# PRODUCTION OF HYDROGEN FROM DARK FERMENTATION EFFLUENTS USING MICROBIAL ELECTROLYSIS CELLS

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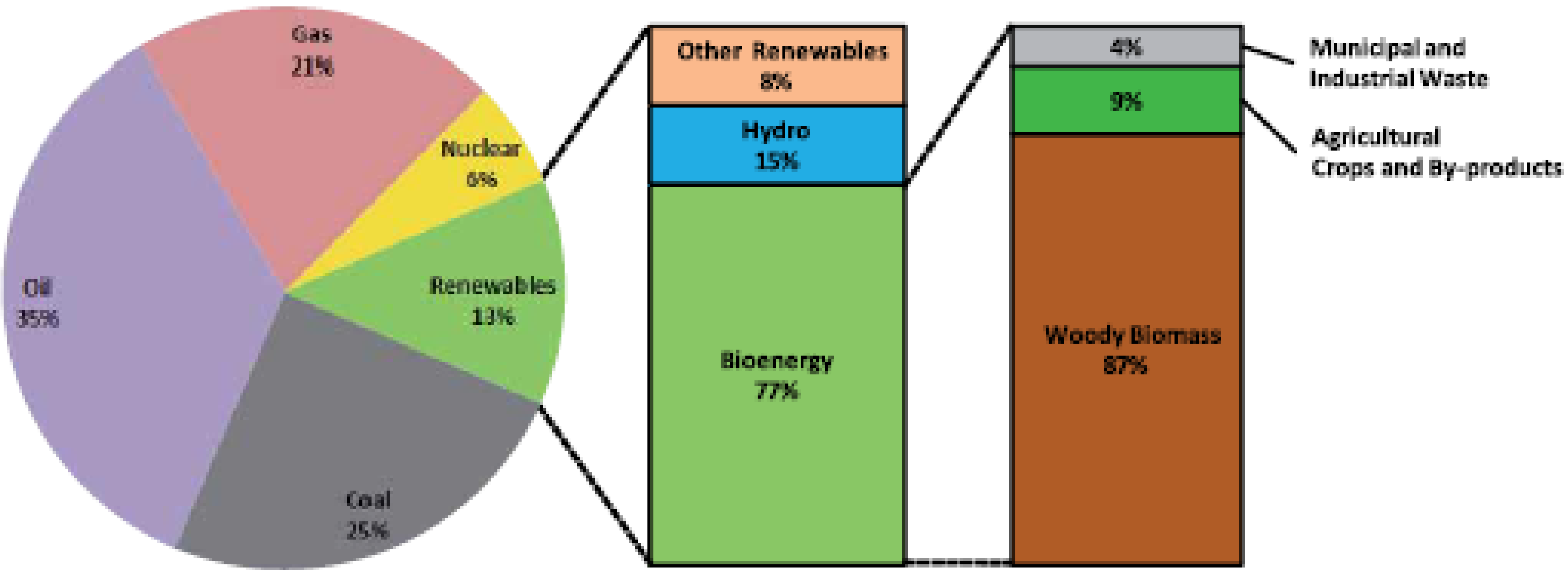
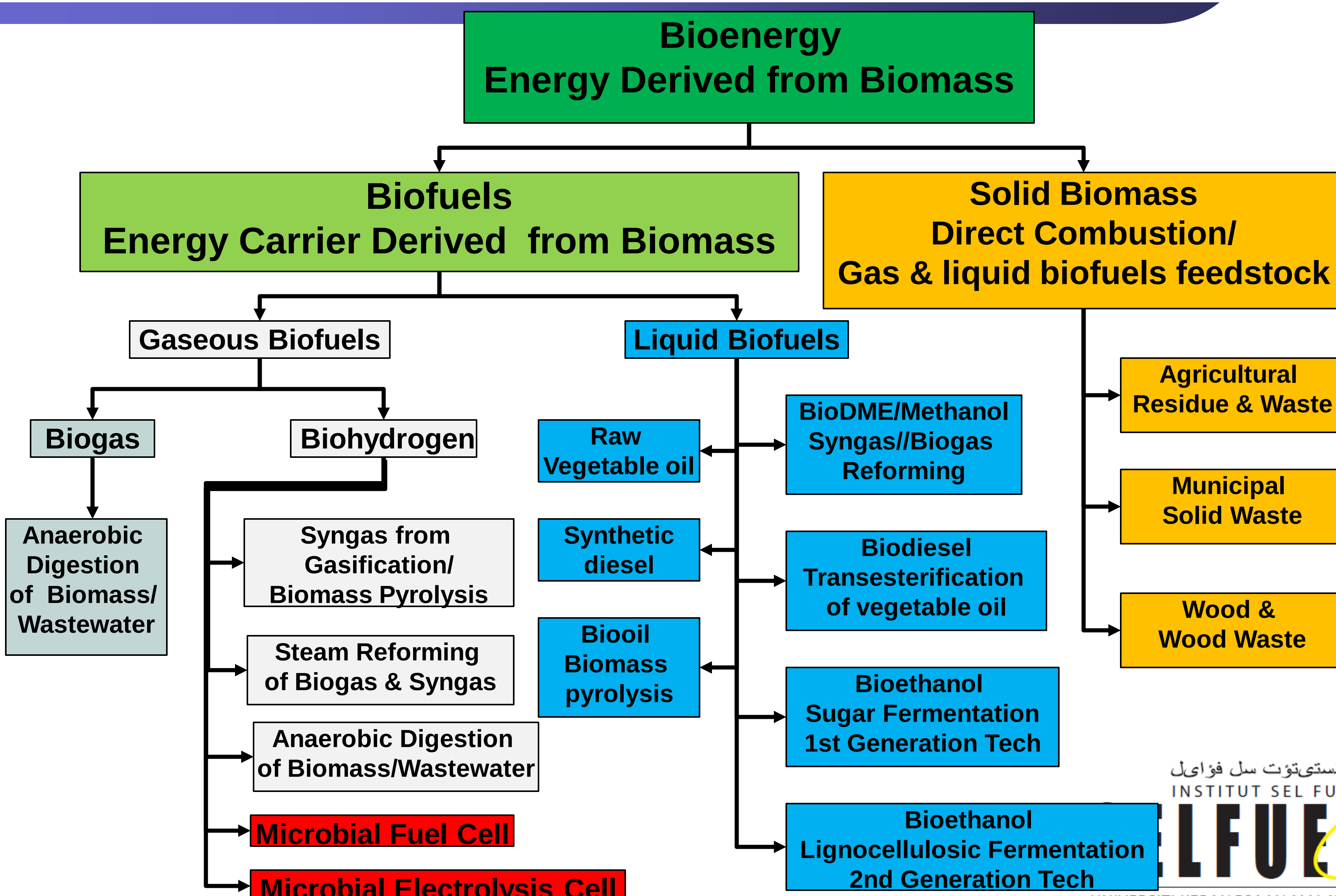
Workshop on POME to Energy
5-6 April 2016

