



Institut
Européen des
Membranes



UNIVERSITÉ
DE MONTPELLIER



Des bactéries pour produire de l'électricité: les biopiles.

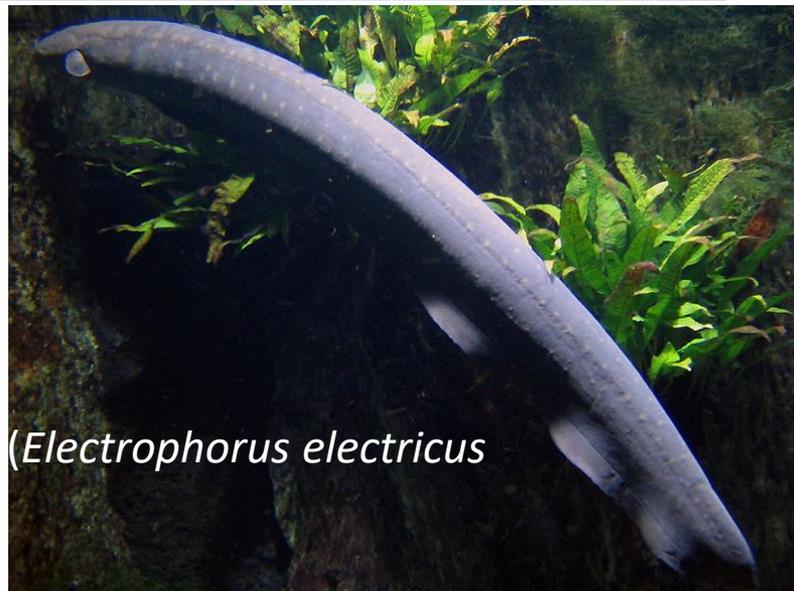
Christophe INNOCENT



Les poissons électriques



Torpille du Pacifique (*Torpedo californica*)

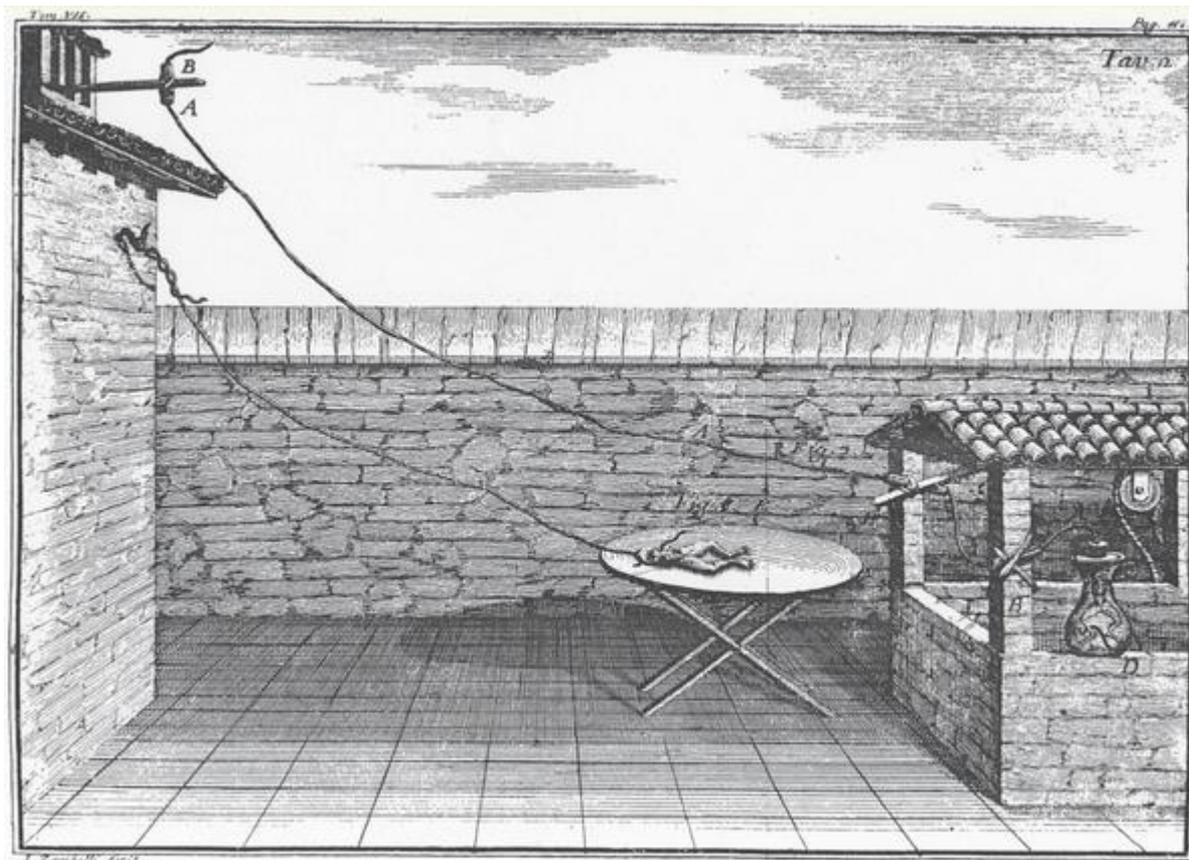


Anguille électrique (*Electrophorus electricus*)



L'électricité animale

L. Galvani, *Commentaire sur les forces électriques dans le mouvement musculaire*, 1791.

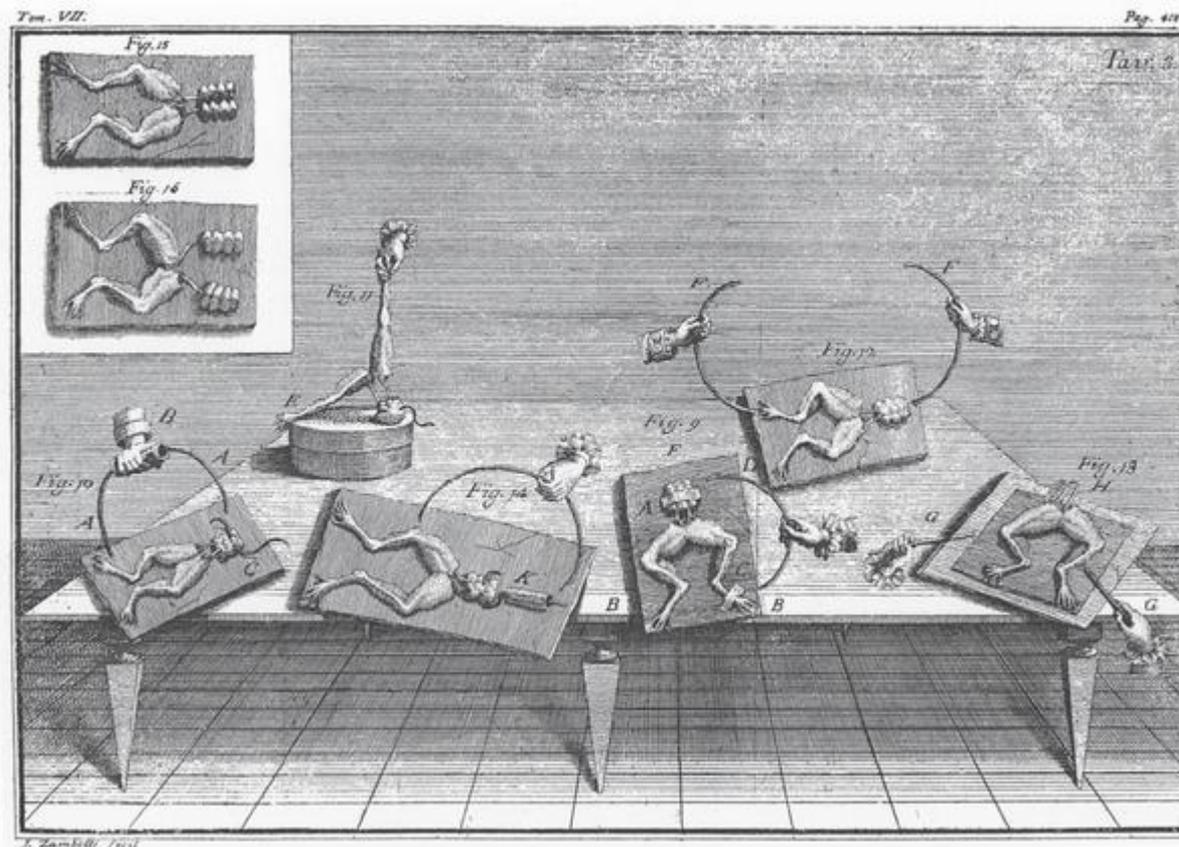


A droite : La grenouille est placée dans un récipient en verre C, AA est un fil de fer isolé. Une extrémité du fil de fer D touche les pattes et l'autre plonge dans l'eau du puits.

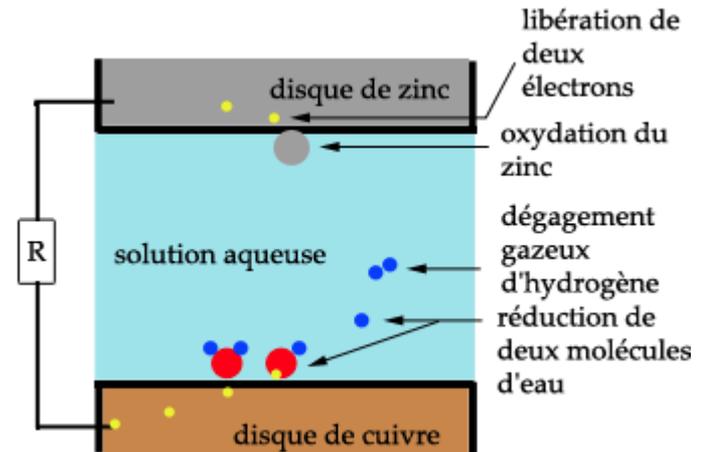
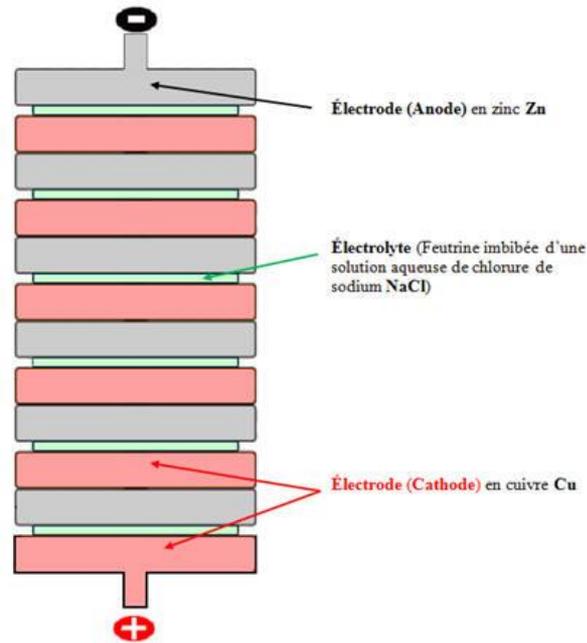
Au centre : La grenouille est posée sur une table recouverte d'un revêtement huileux, un fil de fer la relie au mur. Les phénomènes sont identiques.

L'électricité animale

L. Galvani, *Commentaire sur les forces électriques dans le mouvement musculaire*, 1791.



Pile Volta



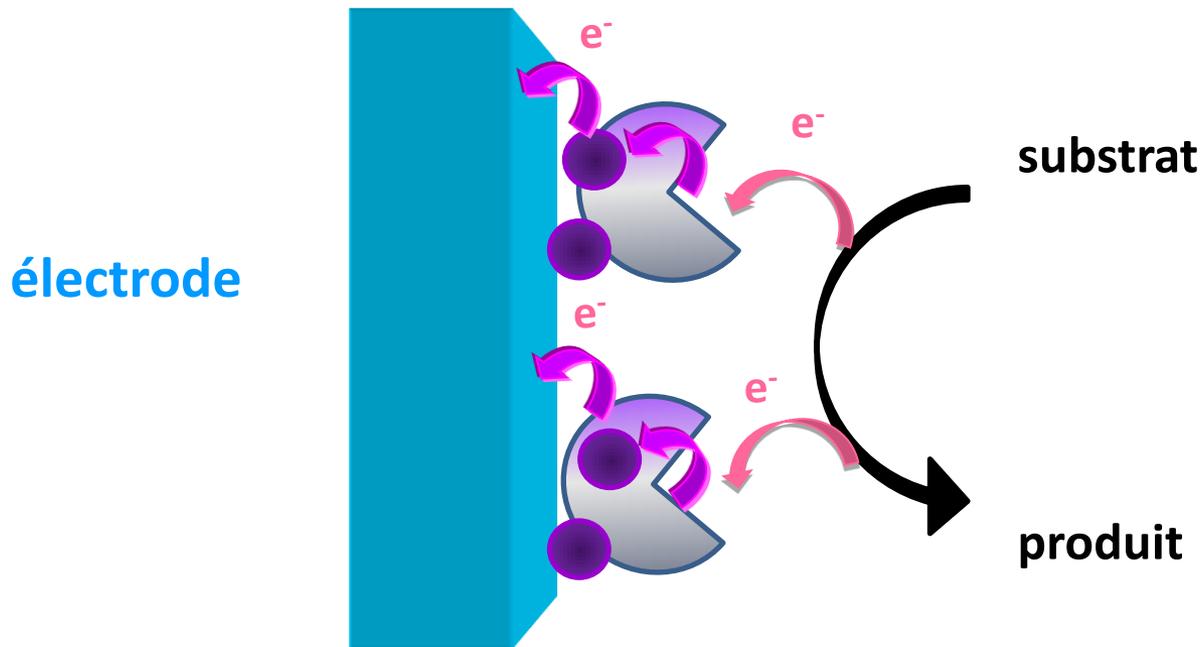
Biopile : principe

Biopile

~

Pile à combustible

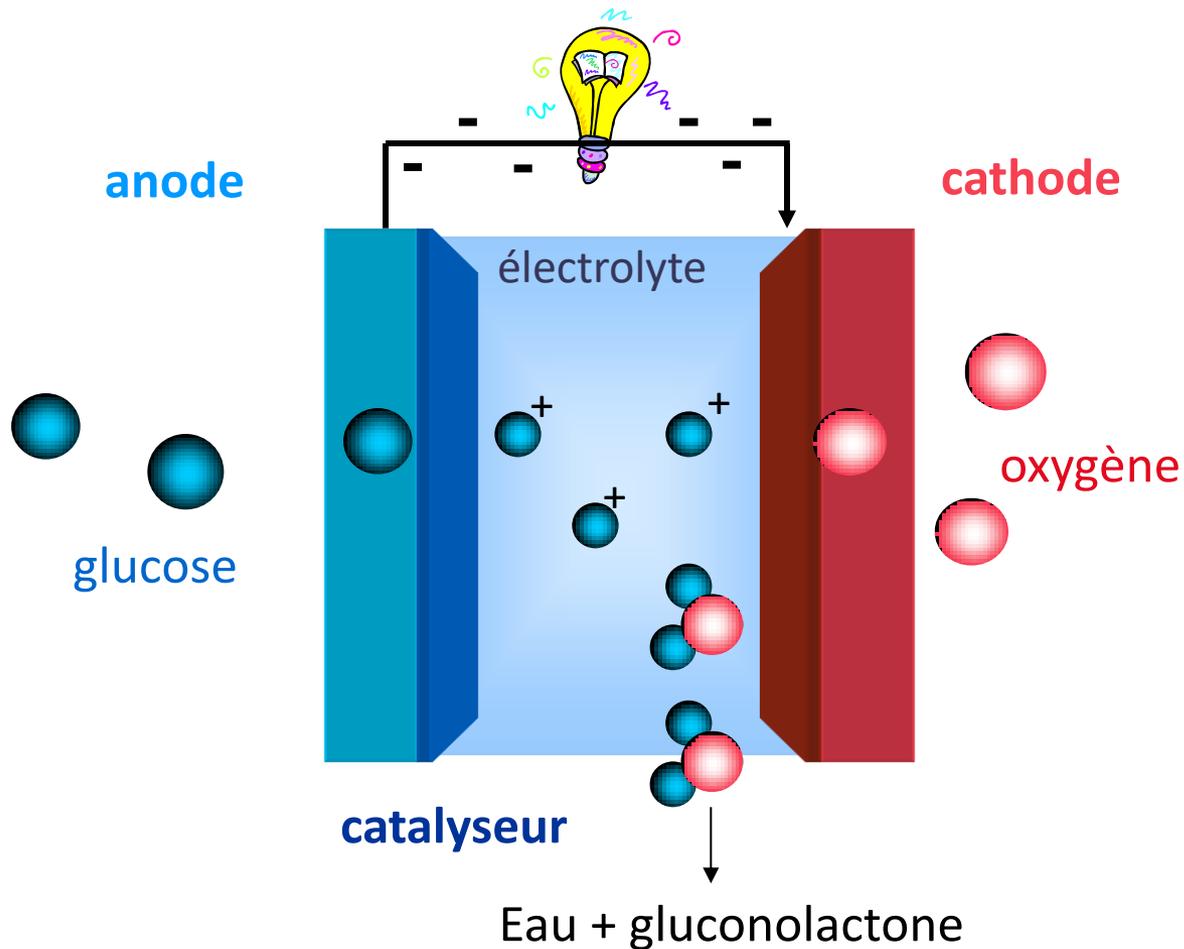
Système utilisant des catalyseurs pour convertir directement de l'énergie chimique en courant électrique.



