



# Bio-catalyzed electrode reactions: from biocorrosion to biofuel celles

D. Feron

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# BIO-CATALYSED ELECTRODE REACTIONS: FROM BIOCORROSION TO BIOFUEL CELLS

Institut of Metal Research, Chinese Academy of Sciences  
Shenyang  
November, 2016

| Damien Féron  
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

## 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-H2" - bio-électrolyse (2009-2013)
- « Bioelec » (2014- 2016)

**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**

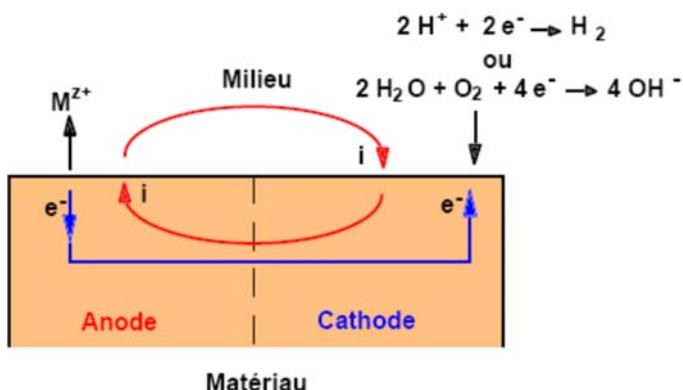
Biocorrosion (MIC), bioprotection (MICI)

- Focus on the works done at Saclay and Toulouse -

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**Background** – **Cathodic reaction** – **Anodic reaction** – **Conclusive remarks**

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

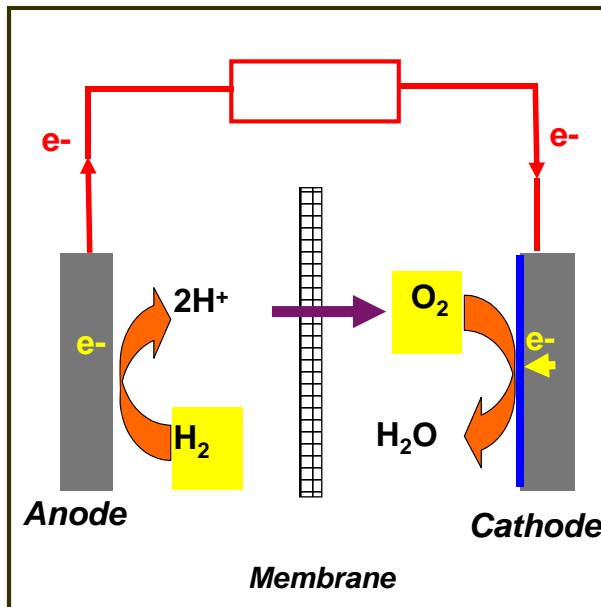


**Biocorrosion: increase of cathodic reaction rates which more often limit the overall kinetics**

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

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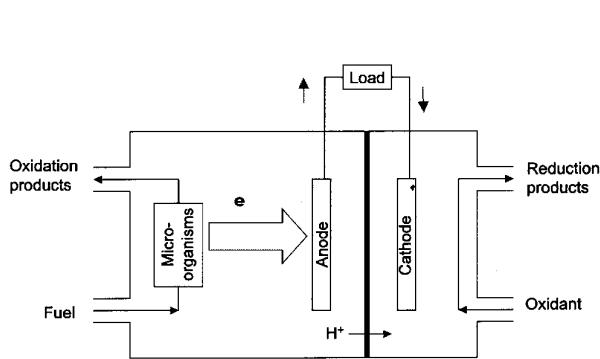
# Fuel cell (PEMFC type)



- 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)

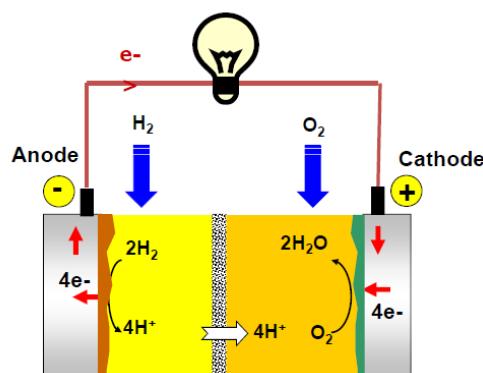
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**"Biofuel cell"** is a wide concept.  
It is has been first used for the biocatalyse of the anodic reaction



«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.)



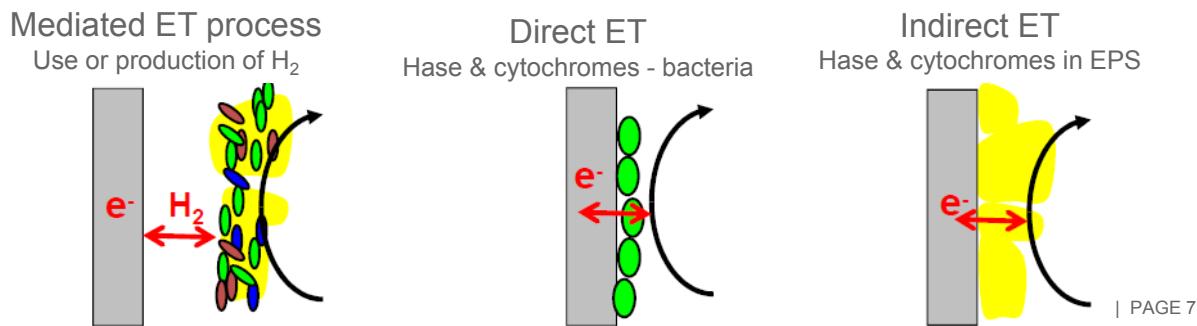
Other used it only when the anodic and cathodic reactions are biocatalysed

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)