# WORLD BIOENERGY




**Share of bioenergy in the world primary energy mix**
**Source: IEA (2006) and IPCC (2007)**

# BIOENERGY

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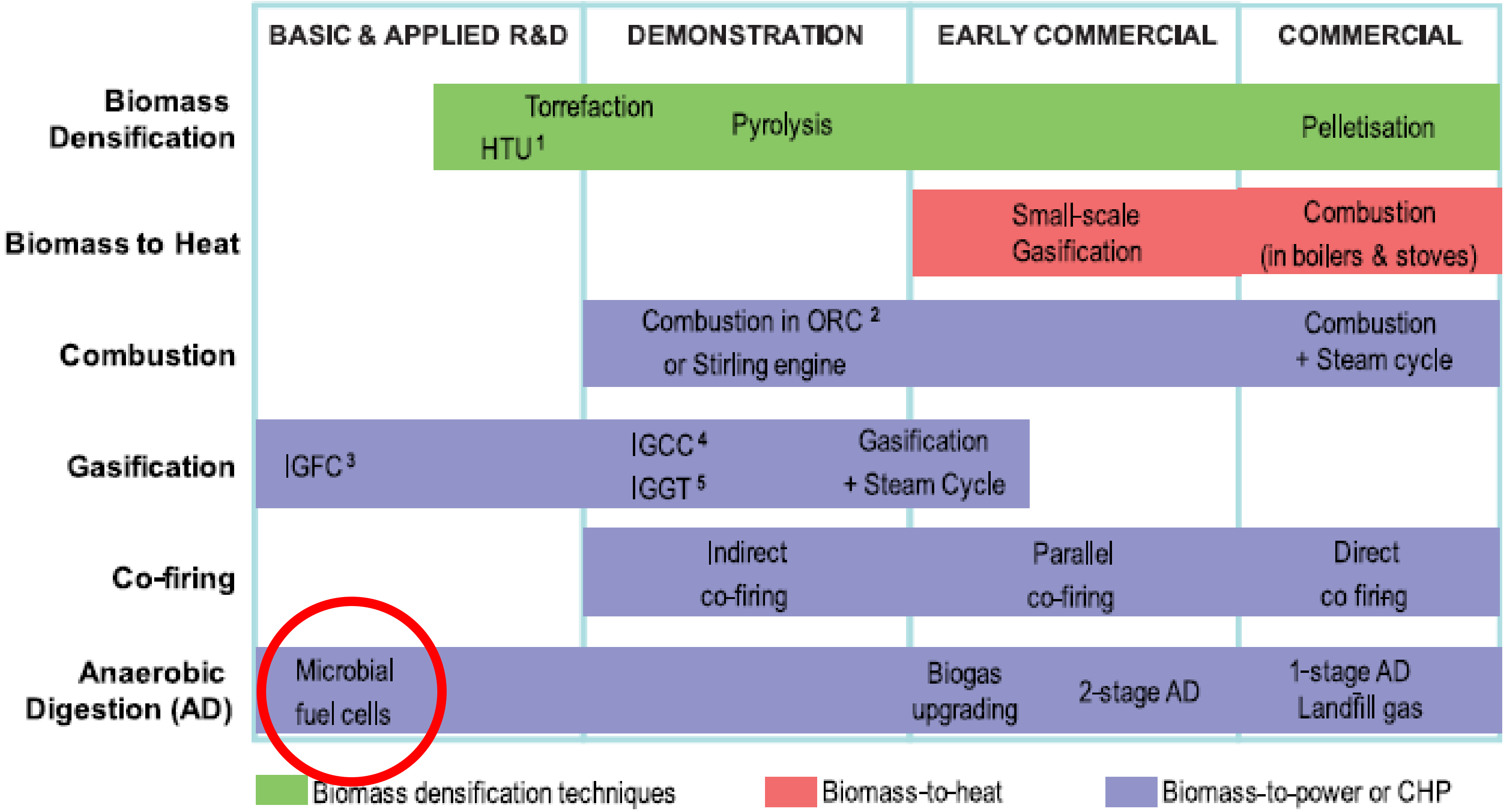
# BIOENERGY CONVERSION TECHNOLOGIES