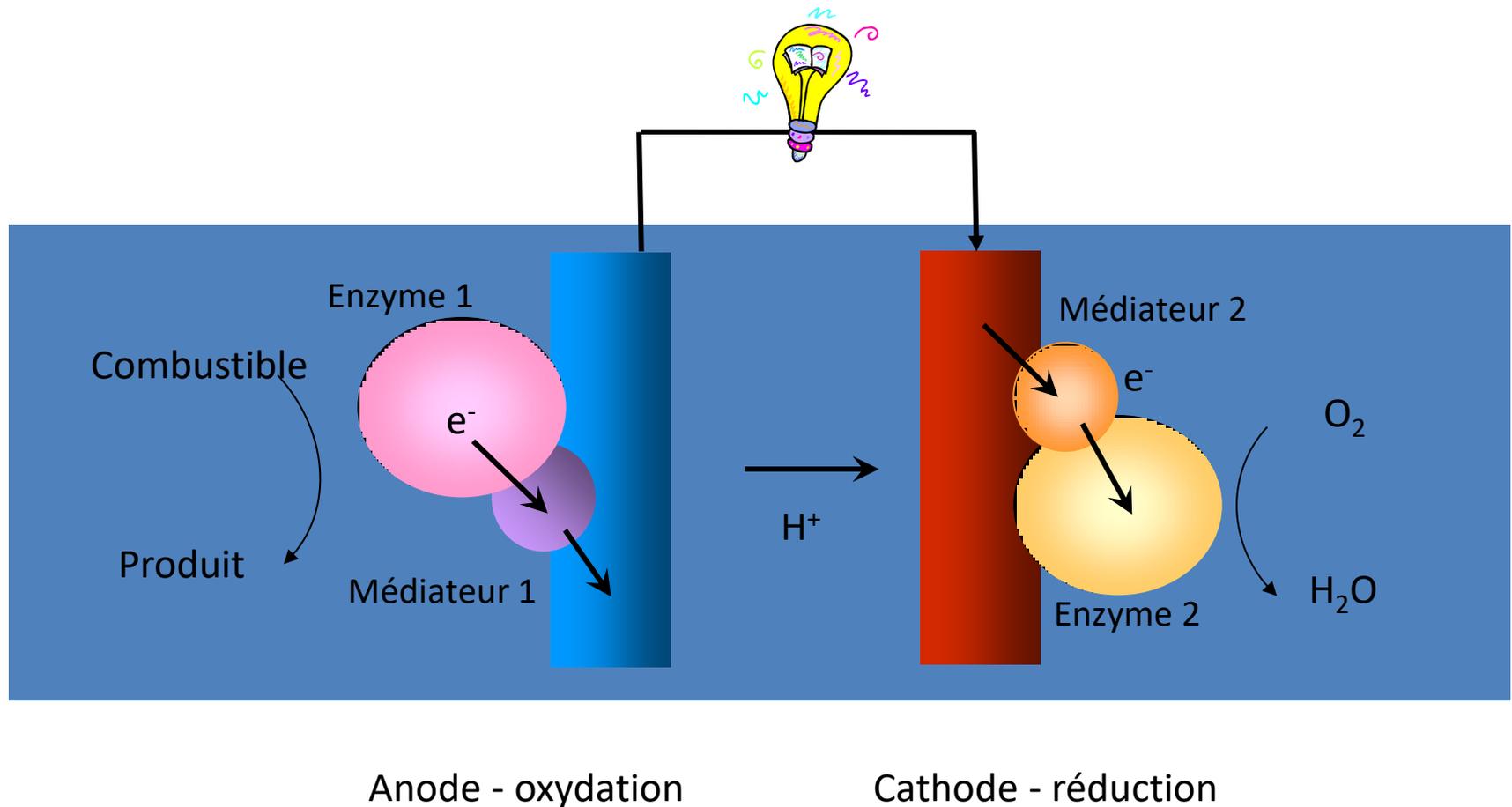
catalyseur = enzymes, micro-organismes

Biopile enzymatique : principe

Biopile glucose/O₂



Principe d'une biopile enzymatique



Exemple de combustible : glucose, méthanol, glycérol...

caractéristiques

- avantages

- Sélectivité des enzymes
spécificité des réactions
- Faibles couts de production
(Biotechnologies)
- Conditions opératoires
(conditions physiologiques)

- inconvénients

- Stabilité limitée du
biocatalyseur
- Faible puissance
Conduction électronique



BBA 45057

BIOELECTROCHEMISTRY

I. ENZYME UTILIZING BIO-FUEL CELL STUDIES

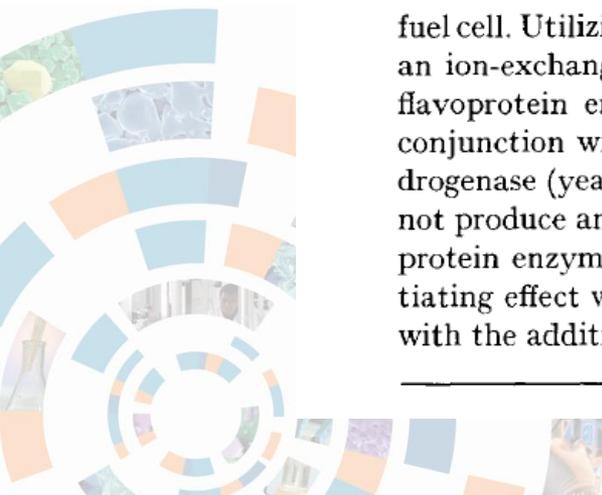
A. T. YAHIRO, S. M. LEE AND D. O. KIMBLE

Space-General Corporation, El Monte, Calif. (U.S.A.)

(Received December 31st, 1963)

SUMMARY

Electron transfer as opposed to hydrogen transfer was demonstrated to be involved in the oxidation-reduction of the flavoprotein enzyme system. A bioelectrochemical investigation of glucose oxidase (EC 1.1.3.4), D-amino acid oxidase (EC 1.4.3.3), and yeast alcohol dehydrogenase (EC 1.1.1.1) systems was conducted in an attempt to utilize the electron-transferring process as a potential anodic reaction in a biochemical fuel cell. Utilizing a bio-fuel cell constructed of plexiglass, platinum-foil electrodes, and an ion-exchange membrane for conduction between the anolyte and catholyte, the flavoprotein enzymes, both glucose oxidase and D-amino acid oxidase systems in conjunction with an O₂ cathode, generated 175–350 mV. In contrast, alcohol dehydrogenase (yeast), a pyridinoprotein enzyme which requires coenzyme I (NAD⁺), did not produce any electrical voltage. Elemental iron was found to potentiate the flavoprotein enzyme reaction yielding voltages ranging from 625 to 750 mV. The potentiating effect was probably due to a faster turnover rate of FADH to FAD⁺ coupled with the additional net oxidation potential of iron.



Biopiles enzymatiques : applications

Principaux avantages = Sélectivité du catalyseur biologique,
Fonctionnement dans des conditions physiologiques (pH, T°)

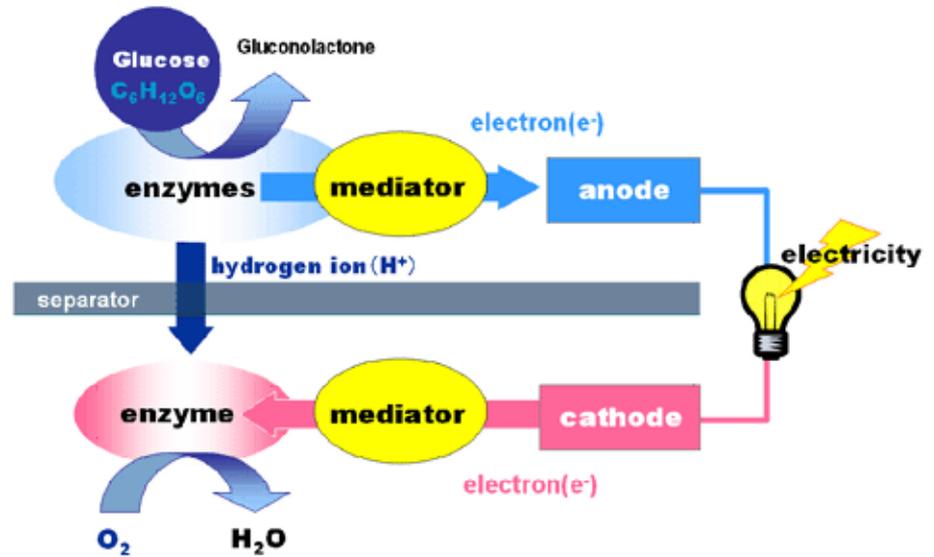
Application sur des marchés « niches » tels que l'alimentation
de dispositifs de faible puissance :



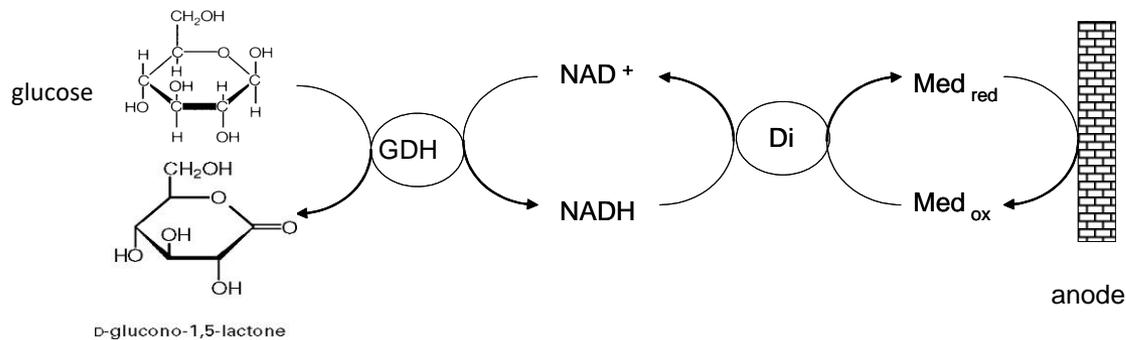
Orientation actuelle :
Miniaturisation des systèmes
pour un gain en densité volumique d'énergie

Biopiles enzymatiques : applications

Biopile de SONY:



Principe de fonctionnement:

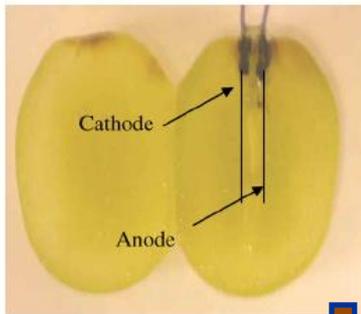


Miniaturisation des systèmes

Différents challenges en terme de : design des systèmes, matériaux et techniques de fabrication mis en œuvre...

Deux concepts de miniaturisation sont actuellement développés :

- Réduction d'échelle des biopiles existantes :



Micro BFC implantable
in vivo, Mano et al.,
JACS



**Bien adapté aux applications *in vivo*
mais pas de contrôle possible
du transport de matière**

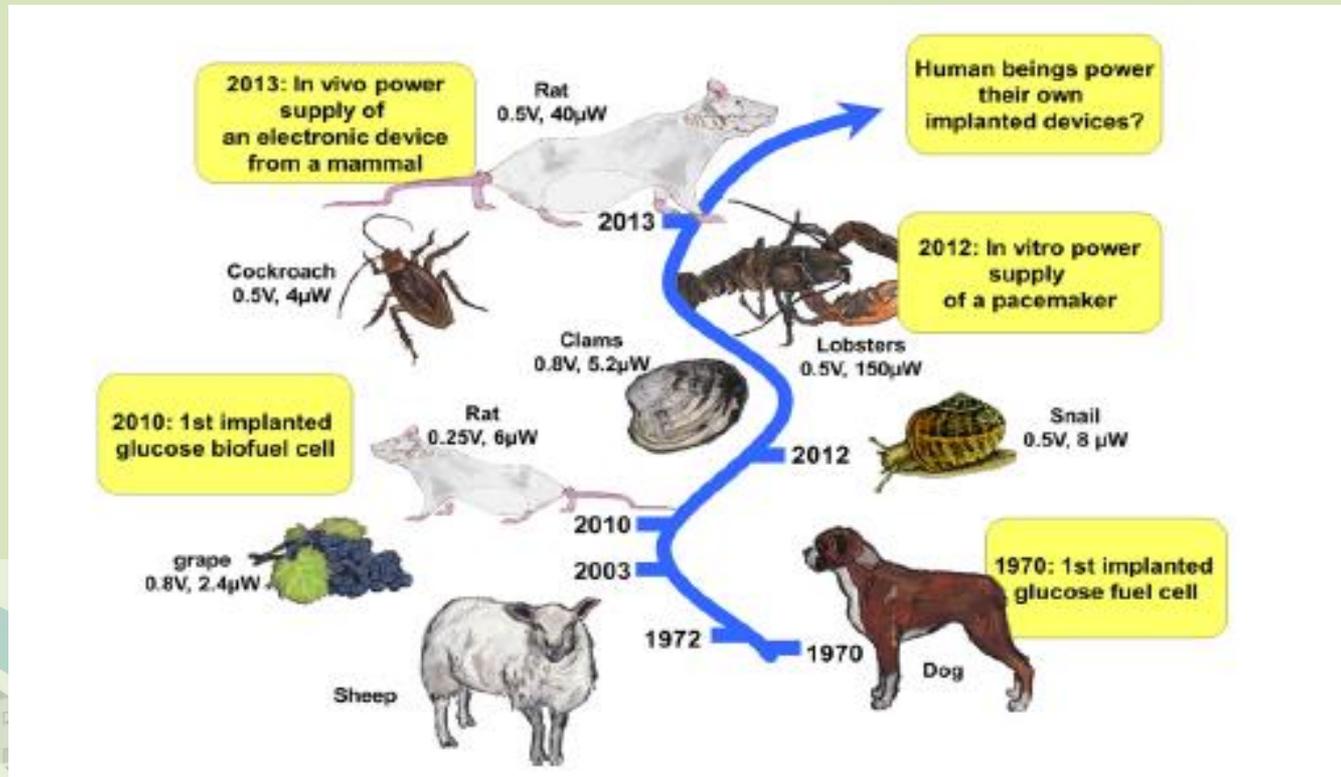
- Développer des microstructures incluant tous les composants du système : électrodes, électrolyte, catalyseur biologique