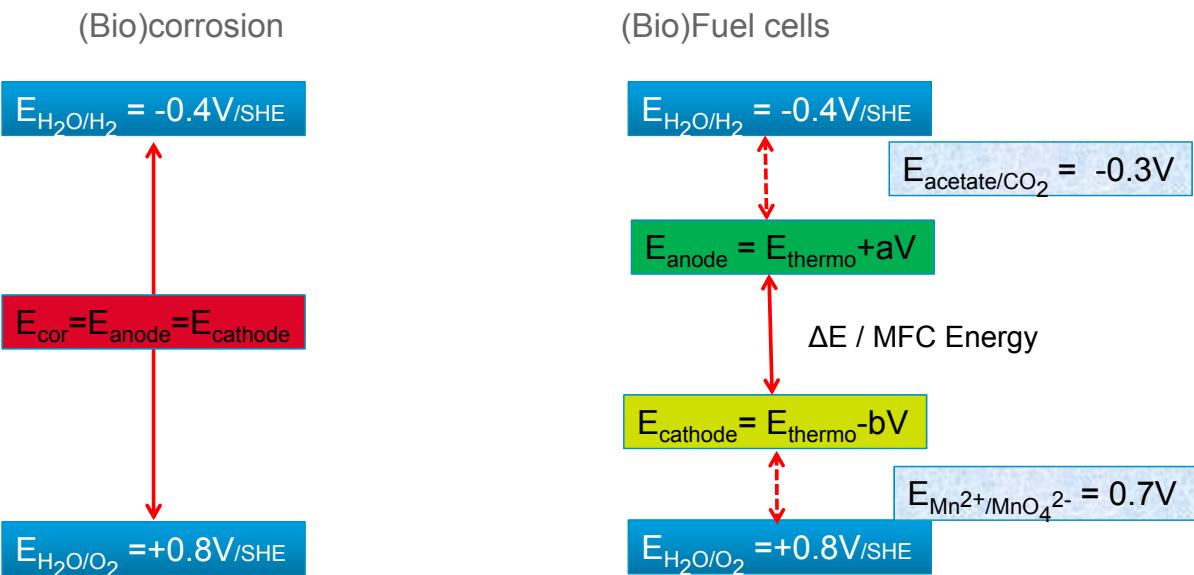
- Mediated process: production or use of chemicals which modify the environment leading to an increase or a decrease the anodic or the cathodic reaction (enzymes, metabolites...)
- Direct electron transfer (ET) through membrane-bound proteins
- Indirect electron transfer by exopolymeric substances, EPS

### Illustration with hydrogenase



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



**In both cases,  $i_{anode} = i_{cathode}$**   
 $I_{cor} = 0.001 \text{ to } 1 \text{ A.m}^{-2} / I_{BFC} = 1 \text{ to } >100 \text{ A.m}^{-2}$

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### Anodic reaction

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- Focus on the works done at Saclay and Toulouse -

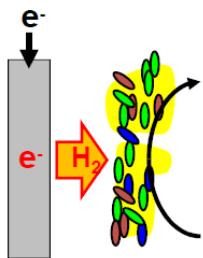
| PAGE 9

Background – Cathodic reaction – Anodic reaction – Conclusive remarks

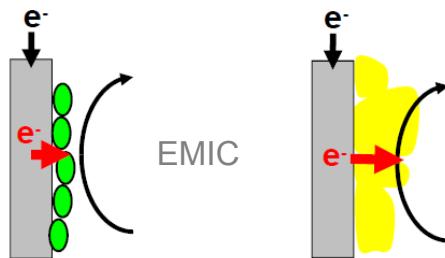
## Biocatalyse of the cathodic reaction

- 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

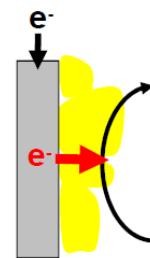
Microbial cathodes: mechanisms largely discussed



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  
Substances  
(enzymes e.g.)

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## Biocatalyse of the cathodic reactions

- Redox systems, redox potentials and reactions

	Couples redox	Potentiels redox (V/ESH)	Reactions redox
Low	CO <sub>2</sub> /glucose	-0,43	$6\text{CO}_2 + 24\text{H}^+ + 24\text{e}^- \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O}$
	CO <sub>2</sub> /formate	-0,43	$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$
	H <sup>+</sup> /H <sub>2</sub>	-0,42	$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$
	Ferredoxin ox/red	-0,42	$\text{Ferredoxin}(\text{Fe}^{3+}) + \text{e}^- \longrightarrow \text{Ferredoxin}(\text{Fe}^{2+})$
	NaD <sup>+</sup> /NaDH	-0,32	$\text{NaD}^+ + \text{H}^+ + 2\text{e}^- \longrightarrow \text{NaDH}$
	CO <sub>2</sub> /acétate	-0,28	$2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \longrightarrow \text{C}_2\text{H}_4\text{O}_2 + 2\text{H}_2\text{O}$
	S <sup>0</sup> /H <sub>2</sub> S	-0,274	$\text{S} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{S}$
Intermediate	CO <sub>2</sub> /CH <sub>4</sub>	-0,22	$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \longrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
	SO <sub>4</sub> <sup>2-</sup> /H <sub>2</sub> S	-0,22	$\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- \longrightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$
	Pyruvate/Lactate	-0,185	$\text{Pyruvate}^{2-} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{Lactate}^{2-}$
	Fumarate/Succinate	+0,033	$\text{Fumarate}^{2-} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{Succinate}^{2-}$
	Cytochrome b <sub>oxx/d</sub>	+0,075	$\text{Cytochrome b}(\text{Fe}^{3+}) + \text{e}^- \longrightarrow \text{Cytochrome b}(\text{Fe}^{2+})$
	Ubiquinone/UbiquinoneH <sub>2</sub>	+0,1	$\text{Ubiquinone} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{Ubiquinone H}_2$
	Cytochrome C <sub>ox/d</sub>	+0,254	$\text{Cytochrome b}(\text{Fe}^{3+}) + \text{e}^- \longrightarrow \text{Cytochrome b}(\text{Fe}^{2+})$
High	Fe(CN) <sub>6</sub> <sup>3-</sup> /Fe(CN) <sub>6</sub> <sup>4-</sup>	+0,36	$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \longrightarrow \text{Fe}(\text{CN})_6^{4-}$
	NO <sub>3</sub> <sup>-</sup> /NO <sub>2</sub> <sup>-</sup>	+0,43	$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{NO}_2^- + \text{H}_2\text{O}$
	NO <sub>2</sub> <sup>-</sup> /NH <sub>4</sub> <sup>+</sup>	+0,44	$\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^- \longrightarrow \text{NH}_4^+ + 2\text{H}_2\text{O}$
	MnO <sub>2</sub> /Mn <sup>2+</sup>	+0,60	$\text{MnO}_{2(i)} + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$
	Fe <sup>3+</sup> /Fe <sup>2+</sup>	+0,771	$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$
	1/2O <sub>2</sub> /H <sub>2</sub> O	+0,84	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$

