000-10000 TON/s

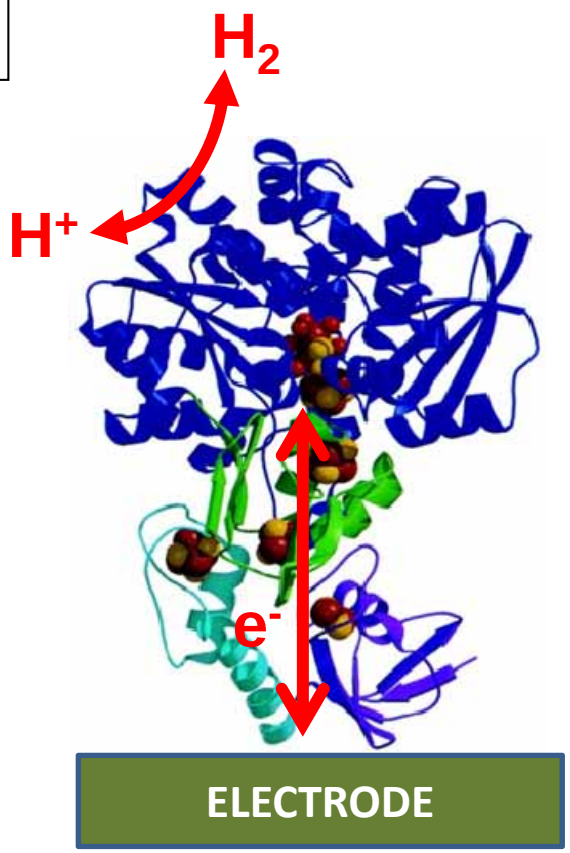


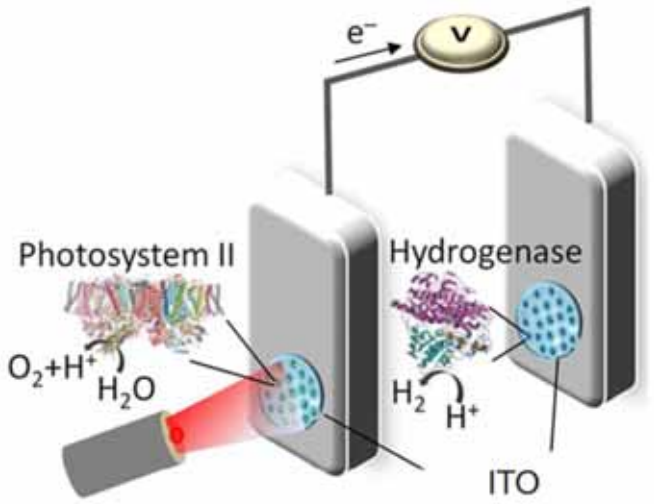
Volbeda, A. et al., *Nature* (1995), **373**, 580-587.
Volbeda, A. et al., *J. Am. Chem. Soc.* (1996), **118**, 12989-12996.

JW Peters et al *Science* (1998) 282, 1853
Y Nicolet et al *Structure* (1999) 7, 13

Hydrogénases





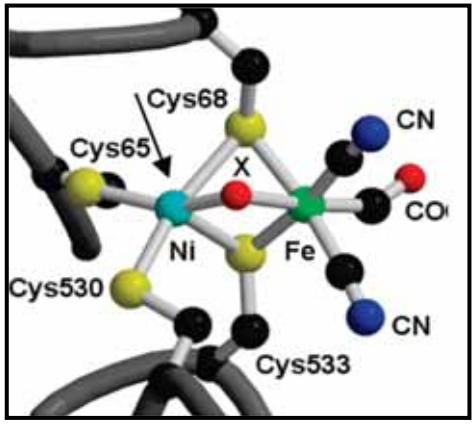


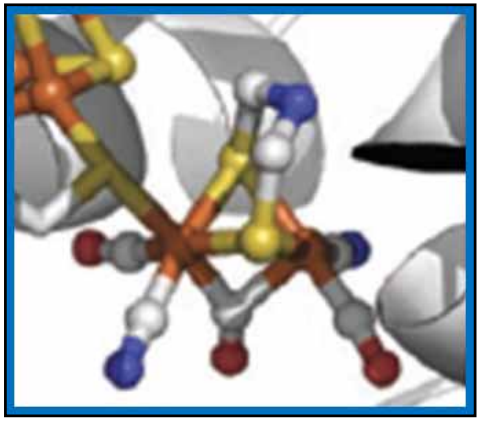
E. Reisner, Cambridge

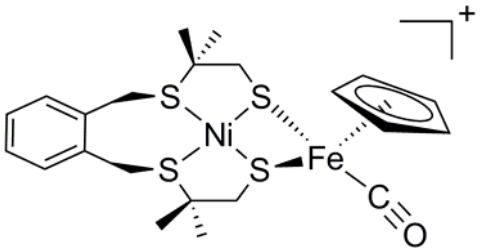
- **Sensibilité à O_2**
- **Expression/purification complexe**

CATALYSEURS BIOINSPIRES

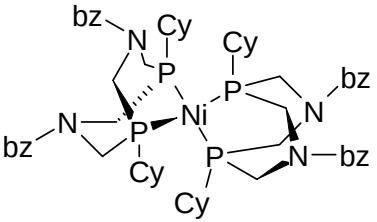
Catalyseurs bioinspirés



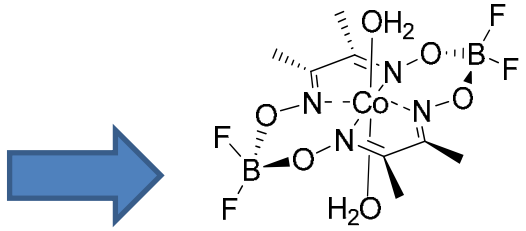




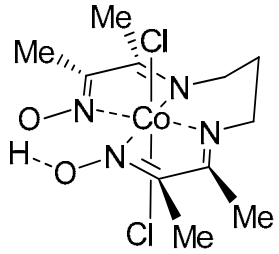
V. Artero, M. Fontecave,
Chem Commun 2010



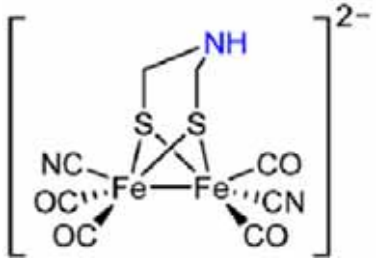
Dubois et al. *J. Am. Chem. Soc.*,
2006 and 2007.