**Technologie basée sur le
concept de pile à combustible en
configuration microfluidique**

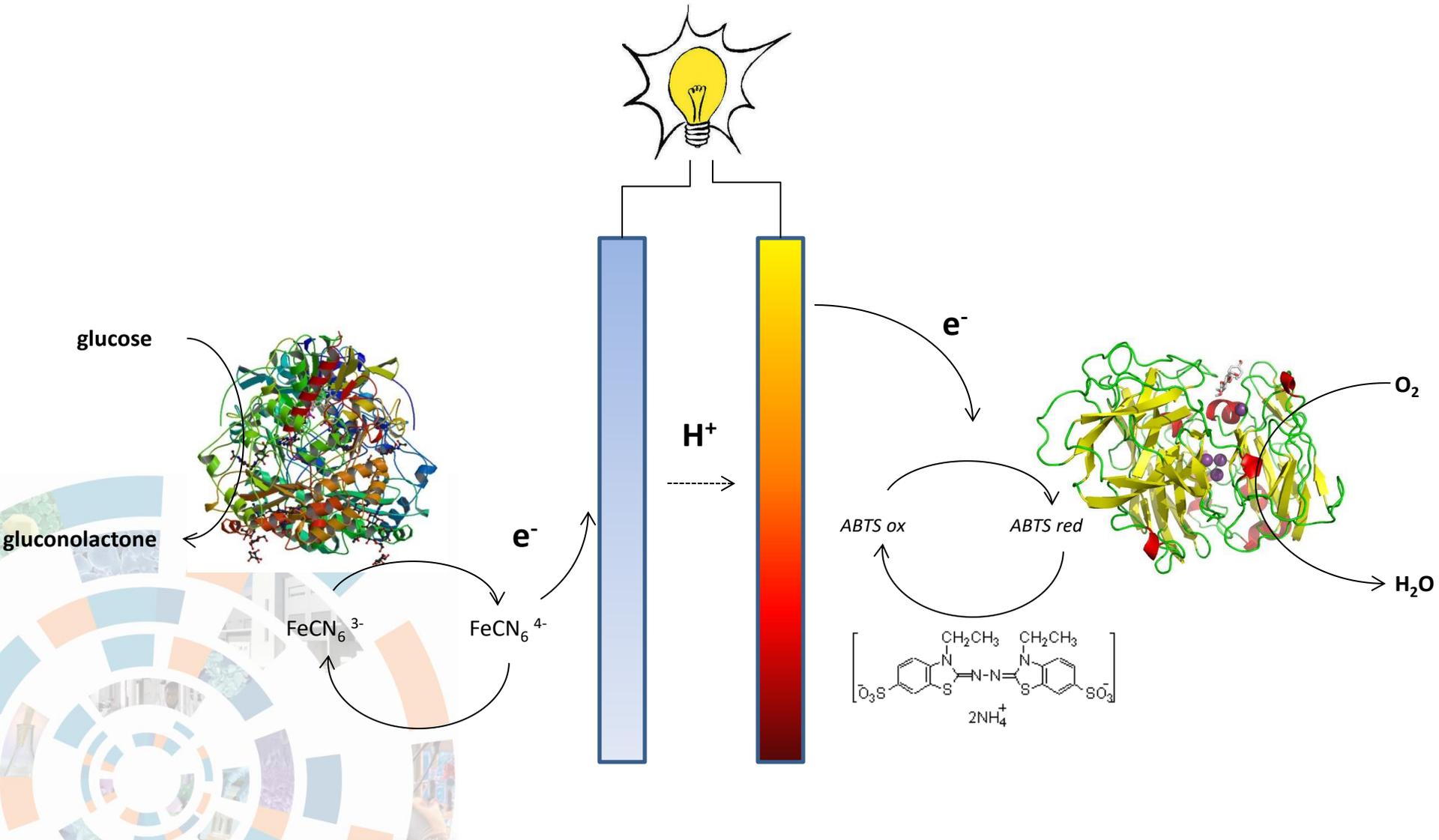
Enzymatic biofuel cell: applications

Implantable biofuel cells

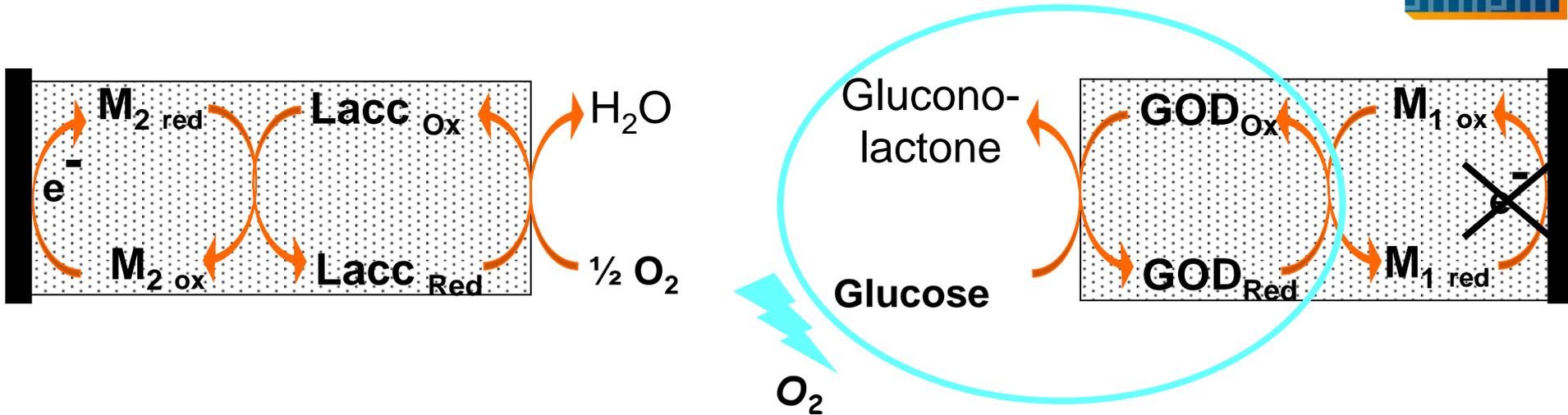


“Towards glucose biofuel cells implanted in human body for powering artificial organs: Review”, S. Cosnier, A. Le Goff, M. Holzinger; *Electrochemistry Communication*, **38**, 19, (2014).

Biopile Glucose/O₂



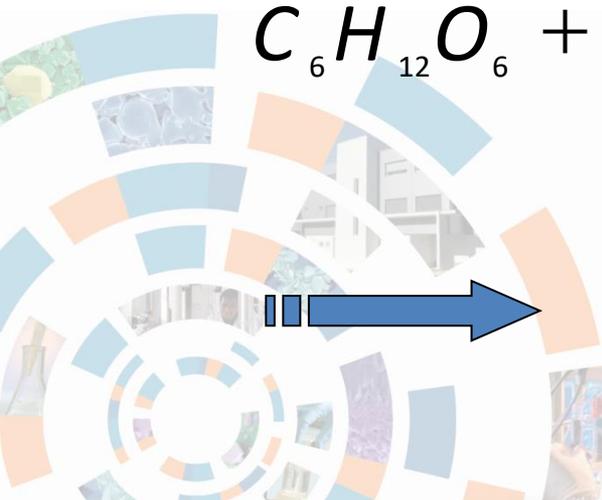
Limitation du système!



Réaction "secondaire"



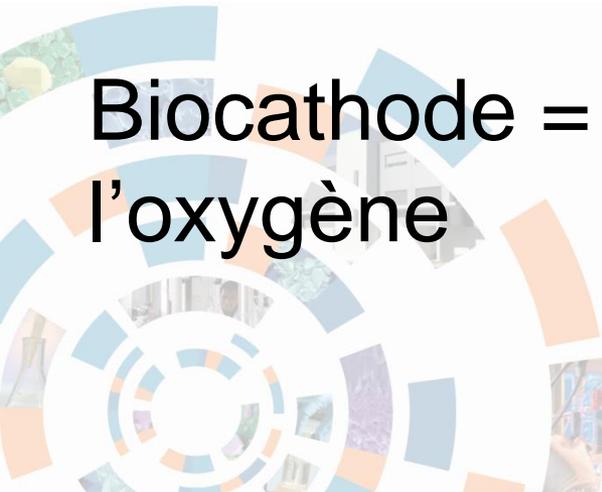
- ✓ diminution des électrons
- ✓ diminution de la tension de sortie



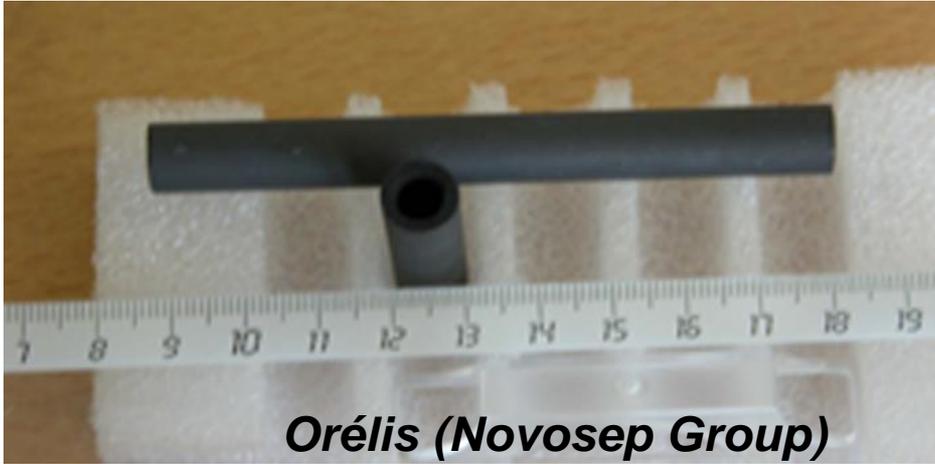
Condition = Alimentation en O₂ séparée de l'électrolyte



Biocathode = séparateur membranaire pour l'oxygène

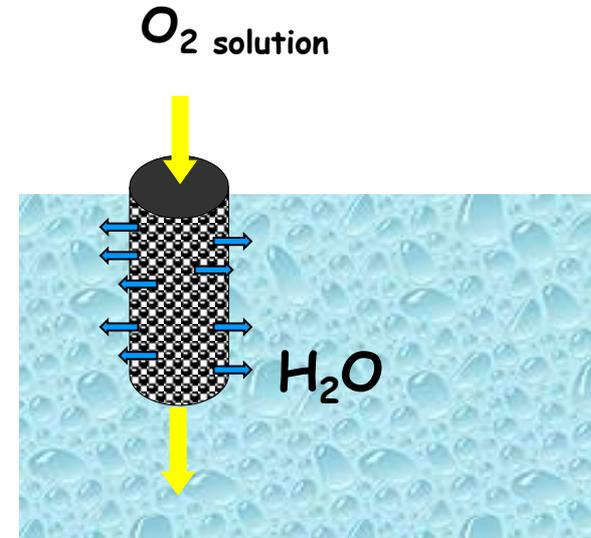
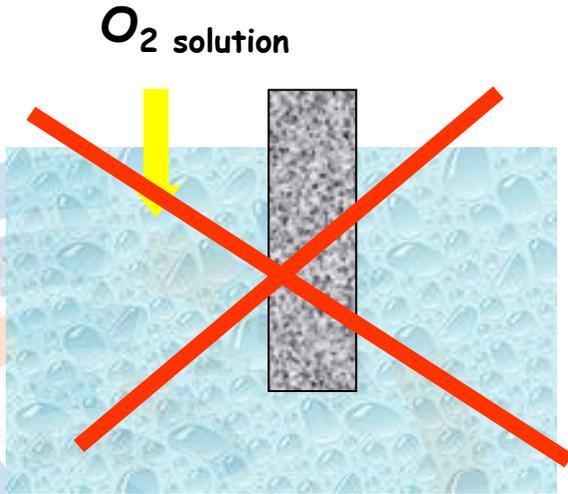


Conception du séparateur membranaire

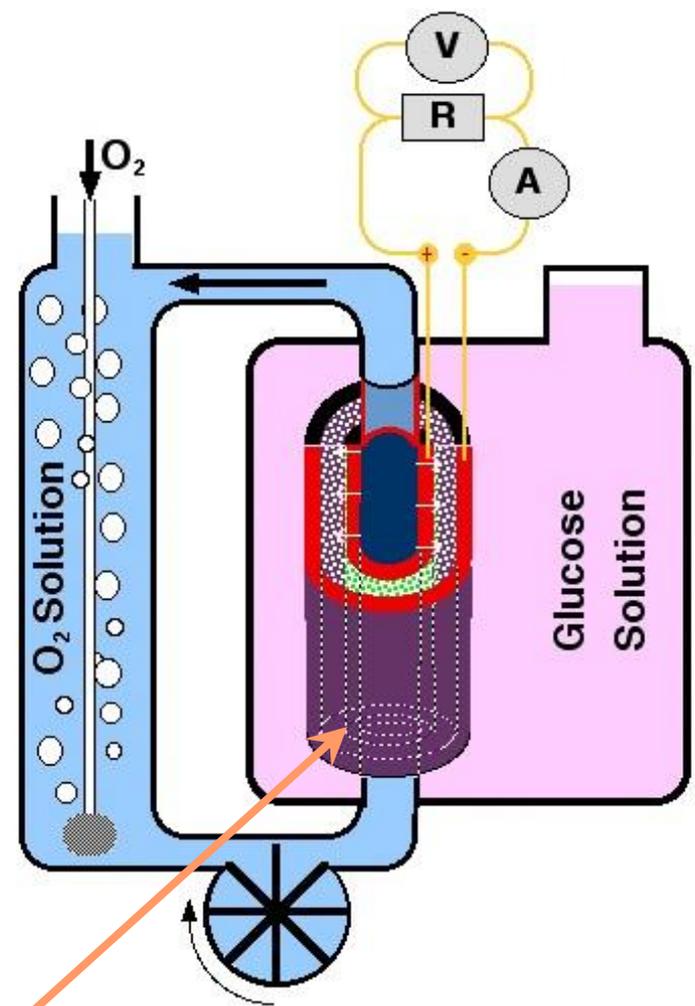
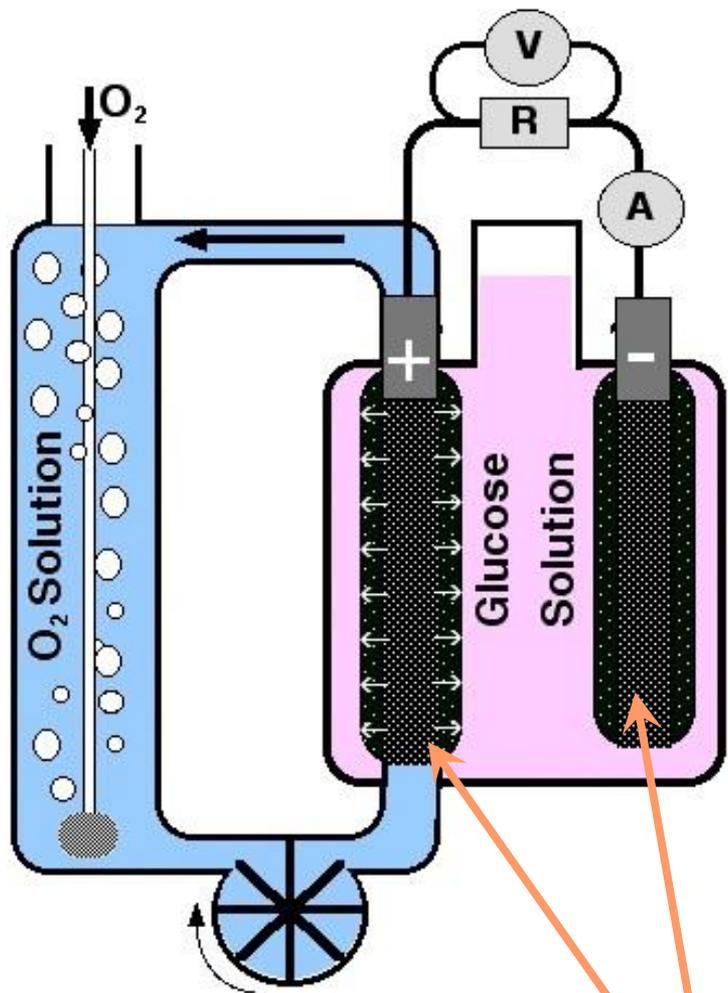


Orélis (Novosep Group)

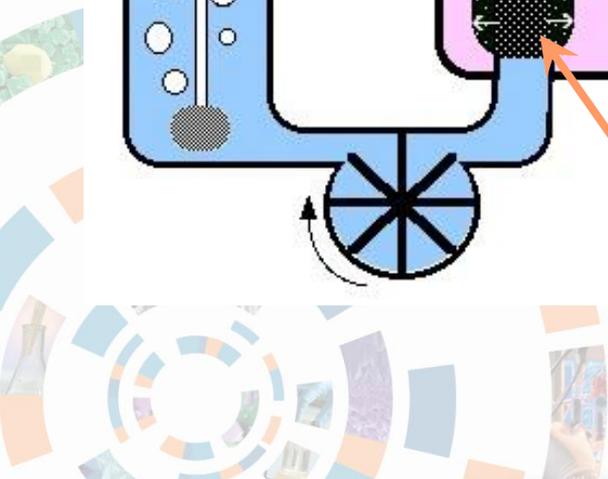
- Matrix = carbon porous tubes (pore diameter = 1-3 μm ,
- porosity 17%)