Corrosion

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## Biocathodes on stainless steels: biofilms, bacteria, enzymes

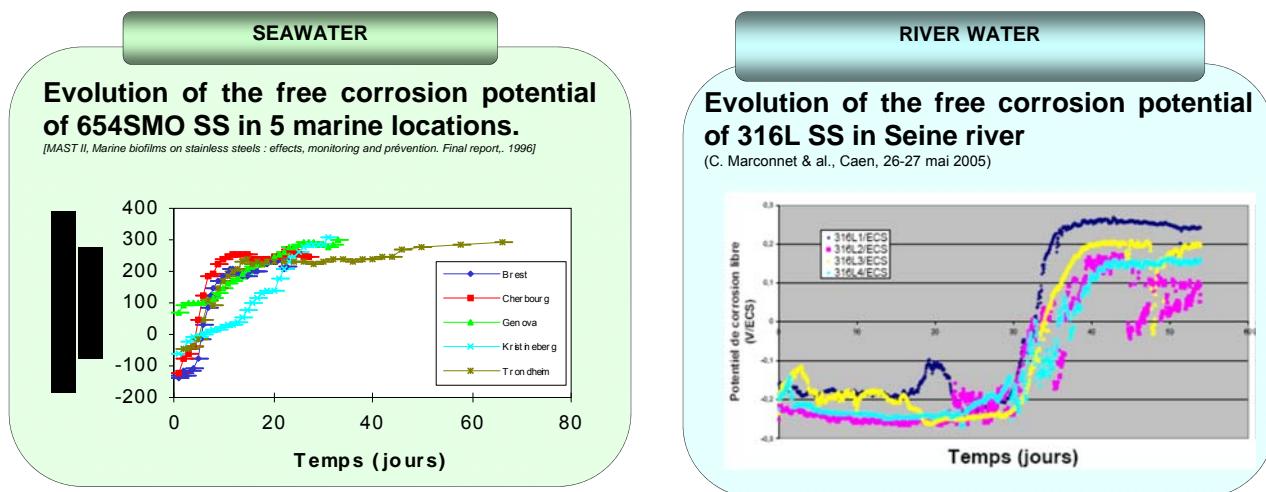
System	Material	W. Potential (/SHE)	Ox/red	Application	Ref.
Marine biofilm	Stainless steel	+0,5 V	O <sub>2</sub> /H <sub>2</sub> O	corrosion	(1)
Marine biofilm	Stainless steel	0,0 / -0,1 V 0,45	O <sub>2</sub> /H <sub>2</sub> O	MFC (current) MFC (OCP)	(2)
Geobacter sulfurreducens	Stainless steel	+0,1 V	Fumarate/ac etate	corrosion	(3)
Geobacter sulfurreducens	Stainless steel	-0,2 / -0,4 V	Succinate+ carbonate/ Glycerol	MFC	(4)
Hydrogenase ( <i>Ralstonia eutropha</i> )	Stainless steel	-0,5 V	H <sub>2</sub> O/H <sub>2</sub>	Corrosion	(5)
Hydrogenase ( <i>Desulfovibrio desulfuricans</i> )	Stainless steel	-0,2 V	H <sub>2</sub> O/H <sub>2</sub>	« Enzymatic » fuel cell	(6)

## Focus on biofilm

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

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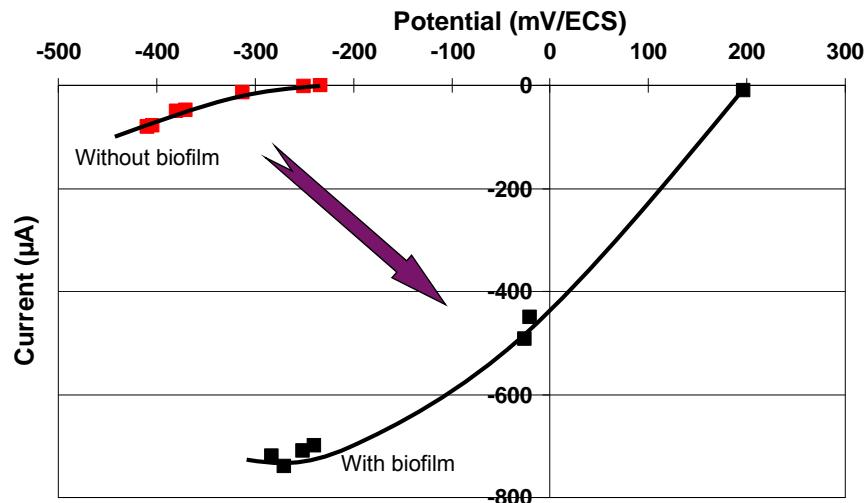
## Stainless steels in natural waters



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

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## Efficient microbial cathode in seawater on SS