V. Artero, M. Fontecave,
Angew. Chem. 2008



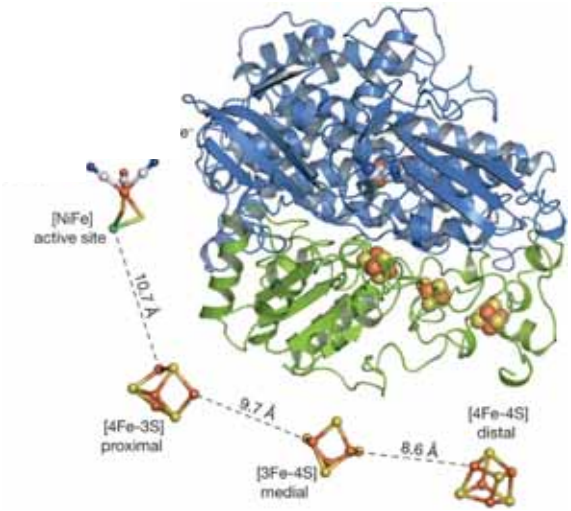
V. Artero, M. Fontecave,
PNAS (2009)



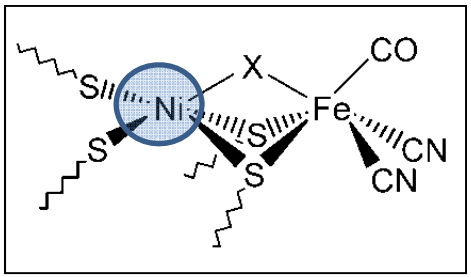
T. Rauchfuss, M. Darensbourg

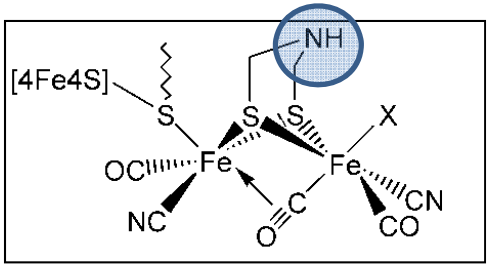
Des hydrogénases aux catalyseurs bioinspirés

Hydrogénases



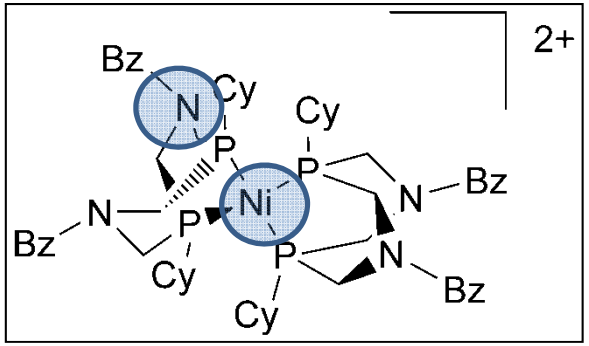
Ni-Fe



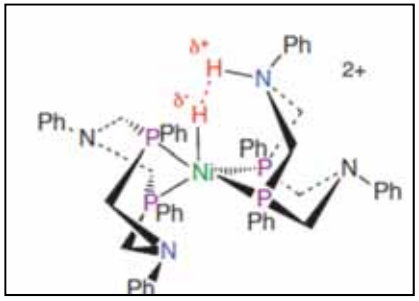


Fe-Fe

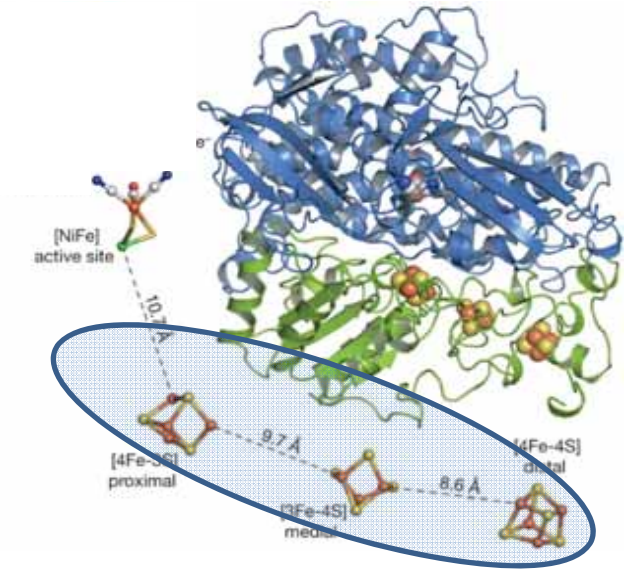
Catalyseur bioinspiré
(site actif)