Prototypes

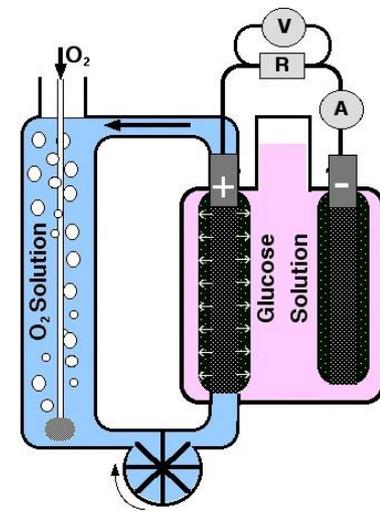


Tubular electrodes



Performances of the biofuel cell

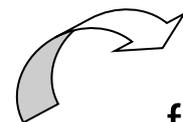
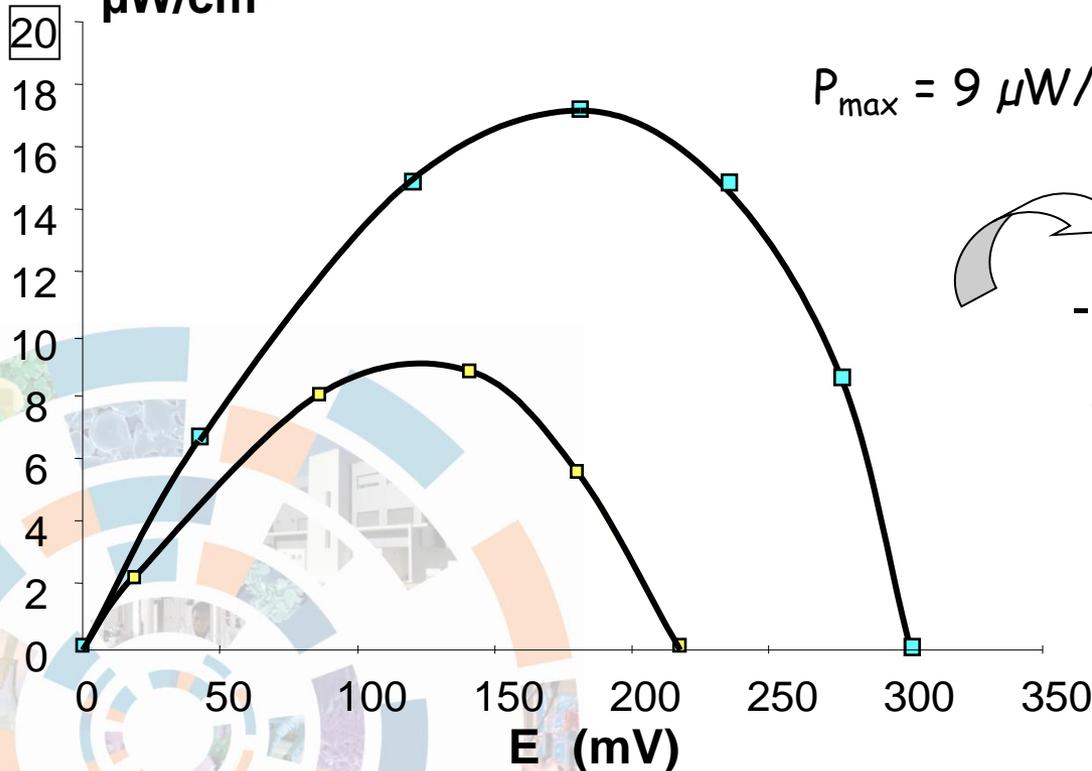
(GOD, Laccase)



Power density
 $\mu\text{W}/\text{cm}^2$

$P_{\max} = 18 \mu\text{W}/\text{cm}^2$ at 0.2 V; pH 7

$P_{\max} = 9 \mu\text{W}/\text{cm}^2$ at 0.13 V; pH 7



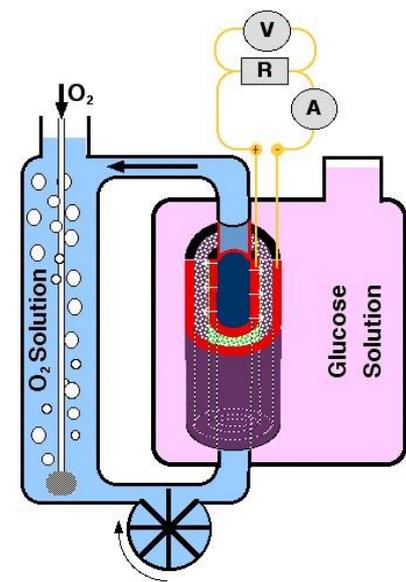
Tubular cathode

- favours O_2 reduction by enzyme
- limits its diffusion to the anode

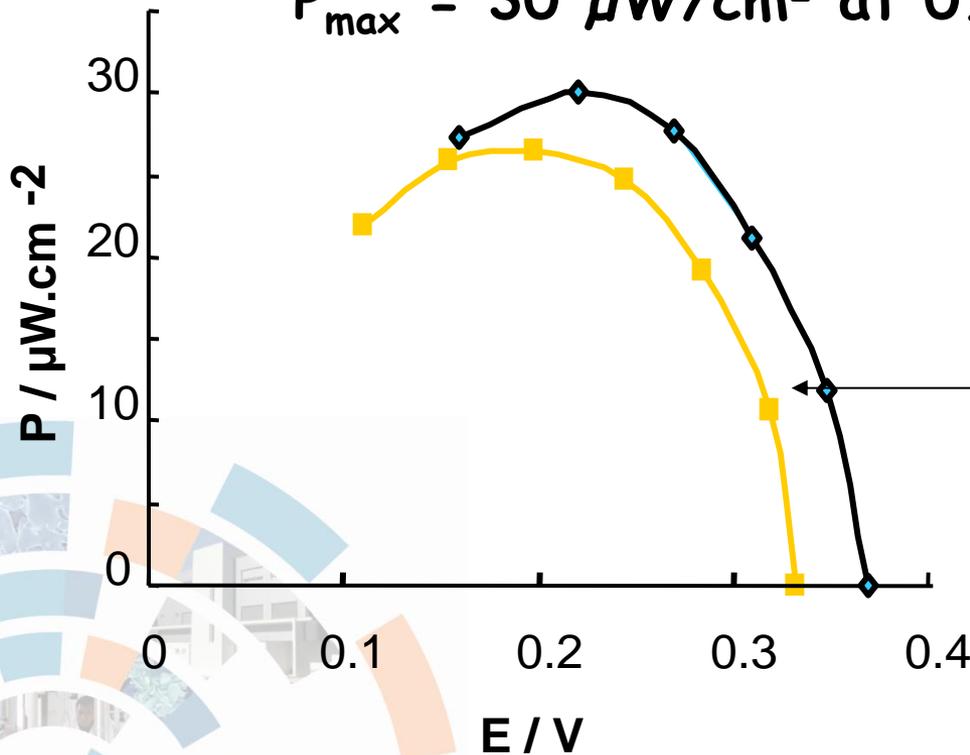
Conditions:
 37°C, pH 7
 10 mM Glucose

Performances of the concentric biofuel cell

(GOD, BOD)



$$P_{\max} = 30 \mu\text{W}/\text{cm}^2 \text{ at } 0.22 \text{ V}$$



After 3 hours of running

$P \sim 95\%$ of its initial value

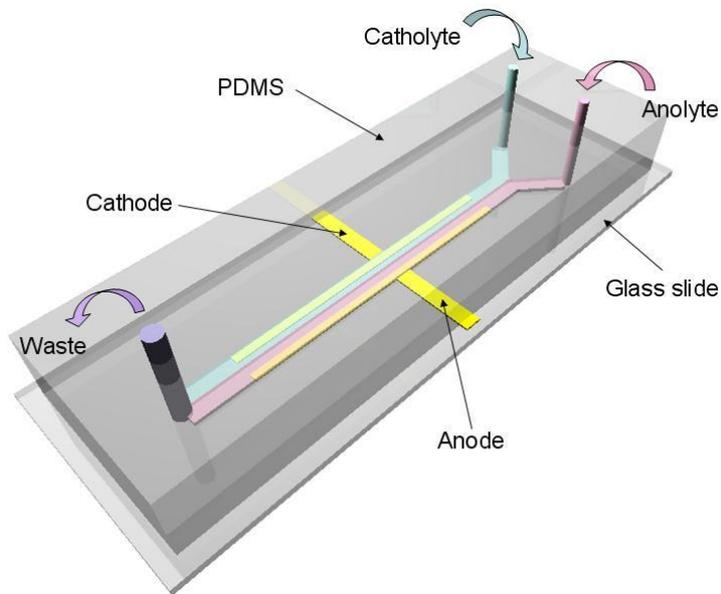
After 2 days of storage

Conditions:
37°C, pH 7.4
10 mM Glucose

Pile à combustible microfluidique

Intégration dans une puce microfluidique :

- des fonctions relatives à la distribution et l'évacuation des fluides
- des composants (électrodes, catalyseurs)
- des réactions électrochimiques



Nombre de Reynolds, $Re = U \cdot D_h / \nu$

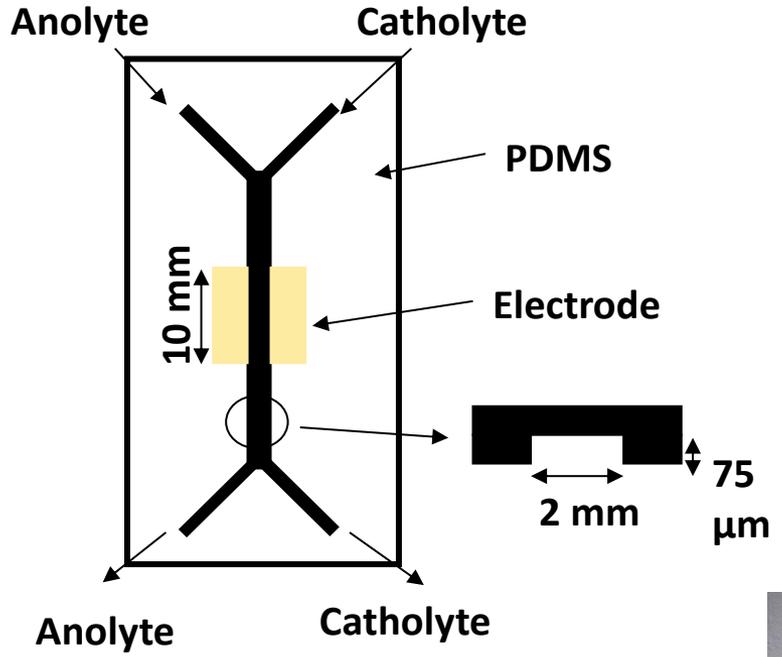
U vitesse moyenne du fluide
 D_h diamètre hydraulique
 ν viscosité cinétique du fluide

**Re < 2000: régime laminaire
de distribution du fluide**

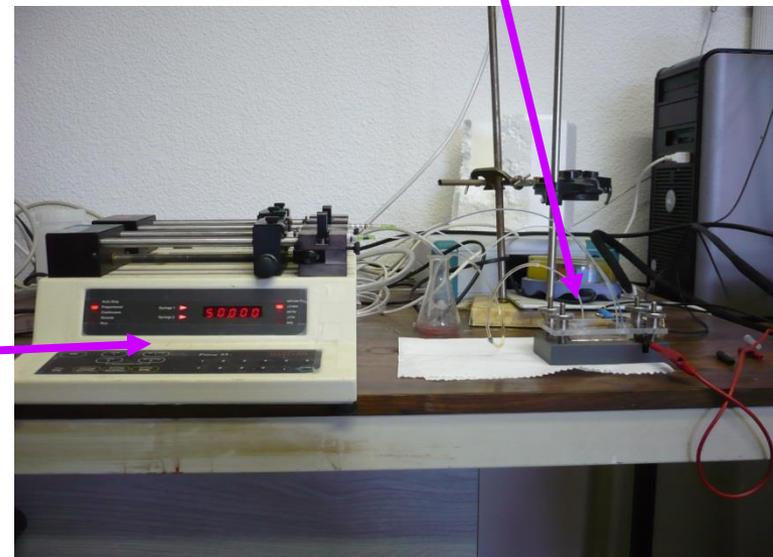


Ecoulement en parallèle du combustible et du comburant sans mélange convectif dans un monocanal microfluidique

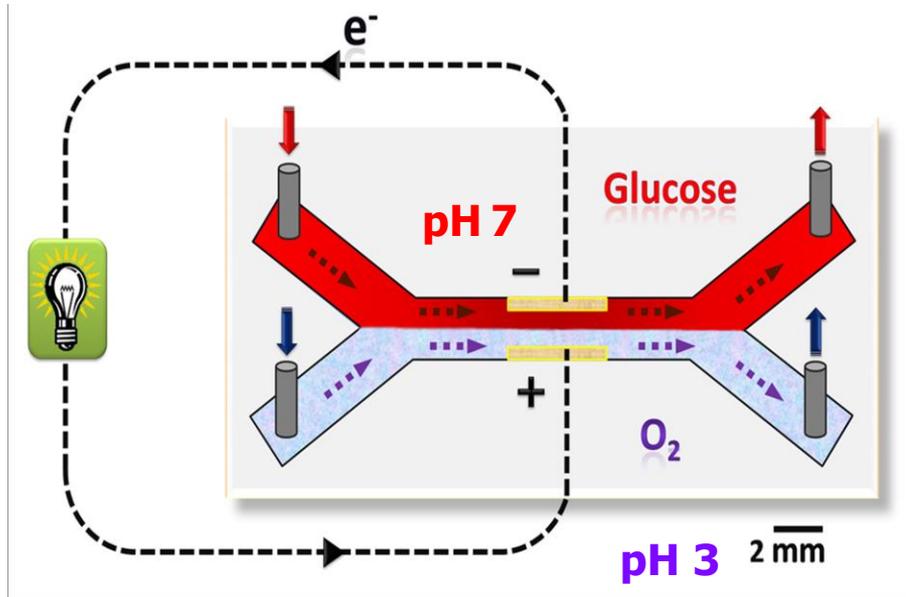
Microfluidic concept: biopile glucose/O₂



syringe pump



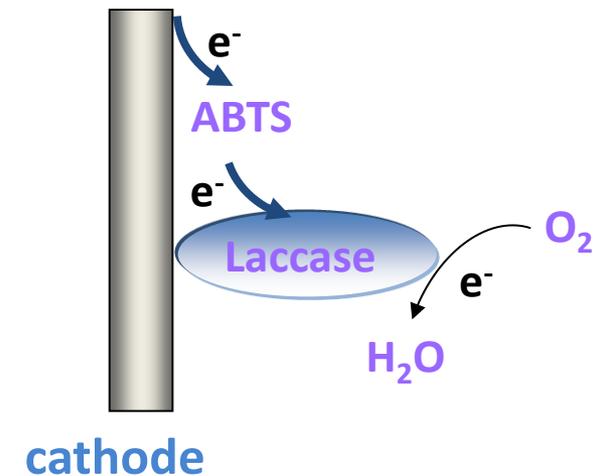
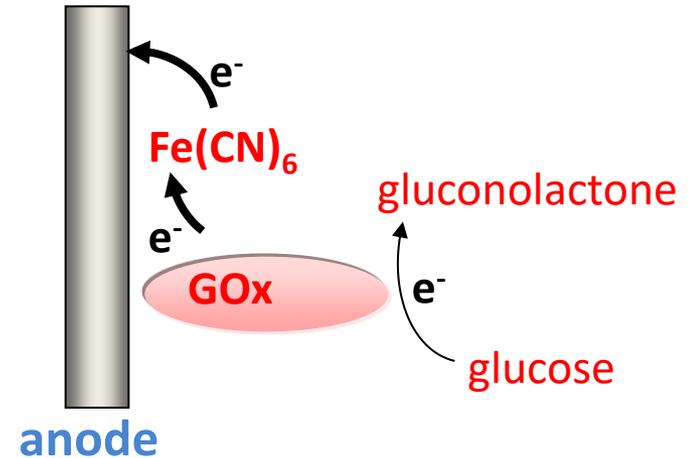
1. Biopile glucose/O₂