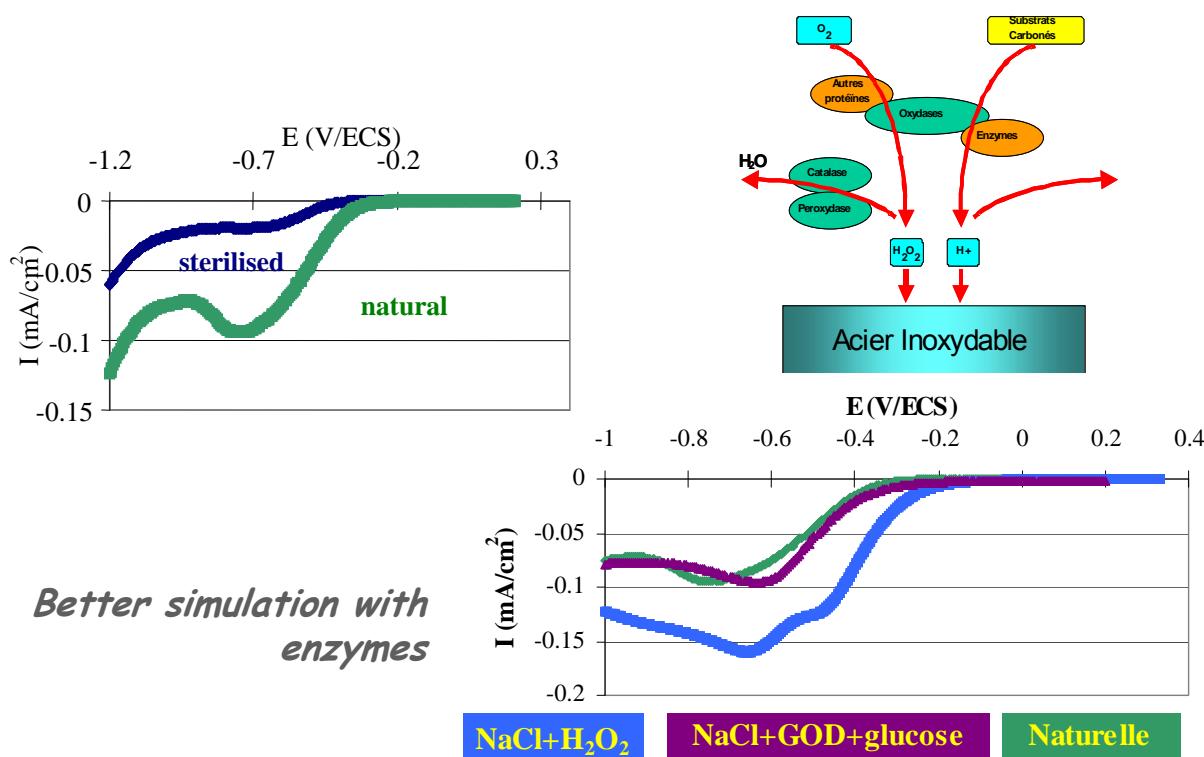


Biofilm formed in seawater on stainless steel

- very efficient to induce microbial corrosion (pitting & crevice corrosion)
- in biofuel cell: current densities up to  $1.3 \text{ Am}^{-2}$

# "ENZYMATIC METHOD"

## BIOSYNTHETIC / NATURAL SEA WATER



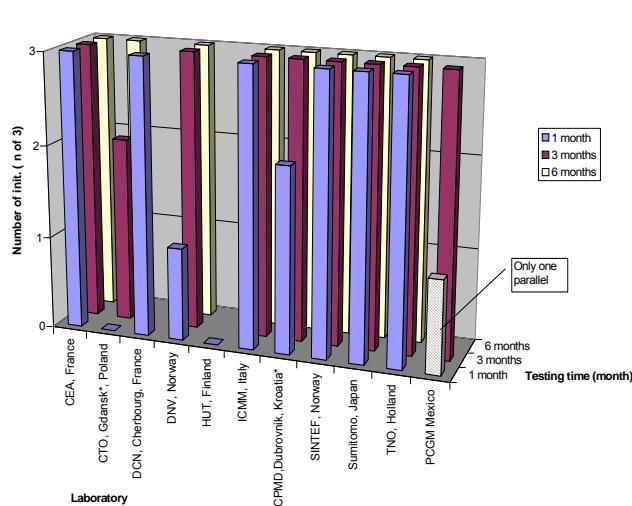
D.Féron &amp; al., EFC series N°22, The Institute of Materials, 1997, 103-113

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

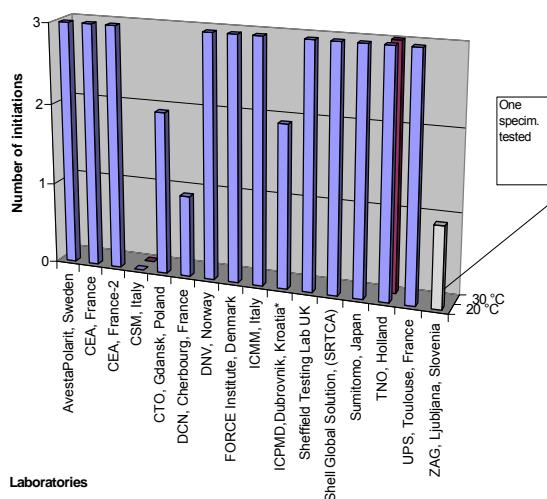
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# "ENZYMATIC METHOD" BIOSYNTHETIC / NATURAL SEA WATER