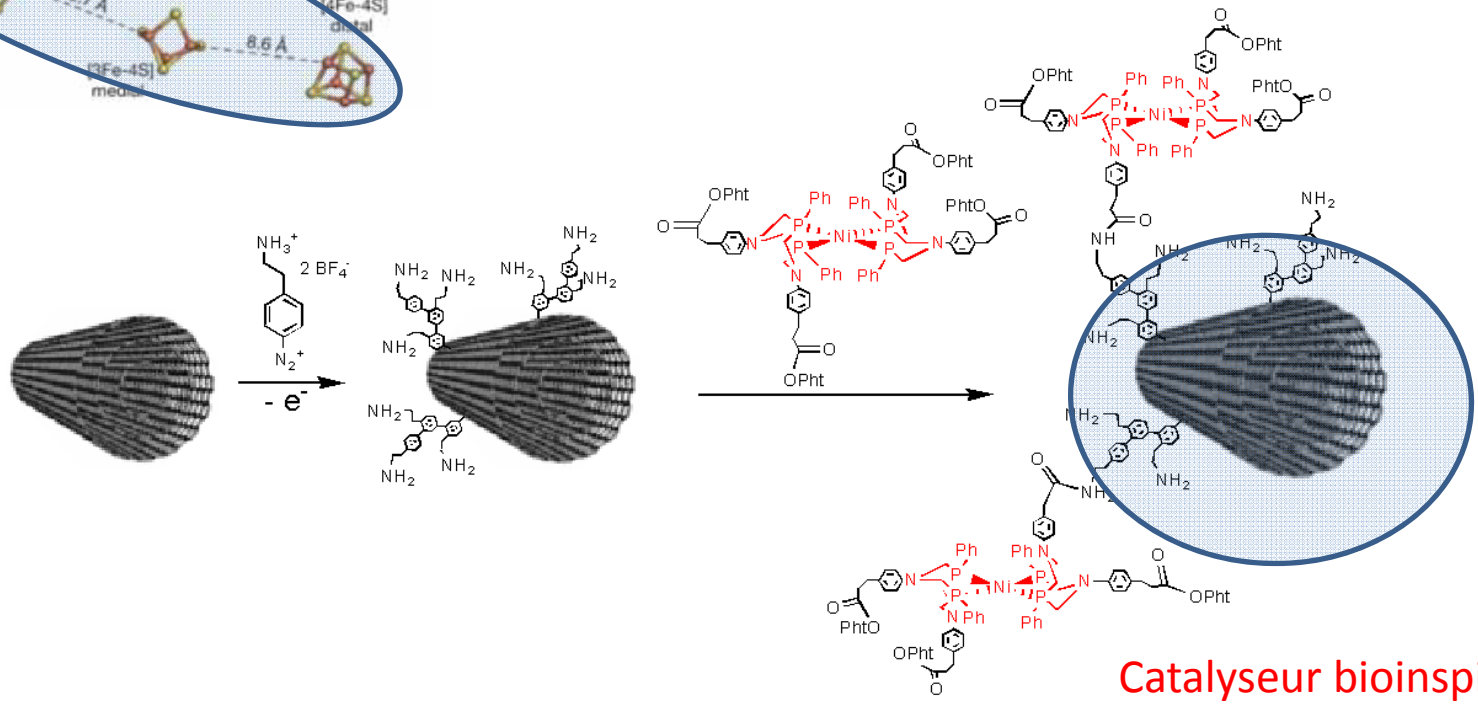
D. Dubois *JACS* 2006, 2007
Science 2011, Angew. Chem. 2012
OV: 100-200 mV
TOF: 500-1000 s^{-1}



Des hydrogénases aux catalyseurs bioinspirés

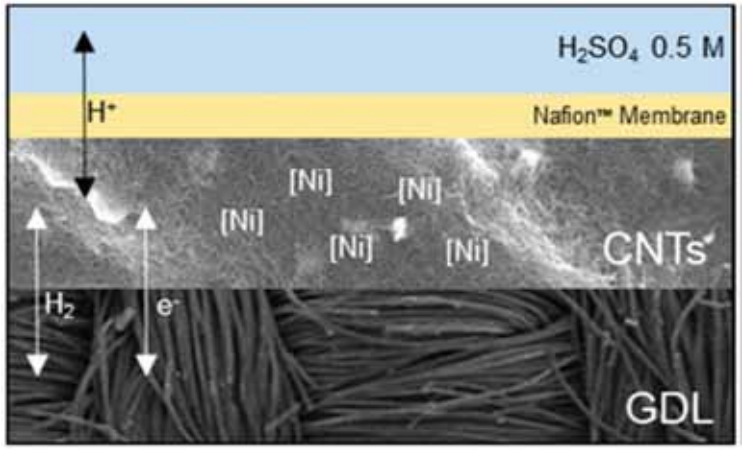


V. ARTERO
(CEA Grenoble)



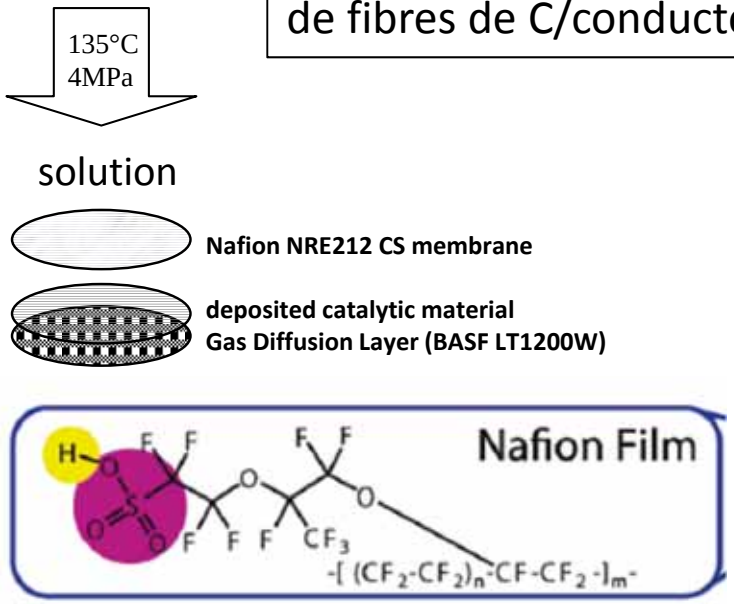
Catalyseur bioinspiré

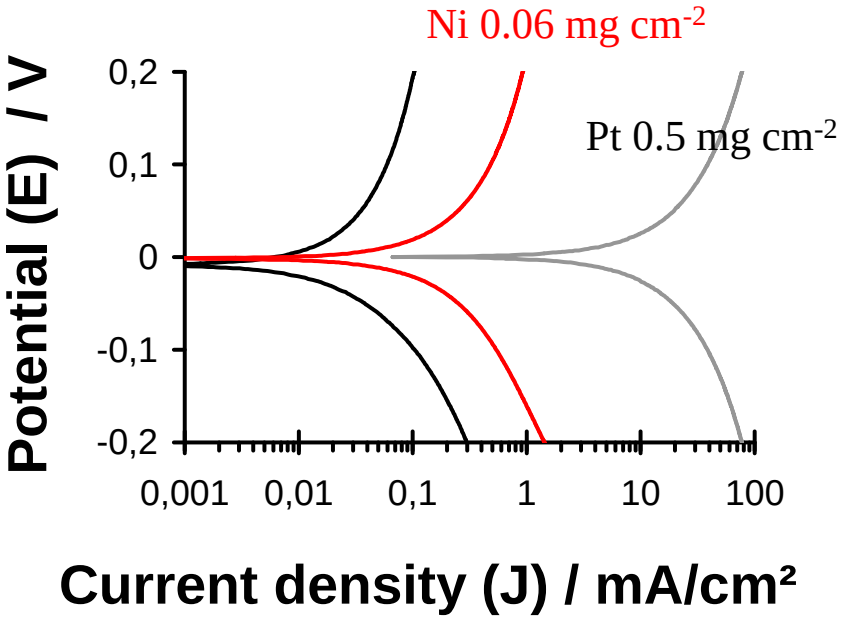
Une cathode pour PEMFC



Catalyseur déposé sur une **GDL** (matériau poreux/réseau dense de fibres de C/conducteur)