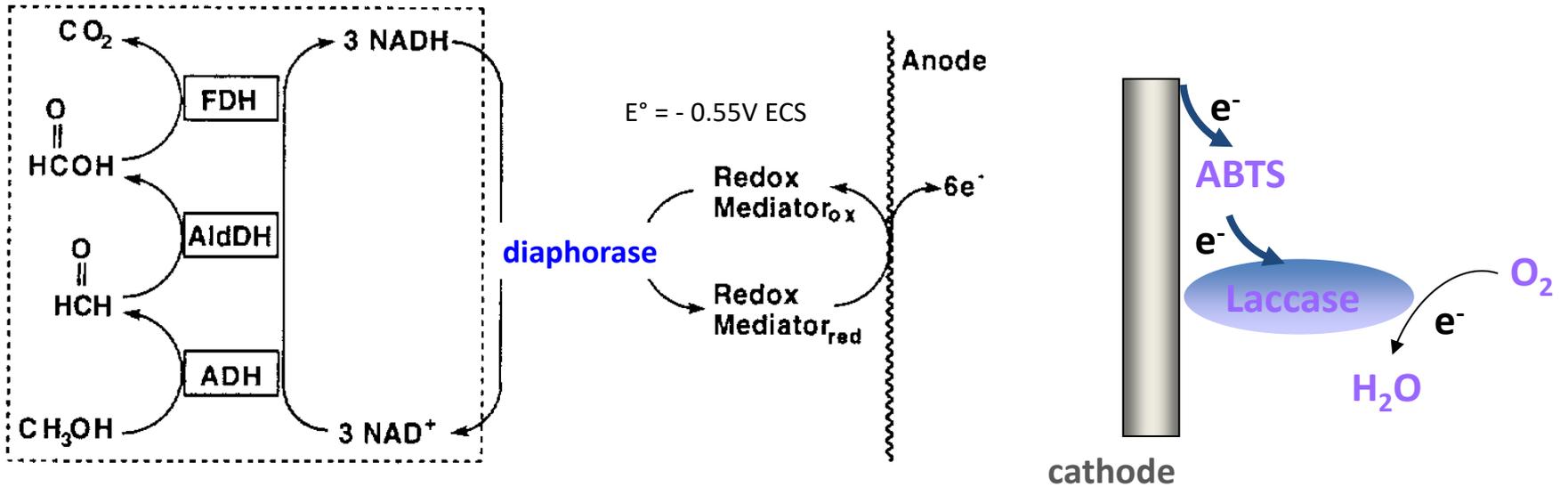
➤ Introduction des solutions sous flux

➤ Mesure de la caractéristique courant/tension en fonction :

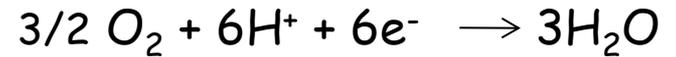
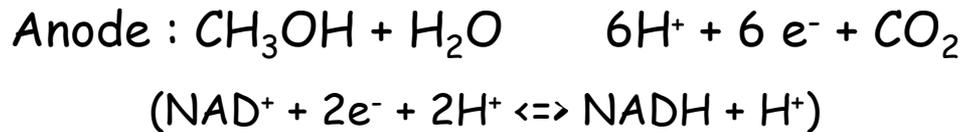
- des conditions chimiques (pH en particulier)
- du flux de comburant et combustible
- de la géométrie des électrodes
- de l'immobilisation ou non du catalyseur



2. Biopile microfluidique méthanol/O₂



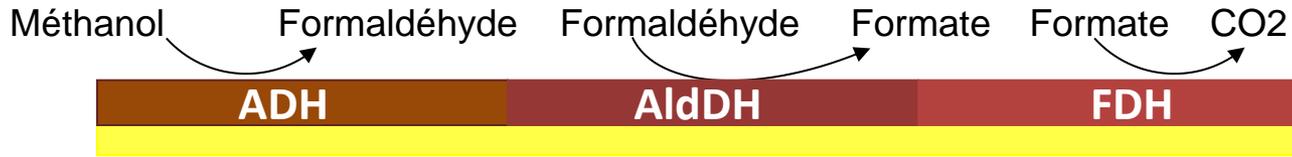
$E^\circ = -0.6V \text{ ECS}$



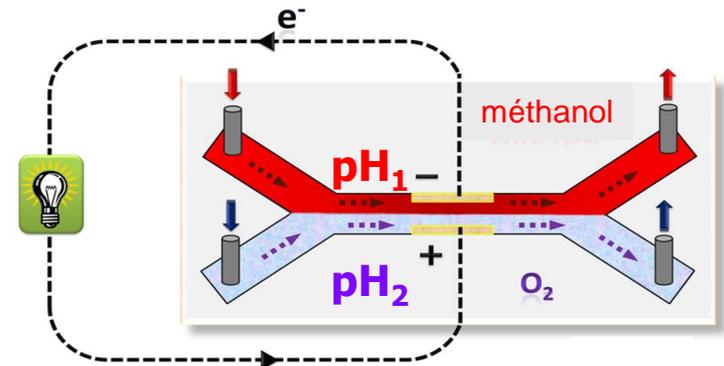
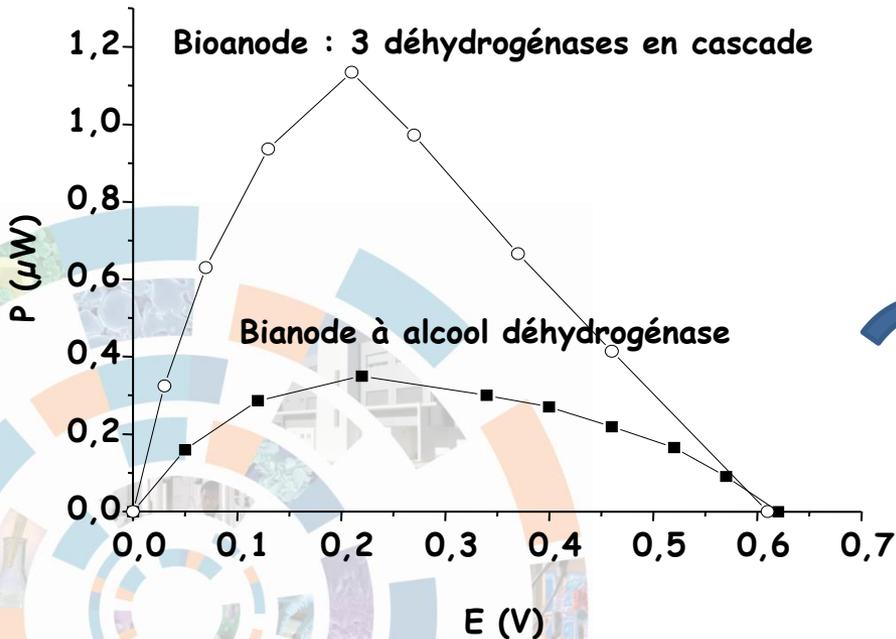
Autres travaux :

- Ethanol/O₂ : oxydation de l'éthanol en acétate en 2 étapes (Minteer et al.)
- Glycerol/O₂ : oxydation du glycérol en CO₂ en 3 étapes (Minteer et al.)

MicroBiopile à alcool



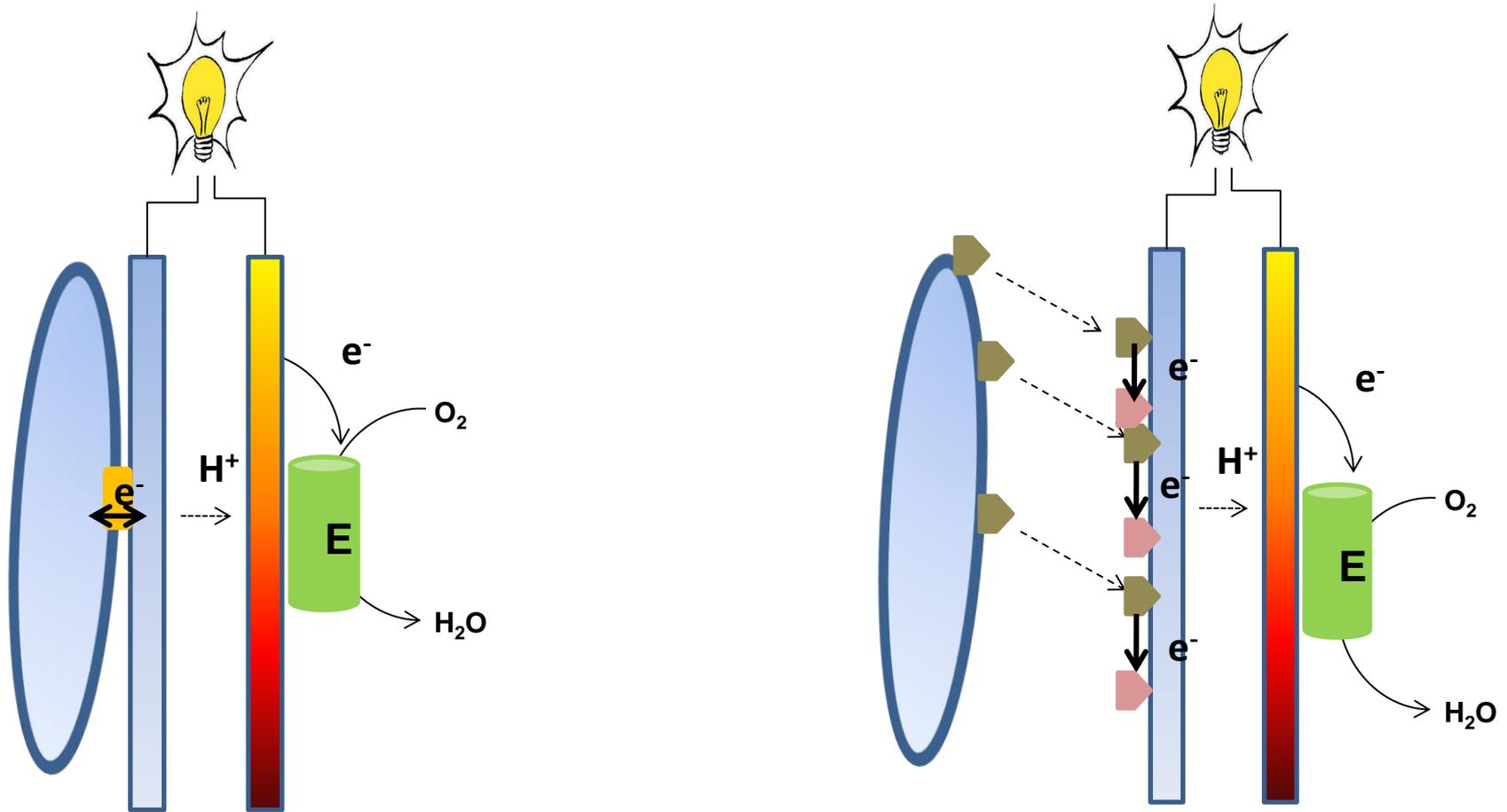
Déhydrogénases, laccase et ABTS encapsulés dans un film de poly-L-lysine
 NAD⁺, BV²⁺ et diaphorase en solution



Augmentation de la puissance
 d'un facteur 3

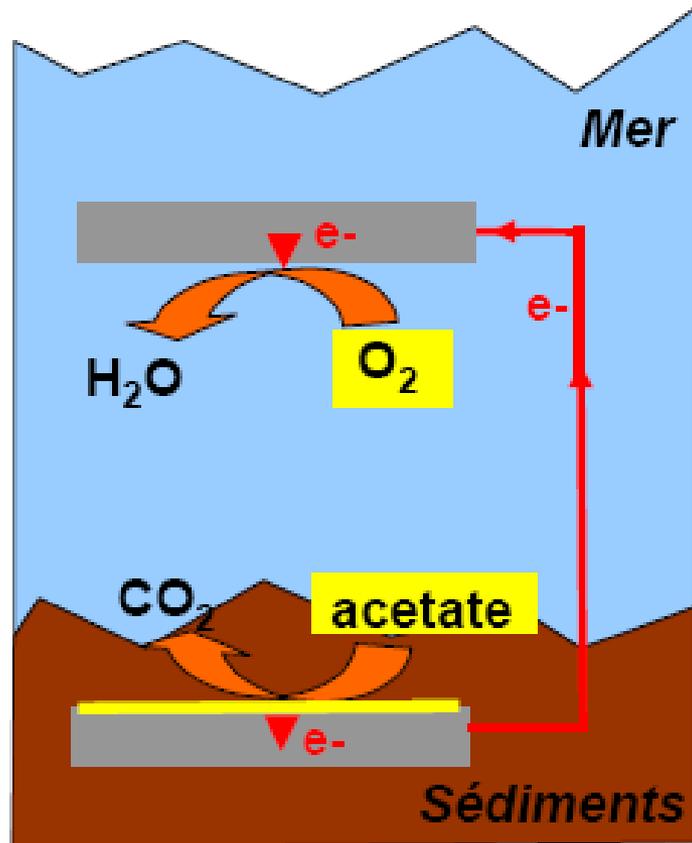
Des enzymes aux micro-organismes

Connexion de bactéries, levures, ... sur électrode



Evacuer les électrons du métabolisme vers l'électrode

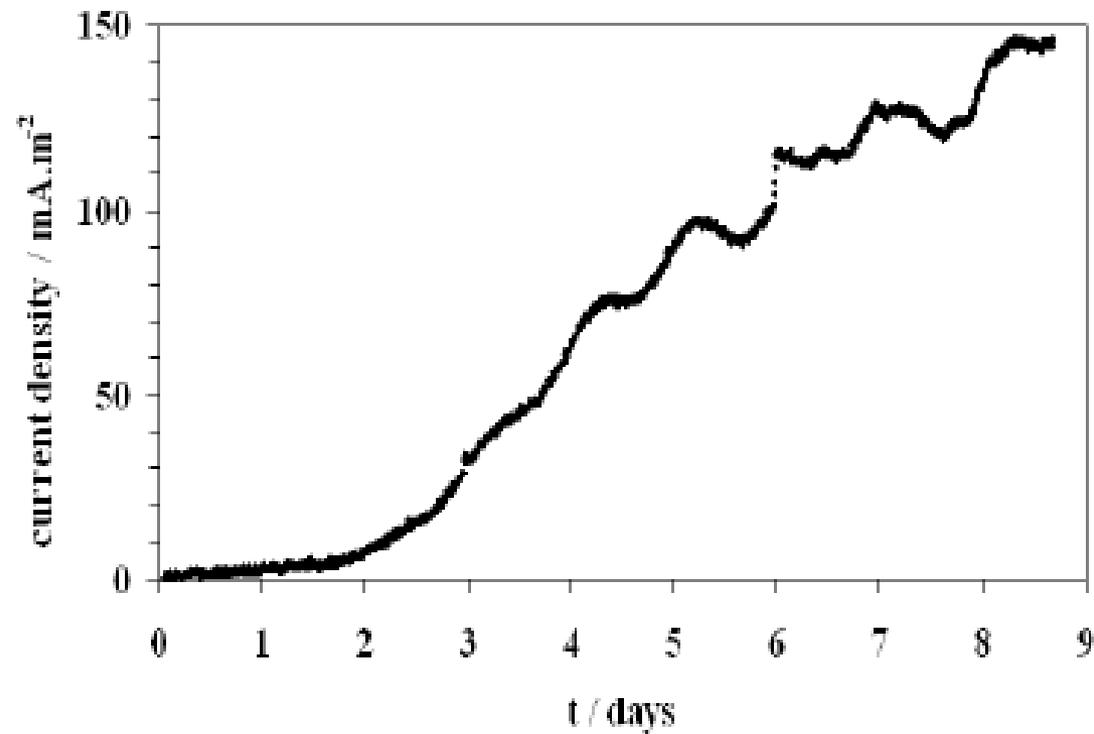
Naissance du concept de biofilm électroactif



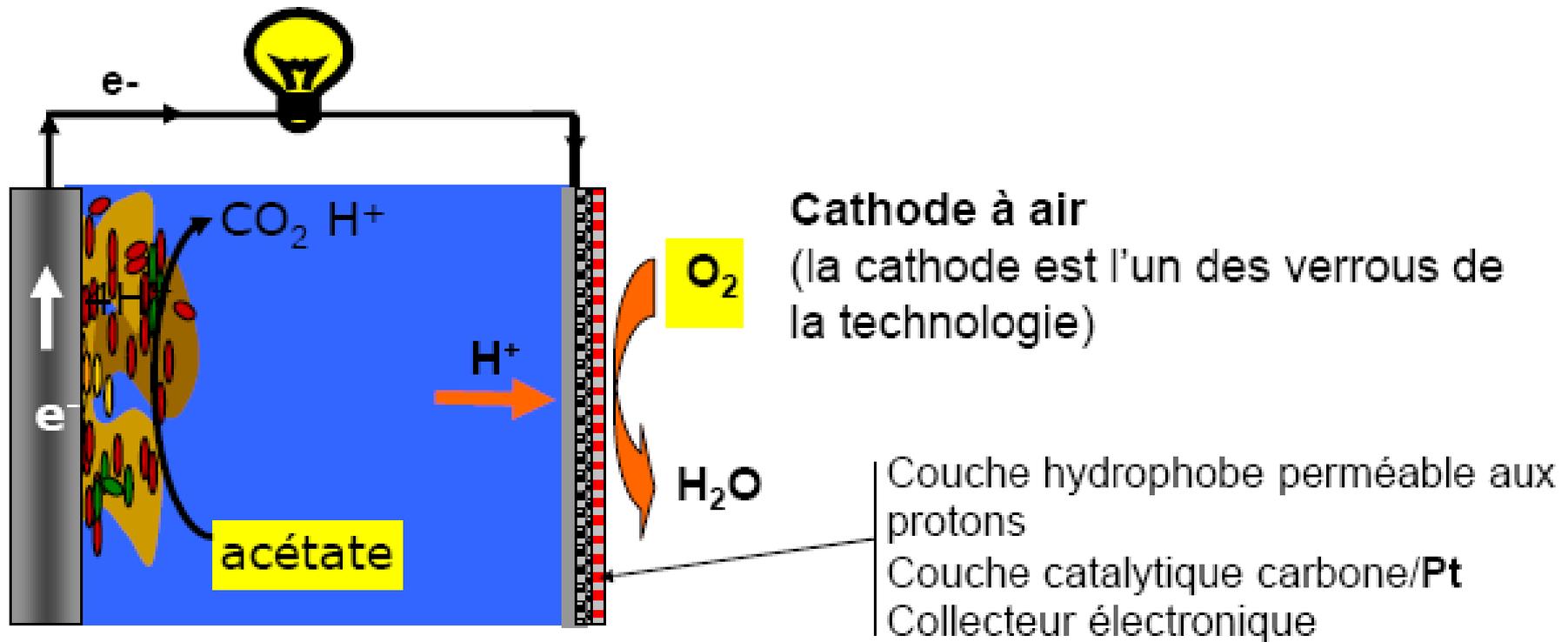
D.R. Bond et al., *Science* 295 (2002) 483