## 316L Crevice corrosion initiation



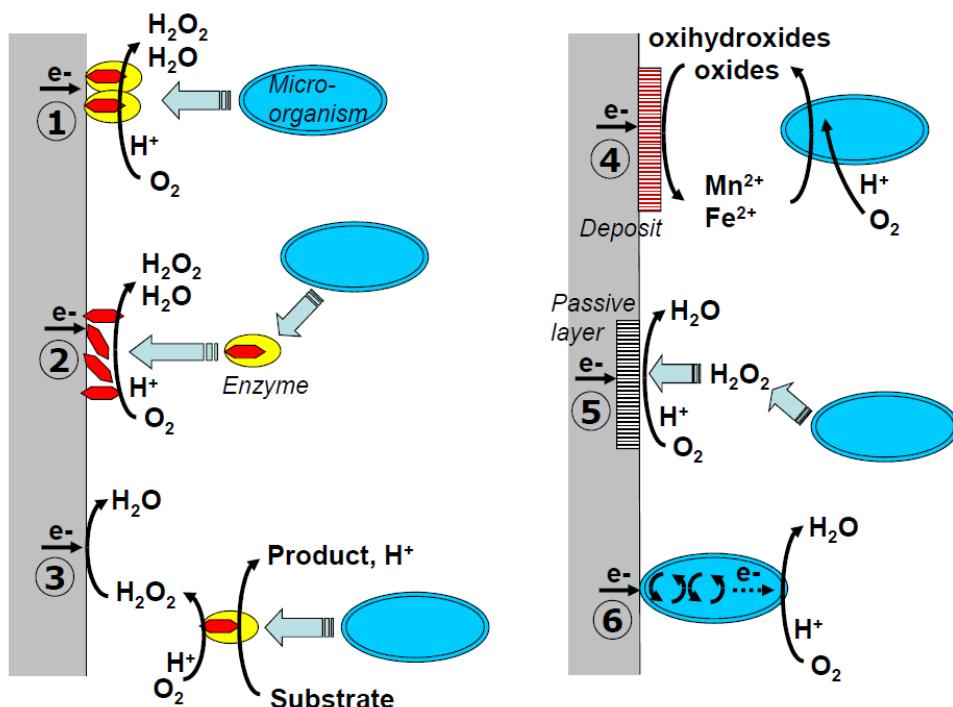
Natural seawater: 74% of coupons corroded



Biosynthetic seawater at 20°C: 91%

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

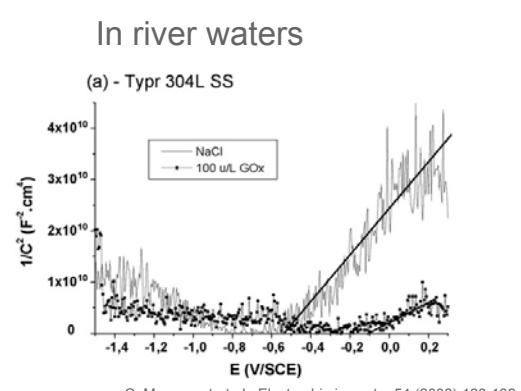
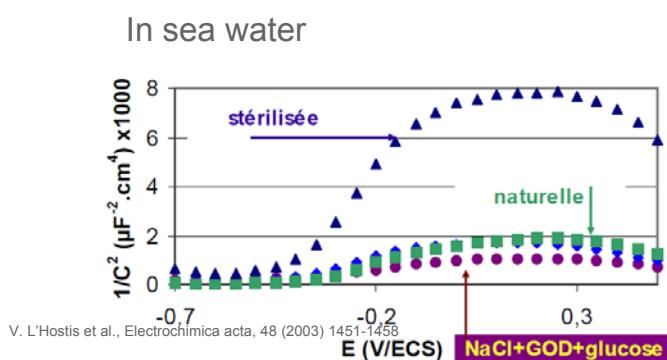
## Different mechanisms postulated to explain microbial catalysis of oxygen reduction by biofilms



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

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## Evolution of the semi-conductive properties SS passive layers / with or without biofilms/enzymes



- 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).

## Current densities reported recently with various oxygen biocathodes in MFC

Electron acceptor	Source inoculum	Operation mode (potencial vs Ag/AgCl)	Current density (A.m <sup>-2</sup> )/power density (W m <sup>-2</sup> )
MFC			
O <sub>2</sub>	Enrichment culture	Batch-fed anode, recirculated catholyte	2.13/0.88
O <sub>2</sub>	Enrichment with Mn (IV) and Mn (II)	Batch-fed anode, recirculated catholyte	2.13/0.88
O <sub>2</sub>	Enrichment culture	Continuous fed, with loop between anode and cathode	3.01/1.2
O <sub>2</sub>	Enrichment culture	Two chamber, batch-fed	1.76/0.37
O <sub>2</sub>	Enrichments and isolates of <i>Acinetobacter calcoaceticus</i>	Two chamber, batch-fed	2.8
O <sub>2</sub>	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<sup>-2</sup> 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 .
<i>Geobacter sulfurreducens</i>	Stainless steel	-0.1 / -0.3 V	30 A.m <sup>-2</sup>	Succinate+carbonate /Glycerol	MFC	(1)
<i>Geobacter sulfurreducens</i>	Stainless steel	-0.3 V	14 A.m <sup>-2</sup>	Fumarate/succinate	MFC	(2)
<i>Geobacter sulfurreducens</i>	graphite	-0.3 V	0.75 A.m <sup>-2</sup>	Fumarate/succinate	MFC	(3)
Hydrogenase ( <i>Clostridium acetobutylicum</i> )	Carbon steel	-0.5 V	0,015 A.m <sup>-2</sup>	H <sub>2</sub> O/H <sub>2</sub>	Corros ion	(4)
Hydrogenase ( <i>Ralstonia eutropha</i> )	Stainless steel	-0.45 V	0,004 A.m <sup>-2</sup>	H <sub>2</sub> O/H <sub>2</sub>	Corros ion	(5)
Hydrogenase ( <i>Desulfovibrio desulfuricans</i> )	Stainless st.	-0.15 V	0,13 A.m <sup>-2</sup>	H <sub>2</sub> O/H <sub>2</sub>	MFC	(6)
	Graphite	-0.15 V	0,27 A.m <sup>-2</sup>			

(1) L. Soussan & al., *Electrochim. 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

