Bio-catalyzed electrode reactions: from biocorrosion to biofuel celles

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DE LA RECHERCHE À L'INDUSTRIE

BIO-CATALYSED ELECTRODE REACTIONS: FROM BIOCORROSION TO BIOFUEL CELLS

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November, 2016

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Service de la corrosion et du comportement des matériaux dans leur environnement
Commissariat à l'énergie atomique et aux énergies alternatives
French atomic energy and alternatives energies Commission
Saclay, France

www.cea.fr

Thanks to EU funded programmes

✓ FP4"Biofilms on stainless steels" in the framework of "MAST II"
✓ FP5 "MIC of industrial materials" in the framework of "BRITE-RAM"
✓ FP5 « CREVCORR » in the framework of "Competitive and Sustainable Growth" Programme.
✓ FP6 « EA-Biofilms » in the framework of "New and Emerging Science and Technology (NEST)"
✓ FP7"biocorrosion" in the framework of Marie Curie programmes

and to French national research agency (ANR)

- "BactérioPile" (2005-2009)
- "Agri-elec" – biofuel cells (2009-2013)
- "Defi-H12" - bio-électrolyse (2009-2013)
- « Bioelec » (2014- 2016)

OVERVIEW

Background

Aqueous corrosion, fuel cells, biocatalyse,

Cathodic reaction

Electron transfer, aerobic and anaerobic environments

Anodic reaction

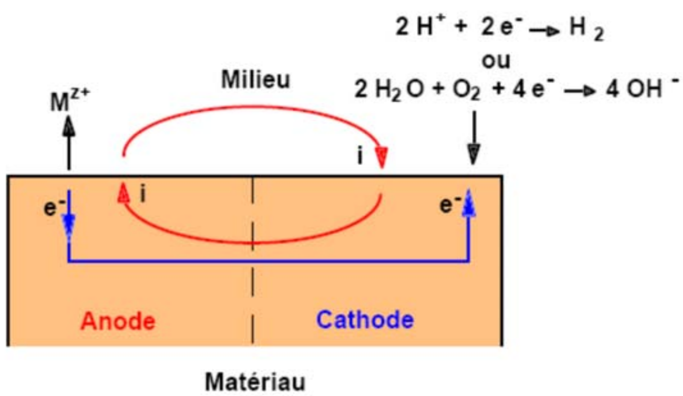
Electron transfer, aerobic and anaerobic environments

Conclusive remarks - Back to corrosion

Biocorrosion (MIC), bioprotection (MICI)

- Focus on the works done at Saclay and Toulouse -

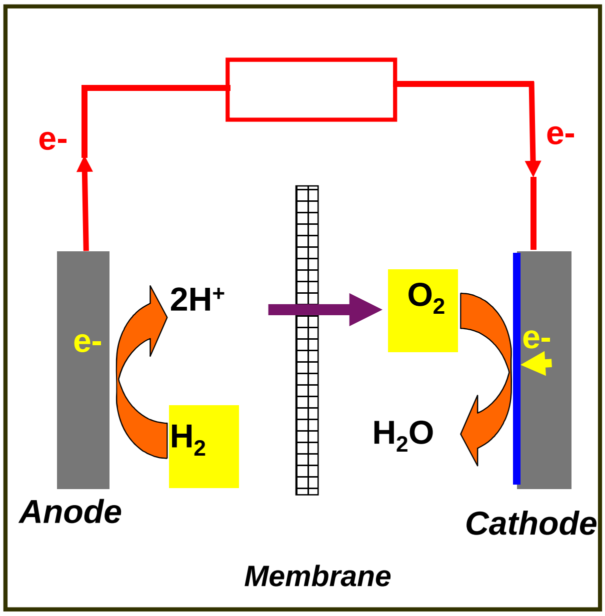
« Aqueous Corrosion: an electrochemical phenomena
corrosion involving at least one anodic reaction and one cathodic reaction"



Biocorrosion: increase of cathodic reaction rates which more often limit the overall kinetics

- Increase of the cathodic reaction in aerated natural seawater (Mollica, 1976 - Dupont & al., Int. Biodete & Biodegra. J., 1998, 41, 13-18)
- Increase of the cathodic reaction in anaerobic environment (Da Silva & al., Bioelectrochemistry, 2002, 56, 77)

Fuel cell
(PEMFC type)



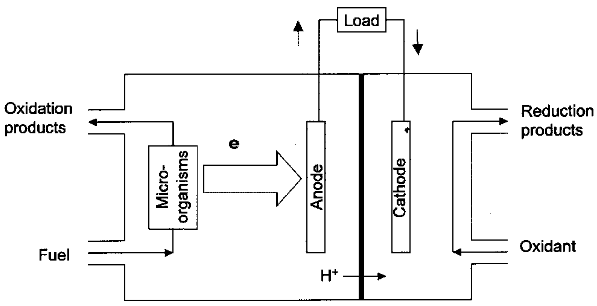
- Cathodic reaction is the same in fuel cells and for corrosion
- Anodic reaction : oxidation of soluble or dissolved species

- Biocatalyse of these anodic & cathodic reactions in MFC: CEA-CNRS Patents 2002

- by enzymes (EN02/01488, February 2002)

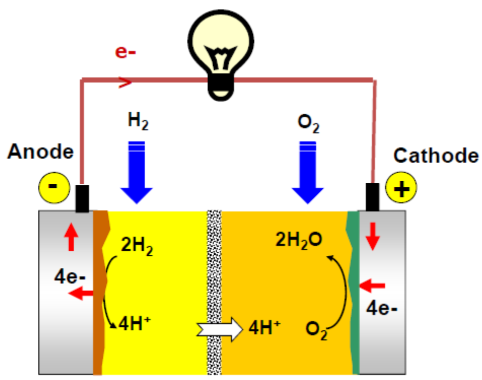
- by biofilms (EN 02/10009, August 2002)

"Biofuel cell" is a wide concept.
It is has been first used for the biocatalyse of the anodic reaction



«Figure 1. A typical biological fuel cell representing current generation with the help of microorganisms. The fuel generated by microbial metabolism gets oxidized at the anode and usually oxygen is reduced at the cathode. »

(from CURRENT SCIENCE, VOL. 87, NO. 4, 25 AUGUST 2004, review article by A. K. Shukla & al.)