[1] Hydrothermal upgrading; [2] Organic Rankine Cycle; [3] Integrated gasification fuel cell; [4/5] Integrated gasification combined cycle (CC) / gas turbine (GT)

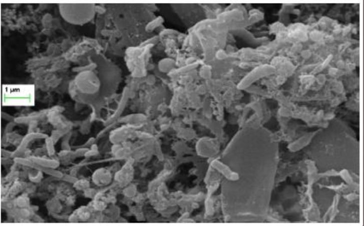
**Status of Main Conversion Technologies of Biomass to Heat & Power**
**Source: E4tech (2009)**

# MICROBIAL FUEL CELL

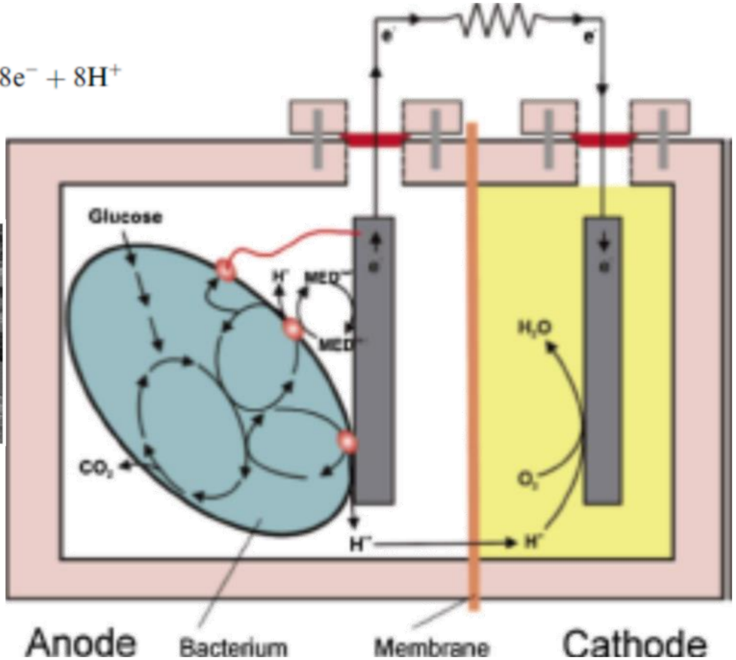
- **Microbial fuel cells (MFC) produce electricity by converting chemical energy from biological substrates & oxygen into electrical energy by using bacteria**
- **In early MFCs, to anode by mediator molecules (Potter 1911, Lewis 1966, Allen & Benetto 1993) – low current density**
- **In mediatorless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