L.M. Tender et al., *Nature Biotechnology* 20 (2002) 281

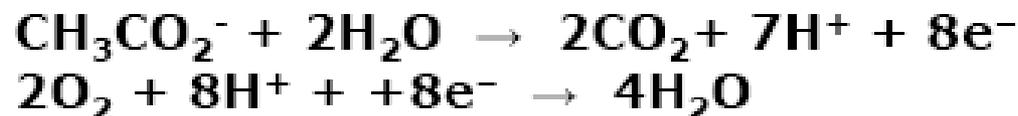
La croissance du courant est due à la formation d'un biofilm sur l'anode qui catalyse l'oxydation d'acétate



PAC microbiennes: Le dispositif le plus utilisé



Anode
 Cathode

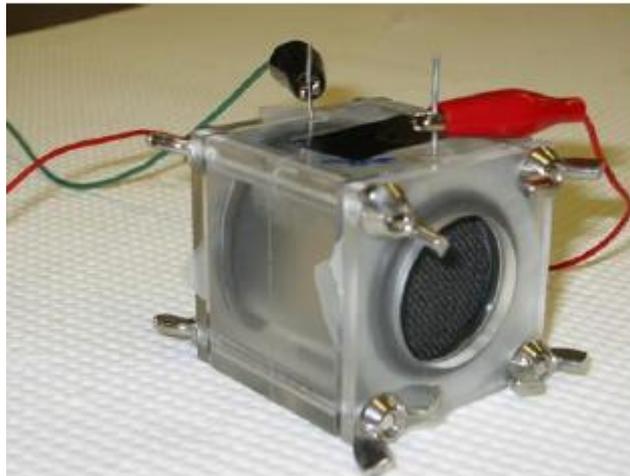


Anode volume (mL)	Synthetic or real wastewater substrate type [b]	Concentration (mg/L) [c]	Maximum power [d]	External resistor (Ω) [e]	Coulombic efficiency (%) [f]
560	Acetate	458	48 W/m ³	20	98
40	Glucose	2000	3600 mW/m ²	<100	89
240	Glucose	NP [g]	4310 mW/m ²	<100	81
390	Glucose	467	35 W/m ³	20	74
22	Acetate	1000	286 mW/m ²	33	65
22	Butyrate	1000	220 mW/m ²	33	50
 390	Hospital wastewater	332	25 W/m³	NP [g]	36
28	Acetate	800	506 mW/m ²	218	29
22	Starch	1000	242 mW/m ²	33	21
28	BSA	1100	354 mW/m ²	>50	20.6
 390	Municipal wastewater	429	10 W/m³	75	20
22	Dextran	1000	150 mW/m ²	33	17
440	Sucrose	800	29 W/m ³	20	14.2
22	Glucose	1000	212 mW/m ²	33	14
520	Sucrose	1000	170 mW/m ²	66	8.1
28	Swine waste (soluble fraction)	8320	261 mW/m²	200	8
28	Butyrate	1000	305 mW/m ²	1000	7.8
 22	Municipal wastewater	379	72 mW/m²	470	6
28	Peptone	500	269 mW/m ²	>50	6.0
 28	Slaughterhouse wastewater	1420	80 mW/m²	>50	5.2
5400	Brewery wastewater	1168	5 W/m³	10	3.6

PAC microbiennes de laboratoire

PaCM dite à un seul compartiment
(28 mL) avec cathode à air

B.E. Logan Penn State university



PAC microbiennes benthiques

Sediment MFC, benthic unattended generator (BUG)

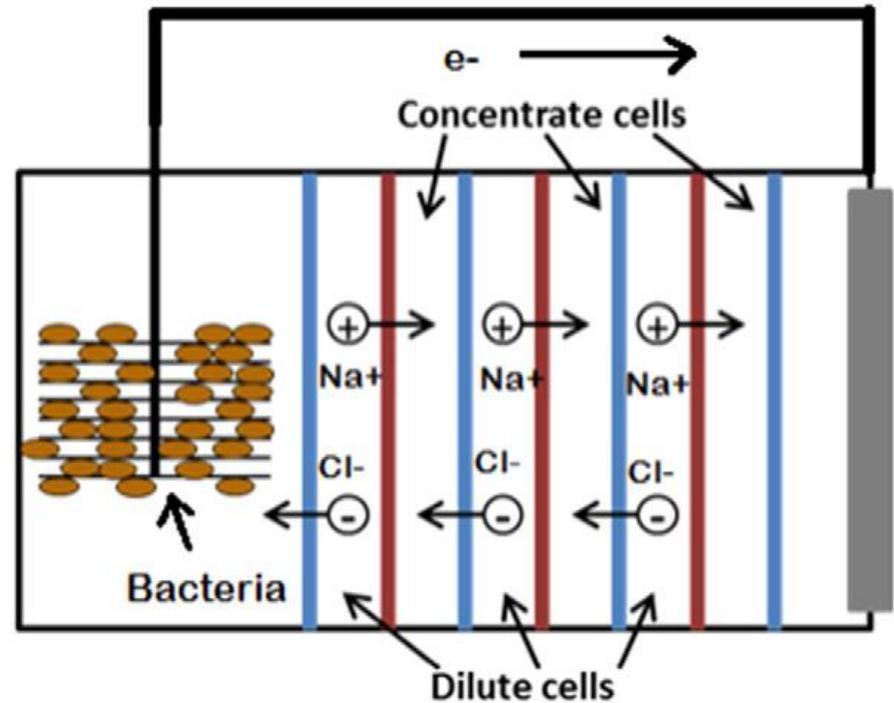
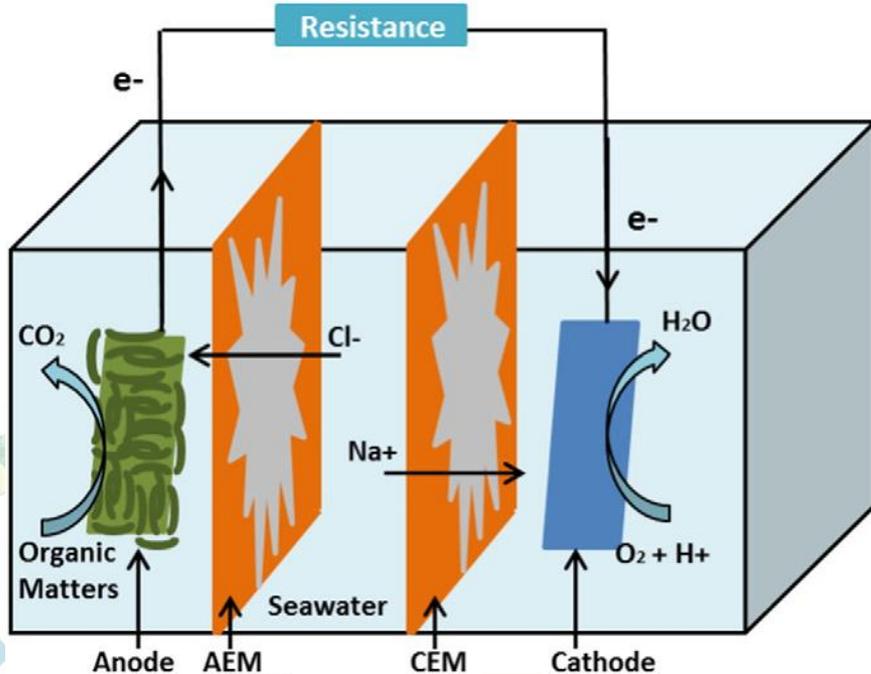


Resistor with connections to
real-time monitoring devices

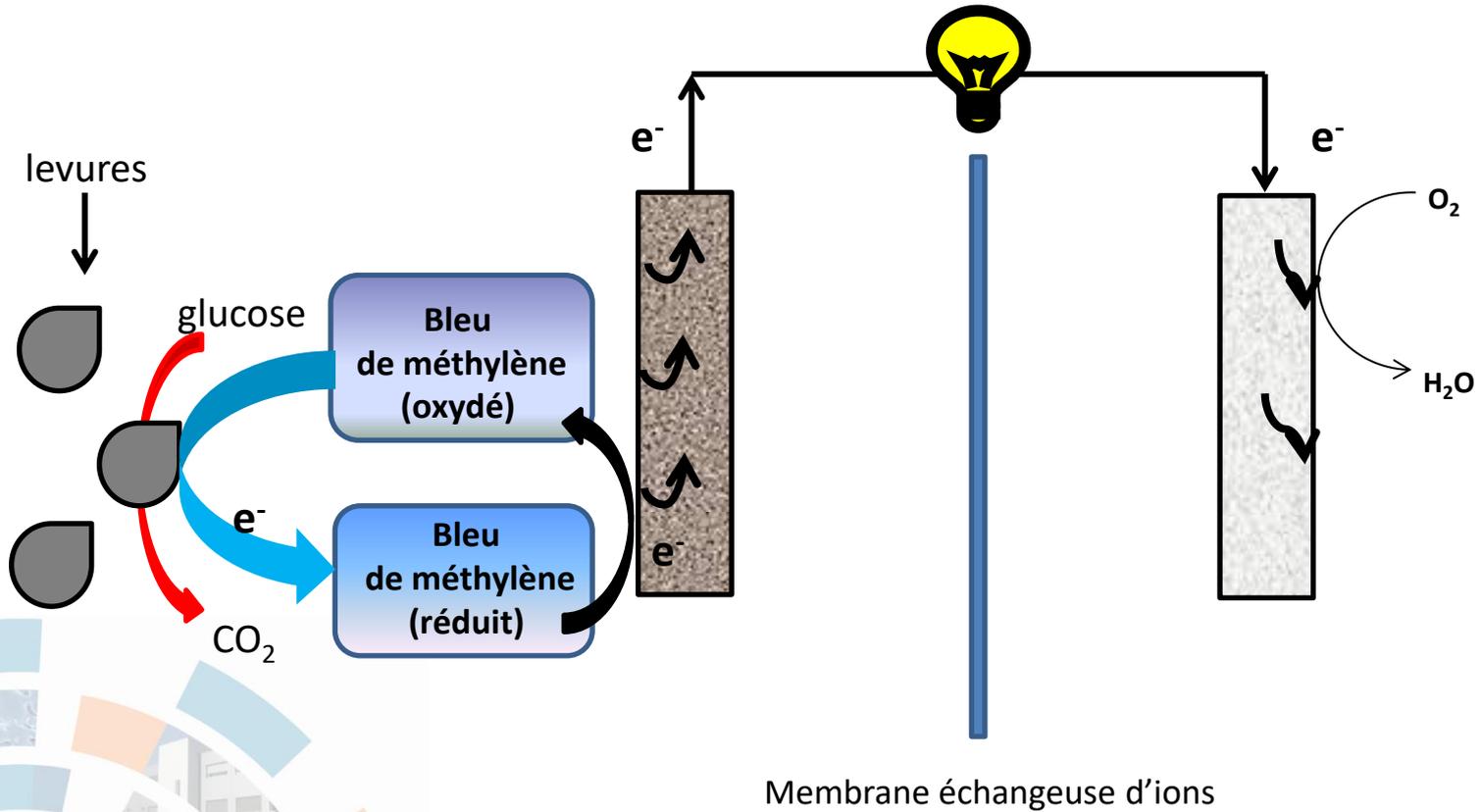
Cathode to be positioned in the
overlying water

Anode to be buried in mud

Microbial fuel cell application: Water desalination

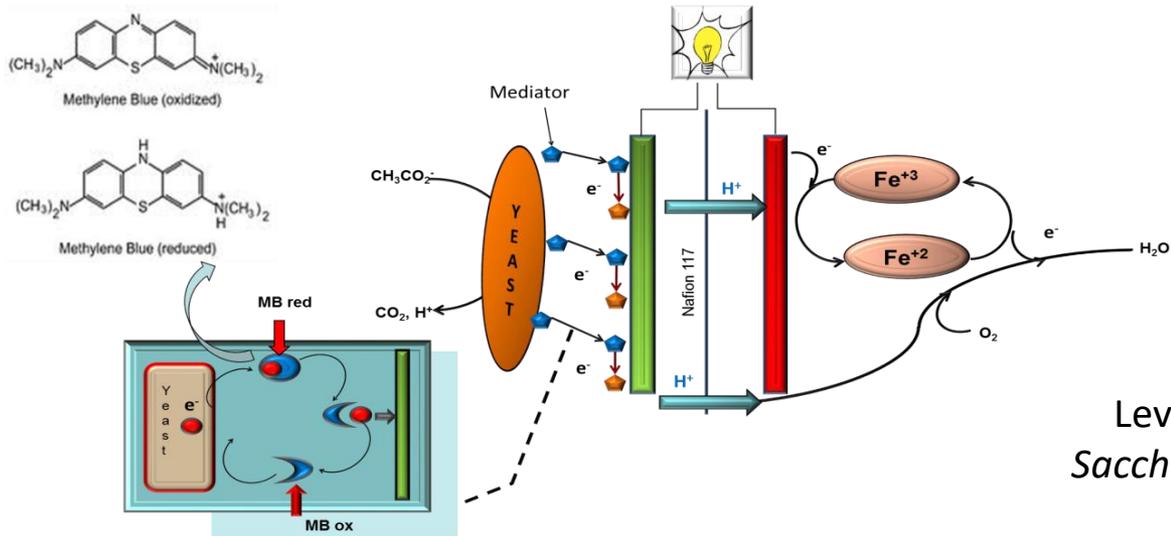


Biopiles à levure

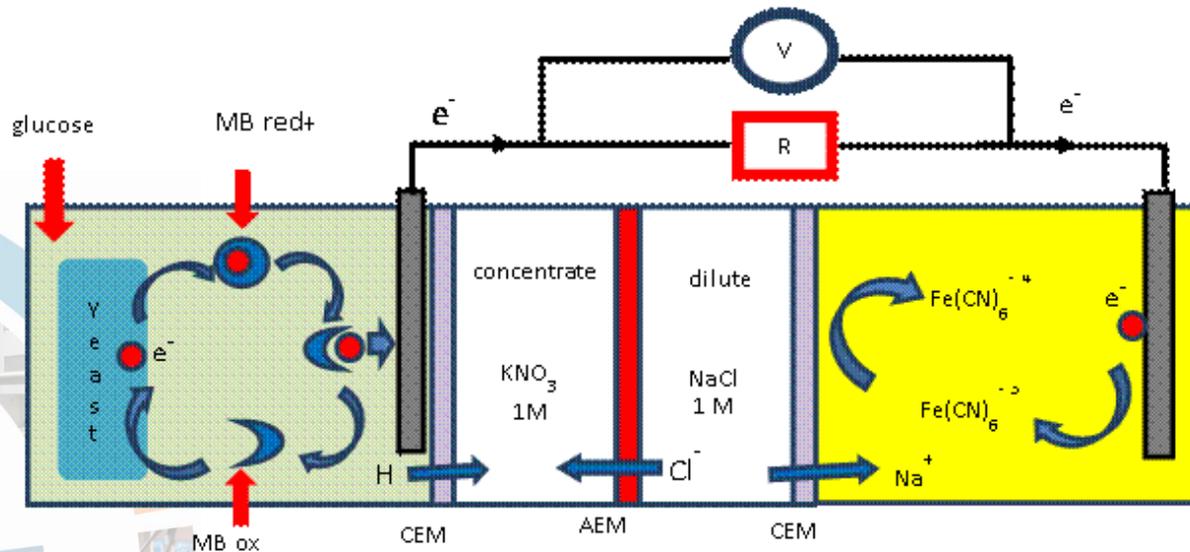


Levure du boulanger: [Saccharomyces cerevisiae](#)