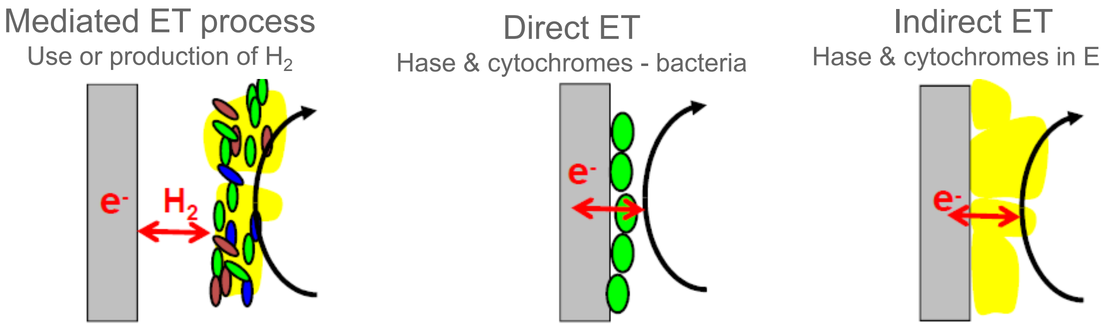
Other used it only when the anodic and cathodic reactions are biocatalysed

D. Féron & A. Bergel, Techniques de l'Ingénieur, RE89-1, 11, 2007

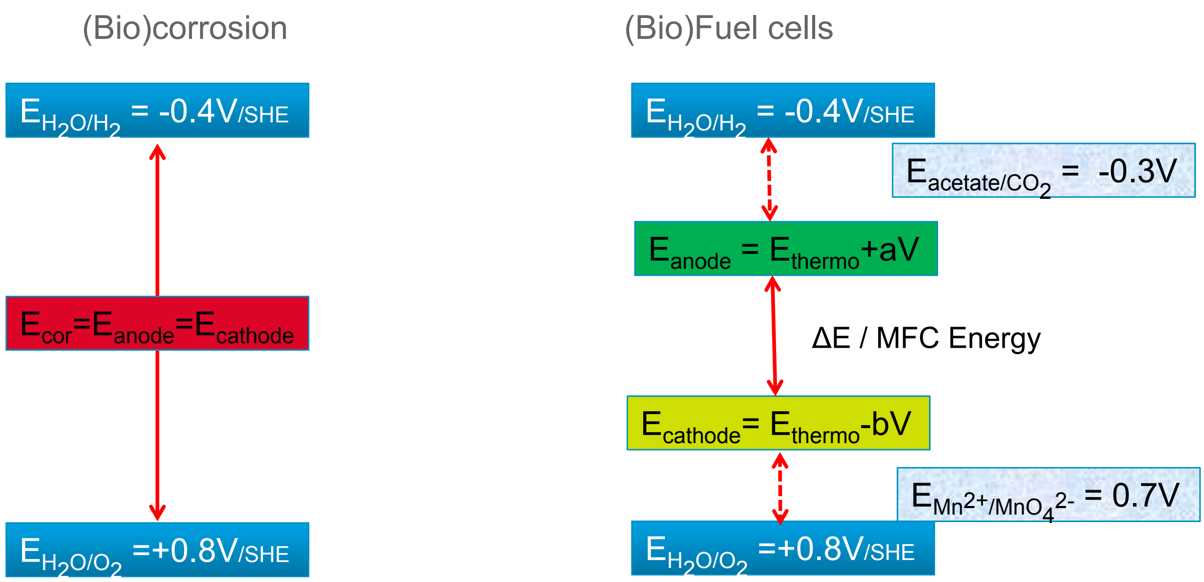
Biocatalyse of electrode reactions: increase of anodic/cathodic reaction via micro-organisms (bacteria)

- Mediated process: production or use of chemicals which modify the environment leading to an increase or a decrease the anodic or the cathodic reaction (enzymes, metabolites…)
- Direct electron transfer (ET) through membrane-bound proteins
- Indirect electron transfer by exopolymeric subtances, EPS

Illustration with hydrogenase



Similarities & differences in terms of potentials & currents (pH~7)



In both cases, $i_{anode} = i_{cathode}$

I_{cor} = 0.001 to 1 $A.m^{-2}$ / I_{BFC} = 1 to >100 $A.m^{-2}$

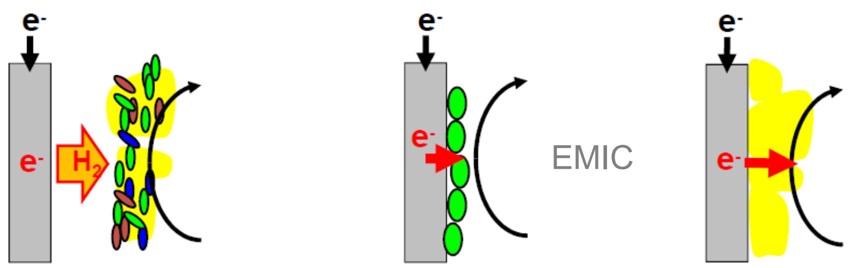
CONTENT

- Focus on the works done at Saclay and Toulouse -

Biocatalyse of the cathodic reaction

- Low potential cathodes (production of hydrogen, reduction of CO_2 or nitrites on the electrode …) / mainly two-step process / Biofuel cells
- Intermediate potential cathode (anaerobic conditions, direct or indirect ET) / Bio –corrosion & -fuel cells
- High potential cathodes (aerobic environments) / Bio-corrosion&-fuel cells

Microbial cathodes: mechanisms largely discussed



Two-step process: the microorganisms use the hydrogen that is generated abiotically on the electrode surface

Direct ET through membrane-bound proteins (hydrogenases e.g.)

Indirect catalysis by ExoPolymeric Subtances (enzymes e.g.)