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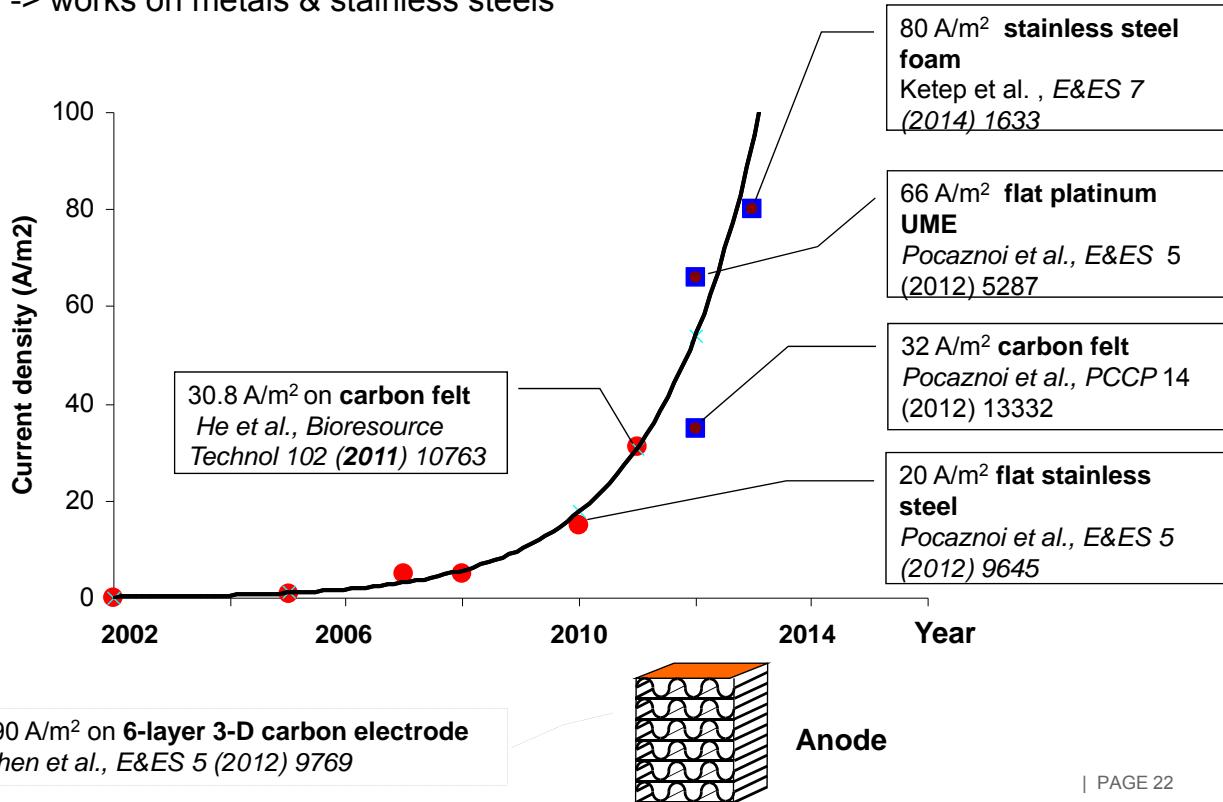
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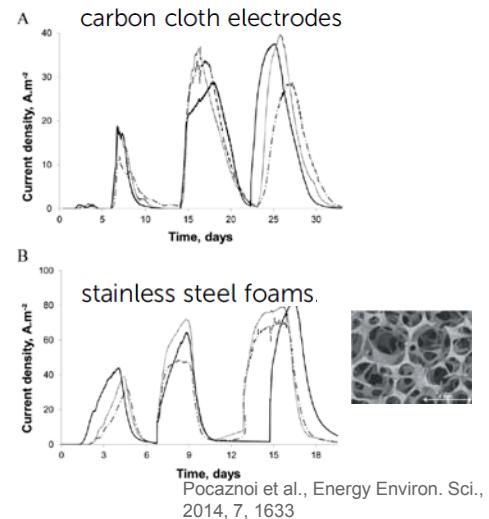
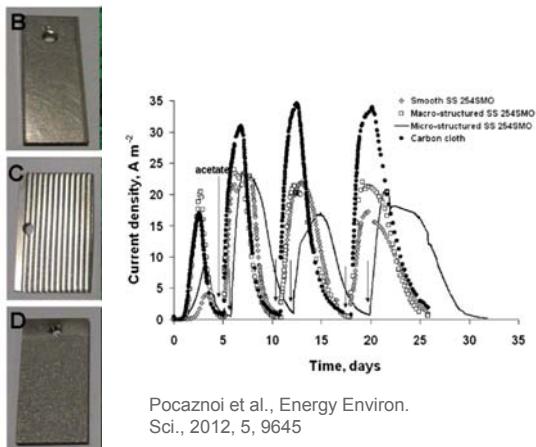
Background – Cathodic reaction – Anodic reaction – Conclusive remarks

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



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## Influence of the surface geometry on stainless steels



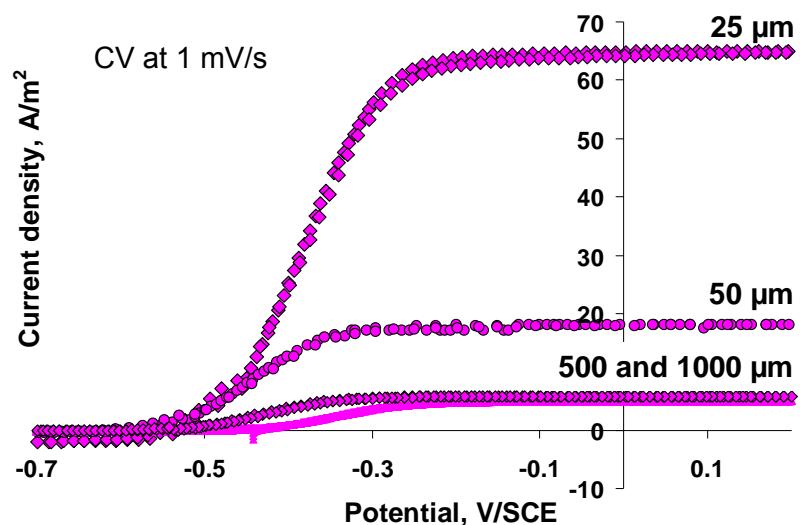
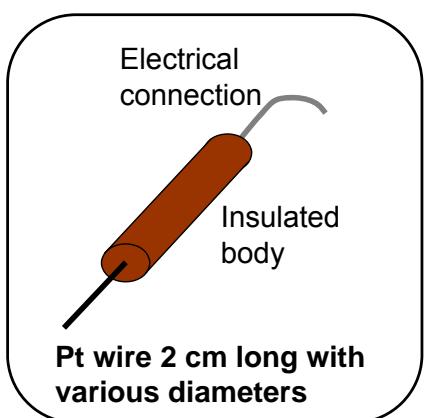
- Soil leachate / acetate addition / polarisation at -0.2 V/SCE
- Stainless steels : promising anode materials for MFC