Biopiles à levures:



Levure du Boulanger:
Saccharomyces cerevisiae

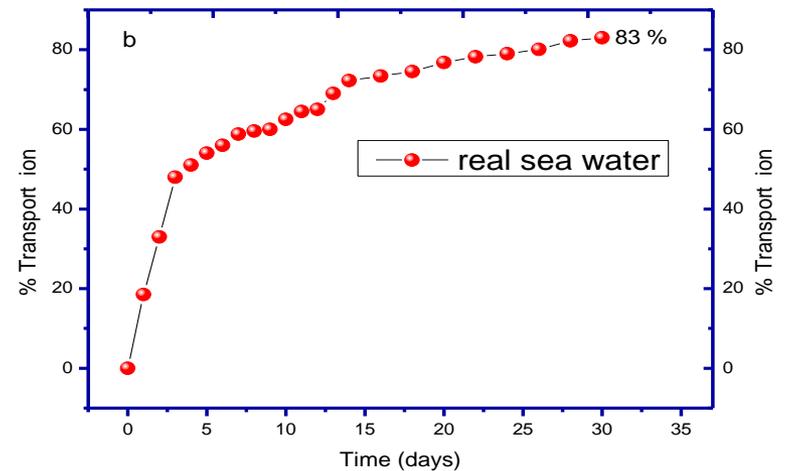
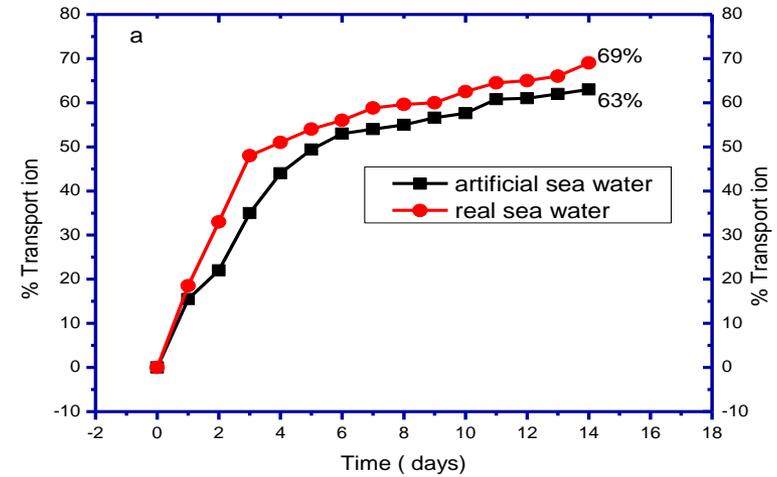
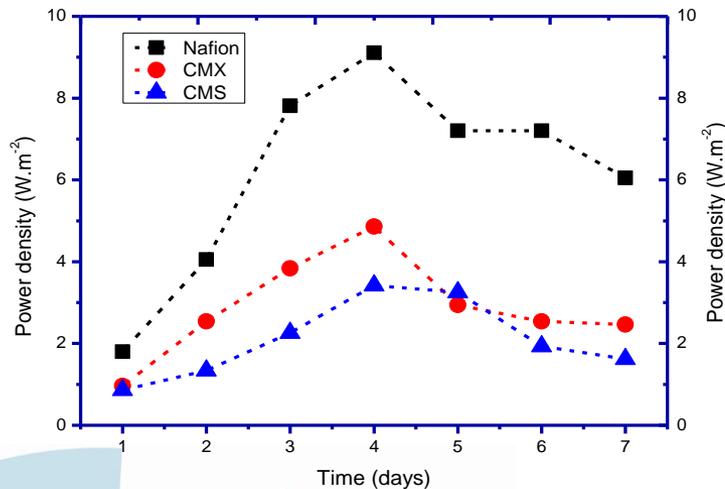


Desalination of seawater with biofuel cell:



Sea water treatment

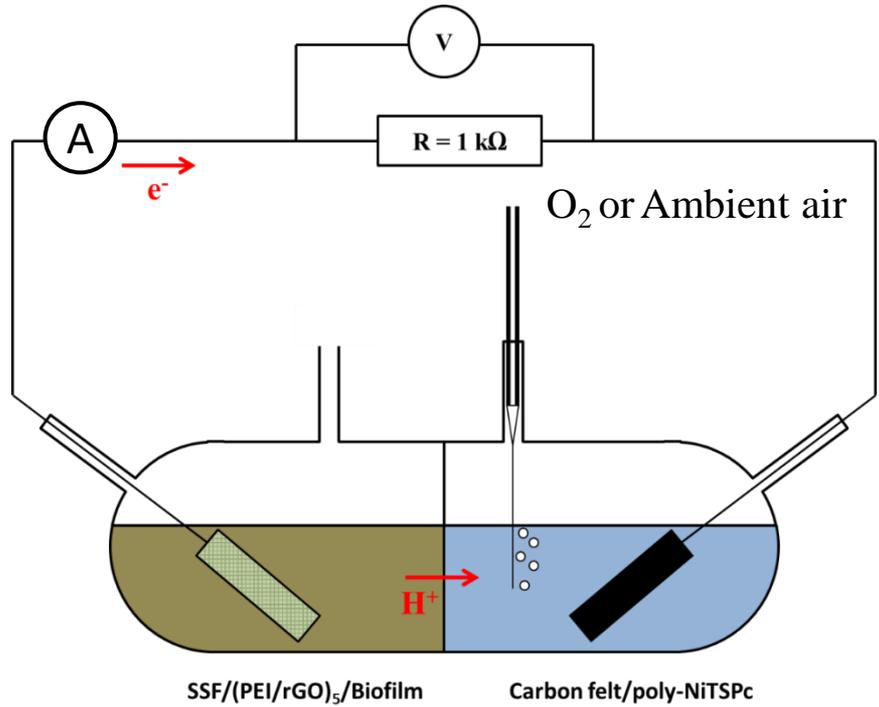
Influence of ion exchange membranes



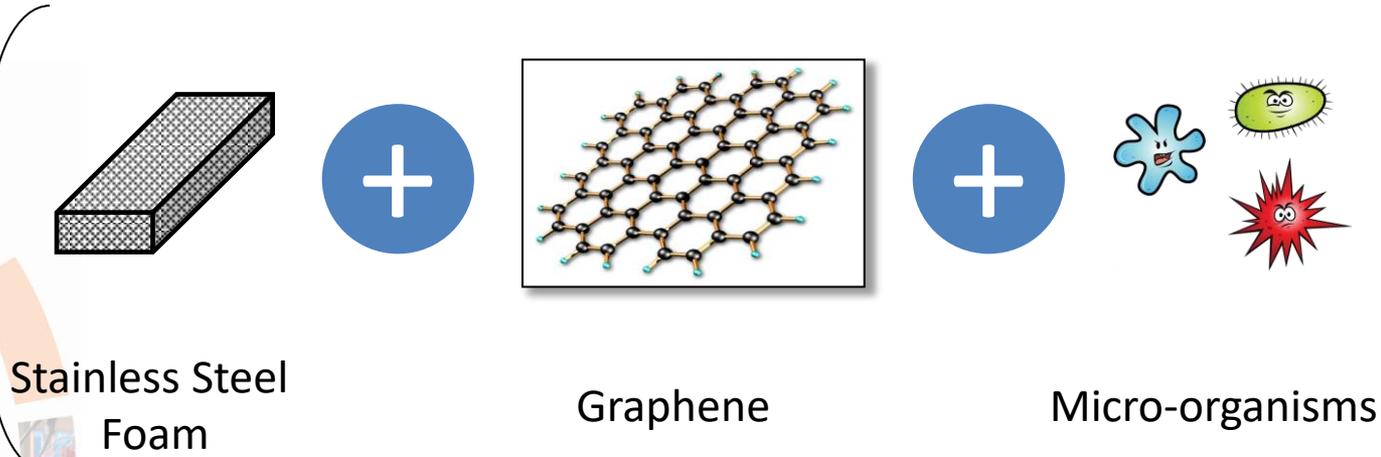
Biopile à base de terreau de jardin

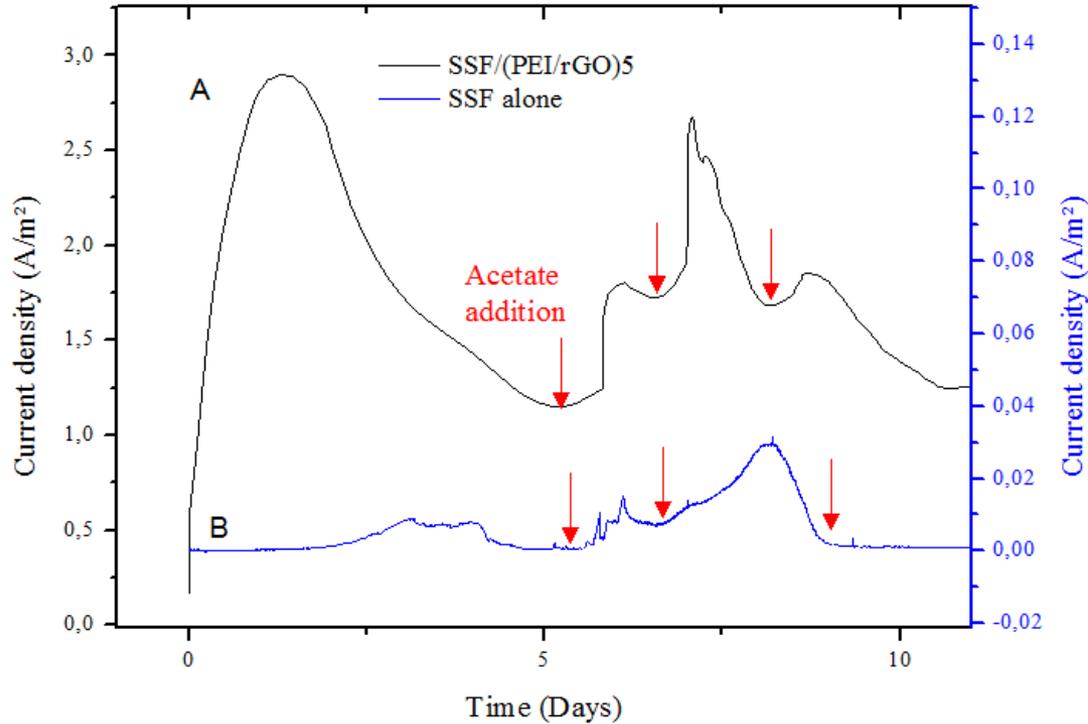


Inoculum: lixiviat de terreau



Bio-Anode

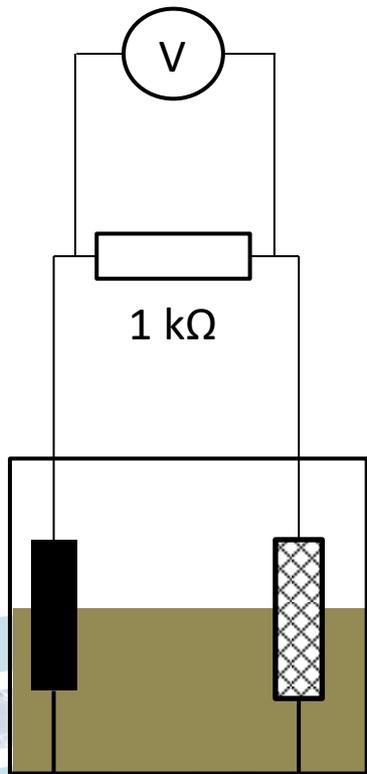




Polarization at -0,246 V vs Ag/AgCl
 in a 3 electrodes system
 Medium: compost garden leachate
 + acetate (20 mM)
 Counter electrode: graphite

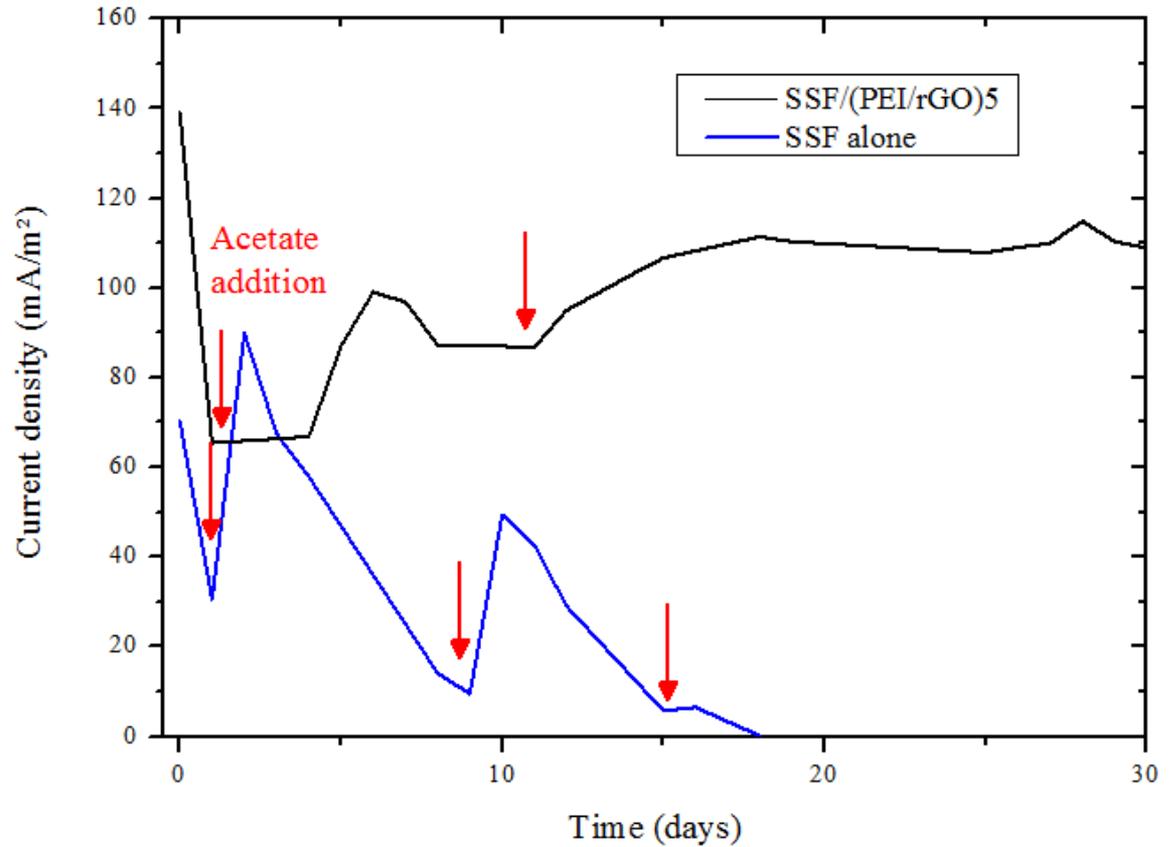
Augmentation du courant après ajout d'acétate.