$$C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$$

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O$$

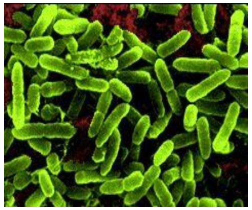


**Microbial catalyst on carbon paper anode Ghasemi et al. 2012**

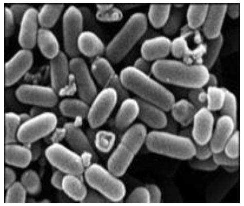



**Mediatorless & Mediatored Microbial Fuel Cells**
**Logan et al. 2006**

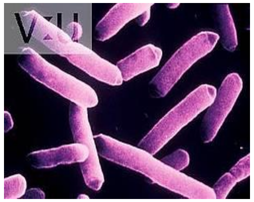
## Microbes for Mediatorless MFCs



*Pseudomonas sp.*



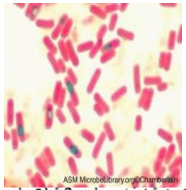
*Clostridium butyricum*



*Enterobacter aerogenes*

## Microbes for Mediatored MFCs

*Escherida coli*



*Bacillus subtilis*

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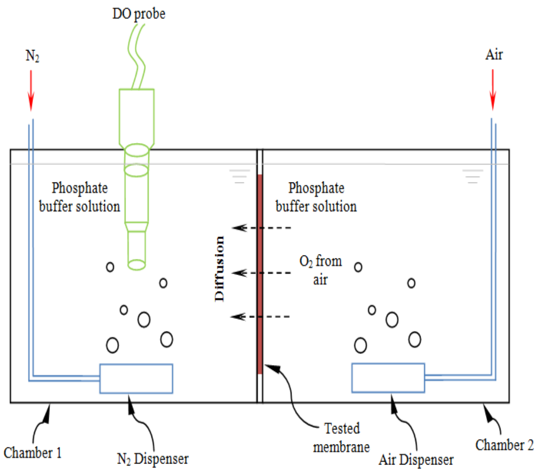
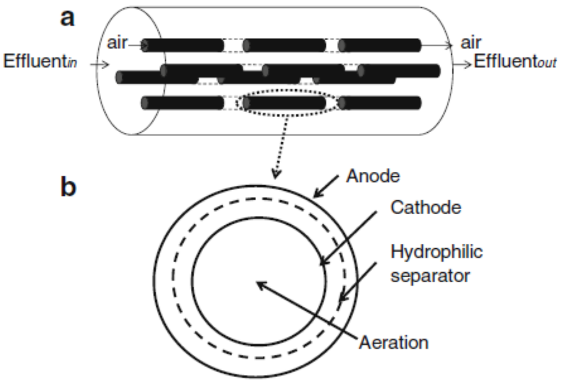
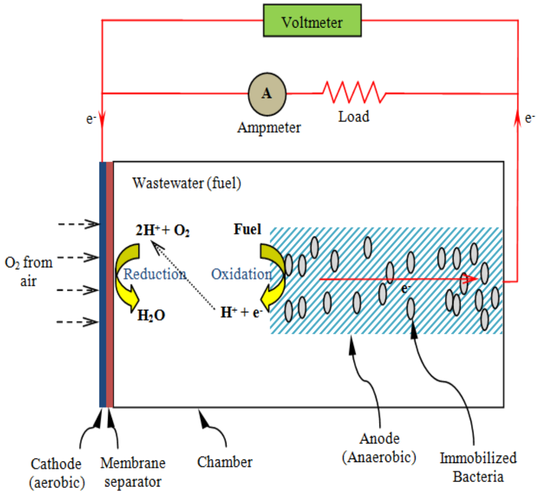
# MICROBIAL FUEL CELL DESIGN & CONFIGURATION



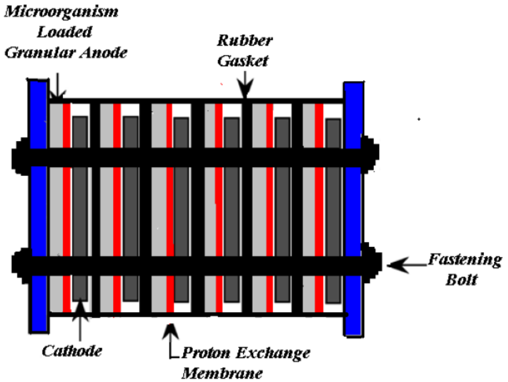




**Stacked tubular single chamber MFCs**
**Lefebvre et al. 2010**

**Two Chamber MFC**
**Jang et al. 2004**




**Single chamber MFC**
**Park et al. 2003**




**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**

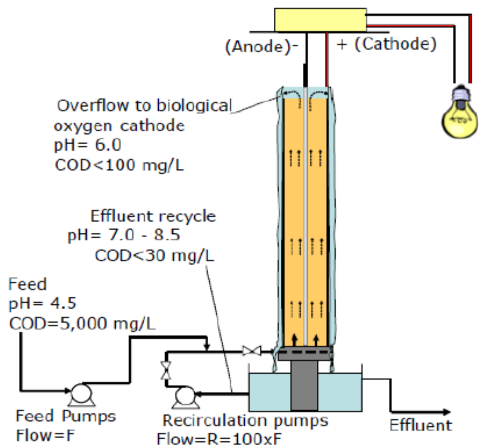
- **Carbon paper, carbon felt, carbon brush, carbon fiber, graphite of various type, granular graphite, reticulated vitreous carbon (RVC)**
- **Carbon cathode has slow ORR kinetic: Modified with metals e.g. Pt ,Cu, Cu–Au, tungsten carbide and conducting polymers e.g. polypyrole**

**Proton & ion transport between anode & cathode chambers through separator:**

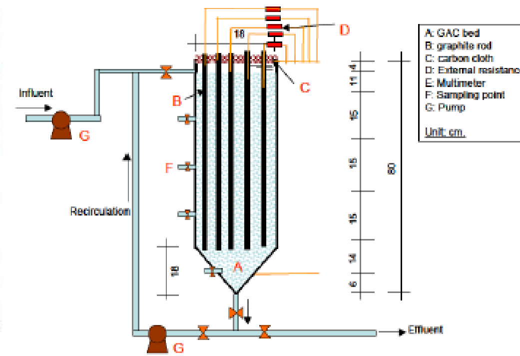
- **Porous membrane e.g. J-cloth, nylon, non-woven cloth, carbon fiber, earthen pot, porous ceramic. Better performance than ion exchange membranes**
- **Cation exchange membranes (CEMs) e.g. Nafion but costly, SPEEK is cheaper alternative CEM. Cause pH imbalance in the course of operation (Daud et al. 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

