PRODUCTION OF HYDROGEN FROM DARK FERMENTATION EFFLUENTS USING MICROBIAL ELECTROLYSIS CELLS

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Share of bioenergy in the world primary energy mix
BIOENERGY

Bioenergy
Energy Derived from Biomass

Biofuels
Energy Carrier Derived from Biomass

Gaseous Biofuels
- Biogas
- Biohydrogen
  - Syngas from Gasification/Biomass Pyrolysis
  - Steam Reforming of Biogas & Syngas
  - Anaerobic Digestion of Biomass/Wastewater

Liquid Biofuels
- Raw Vegetable oil
- Synthetic diesel
- Biooil Biomass pyrolysis

Solid Biomass Direct Combustion/Gas & liquid biofuels feedstock
- BioDME/Methanol Syngas/Biogas Reforming
- Biodiesel Transesterification of vegetable oil
- Bioethanol Sugar Fermentation 1st Generation Tech
- Bioethanol Lignocellulosic Fermentation 2nd Generation Tech

Agricultural Residue & Waste
- Municipal Solid Waste
- Wood & Wood Waste

Microbial Fuel Cell
Microbial Electrolysis Cell
### Status of Main Conversion Technologies of Biomass to Heat & Power

Source: E4tech (2009)

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Microbial fuel cells (MFC) produce electricity by converting chemical energy from biological substrates & oxygen into electrical energy by using bacteria. In early MFCs, electron transfer from cells to anode occurs by mediator molecules (Potter 1911, Lewis 1966, Allen & Benetto 1993) – low current density. In mediatorless MFCs, electron transfer occurs directly without mediator molecules (Kim et al. 1999) – higher current density.

Microbes for Mediatorless MFCs:
- Pseudomonas sp.
- Clostridium butyricum
- Enterobacter aerogenes

Microbes for Mediated MFCs:
- Escherichia coli
- Bacillus subtilis

Mediatorless & Mediated MFCs
Logan et al. 2006

Microbial catalyst on carbon paper anode
Ghasemi et al. 2012
MICROBIAL FUEL CELL DESIGN & CONFIGURATION

Two Chamber MFC
Jang et al. 2004

Single chamber MFC
Park et al. 2003

Stacked tubular single chamber MFCs
Lefebvre et al. 2010

Stacked rectangular single chamber MFCs
Aelterman et al. 2006
MICROBIAL FUEL CELL PERFORMANCE LIMITATION

Anodic catalytic activity:
- Anode material from carbon: graphite fiber brush, carbon cloth, graphite rod, carbon paper, reticulated vitreous carbon (RVC) & carbon felt
- Stable in microbial cultures, high electric conductivity & vast surface area
- Modified with metals and conducting polymers

Cathodic oxygen reduction activity
- Carbon paper, carbon felt, carbon brush, carbon fiber, graphite of various type, granular graphite, reticulated vitreous carbon (RVC)
- Carbon cathode has slow ORR kinetic: Modified with metals e.g. Pt, Cu, Cu–Au, tungsten carbide and conducting polymers e.g. polypyrole

Proton & ion transport between anode & cathode chambers through separator:
- Porous membrane e.g. J-cloth, nylon, non-woven cloth, carbon fiber, earthen pot, porous ceramic. Better performance than ion exchange membranes
- Cation exchange membranes (CEMs) e.g. Nafion but costly, SPEEEK is cheaper alternative CEM. Cause pH imbalance in the course of operation (Daud et al. 2015, Leong et al. 2013)
- Anion exchange membranes (AEMs) perform better than CEM – higher power density because it has lower resistance to ion transport and less liable to biofouling than CEM (Daud et al. 2015, Leong et al. 2013)
MICROBIAL FUEL CELL
SCALING UP PROBLEM

The large MFC reactor at Foster’s Brewery in Queensland, Australia
Keller & Rabaey 2008

NYSERDA/WERF MFC pilot test in Johnstown, New York
Li et al. 2011

Significant problems:
- Electrode fouling that raised internal resistance & reduced voltage
- Uneven flow and composition in wastewater feed
- Difficult to regulate wastewater feed pH & conductivity
- Clogging of external & internal surfaces by biofilm growth

Lessons learnt from large-scale MFC for wastewater treatment tests:
- Use assembly of many small reactors that minimize electrode spacing and electrode material resistivity losses
- Increase conductivity on the cathode side
- Form initial biofilm growth before application but minimize electrode fouling to avoid high maintenance
- Use low-cost materials.
- Stacking to increase power outputs but performance may drop due voltage reversal

Significant problems:
- Cathode fouling after 3-4 weeks that raised internal resistance and reduced voltage
- Low electron acceptance rate at cathode
- Low coulombic efficiency
- High internal resistance from anode/cathode separation distance due to scale-up
MICROBIAL FUEL CELL

MFC’s (a) voltage (b) power density using PEEK/PES composite membranes (Lim et al. 2012)

MFC’s (a) power (b) polarization curves MFCs with AC cathodes (Ghasemi et al. 2012a)

MFC’s (a) Power (b) Polarization with nanocomposite membrane (Ghasemi et al. 2012b,c,d)
Improvements in MFC Membrane Separators

Power density of MFC using Nafion-activated carbon nanofiber membrane (Ghasemi et al. 2012b & c)

Power density of MFCs using GO-SPEEK membrane (Leong et al. 2015)

Power density graph of the MFCs using PS/PANI membrane (Ghasemi et al. 2013d)
IMPROVEMENTS IN MFC ELECTRODES

- Power density of MFC using CP, CNT, Pt & Pt-CNT cathode (Ghasemi et al. 2012a)
- Current density of MFCs using Pani/V2O5 catalysts (Ghoreishi et al. 2013a)
- Power curves of MFCs using CuPc/C (Ghasemi et al. 2013)
- Power curves of MFCs using Ceramic membrane (Daud et al. 2016)
IMPROVEMENT IN MFC ELECTRODES

