BIOFUEL CELL: An alternative Method for energy production?

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What is biofuel cell?

Biofuel cell ~ Fuel cell

System using catalysts to convert chemical energy directly in electric current.

Originality = catalysts are biological

- enzymes
- cells
- microorganisms
Principle

- **Combustion** (O₂, H₂O₂...)
- **Fuel** (H₂, methanol, organic acids, glucose...)
- **Oxidation product** H₂O

**Conductive electrodes**
(colecting and carrying e⁻)

**Bio-cathode**
**Bio-anode**

**Electrolyte medium**
(transporting ions between electrodes)
## Fuel Cell / Biofuel Cell Performances

<table>
<thead>
<tr>
<th>Fuel cells</th>
<th>Medium</th>
<th>Power released</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkaline</td>
<td>80°C, KOH concentrated</td>
<td>100 mW/cm²</td>
</tr>
<tr>
<td>polymer membrane</td>
<td>80°C, Nafion</td>
<td>200-350 mW/cm²</td>
</tr>
<tr>
<td>solid electrolyte</td>
<td>900-1000°C, solid oxide ceramic</td>
<td>200-350 mW/cm²</td>
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<tr>
<td>methanol/O₂</td>
<td>ambient T°, neutral pH (physiological serum)</td>
<td>680 μW/cm²</td>
</tr>
<tr>
<td>glucose/O₂</td>
<td>selective catalytic activity</td>
<td>4-830 μW/cm²</td>
</tr>
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Potentials Applications

in medicine:

Medical implants
Integrable into medical devices (Sensors, Drug delivery…)

in computing and communication:

Micro-chips, portable power supplies for mobil phone or laptop computer
(systems releasing low powers on long time periods, and micro-engines realization)
### Assets and Weaknesses

<table>
<thead>
<tr>
<th>Assets</th>
<th>Weaknesses</th>
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</thead>
<tbody>
<tr>
<td>- Selectivity of enzymes</td>
<td>- Short lifetime</td>
</tr>
<tr>
<td>specific and defined reactions</td>
<td>low stability of biocatalysts</td>
</tr>
<tr>
<td>- Potentially low cost production</td>
<td>- Low power density</td>
</tr>
<tr>
<td>(Biotechnologies)</td>
<td>electron conduction</td>
</tr>
<tr>
<td>- Operational conditions</td>
<td></td>
</tr>
<tr>
<td>(physiological conditions)</td>
<td></td>
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</table>
Biofuel cell studied:

Glucose/O$_2$

Gluconolactone + 2H$^+$ + 2e$^-$

Oxygen + 4H$^+$ + 4e$^-$

Redox mediator

2 H$_2$O
Differences between the existing biofuel cells

1. Redox enzymes (for biocathode: laccase, bilirubin oxidase..)

2. Redox mediators (for glucose oxidation: ferrocene, Os, Ru, quinone…)

3. Immobilization methods
• **OBJECTIVE**

Development of tubular bioelectrodes modified by co-immobilized enzyme/mediator system. Application to glucose/oxygen biofuel cell.

• **ORIGINALITY**

1. *design of the system*

2. *co-immobilization of enzyme/mediator system on electrode*
Glucose/O$_2$ biofuel cell

1. Design of the system

\[ \text{Glucose} \rightarrow \frac{1}{2} \text{O}_2 \rightarrow \text{Glucono-lactone} \rightarrow \text{Gluconolactone} \]

\[ \text{M}_2 \text{ red} \rightarrow \text{Lacc}_{\text{ox}} \rightarrow \text{H}_2\text{O} \rightarrow \text{M}_2 \text{ ox} \rightarrow \text{Lacc}_{\text{red}} \rightarrow \text{Glucose} \]

\[ \text{GOD}_{\text{ox}} \rightarrow \text{M}_1 \text{ ox} \rightarrow \text{GOD}_{\text{red}} \rightarrow \text{M}_1 \text{ red} \]
Limit of the system!