Biocatalyse of the cathodic reactions

- Redox systems, redox potentials and reactions

	Couples redox		Potentiels redox (V/ESH)	Reactions redox
	CO_2/glucose		-0,43	$6C0_2 + 24H^+ + 24e^- \longrightarrow C_6H_{12}O_6 + 6H_20$
	CO_2/formate		- 0,43	$C0_2 + 4H^+ + 4e^- \longrightarrow CH_2O_2 + H_2O$
Low	H^+/H_2	✹	- 0,42	$2H^+ + 2\,e^- \longrightarrow H_2$
	Ferredoxin ox/red		-0,42	Ferredoxin(Fe^{3+}) + e^- $\longrightarrow$ Ferredoxin (Fe^{2+})
	NaD^+/NaDH		-0,32	$NaD^+ + H^+ + 2\,e^- \longrightarrow NaDH$
	CO_2/acétate		-0,28	$2CO_2 + 8H^+ + 8e^- \longrightarrow C_2H_4O_2 + 2H_2O$
	S^0/H_2S	✹	-0,274	$S + 2H^+ + 2\,e^- \longrightarrow H_2S$
	CO_2/CH_4		-0,22	$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$
	SO_4^{2-}/H_2S	✹	-0,22	$SO_4^{2-} + 10\,H^+ + 8e^- \longrightarrow H_2S + 4\,H_20$
Intermediate	Pyruvate/Lactate		-0,185	$Pyruvate^{2-} + 2H^+ + 2e^- \longrightarrow Lactate^{2-}$
	Fumarate/Succinate		+0,033	$Fumarate^{2-} + 2H^+ + 2e^- \longrightarrow Succinate^{2-}$
	Cytochrome $b_{ox/red}$		+0,075	Cytochromeb(Fe^{3+}) + e^- $\longrightarrow$ Cytochromeb(Fe^{2+})
	Ubiquinone/UbiquinoneH_2		+0,1	Ubiquinone + $2H^+$ + 2 e- $\longrightarrow$ Ubiquinone H_2
	Cytochrome $C_{ox/red}$		+0,254	Cytochrome b(Fe^{3+}) + e^- $\longrightarrow$ Cytochrome b(Fe^{2+})
	$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$		+0,36	$Fe(CN)_6^{3-} + e^- \longrightarrow Fe(CN)_6^{4-}$
	NO^{3-}/NO^{2-}	✹	+0,43	$NO_3^- + 2H^+ + 2\,e^- \longrightarrow NO_2^- + H_2O$
High	NO^{2-}/NH_4^+		+0,44	$NO_2^- + 8H + 6\,e^- \longrightarrow NH4^+ + 2H_2O$
	MnO_2/Mn^{2+}	✹	+0,60	$MnO_{2(s)} + 4H + 3e^- \longrightarrow Mn^{2+} + 2H_2O$
	Fe^{3+}/Fe^{2+}	✹	+0,771	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$
	$1/2O_2/H_2O$	✹	+0,84	$O_2 + 4H^+ + 4\,e^- \longrightarrow 2H_2O$

✹ Corrosion

Biocathodes on stainless steels: biofilms, bacteria, enzymes

System	Material	W. Potential (/SHE)	Ox/red	Application	Ref.
Marine biofilm	Stainless steel	+0.5 V	O_2/H_2O	corrosion	(1)
Marine biofilm	Stainless steel	0.0 / -0.1 V 0.45	O_2/H_2O	MFC (current) MFC (OCP)	(2)
Geobacter sulfurreducens	Stainless steel	+0,1 V	Fumarate/acetate	corrosion	(3)
Geobacter sulfurreducens	Stainless steel	-0.2 / -0.4 V	Succinate+ carbonate/ Glycerol	MFC	(4)
Hydrogenase *(Ralstonia eutropha)*	Stainless steel	-0.5 V	H_2O/H_2	Corrosion	(5)
Hydrogenase *(Desulfovibrio desulfuricans)*	Stainless steel	-0.2 V	H_2O/H_2	« Enzymatic » fuel cell	(6)

Focus on biofilm

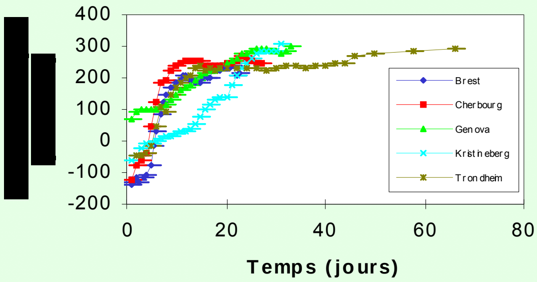
(1) Dupont & al., Int. Biodete & Biodegra. J., 1998, 41, 13-18
(2) A. Bergel & al., Electrochem. Commu., 2005, 7, 900-904
(3) M. Mehanna & al., Electrochem. Com., 2009, 11, 568-571
(4) L. Soussan & al., Electrochem. Comm., 2013, 27-30
(5) Da Silva & al., Bioelectrochemistry, 2002, 56, 77
(6) Cordas *et al.*, Electrochimica Acta, 2008, 54, 29-34

Stainless steels in natural waters

SEAWATER

Evolution of the free corrosion potential of 654SMO SS in 5 marine locations.

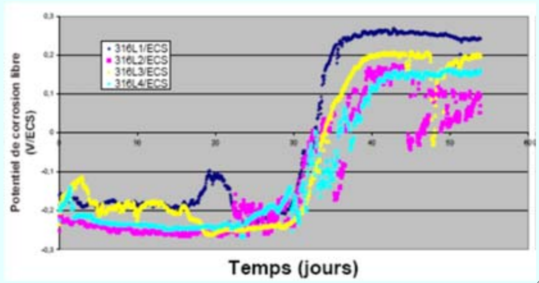
[MAST II, Marine biofilms on stainless steels : effects, monitoring and prévention. Final report,. 1996]