- Power density of MFCs using CNT/Ppy cathode (Ghasemi et al. 2013c)
- Power density of MFCs using PANI nanoparticle based anode (Ghasemi et al. 2013a)
- Power density of MFCs using PPy/KC cathode (Ghasemi et al. 2014)
- Power and current densities of MFCs using CNT & MnO2/CNT cathode (Liew et al. 2015)
BIOHYDROGEN FROM ORGANIC WASTE

**Organic waste**

**Light dependent**

**Bio-photolysis:**

\[ 12H_2O \rightarrow 12H_2 + 6O_2 \text{ (Green algae)} \]

\[ CO + H_2O \rightarrow H_2 + CO_2 \text{ (Photosynthetic bacteria)} \]

**Light independent**

**Photo-fermentation:**

\[ C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2 \text{ (Phototropic bacteria)} \]

**Dark-fermentation:**

\[ C_6H_{12}O_6 + 2H_2O \rightarrow CH_3COOH + 8H_2 + 2CO_2 \]

**Microbial electrolysis cells (MECs):**

**Anode:** \[ CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+ \]

**Cathode:** \[ 8H^+ + 8e^- \rightarrow 4H_2 \]

**Overall:** \[ CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2 \]
MICROBIAL FUEL CELL VERSUS MICROBIAL ELECTROLYSIS CELL

**Anode**:

- MFC: \( \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \)
- MEC: \( \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \)

**Cathode**:

- MFC: \( 2\text{O}_2 + 8\text{e}^- + 8\text{H}^+ \rightarrow 4\text{H}_2\text{O} \)
- MEC: \( 8\text{e}^- + 8\text{H}^+ \rightarrow 4\text{H}_2 \)

**Overall**:

- MFC: \( \text{CH}_3\text{COOH} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \)
- MEC: \( \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 4\text{H}_2 \)

**Electrode Potentials**:

- **acetate / CO\(_2\)**: \( E^\circ = -0.289 \text{V} \)
- **H\(^+\)/H\(_2\)O**: \( E^\circ = +0.818 \text{V} \)

- **acetate / CO\(_2\)**: \( E^\circ = -0.289 \text{V} \)
- **H\(^+\)/H\(_2\)**: \( E^\circ = -0.412 \text{V} \)

- Hydrogen evolution in MEC not spontaneous.
- Require energy input from a power source (PS).
- MFC using the same waste water can provide the energy as the power source.
DARK FERMENTATION-MICROBIAL FUEL CELL-MICROBIAL ELECTROLYSIS CELL HYDROGEN PRODUCTION PROCESS

Stage 1: Fermentation Process

- Medium
- Peristaltic Pump
- Stirrer
- Fermentator
- Effluent

Pretreatment

Stage 2: MCF-MEC system

- Anode
- Cathode
- MFC 1
- MFC 2
- Power source from MFCs
- Anode
- Cathode
- MEC
- Resistor

H₂ collector
Continuous Dark fermentation

Gas analysis
- $\text{H}_2$ 6.81%
- $\text{CO}_2$ 93.19%

Liquid effluent
- Acetic acid 53%
- Lactic acid 35%

Batch MFC-MEC

Gas analysis
- $\text{H}_2$ 98.8%
- $\text{CH}_4$ 1.2%

Coulombic efficiency 33%
COD Removal 82%
DARK FERMENTATION-MICROBIAL FUEL CELL-MICROBIAL ELECTROLYSIS CELL HYDROGEN PRODUCTION PROCESS

- Enrichment stage
- Gases production stage

Current (mA) vs. Time (days)
Main Challenges
- Low hydrogen production rate
- High energy input
- High cost of electrodes and separator membranes

Proposed Solutions
- Increasing the hydrogen production rate by integrating MEC with Dark Fermentation
- Lowering energy input by using MFC
- Lowering cost by using biocathode instead of costly metal based catalyst
“Biocathode” is a cathode that employs electrochemically-active microbes as catalysts to reduce either oxygen in microbial fuel cells (MFCs) or protons in microbial electrolysis cells (MECs).

- Microbial catalysts of biocathodes have several advantages over inorganic catalysts like Pt
  - Inexpensive
  - Sustainable
  - Resistant to sulfide poisoning.
CONVERSION OF MFC TO MEC SYSTEM & IN-SITU ENRICHMENT

MFC to MEC conversion

Hydrogen production startup

MEC biocathode origin system

Hydrogen production startup
Recirculation batch systems compared to batch and continuous systems

- Highest volumetric density
- Lowest charge transfer resistance
- Highest oxidation peak
FUTURE WORK

• Fundamental understanding are needed to characterize effective parameters individually and integrally to improve process yield in energy and product.
• More efforts are needed to improve hydrogen production rate and required applied voltage of biocathode MEC comparable to metal based cathode.
• Better reactor design such as size and cathodic flow pattern have also demonstrated considerable effects on microbial community of the biocathode biofilm.
• Biocatalyst type, enrichment process and nutrient medium are other factors that have affected product evolution yield.
• More research are needed on the investigation and enrichment procedure of the bacterial communities as the main catalyst in cathode chamber to improve hydrogen formation.
• In spite of assumptions and hypothesis that were discussed on electron uptake mechanism from the cathode theoretically, it still lacks experimental data to validate them.
• In addition, better understanding of reaction mechanism involved in biocathode will help understand whether energy is used by biocathode for product formation purpose or consumed by microorganisms for growth, while the link of hydrogen production to energy conservation and biocatalyst growth is not clear yet.
BIOFUEL CELL GROUP
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Terima kasih
Thank you
谢谢