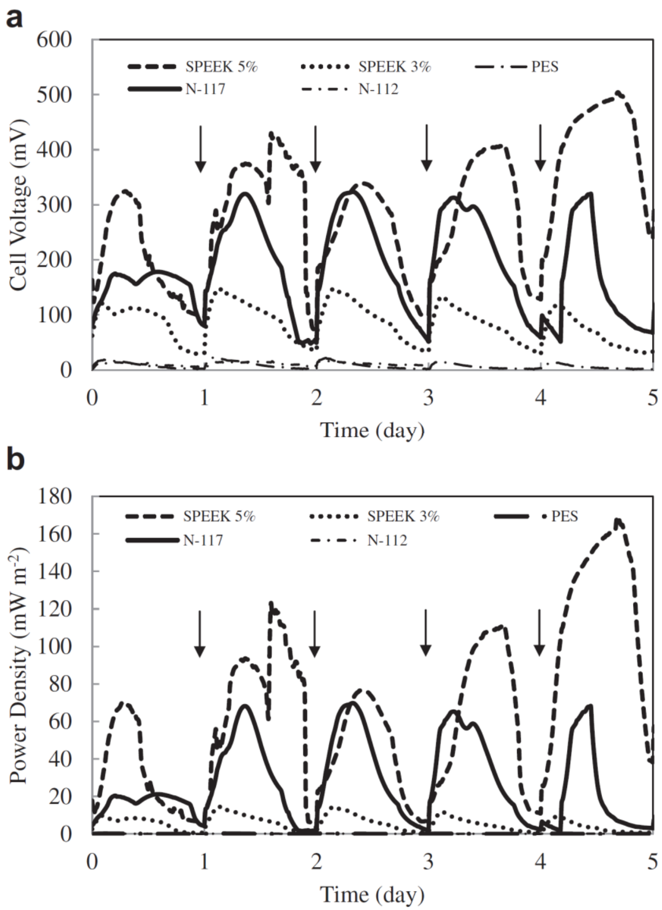
**Significant problems :**

- 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

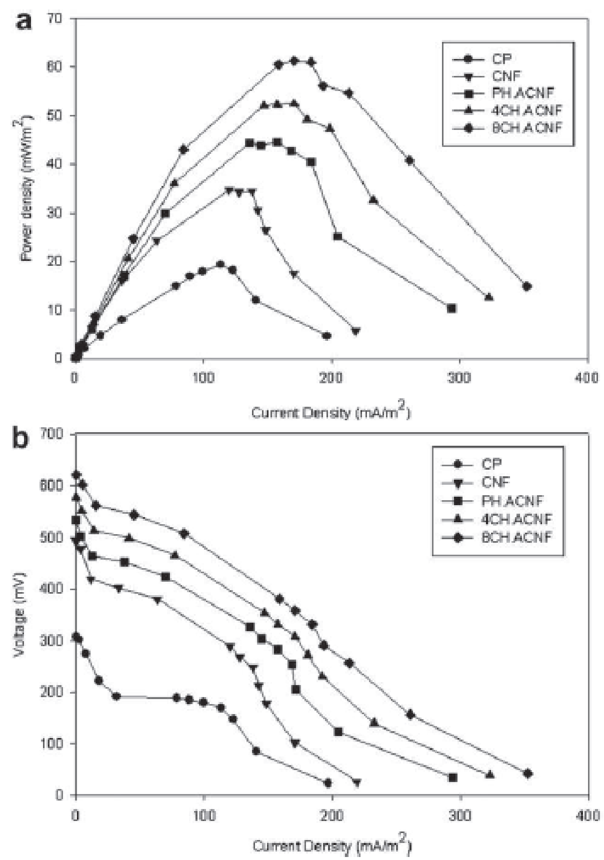
**Lessons learnt from large-scale MFC for wastewater treatment tests:**