1. Design of the system

\[ C_6H_{12}O_6 + O_2 + H_2O \rightarrow C_6H_{12}O_7 + H_2O_2 \]

- electron flow through the anode
- output voltage

Secondary reaction:

\[ \frac{1}{2} O_2 \rightarrow H_2O + e^- \]
Strategy

1. Design of the system

1. Engineering of the enzymes and mediators
   - Reconstituted GOD less sensitive to the presence of oxygen
   - Mediators generating more effective electron mediation with GOD than \( O_2 \)

2. Engineering of the system
Strategy of the work

1. Design of the system

Development of a new configuration of the system to supply $O_2$ separately from the electrolyte.

The inside of the cathode tube is continuously supplied by saturated dioxygen solution that is likely to diffuse from the inner to the external surface of the porous tube.
Prototype

1. **Design of the system**

![Diagram of tubular electrodes](image)

- **O₂ Solution**
- **Glucose Solution**
- **Tubular electrodes**

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www.iemm.univ-montp2.fr
2. Co-immobilization of the Enzyme/mediator system on conducting support

Modification of the electrode surface with an original conducting polymer

Polyaminopyrrole film

Porous carbon tube

6 microns
2. Co-immobilization of the Enzyme/mediator system on conducting support

- Modification of the electrode surface with an original conducting polymer
- Covalent binding of enzyme via an electropolymerized functionnalized film
- Entrapment of mediator within an derivative of Polyethylene glycol matrix

Enzymatic activity of modified electrodes determined by UV spectrophotometry

**Diagram:**
- Polyaminopyrrole film
- Mediator
- PEGDGE
- ENZ
- With spacer or without spacer
Construction of the Biofuel Cell

**Bio- cathode:**
- Covalent grafting of BOD with a long spacer,
- Adsorption and entrapment of mediator in PEG

**Bio- anode:**
- Covalent grafting of GOD without spacer,
- Adsorption and entrapment of mediator in PEG
Performances of the biofuel cell (GOD, BOD)

Conditions: 37°C, pH 7.4
10 mM Glucose

$P_{\text{max}} = 25 \ \mu\text{W/cm}^2 \text{ at } 0.3 \ \text{V}$

After 2 months, $P \sim 99 \%$ of its initial value!!!
Nature of electrode:

Carbon porous tubes are original conducting supports:
- for enzyme and mediator co-immobilization
- for transport of dissolved O₂ solution via laminar flow through the porosity

The feasibility of the co-immobilization of both enzyme and its mediator on a modified conducting support.

Biofuel cell efficiency improved by using an electrode as membrane separator.
Outlooks

2 objectives

• Improvement of the interaction between enzyme-mediator-electrode: (in using another mediators : Ru and Os complexes)

• Improvement of the nature of the carbon tube. (porosity, surface)
MANY THANKS TO...

- My Supervisors from European Membrane Institute
  *Dr. Tingry, Dr. Rolland, Dr. Cretin and Dr. Innocent*

- My colleagues from Laboratoire de Catalyse Chimie Organique (Poitiers)
  *A. Habrioux; K. Servat; B. Kokoh.*

*Société Orélis*

*ACI – Jeunes Chercheurs*
Originality of the work

carbon porous tubes (porosity = 1-3 mm)
as original conducting support as cathode and oxygen contactor

Orélis (Novosep Group)
Working principle

- Fuel cell core = cathode/electrolyte/anode assembly
  - Anode: Oxidation of hydrogen
  - Cathode: Reduction of oxygen
  - Electrolyte: diffusion of ions / tightness to input gases

- Exothermic reaction with production of water

Proton Exchange Membrane Fuel Cell (PEMFC)

\[
\text{H}_2 \rightarrow 2 \text{H}^+ + 2\text{e}^- \\
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}
\]

Solid Oxide Fuel Cell (SOFC)

\[
\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \\
\frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}
\]
Résultats électrochimiques

Courbes de polarisation en milieu tampon phosphate 0,2 M (pH = 7,4) à 37°C.

L’activité de la BOD greffée sur une chaîne longue semble très supérieure à celle de la BOD greffée sur chaîne courte. Vous noterez que l’écart entre les potentiels d’équilibre des deux électrodes est très important.
Résultats électrochimiques

Courbes de polarisation obtenues en milieu tampon phosphate 0,2 M (pH = 7,4) 37°C en présence de 10 mM de glucose.

Ces deux courbes montrent qu’aucune différence d’activité électrochimique significative n’est observée entre la configuration chaîne courte et la configuration chaîne longue.