Biofuel Cells and Electrode Kinetics

Chemistry 671: Introduction to Green Chemistry
Outline

• Biofuel
• What is a Biofuel Cell?
• Green Principles Analysis
• Possible Scenarios for Hydrogen Technology Development and Market Transformation
• Technical Hurdles to Achieve Competition with Primary Batteries as a Power Source
Comparison 12.

- Ethanol derived from corn
  - 1 acre of land produces \(~18\) gallons of ethanol per acre per year.

- Ethanol derived from palm
  - 1 acre of land produces \(~700-800\) gallons of ethanol per acre per year

- Ethanol derived from algae
  - 1 acre of land produces \(~20,000\) gallons of ethanol per acre per year
Valcent Products Inc.

- “If we took \( \frac{1}{10} \) of the state of New Mexico and converted it into algae production we could meet all of the energy demands for the entire United States.” – CEO of Valcent Products Inc. Glen Kertz

- High density vertical growth systems.

- Selectivity
  - Jet Fuel
  - Diesel
Similar Research, Development, and Production

- PetroAlgae
  - “98% of the water used in production is recycled.”

- Coskata Inc.
  - Feedstock flexible bioethanol
    - Municipal solid waste, agricultural waste, wood by-products, construction debris, etc.
  - Their product is cost competitive and environmentally superior than current fuel.

- Arizona State University
  - Microalgae naturally remove and recycle nutrients (such as nitrogen and phosphorous) from water and wastewater and carbon dioxide from flue-gases emitted from fossil fuel-fired power plants, providing an added environmental benefit. The integration of wastewater bioremediation and carbon sequestration with biofuel production in a novel field-scale bioreactor has been demonstrated.
Arizona State University
What is a Biofuel Cell?

- A type of energy conversion device that uses biocatalysts (either completely living cells or enzymes) to convert the chemical energy of a fuel into electrical energy.\(^4\).
- Biofuel cells are a subset of fuel cells that employ biocatalysts.\(^{16}\).

<table>
<thead>
<tr>
<th>Enzyme Catalyzed Biofuel Cells</th>
<th>Microbial Biofuel Cells</th>
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<tr>
<td>Use enzymes to catalyze the oxidation of the fuel</td>
<td>Employ living cells to catalyze the oxidation of the fuel</td>
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<tr>
<td>Possess orders of magnitude higher power densities</td>
<td>Low power densities</td>
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<tr>
<td>Can only partially oxidize the fuel</td>
<td>Are capable of completely oxidizing simple sugars to carbon dioxide</td>
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<td>Have limited lifetimes (typically 7–10 days)</td>
<td>Have long lifetimes (up to 5 years)</td>
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Twelve Principles of Green Chemistry

1) **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.

2) **Atom Economy**
   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3) **Less Hazardous Chemical Syntheses**
   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4) **Designing Safer Chemicals**
   Chemical products should be designed to effect their desired function while minimizing their toxicity.

5) **Safer Solvents and Auxiliaries**
   The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6) **Design for Energy Efficiency**
   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

[NiFe]-hydrogenase from *D. fructosovorans*
7) **Use of Renewable Feedstock's**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8) **Reduce Derivatives**
   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9) **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10) **Design for Degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11) **Real-time analysis for Pollution Prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12) **Inherently Safer Chemistry for Accident Prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.
Overall reaction - redox reaction
\[ \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{CO}_2 \]
Mediators
Commercially Available Electrodes