Conditions:
Technologie PEM
(membrane Nafion,
Solution aqueuse
pH acide)

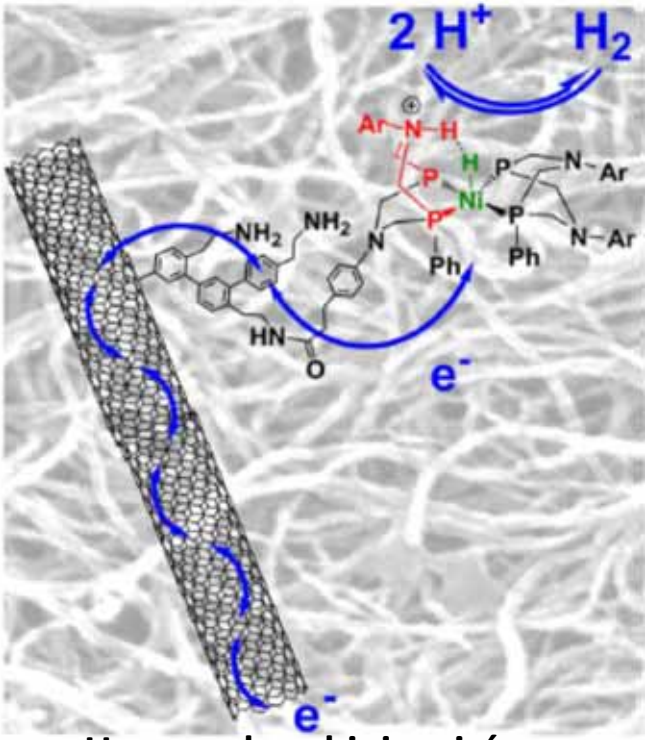




Des hydrogénases aux nanocatalyseurs bio-inspirés

From Hydrogenase Mimics to Noble-Metal Free Hydrogen-Evolving Electrocatalytic Nanomaterials
A. Le Goff, V. Artero, B. Jousselme, N. Guillet, R. Métayé, A. Fihri, S. Palacin, M. Fontecave
Science 2009, 326, 1384-1387

Noncovalent Modification of Carbon Nanotubes with Pyrene-functionalized Ni complexes: Carbon Monoxide Tolerant Catalysts for H2 Evolution and Uptake
P. D. Tran, A. Le Goff, J. Heidkamp, B. Jousselme, N. Guillet, S. Palacin, H. Dau, M. Fontecave, V. Artero
Angew. Chem. 2011, 50, 1371 –1374



Un complexe bioinspiré de Ni gréffé sur des NTCs déposés sur électrode

+++

Un matériau « moléculaire » catalytique pour l'oxydation et la production d'H_2

Métal non noble (Ni)

Coût: 20 euros/kg (Pt: 20000 euros/kg)

Grande stabilité (>100.000 cycles !!)

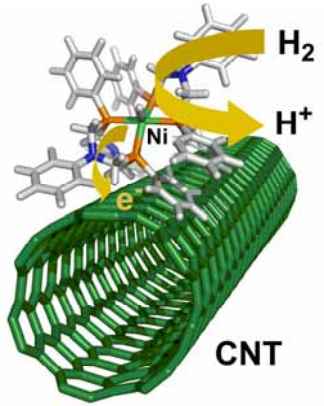
Compatible avec la technologie PEM

surtension= < 20 mV !!

Résistance à CO

- - -

Faibles densités de courant
(1/10 vs Pt)

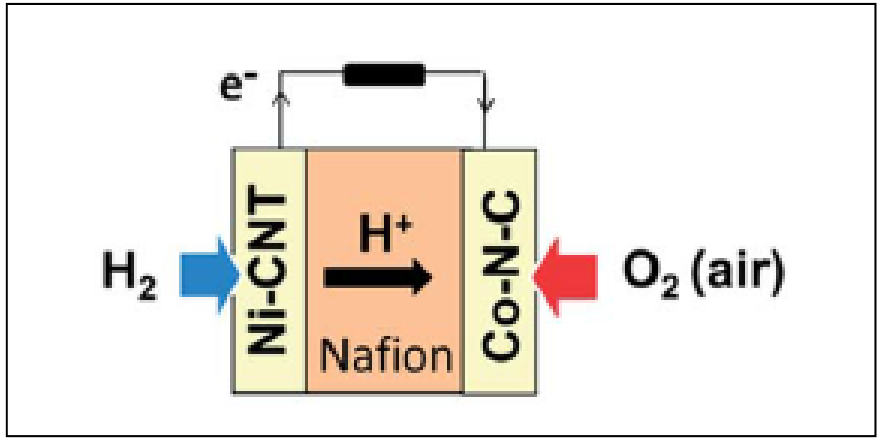


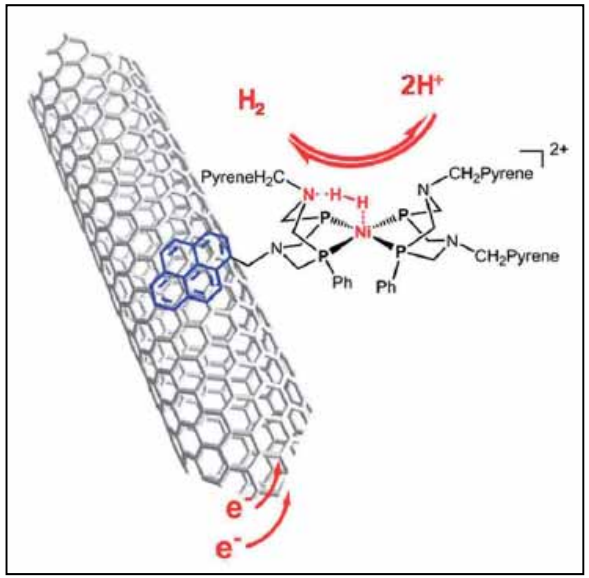
Cite this: *Chem. Sci.*, 2015, **6**, 2050

A noble metal-free proton-exchange membrane fuel cell based on bio-inspired molecular catalysts†