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## Soil microbial ultra-microanodes

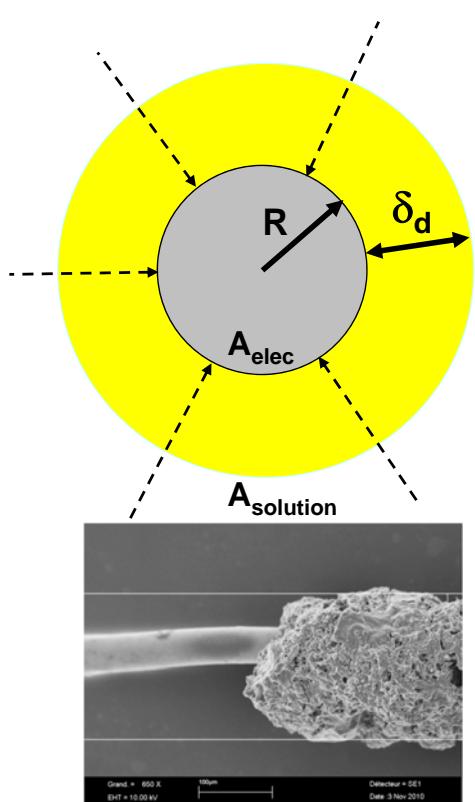
### (non optimal) conditions

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  $\mu\text{m}$  increases  $J_{\max}$  from 7 to 66  $\text{A/m}^2$

# Ultra-microelectrode: principle



Wire radius  $R$  of the same order of magnitude than the diffusion layer thickness  $\delta_d$  ( $R < 25 \mu\text{m}$ )



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- $\mu\text{m}$  diameter  
19 days  
polarisation at -0.2 V/SCE  
Biofilm thickness 75  $\mu\text{m}$

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

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## CONTENT

### Background

Aqueous corrosion, fuel cells, biocatalyse,

### Cathodic reaction

Electron transfer, aerobic and anaerobic environments

### Anodic reaction

Electron transfer, aerobic and anaerobic environments

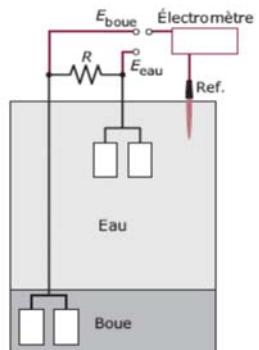
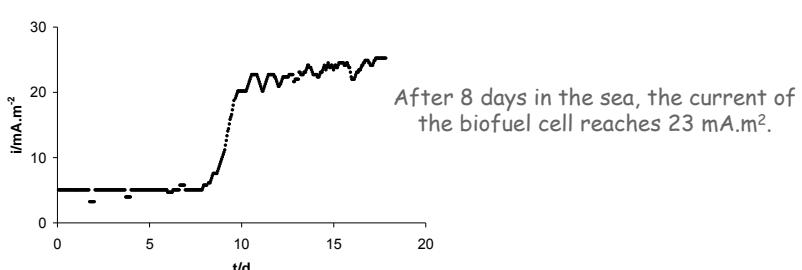
## Conclusive remarks – back to corrosion

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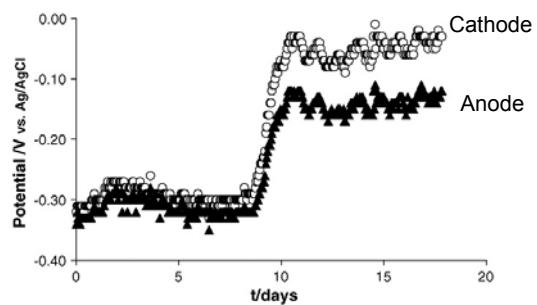
- Focus on the works done at Saclay and Toulouse -

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# BIOFUEL CELLS or BIOPROTECTION



**Stainless steel electrodes ( $0.12 \text{ m}^2$ ) located in aerated seawater and in the mud**



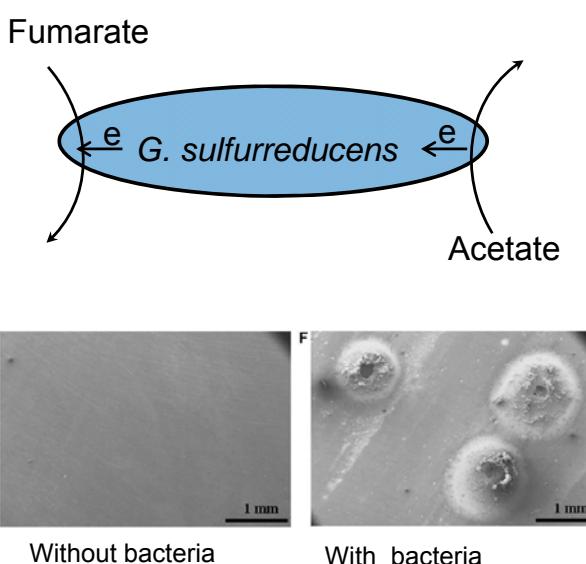
Potential of the cathode lower than  $0.0 \text{ mV/Ag.AgCl}$  instead of  $+300 \text{ mV/Ag.AgCl}$  (free corrosion potential)