- Lanthanum strontium cobalt ferrite LSCF 6428
- Lanthanum strontium cobalt ferrite composite cathode powder, LSCF/GDC
- Lanthanum strontium manganite LSM-20, ≥99%
- Lanthanum strontium manganite LSM
- Lanthanum strontium manganite composite cathode powder, LSM-20/YSZ, ≥99%
- Lanthanum strontium manganite composite cathode powder, LSM20-GDC10
- Lithium cobalt(III) oxide 99.8% trace metals basis
- Lithium dichromate hydrate technical grade
- Lithium granular, high sodium, 99% (metals basis)
- Lithium iron(III) oxide 95%
- Lithium manganese(III,IV) oxide electrochemical grade
- Lithium molybdate 99.9% trace metals basis
- Lithium titanate −325 mesh
- Lithium wire, diam. 3.2 mm, in mineral oil, ≥98%
- Lithium-aluminum alloy
- Manganese(IV) oxide 99.99% trace metals basis
- Molybdenum(IV) sulfide powder, <2 μm, 99%
- Vanadium(V) oxide 99.99% trace metals basis
- Nickel oxide - Cerium samarium oxide for coatings, NiO/SDC, ≥99% trace metals basis
- Nickel oxide - Yttria-stabilized zirconia for coatings, NiO/YSZ
- Nickel powder, <150 μm, 99.999% trace metals basis
- Nickel sulfide 99.7% trace metals basis, −150 mesh
- Nickel(II) oxide <10 μm, Black
- Nickel(II) oxide 99.99% trace metals basis
- Nickel(II) peroxide hydrate
- Niobium(V) oxide mesoporous, pore size 22 Å, 99.5% trace metals basis
- Platinum wire, diam. 0.5 mm, 99.9% trace metals basis
- Platinum wire, diam. 0.5 mm, 99.99% trace metals basis
- Platinum wire, diam. 1.0 mm, 99.9% trace metals basis
- Platinum wire, diam. 1.0 mm, 99.99% trace metals basis
- Platinum wire, diam. 1.5 mm, ≥99.9% trace metals basis
- Platinum wire, diam. 2.0 mm, 99.9% trace metals basis
- Platinum(IV) oxide
- Platinum(IV) oxide
- Platinum(IV) oxide hydrate ≥99.9%
- Vanadium(III) oxide 99.99% trace metals basis
- Vanadium(V) oxide 99.99% trace metals basis
Enzyme(s)
I. Technology Development
Research to meet technology performance and cost targets and establish technology readiness

II. Initial Market Penetration
Portable power and stationary/transport systems are validated; infrastructure investment begins with governmental policies

III. Expansion of Markets and Infrastructure
H₂ power and transport systems commercially available infrastructure business case realized

IV. Fully Developed Markets and Infrastructure
H₂ power and transport systems commercially available in all regions; national infrastructure
How do we interpret?

Is there a better way?
Technical Hurdles to Achieve Competition with Primary Batteries as a Power Source

1. Biofuel cell anodes should be three-dimensional thereby increasing the surface area available for electron transport.

2. The successful immobilization of multi-enzyme systems that can completely oxidize the fuel to carbon dioxide is needed.

3. The anode must support efficient charge transfer mechanisms, whether it be direct or mediated, and balance electron transfer with proton transfer.
1. Biofuel cell anodes should be three-dimensional thereby increasing the surface area available for electron transport.

\[ V = IR \quad \text{(Ohm’s Law)} \]
\[ P = IV = I^2R = V^2/R \]
\[ V = \sqrt{PR} \]

\[ v_{\text{net}} = \frac{i}{nFA} \]

\[ A \overset{k_f}{\underset{k_b}{\rightleftharpoons}} B \]
\[ v_f = k_f C_A \]
\[ v_b = k_b C_B \]

\[ v_{\text{net}} = k_f C_A - k_b C_B \]
Porous chitosan scaffolds can be made through a thermally induced phase separation. 17.
2. The successful immobilization of multi-enzyme systems that can completely oxidize the fuel to carbon dioxide is needed. 18.

- Biomimicry!
- Mimicking the Krebs cycle, Citric acid cycle, for the complete oxidation of biofuel to form carbon dioxide and water
- Power density was increased 8.71-fold compared to a single enzyme (alcohol dehydrogenase)-based ethanol/air biofuel cell