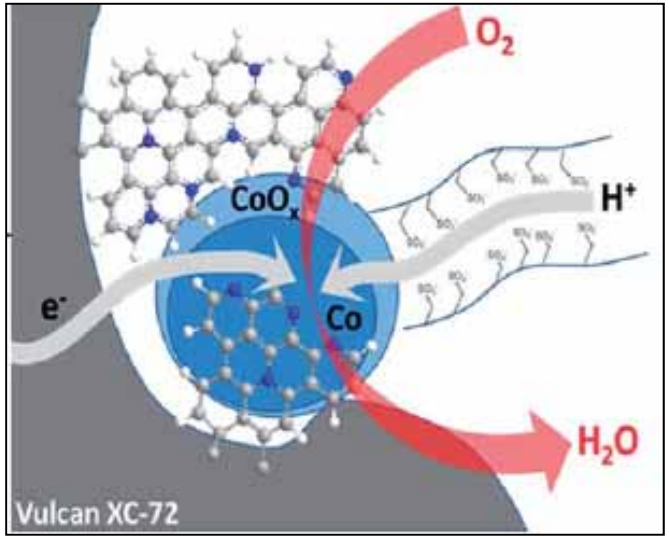
P. D. Tran,‡[a] A. Morozan,‡[b] S. Archambault,‡[c] J. Heidkamp,‡[d] P. Chenevier,[e] H. Dau,[d] M. Fontecave,[af] A. Martinent,*[c] B. Jousselme*[b] and V. Artero*[a]

La première PEMFC sans métaux nobles





Anode	Cathode	OCV/V	I@0.2 V/μA cm^{-2}	P_{max}/μW cm^{-2}
Pt	Co–N–C	0.79	1.3×10^4	2600
Ni–CNT	Pt	0.85	224	70
Ni–CNT	Co–N–C	0.74	94	23
Pt	Pt	1.00	1.75×10^5	1.05×10^3



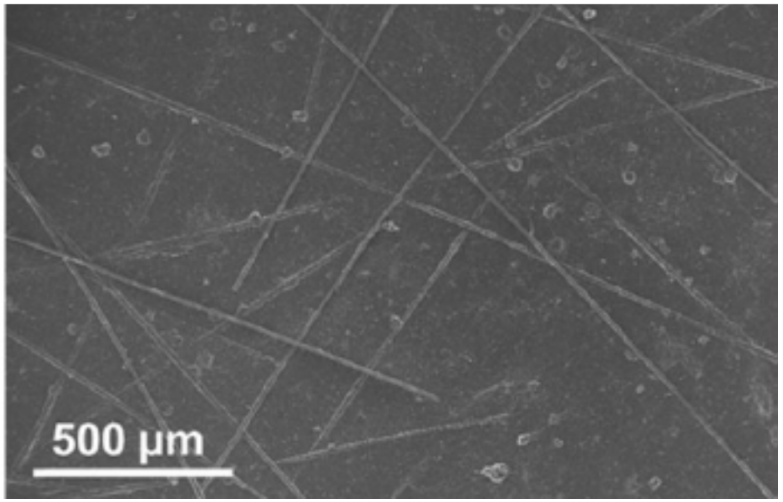
N-heterocyclic polymer
$Co^{2+/3+;}$ metallic Co

Plus d'optimisation…

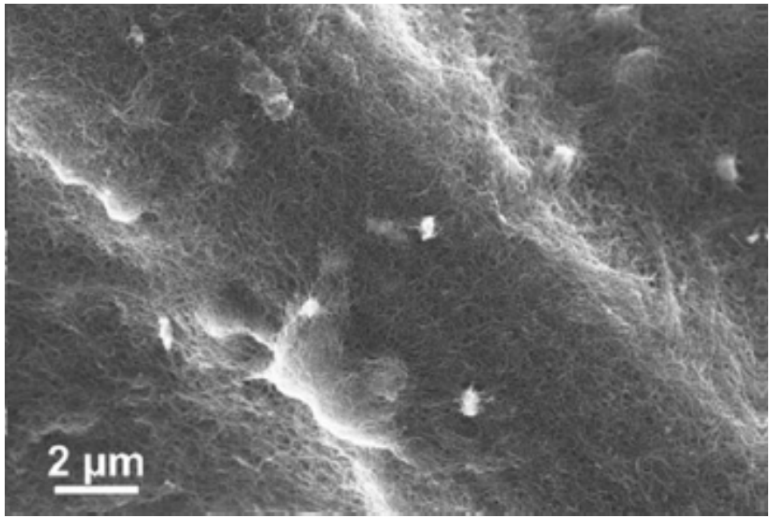
Un support mieux *nanostructuré*
pour obtenir de plus *grandes surfaces spécifiques*
plus *perméable à l'hydrogène*
permettant un *meilleur transport* de l'électrolyte