- 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

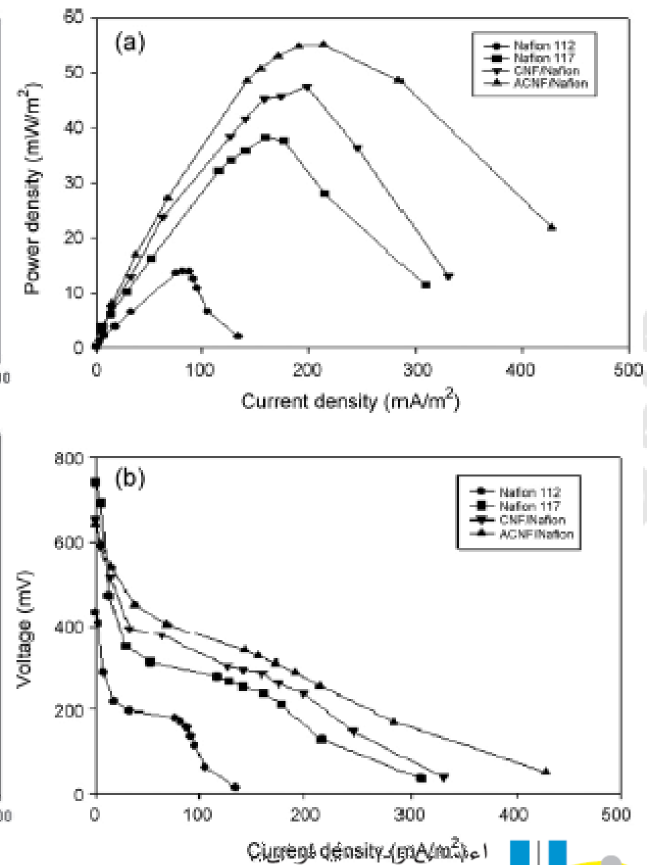
# MICROBIAL FUEL CELL




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

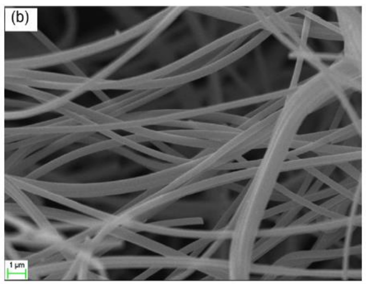


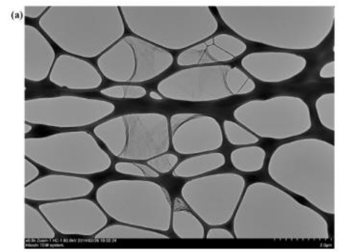

**MFC's (a) power (b) polarization curves MFCs with AC cathodes (Ghasemi et al. 2012a)**

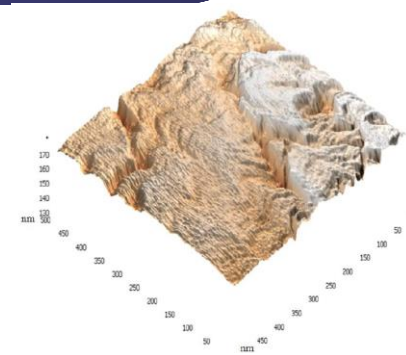


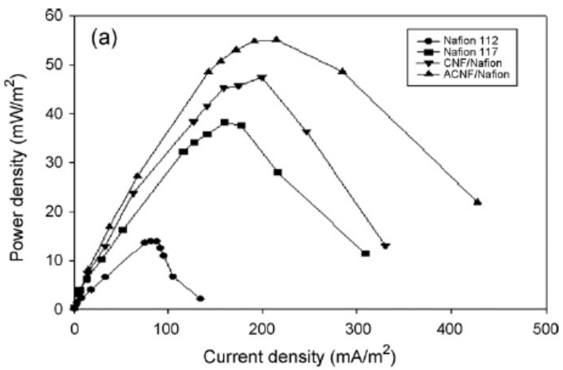

**MFC's (a) Power (b) Polarization with nanocomposite membrane (Ghasemi et al. 2012b,c,d)**

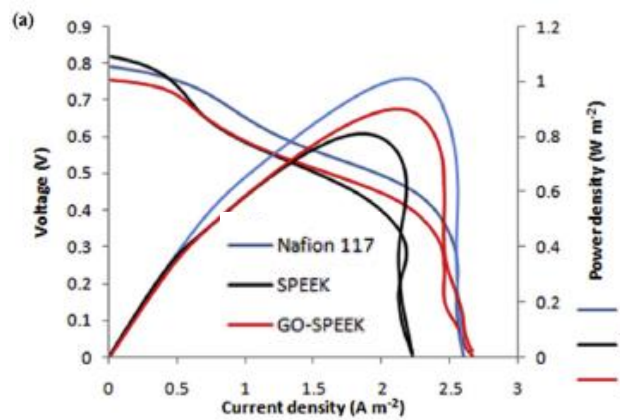
# IMPROVEMENTS IN MFC MEMBRANE SEPARATORS

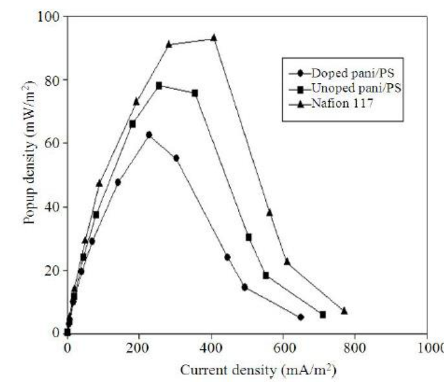


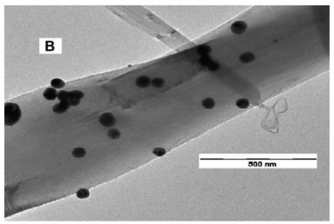



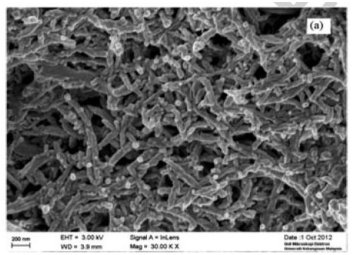

**Power density of MFC using Nafion-activated carbon nanofiber membrane (Ghasemi et al. 2012b & c)**

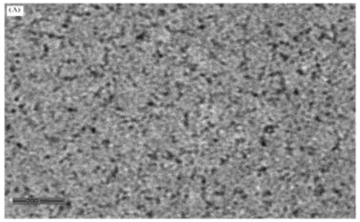
**Power density of MFCs using GO-SPEEK membrane (Leong et al. 2015)**

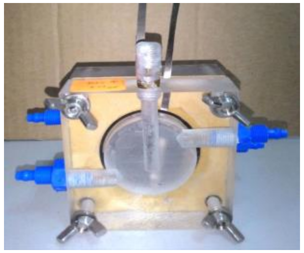
**Power density graph of the MFCs using PS/PANI membrane (Ghasemi et al. 2013d)**