<table>
<thead>
<tr>
<th>Dehydrogenase cascades</th>
<th>Current density (A/cm²)</th>
<th>Power density (W/cm²)</th>
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<tbody>
<tr>
<td>ADH</td>
<td>3.77 ± 1.97 × 10⁻⁴</td>
<td>1.16 ± 0.88 × 10⁻⁴</td>
</tr>
<tr>
<td>ADH, AldDH</td>
<td>5.30 ± 2.50 × 10⁻⁴</td>
<td>1.30 ± 0.52 × 10⁻⁴</td>
</tr>
<tr>
<td>ADH, AldDH, IDH</td>
<td>8.02 ± 1.98 × 10⁻⁴</td>
<td>1.63 ± 0.37 × 10⁻⁴</td>
</tr>
<tr>
<td>ADH, AldDH, IDH, KDH</td>
<td>9.84 ± 6.47 × 10⁻⁴</td>
<td>2.02 ± 0.83 × 10⁻⁴</td>
</tr>
<tr>
<td>ADH, AldDH, IDH, KDH, SDH</td>
<td>1.62 ± 0.35 × 10⁻³</td>
<td>2.86 ± 0.36 × 10⁻⁴</td>
</tr>
<tr>
<td>ADH, AldDH, IDH, KDH, SDH, MDH</td>
<td>3.60 ± 0.23 × 10⁻³</td>
<td>1.01 ± 0.01 × 10⁻³</td>
</tr>
</tbody>
</table>
3. The anode must support efficient charge transfer mechanisms, whether it be direct or mediated, and balance electron transfer with proton transfer.

\[ k_0(d) = k_0^{\text{max}} \exp(-\beta d) \]
\[ \text{O} + \text{n}e \xrightleftharpoons[\text{k}_b]{\text{k}_f} \text{R} \]

\( n = \text{Number of electrons participating in the reaction} \)
\( F = \text{Faraday Constant} = 96485.3415 \text{ coulombs/mol} \)
\( A = \text{Electrode surface area} \)

\[ v_f = k_f C_O(0, t) = \frac{i_c}{nFA} \]
\[ v_b = k_b C_R(0, t) = \frac{i_a}{nFA} \]

\[ v_{\text{net}} = v_f - v_b = k_f C_O(0, t) - k_b C_R(0, t) = \frac{i}{nFA} \]

\[ i = i_c - i_a = nFA[k_f C_O(0, t) - k_b C_R(0, t)] \]
Butler-Volmer Equation

\[ k = A e^{-E_A/RT} \]

\[ \Delta G^\ddagger_a = \Delta G^\ddagger_{0a} - (1 - \alpha)F(E - E^{0'}) \]

\[ \Delta G^\ddagger_c = \Delta G^\ddagger_{0c} + \alpha F(E - E^{0'}) \]

\[ k_f = A_f \exp \left( -\frac{\Delta G^\ddagger_c}{RT} \right) \]

\[ k_b = A_b \exp \left( -\frac{\Delta G^\ddagger_a}{RT} \right) \]

\[ k_f = A_f \exp \left( -\frac{\Delta G^\ddagger_{0c}}{RT} \right) \exp \left[ -\alpha f(E - E^{0'}) \right] \]

\[ k_b = A_b \exp \left( -\frac{\Delta G^\ddagger_{0a}}{RT} \right) \exp \left[ (1 - \alpha) f(E - E^{0'}) \right] \]

\[ f = F/RT \]

\[ k_f = k^0 \exp \left[ -\alpha f(E - E^{0'}) \right] \]

\[ k_b = k^0 \exp \left[ (1 - \alpha) f(E - E^{0'}) \right] \]
Summary

1. By making the biofuel cell anode three-dimensional we can promote an increase in the concentration of electro-active species. The catalytic current that is obtained is directly proportional to the enzyme’s turnover rate and this will directly influence the voltage.

2. It is possible to immobilize multi-enzyme systems that can completely oxidize a biofuel to carbon dioxide. In an experiment using the principles of biomimicry, power density was increased 8.71-fold compared to a single enzyme (alcohol dehydrogenase)-based ethanol/air biofuel cell.

3. The anode must support efficient charge transfer mechanisms. Efforts to reduce the distance between the enzyme and the electrode and to achieve greater homogeneity among enzymes will provide this important improvement in the performance of enzymes as electrocatalysts.
References

16. “Enzyme-based biofuel cells” Shelley D Minteer1, Bor Yann Liaw and Michael J Cooney, © 2006