Mélange NTCs et **microfibres de C** puis dépôt sur GDL

n = de 1.5 10^{-9} mol.cm^{-2} à 2.5 10^{-8} mol.cm^{-2}



L = 6 mm; d = 7 µM



En Env Sci 2016 9 240

Plus d'optimisation…

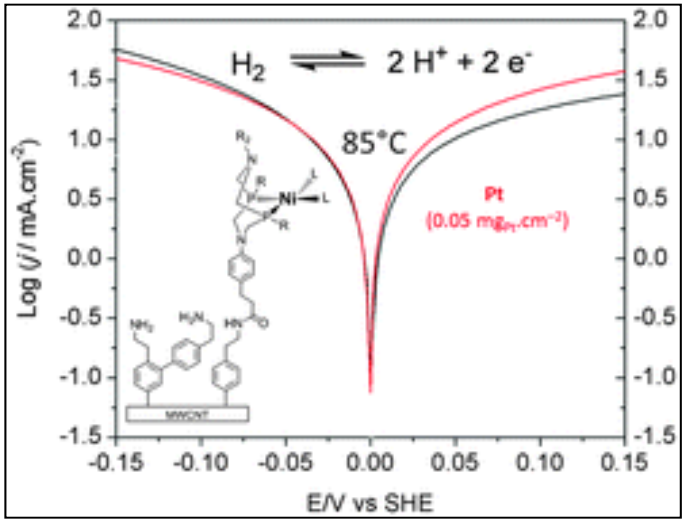
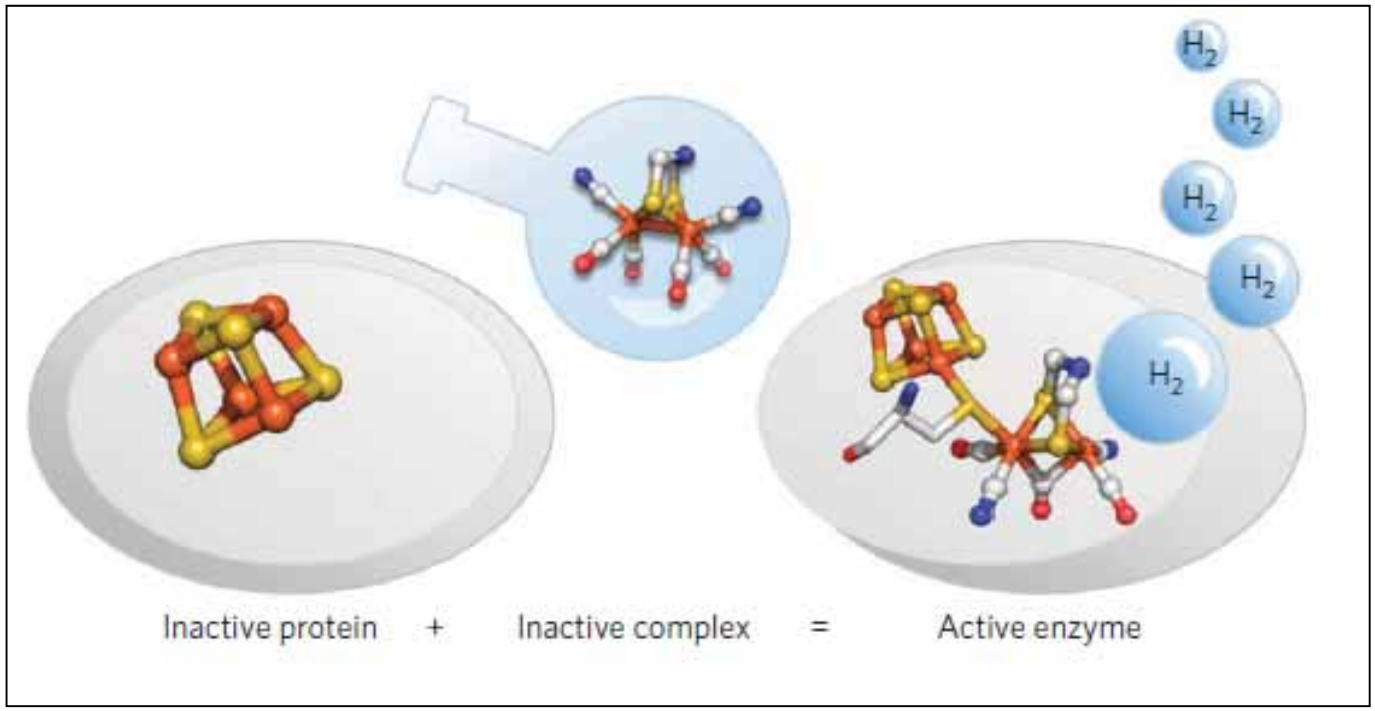


Table 1 Current obtained for hydrogen oxidation at 100 mV and 300 mV overpotential, and for hydrogen evolution at 100 mV overpotential with the NiP^{Cy}_2-functionalized MWCNT + carbon microfiber (2.5×10^{-8} mol_{Ni} cm^{-2}) and Pt/C (2.5×10^{-7} mol_{Pt} cm^{-2}) electrodes at 25 °C and 85 °C

	E vs. SHE	NiP^{Cy}_2 (2.5×10^{-8} mol_{Ni} cm^{-2})	Pt/C (2.5×10^{-7} mol_{Pt} cm^{-2})
25 °C	+100 mV (H_2 ox)	6.1 mA cm^{-2}	14.0 mA cm^{-2}
	+300 mV (H_2 ox)	11.67 mA cm^{-2}	36.4 mA cm^{-2}
	−100 mV (H_2 prod)	7.1 mA cm^{-2}	18.4 mA cm^{-2}
85 °C	+100 mV (H_2 ox)	16.8 mA cm^{-2}	26.6 mA cm^{-2}
	+300 mV (H_2 ox)	40.1 mA cm^{-2}	60.9 mA cm^{-2}
	−100 mV (H_2 prod)	38.3 mA cm^{-2}	32.2 mA cm^{-2}

En Env Sci 2016 9 240

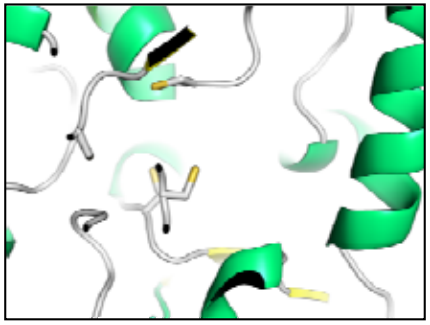
Hydrogénases et maturation « synthétique »

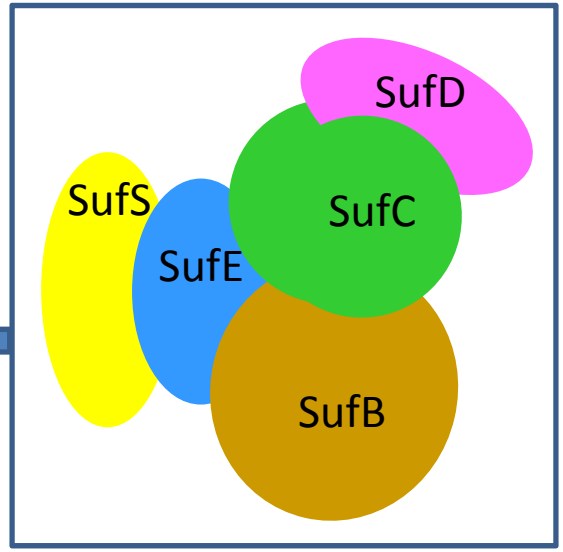


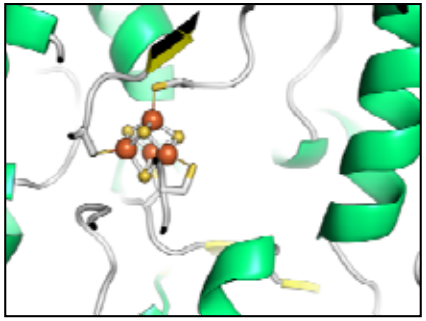
Nature 2013, Nature Chem Biol 2013,
BBA 2016, Nature Chem Biol 2017