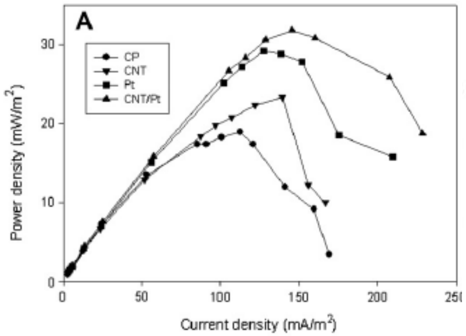
# IMPROVEMENTS IN MFC ELECTRODES

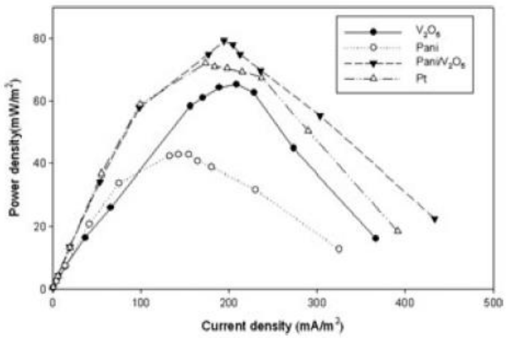


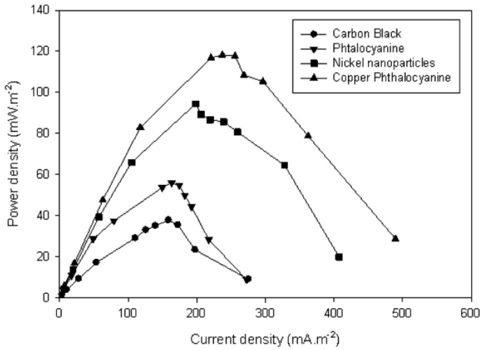



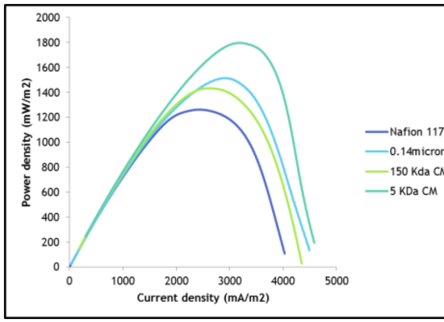







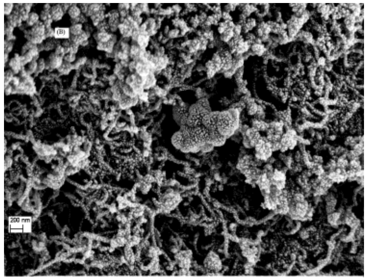

**Power density of MFC using CP, CNT, Pt & Pt-CNT cathode (Ghasemi et al. 2012a)**

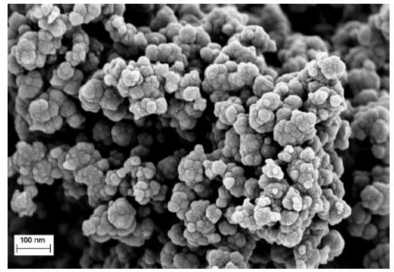
**Current density of MFCs using Pani/V2O5 catalysts (Ghoreishi et al. 2013a)**

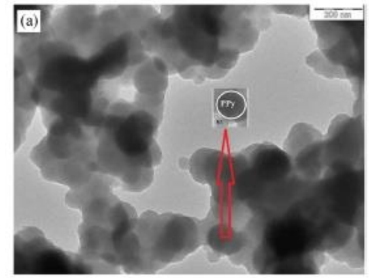
**Power curves of MFCs using CuPc/C (Ghasemi et al. 2013**

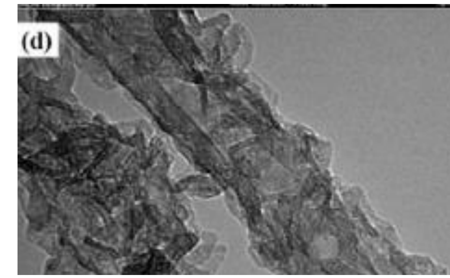
**Power curves of MFCs using Ceramic membrane (Daud et al. 2016)**