=> Cathodic protection

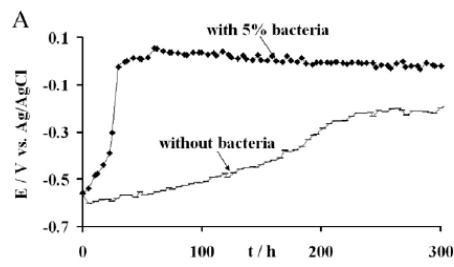
C. Daumas et al., Electrochimica Acta 53 (2007) 468–473

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



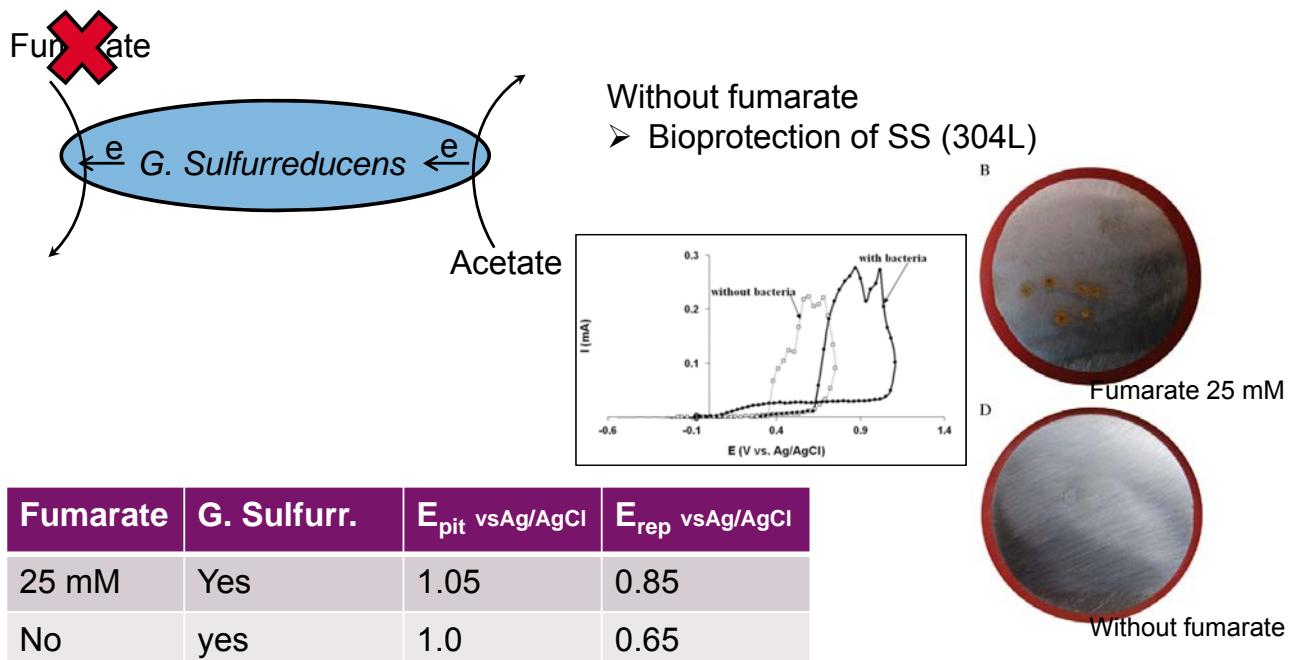
- Increase of the cathodic reaction
- Increase of the pitting or localised corrosion risk on SS (304L)
  - Decrease of the pitting potential (304L)



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

## Biocorrosion or bioprotection

The ubiquitous role of *Geobacter sulfurreducens* (304L)

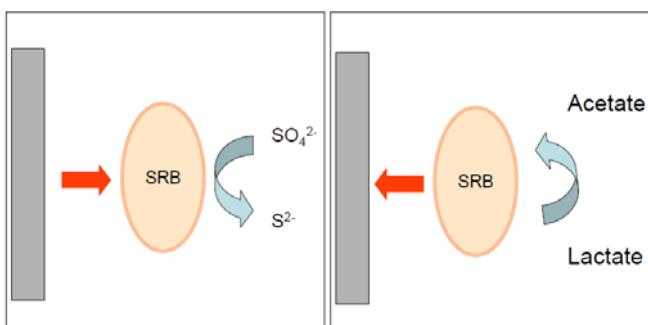


M. Mehanna & al.al., Electrochemistry communications, 2010, 12, 724-728

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**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)



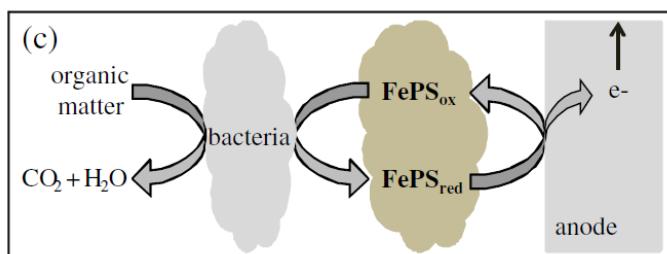
Cordas et al., Electrochimica Acta, 2008, 54, 29-34  
 S. Da Silva et al. J. Electroanal. Chem. 561 (2004) 93  
 S. Da Silva et al., Bioelectrochemistry 56 (2002), 77.

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## 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 donor reactions (direct, indirect or mediated ET)

*Deposition of a Fe-P-S-graphite layer ( $\text{FeSO}_4$ ,  $\text{Na}_2\text{S}$ ,  $\text{NaH}_2\text{PO}_4$  and graphite powder) on stainless steel*



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## 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 donor 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

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## 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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environnement

Damien Féron