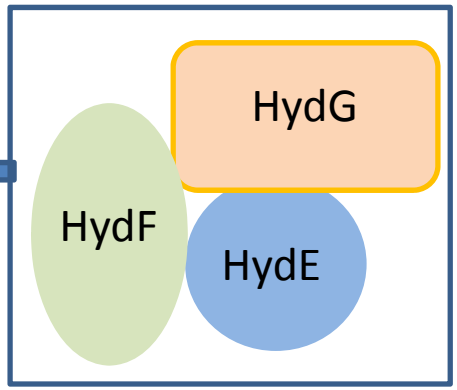
Hydrogénases: une maturation biologique complexe

Inactif HydA

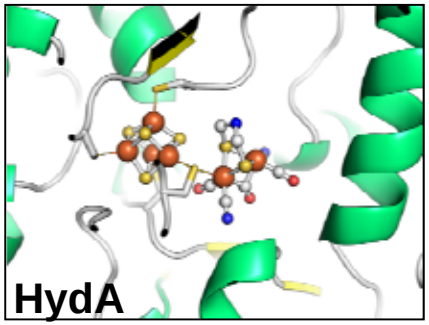


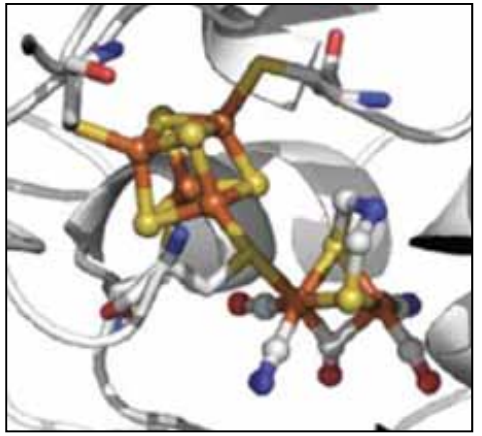






Actif HydA

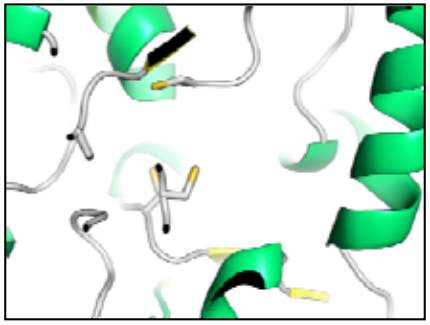




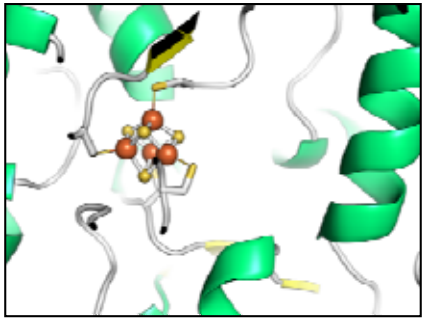
J.W. Peters, J.B. Broderick et al. *Biochemistry* 2014 53 4090
V. Artero, M. Fontecave et al *Acc. Chem. Res.* 2015, 48, 2380

Hydrogénases: une maturation « chimique » simple

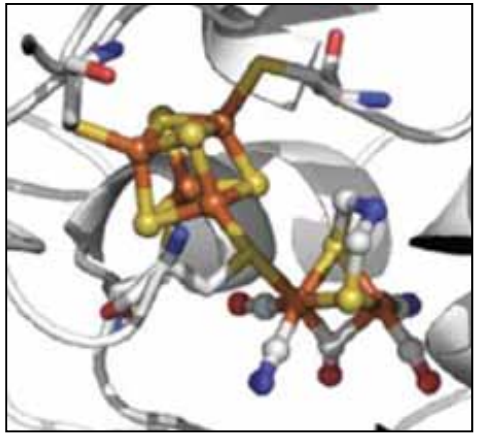
Inactif HydA



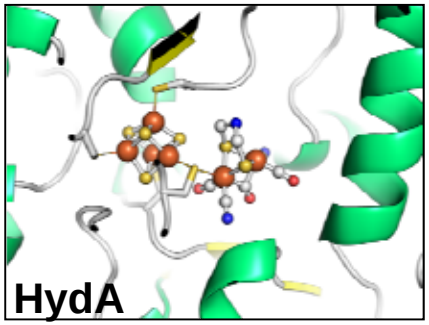
Sel de fer
+
Sulfure de sodium



complexe biomimétique



Actif HydA



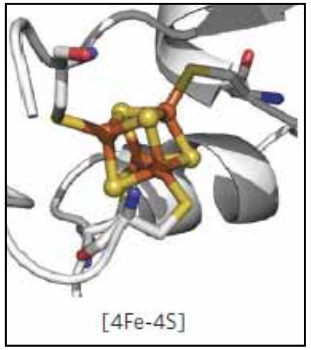
J. Esselborn et al. *Nature Chem Biol* 2013 9 607
G. Caserta et al *Acc. BBA* 20156 1857 1734
G. Caserta et al Nature Chem Biol 2017 13 779;

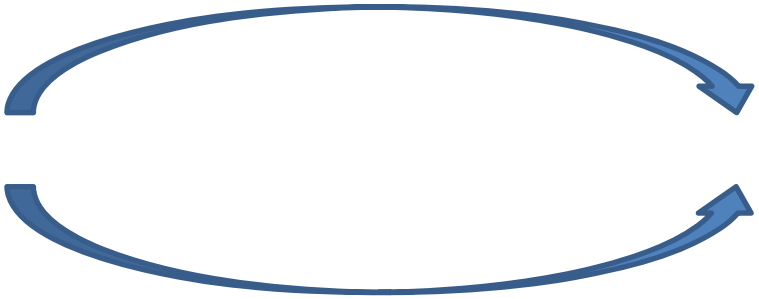
Maturation « chimique » des hydrogénases: applications