RIVER WATER

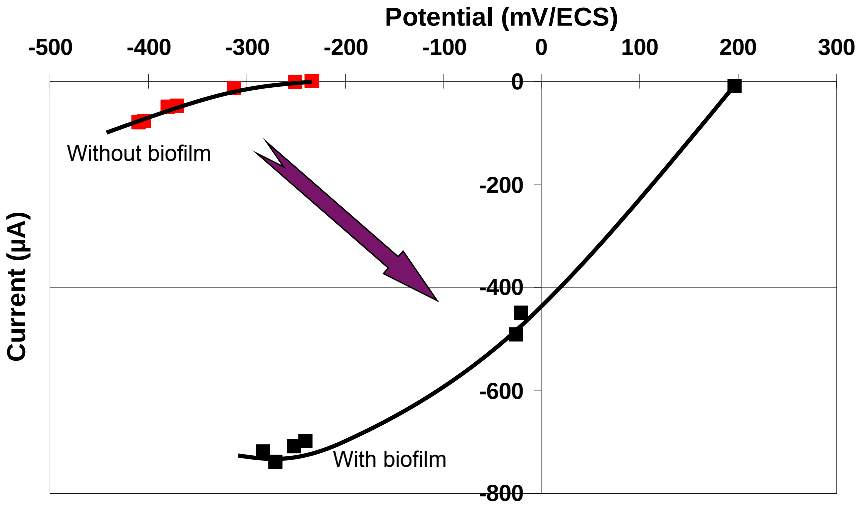
Evolution of the free corrosion potential of 316L SS in Seine river

(C. Marconnet & al., Caen, 26-27 mai 2005)



In natural aerated waters, the free corrosion potentials increase due to the biofilm formation

Efficient microbial cathode in seawater on SS



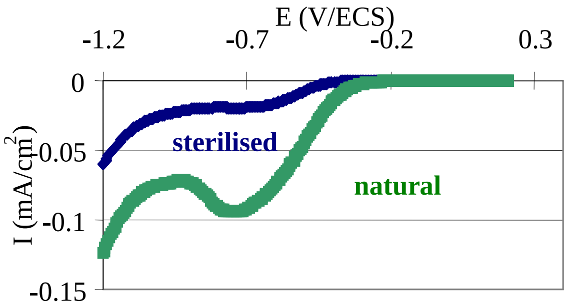
Biofilm formed in seawater on stainless steel

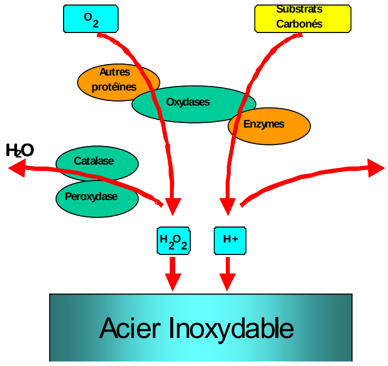
→ very efficient to induce microbial corrosion (pitting & crevice corrosion)

→ **in biofuel cell: current densities up to 1.3Am^{-2}**

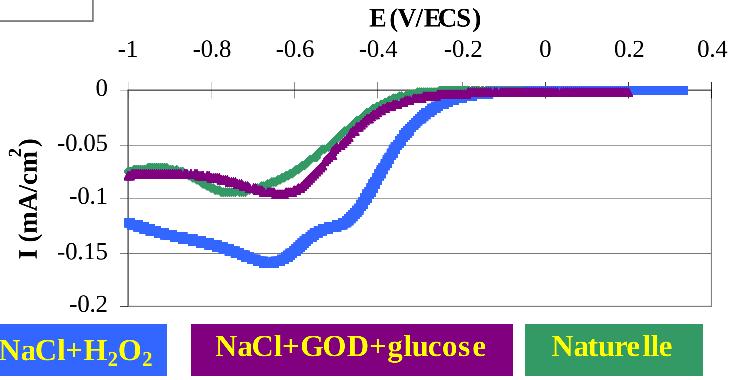
A.Bergel & al., Electrochem. Comm. ***7*** *(2005) 900 - 904*

"ENZYMATIC METHOD" BIOSYNTHETIC / NATURAL SEA WATER





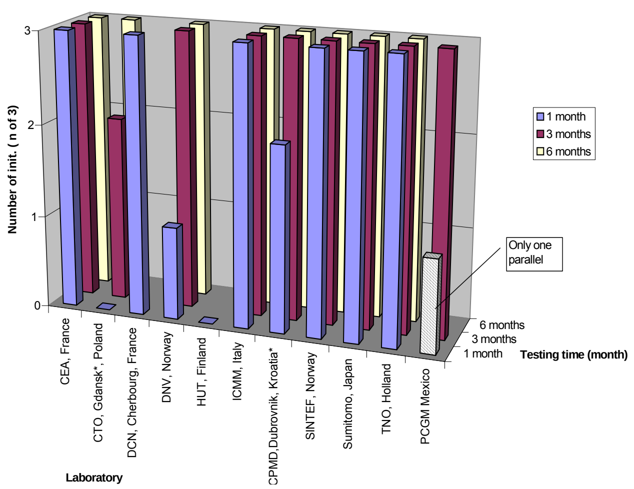
Better simulation with enzymes

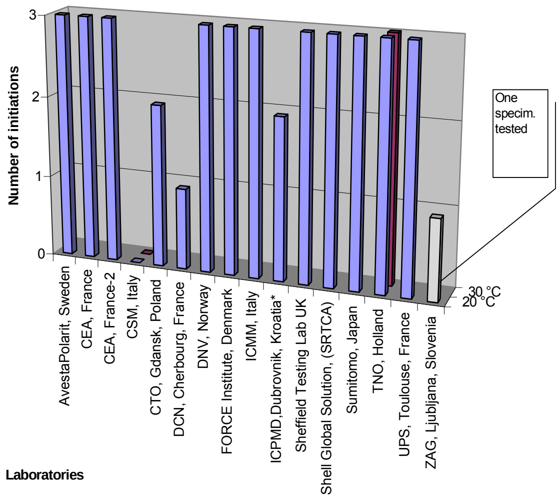


D.Féron & al., EFC series N°22, The Institute of Materials, 1997, 103-113

U. Kivissac & al., EFC series N°60, Maney Publishing, 2010, 134 pages

"ENZYMATIC METHOD" BIOSYNTHETIC / NATURAL SEA WATER
316L Crevice corrosion initiation