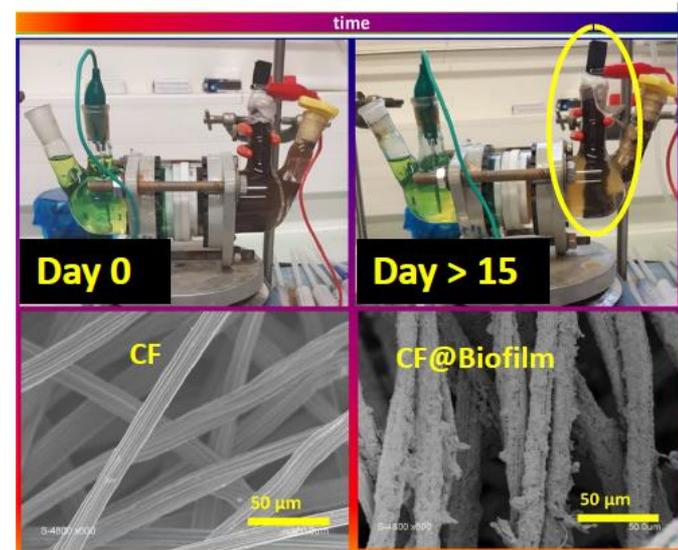
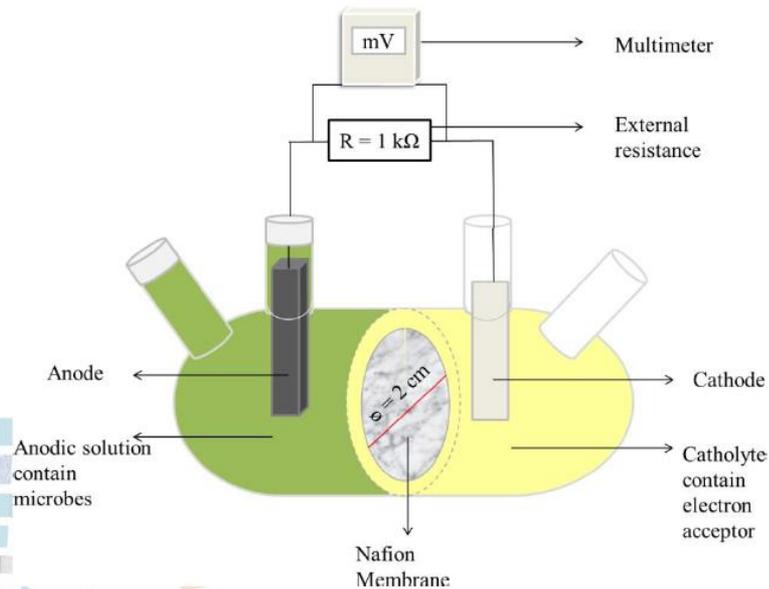
Graphite

Working
electrode



Dispositif expérimental

Cellule de mesure



On the cathode:

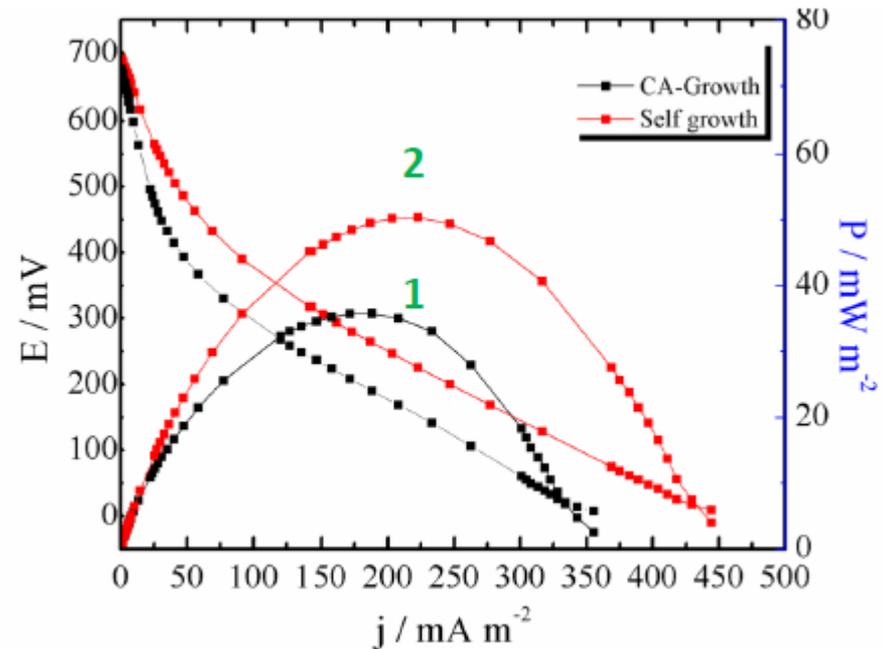
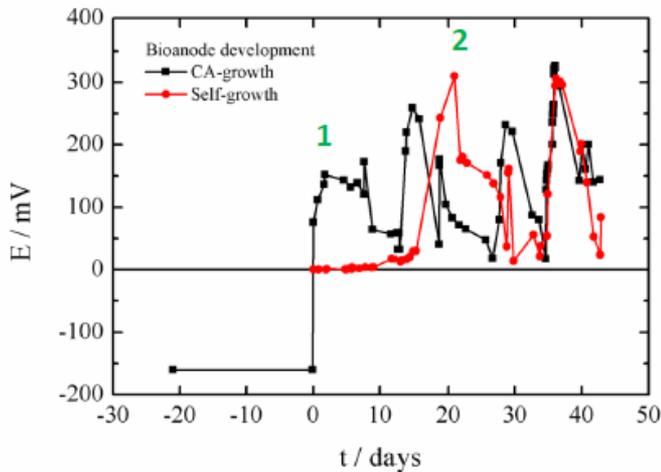
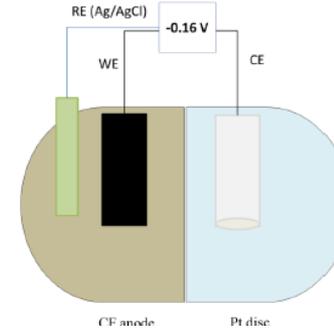


Formation de biofilm Electroactif

Comparaison de 2 méthodes:

1) Potentiel appliqué

2) Croissance autonome sur circuit fermé

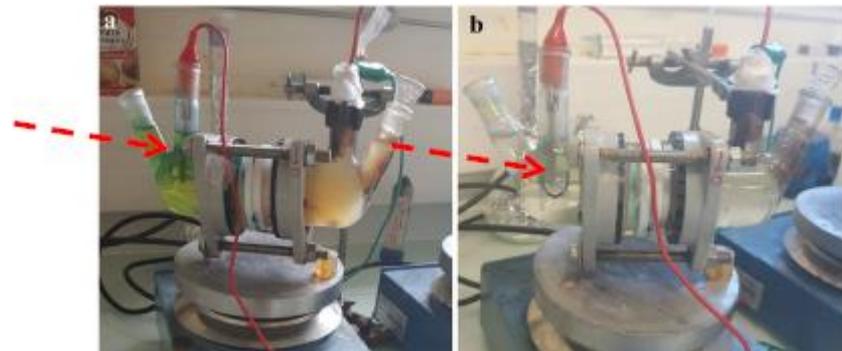


Conclusion: Croissance autonome est plus efficace

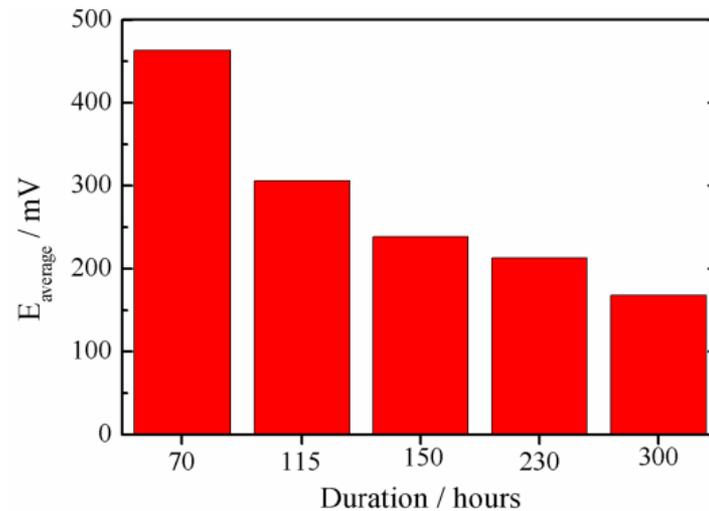
Compartiment cathodique

Accepteur d'électrons :
Potassium Ferricyanide

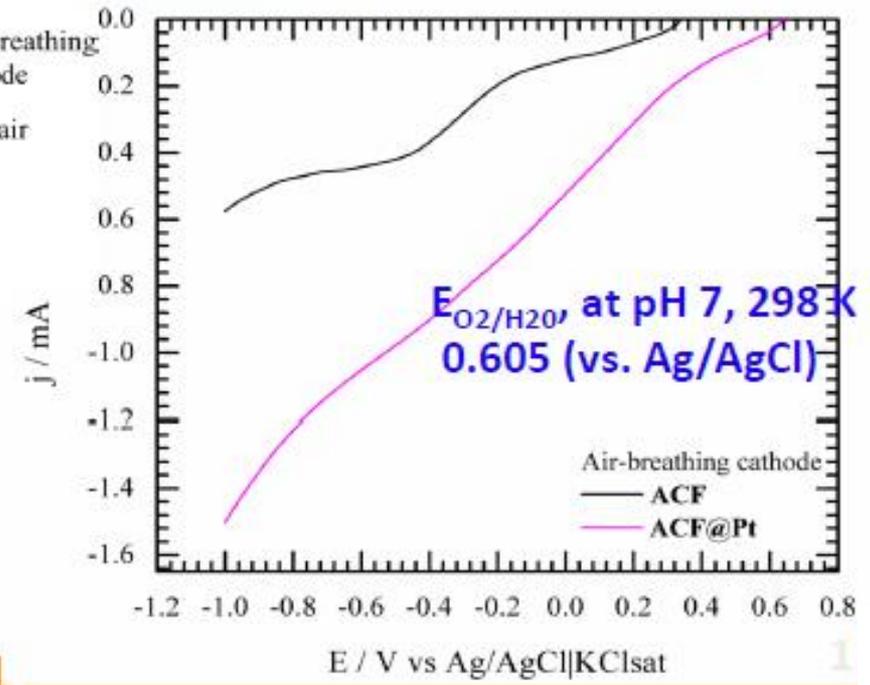
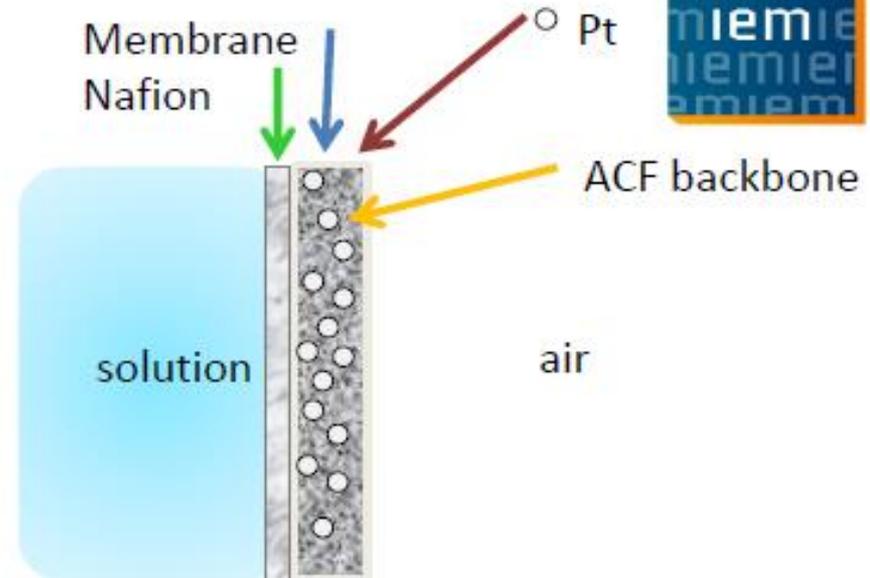
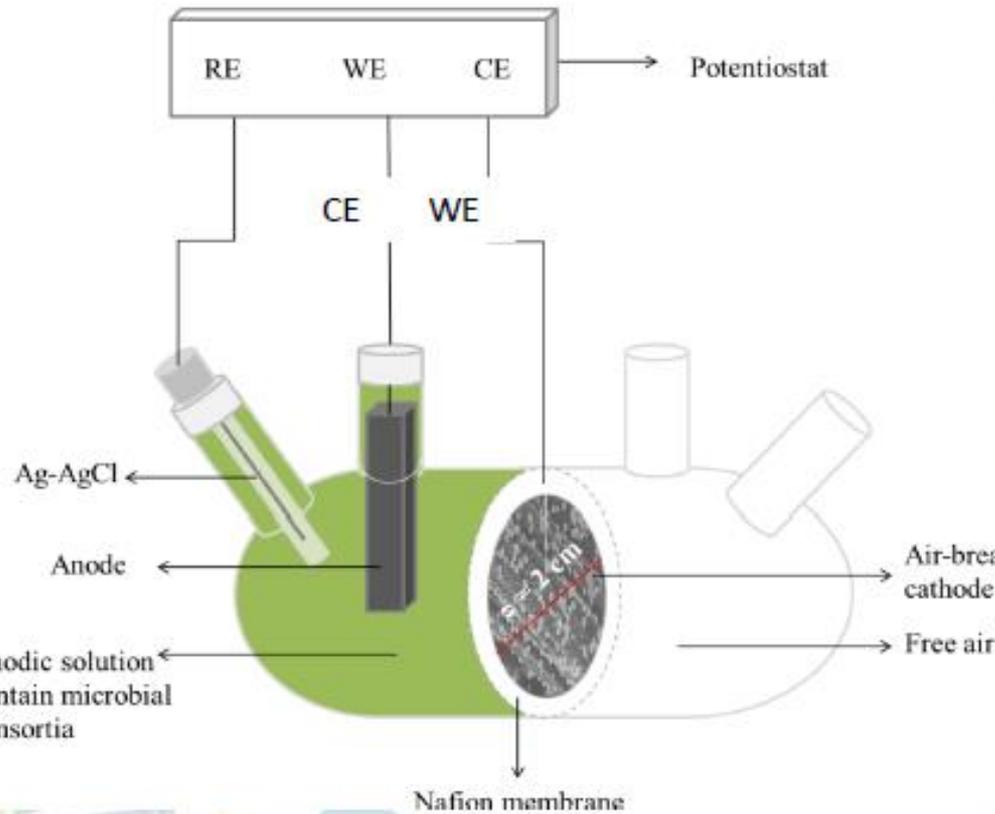
Observation:
Décoloration de la solution



Stabilité de la biopile:



Air-breathing cathode installation



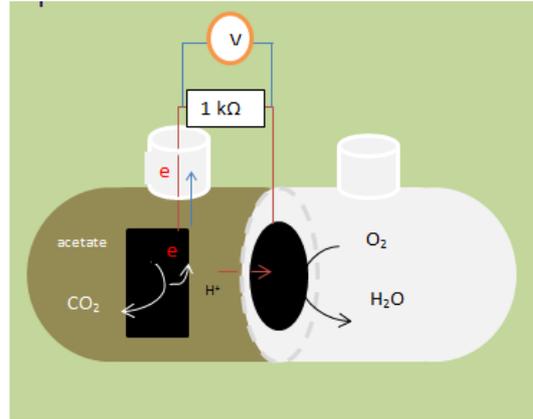
Garden compost leachate + 20 mM acetate, pH 6.5

Comparaison cathode à air et cathode conventionnelle

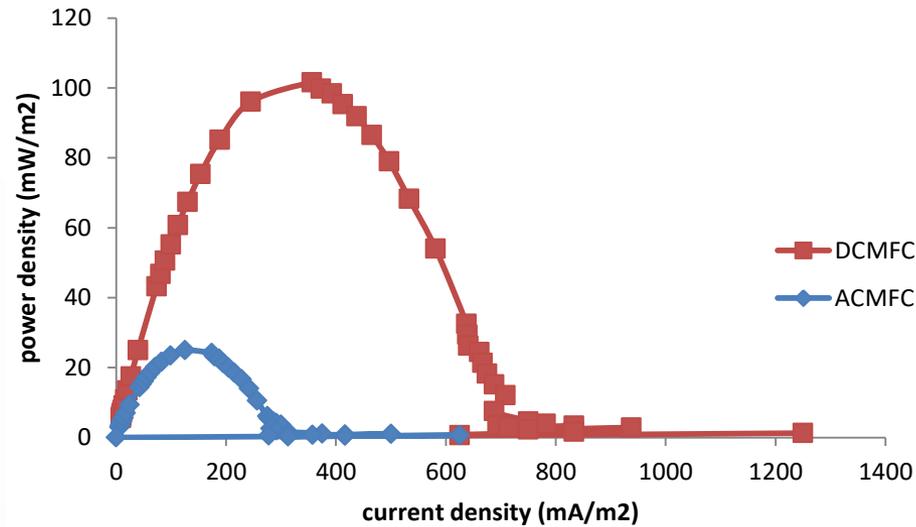
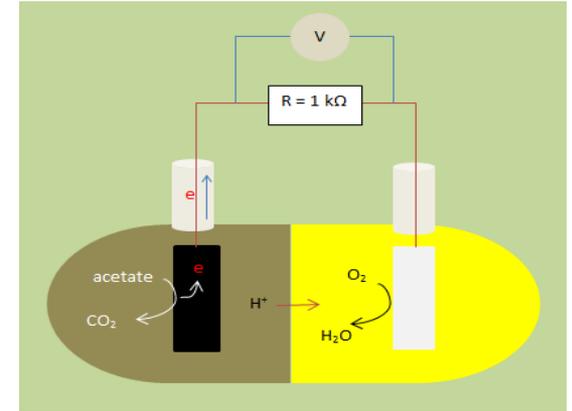
Microbial source:
garden compost with 60 mM KCl

Substrate: acetate, 20 mM

ACMF



DCMF



Conclusion

Biopiles : Source alternative d'énergie pour la production d'électricité

Solution « développement durable », respectueuse de l'environnement

Faibles puissances délivrées :



Miniaturisation pour des applications portables