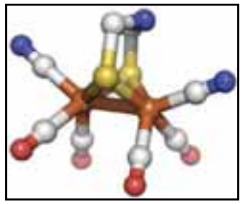
FeSHydA

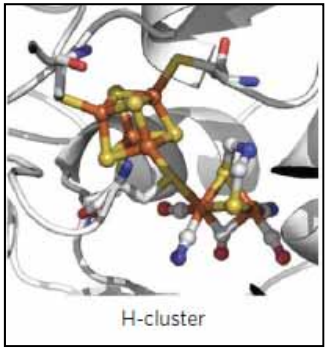
Maturation cellulaire

HoloHydA







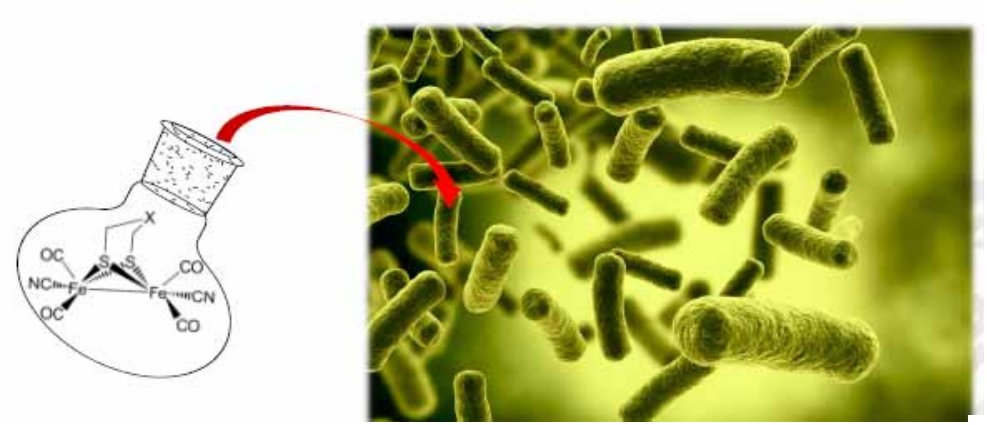


Applications :

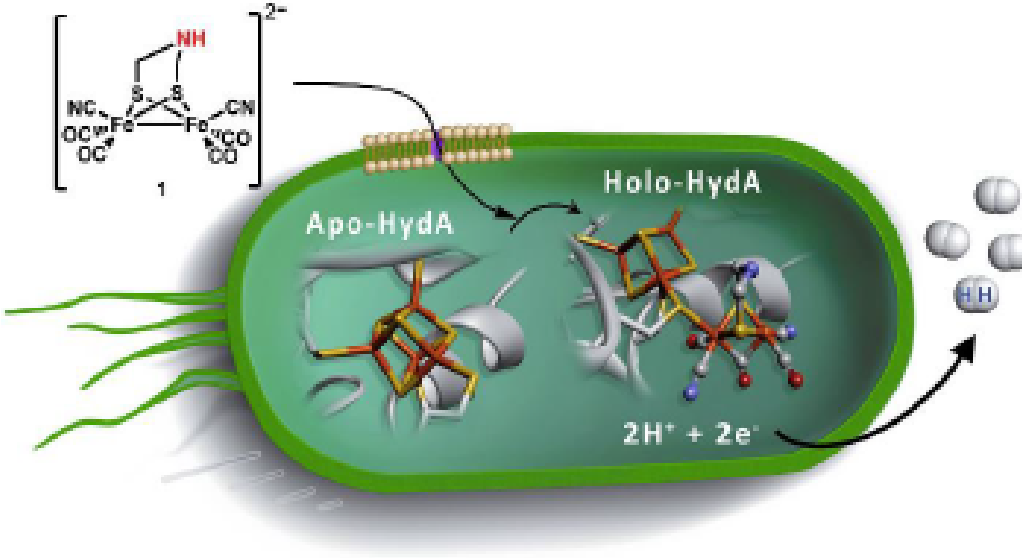
- Manipulation du site actif (marquage sélectif,..);
- Vers des sites actifs “non naturels” et de “nouvelles” hydrogénases
- Vers des hydrogénases artificielles
- Cribler des hydrogénases et mutants (*in vitro* / *in vivo*)

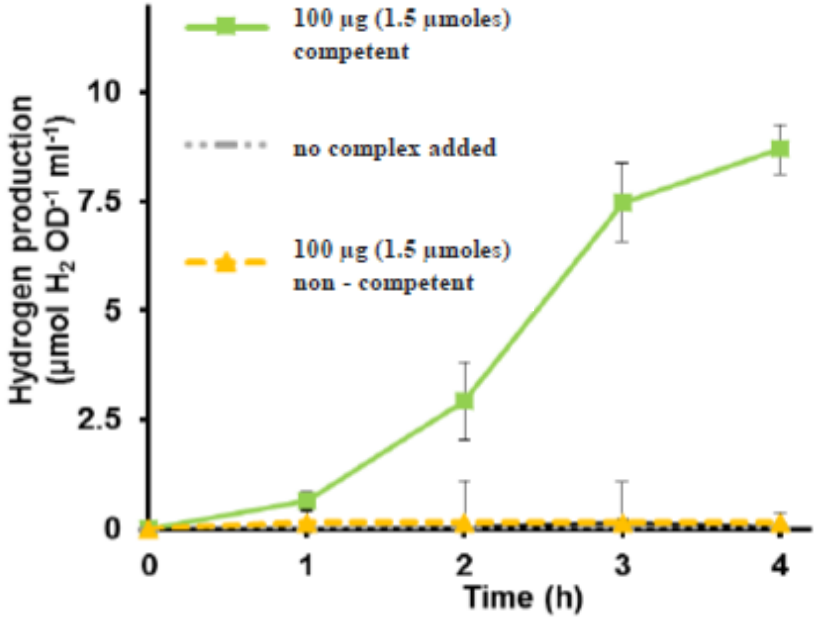
See: *Biochemistry* 2015 54 1474; *J. Am Chem Soc.* 2014 136 11339;
Phys Chem Chem Phys. 2015 17 5421; *J. Am. Chem. Soc.* 2015 137, 8998;
J. Am. Chem. Soc. 2015, 137, 12744; *BBA* 2016 1857 1734; EES 2017 10 2563

Maturation chimique des hydrogénases *in vivo*: Des organismes chimiquement modifiés pour la production d'H_2 (*biologie synthétique*)



G. Berggren
En. Env. Sci. 2017 10 1563





Hydrogénases et catalyseurs bioinspirés

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