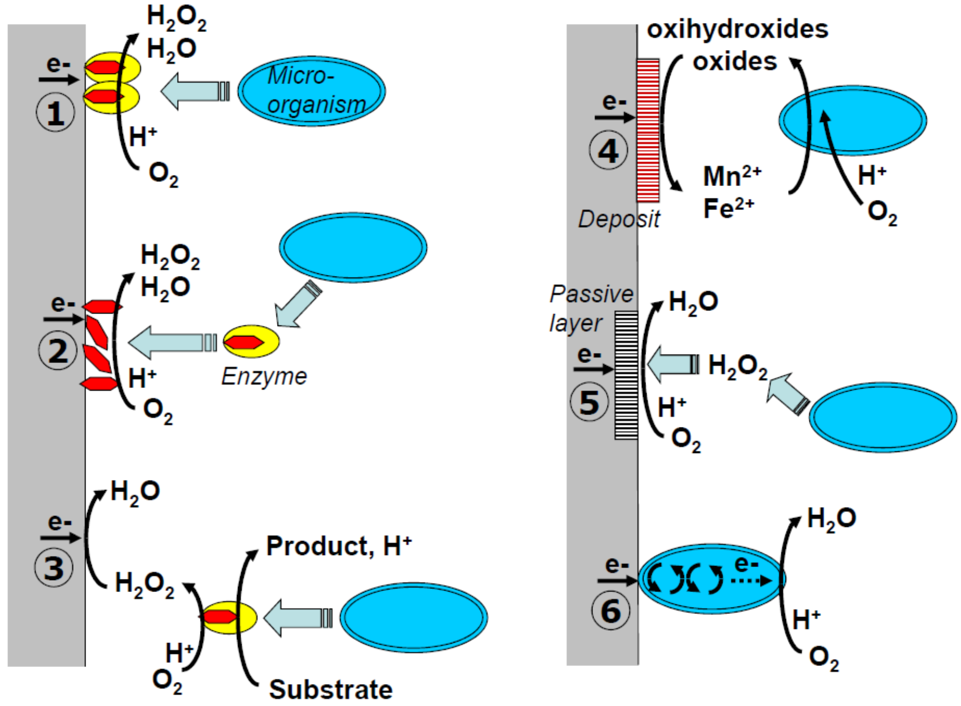
Natural seawater: 74% of coupons corroded

Biosynthetic seawater at 20°C: 91%

The biochemical synthetic sea or ocean water "reproduces the corrosivity" of natural seawaters

U. Kivissac & al., EFC series N°60, Maney Publishing, 2010, 134 pages

Different mechanisms postulated to explain microbial catalysis of oxygen reduction by biofilms

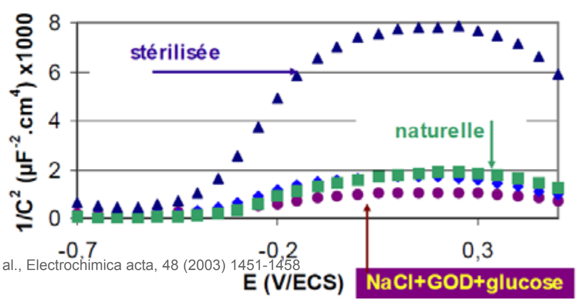


B. Erable & al., Chemsuschem, 2012, 5, 6, 975-987

Evolution of the semi-conductive properties

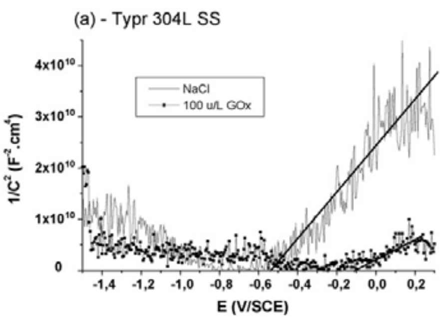
SS passive layers / with or without biofilms/enzymes

In sea water



V. L'Hostis et al., Electrochimica acta, 48 (2003) 1451-1458

In river waters



C. Marconnet et al., Electrochimica acta, 54 (2008) 123-132

- No biocatalyse of the cathodic reaction on p-type oxide films
- Biocatalyse of the cathodic reaction on n-type oxide films provokes an increase of the electron density (sea and river waters, pure cultures)
- Same evolution of semi-conductive properties with bacteria (biofilms) or only addition of enzymes (oxidases).

L. Ponz et al., Electrochimica acta, 56 (2011) 2682-2688

Current densities reported recently with various oxygen biocathodes in MFC

Electron acceptor	Source inoculum	Operation mode (potencial vs Ag/AgCl)	Current density (Am^{-2})/power density ($W m^{-2}$)
MFC			
O_2	Enrichment culture	Batch-fed anode, recirculated catholyte	2.13/0.88
O_2	Enrichment with Mn (IV) and Mn (II)	Batch-fed anode, recirculated catholyte	2.13/0.88
O_2	Enrichment culture	Continuous fed, with loop between anode and cathode	3.01/1.2
O_2	Enrichment culture	Two chamber, batch-fed	1.76/0.37
O_2	Enrichments and isolates of *Acinetobacter calcoaceticus*	Two chamber, batch-fed	2.8
O_2	Enrichment culture	Two chamber, batch-fed	3.58/1.36

From M. Sharma & Al., Electrochimica acta, 2014, http://dx,doi,org/10,1016/J.electacta,204,02,111

- Densities of few $A.m^{-2}$ max
- Oxygen reduction biocatalyse is a key factor in biocorrosion
- Oxygen biocathodes are very often the limiting step in a MFC

Performances of other biocathodes

System	Material	Working Potential	Max. current density	Ox/red	Appli cation	Ref .
Geobacter sulfurreducens	Stainless steel	-0.1 / -0.3 V	30 $A.m^{-2}$	Succinate+carbonate /Glycerol	MFC	(1)
Geobacter sulfurreducens	Stainless steel	-0.3 V	14 $A.m^{-2}$	Fumarate/succinate	MFC	(2)
Geobacter sulfurreducens	graphite	-0.3 V	0.75 $A.m^{-2}$	Fumarate/succinate	MFC	(3)
Hydrogenase *(Clostridium acetobutyllicum)*	Carbon steel	-0.5 V	0,015 $A.m^{-2}$	H_2O/H_2	Corros ion	(4)
Hydrogenase (*Ralstonia eutropha*)	Stainless steel	-0.45 V	0,004 $A.m^{-2}$	H_2O/H_2	Corros ion	(5)
Hydrogenase (*Desulfovibrio desulfuricans)*	Stainless st. Graphite	-0.15 V -0.15 V	0,13 $A.m^{-2}$ 0,27 $A.m^{-2}$	H_2O/H_2	MFC	(6)

(1) L. Soussan & al., Electrochem. Comm., 2013, 27-30
(2) L.Pons, Electrochimica acta, 2011, 56, 2682
(3) C. Dumas & al., Electrochimica acta, 2008, 53, 2494
(4) M. Mehanna, Electrochimica acta, 2008, 54, 140-147
(5) Da Silva & al., Bioelectrochemistry, 2002, 56, 77
(6) Cordas *et al.,* Electrochimica Acta, 2008, 54, 29-34

current densities & potentials

CONTENT

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Cathodic reaction

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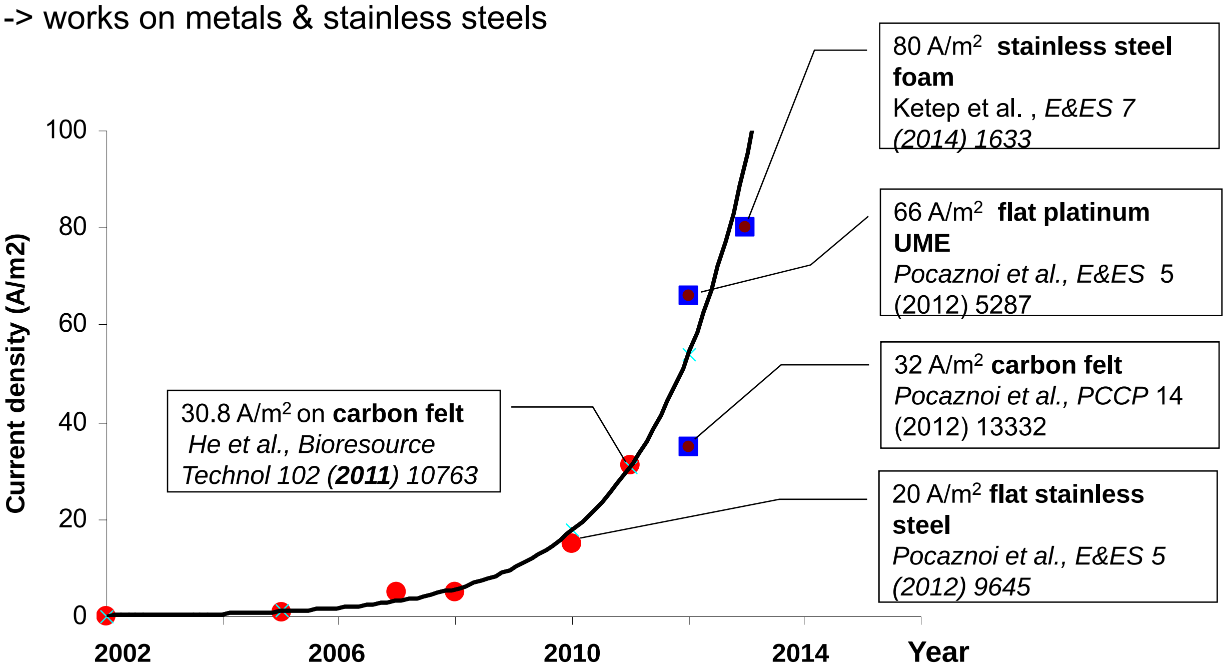
Conclusive remarks

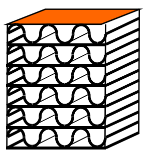
Biocorrosion (MIC), bioprotection (MICI)

- Focus on the works done at Saclay and Toulouse -

Exponential evolution of the anodic current densities
-> works on metals & stainless steels

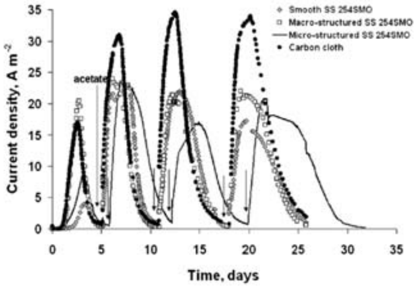


390 A/m² on **6-layer 3-D carbon electrode**
Chen et al., E&ES 5 (2012) 9769

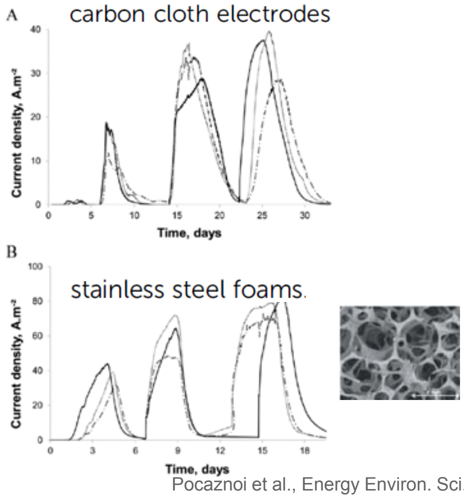


Anode

Influence of the surface geometry on stainless steels



Pocaznoi et al., Energy Environ. Sci., 2012, 5, 9645

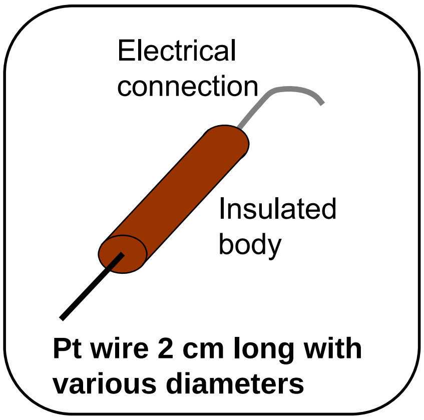


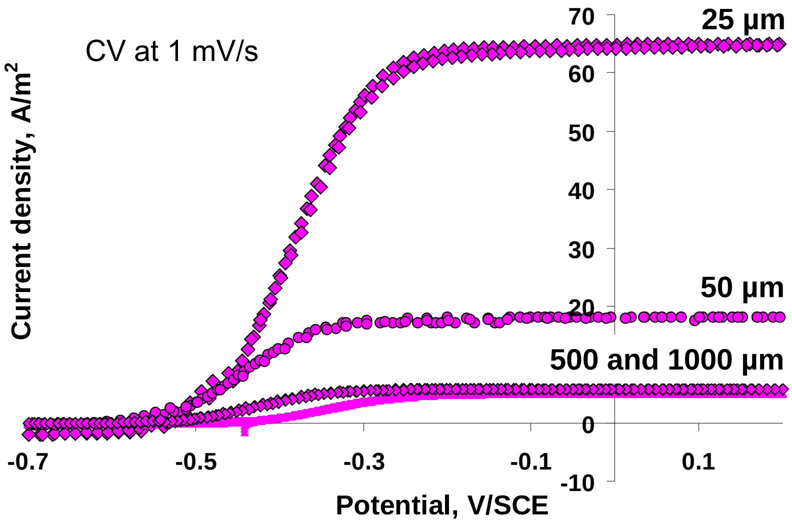
Pocaznoi et al., Energy Environ. Sci., 2014, 7, 1633

- Soil leachate / acetate addition / polarisation at -0.2 V/SCE
- Stainless steels : promising anode materials for MFC

Soil microbial ultra-microanodes

(non optimal) conditions
Soil leachate with 60 mM NaCl
Acetate 10 mM, ambient T
Polarization at -0.2 V/SCE
Biofilm age > two acetate additions

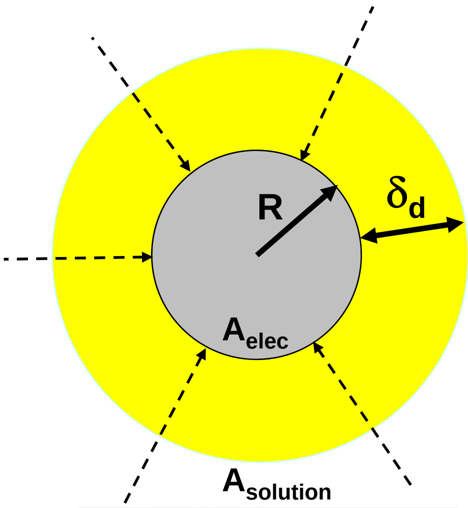




Decreasing the diameter to 25 µm increases J_{max} from 7 to 66 A/m^2

D.Pocaznoi, B.Erable, M.-L.Délia, A.Bergel, *Energy and Environ. Sci.* **5** (2012) 5287 - 5296

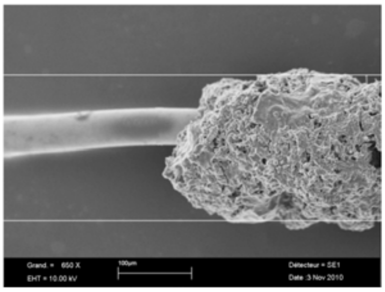
Ultra-microelectrode: principle

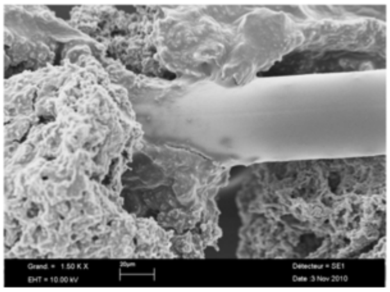


Wire radius R of the same order of magnitude than the diffusion layer thickness δ_d (R < 25 µm)

The area of the electrode surface (A_{elec}) is smaller than the surface area of the biofilm/solution from which diffusion occurs ($A_{solution}$)

The diffusion pattern concentrates the flux towards the electrode surface





Wire 50-µm diameter
19 days
polarisation at -0.2 V/SCE
Biofilm thickness 75 µm

D.Pocaznoi, B.Erable, M.-L.Délia, A.Bergel
Energy and Environ. Sci. **5** (2012) 5287 - 5296

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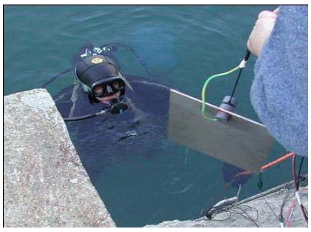
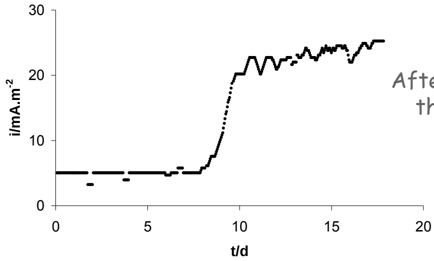
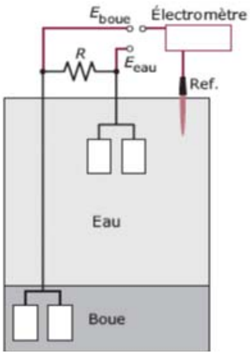
BIOFUEL CELLS or BIOPROTECTION

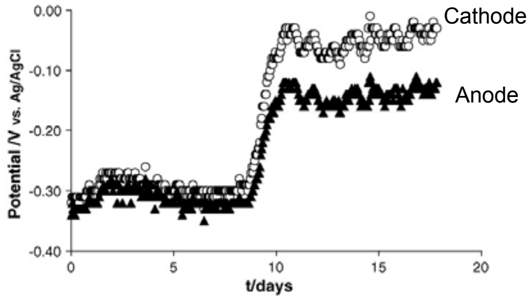




After 8 days in the sea, the current of the biofuel cell reaches 23 $mA.m^2$.



Stainless steel electrodes (0.12 m2) located in aerated seawater and in the mud

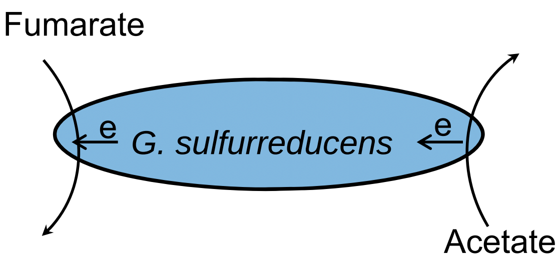


Potential of the cathode lower than 0.0mV/Ag.AgCl instead of +300mV/Ag.AgCl (free corrosion potential)

=> Cathodic protection

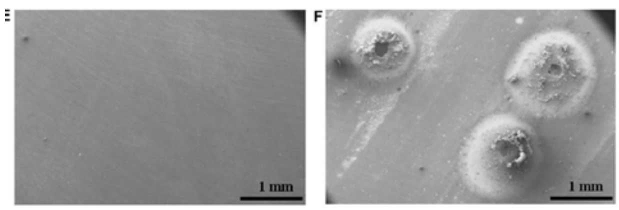
C. Daumas et al.., Electrochimica Acta 53 (2007) 468–473

Biocorrosion or bioprotection
The ubiquitous role of *Geobacter sulfurreducens (304L)*

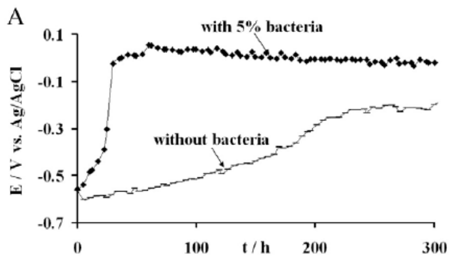


Increase of the cathodic reaction

- Increase of the pitting or localised corrosion risk on SS (304L)
- Decrease of the pitting potential (304L)



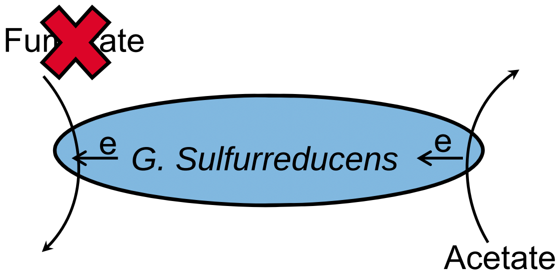
Without bacteria   With bacteria



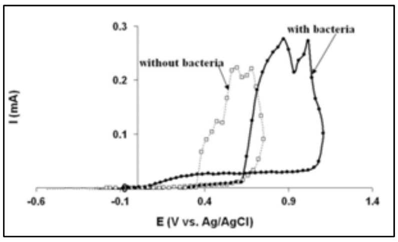
Acetate (mM)	Epit with *G. sulf.* vs Ag/AgCl
0	0.79 – 0.90
1	0.84 – 1.09
5	1.07 – 1.22

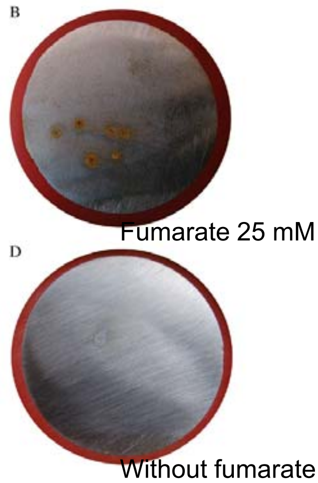
M. Mehanna & al.al.., Electrochemistry communications, 2009, 11, 1476-1481

Biocorrosion or bioprotection
The ubiquitous role of *Geobacter sulfurreducens (304L)*



Without fumarate
- Bioprotection of SS (304L)



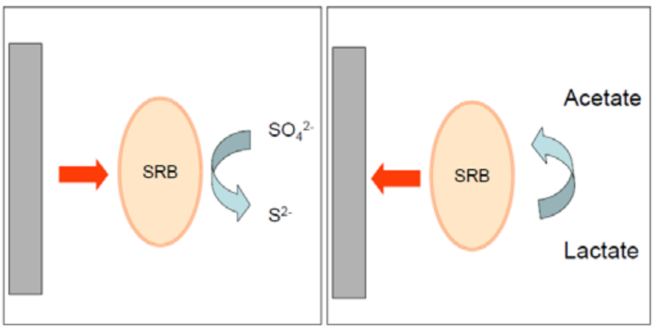


Fumarate	G. Sulfurr.	E_{pit} vsAg/AgCl	E_{rep} vsAg/AgCl
25 mM	Yes	1.05	0.85
No	yes	1.0	0.65

M. Mehanna & al.al.., Electrochemistry communications, 2010, 12, 724-728

Corrosive biofilms: those with bacteria able to accept electrons, to increase cathodic reaction (direct electron transfer?) at the free corrosion potential

With SRBs, direct electron transfer are claimed also (biofuel cells - cathode /anode)

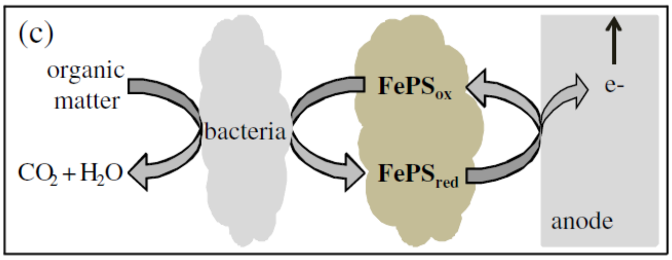


Cordas *et al.,* Electrochimica Acta, 2008, 54, 29-34
S. Da Silva et al. J. Electroanal. Chem. 561 (2004) 93
S. Da Silva et al;, Bioelectrochemistry 56 (2002), 77.
.

Proactive bioprotection – Proactive MIC inhibition

- Cathodic protection (coupling anodes & cathodes – biofuel cells)
- Electron acceptors in the solution
- Construction of a protective biofilms with bacteria able to increase electron donnor reactions (direct, indirect or mediated ET)

Deposition of a Fe-P-S-graphite layer (FeSO4, Na2S, NaH2PO4 and graphite powder) on stainless steel



From biocorrosion to biofuel cells…

… from biofuel cells to bioprotection

- Electron acceptor biofilms (cathode)
  - Increase of the cathodic reaction (direct ET transfer ?)
  - Increase of generalized or localized corrosion
  - Biocorrosion / MIC
- Electron donnor biofilms (biofuel cell anode)
  - Decrease of the anodic corrosion reaction (metal oxidation) / decrease of the corrosion potential
  - Decrease of generalized or localized corrosion
  - Bioprotection / MICI
- Proactive
  - Electro Active Biofilms (EA-biofilms)

Electron acceptor or donor / Biocorrosion or bioprotection

Back to old times

At the end of the XVIII century on the origins of electricity, between "anatomists" and "physicists",

"animal electricity"
Luigi Galvani

"physical electricity"
Alessandro Volta

THANK YOU FOR YOUR ATTENTION

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SERVICE DE LA CORROSION et du comportement des matériaux dans leur environnement

Damien Féron