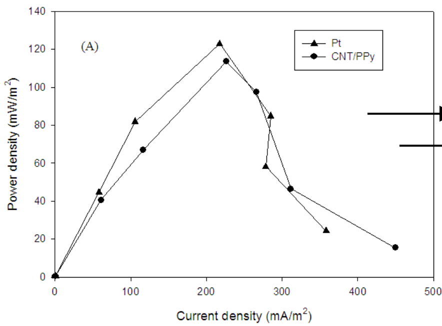
# IMPROVEMENT IN MFC ELECTRODES

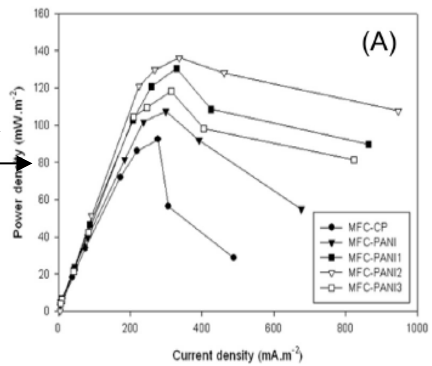


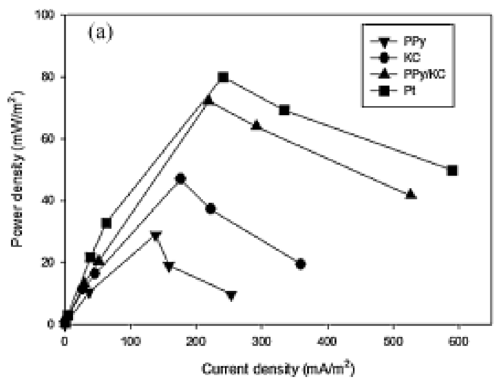


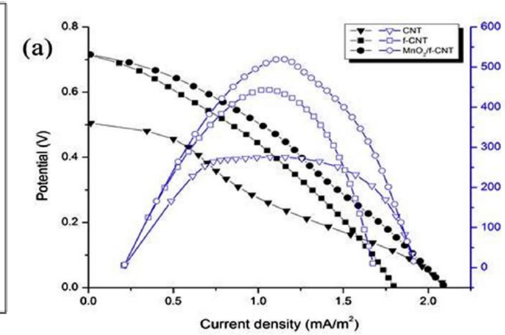




**Power density of MFCs using CNT/Ppy cathode (Ghasemi et al. (2013c)**

**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** / **Light independent**

**Light dependent** → Bio-photolysis / Photo-fermentation

**Bio-photolysis:**

$12H_2O \rightarrow 12H_2 + 6O_2$ (Green algae)

$CO + H_2O \rightarrow H_2 + CO_2$ (Photosynthetic bacteria)

**Photo-fermentation:**

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

**Light independent** → Dark-fermentation

**Dark-fermentation:**

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

↓

**Microbial electrolysis cells (MECs):**

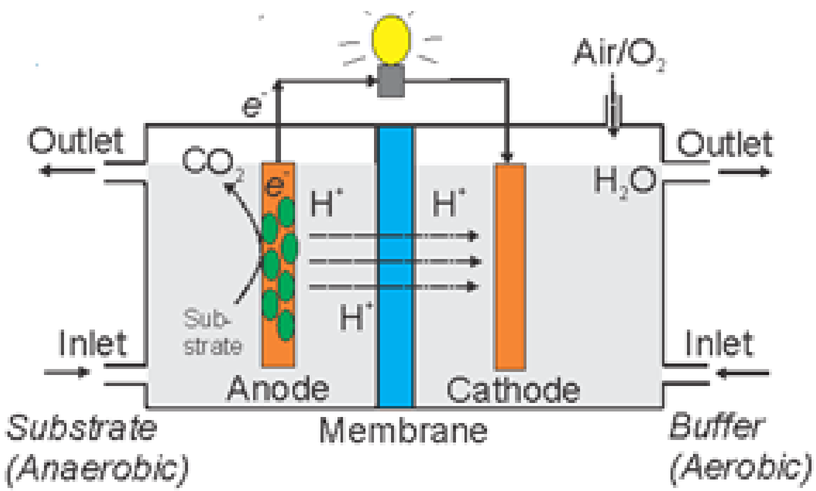
Anode: $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$

Cathode: $8H^+ + 8e^- \rightarrow 4H_2$

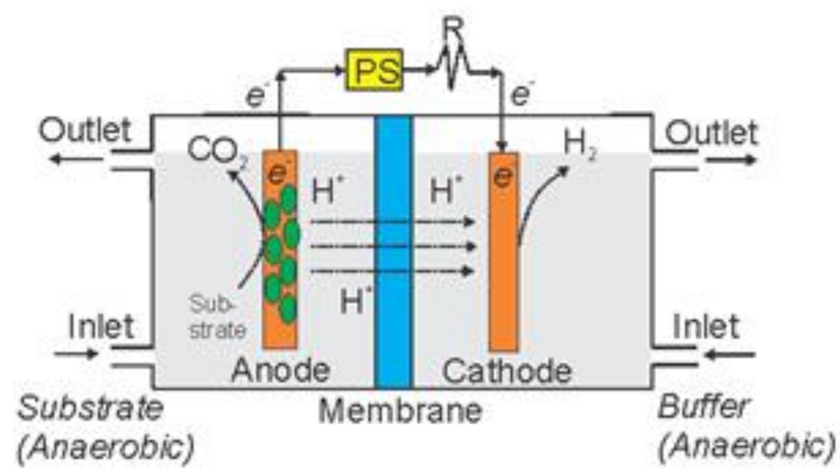
Overall: $CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2$

# MICROBIAL FUEL CELL VERSUS MICROBIAL ELECTROLYSIS CELL

**MFC**




**MEC**




**MFC**

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

**Cathode:** $2O_2 + 8e^- + 8H^+ \rightarrow 4H_2O$

**Overall:** $CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$

$E^\circ_{acetate / CO2}$=-0.289V $E^\circ_{H+/H2O}$=+0.818V

**MEC**

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

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

**Overall:** $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2$

$E^\circ_{acetate / CO2}$=-0.289V $E^\circ_{H+/H2}$=-0.412V

- **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.**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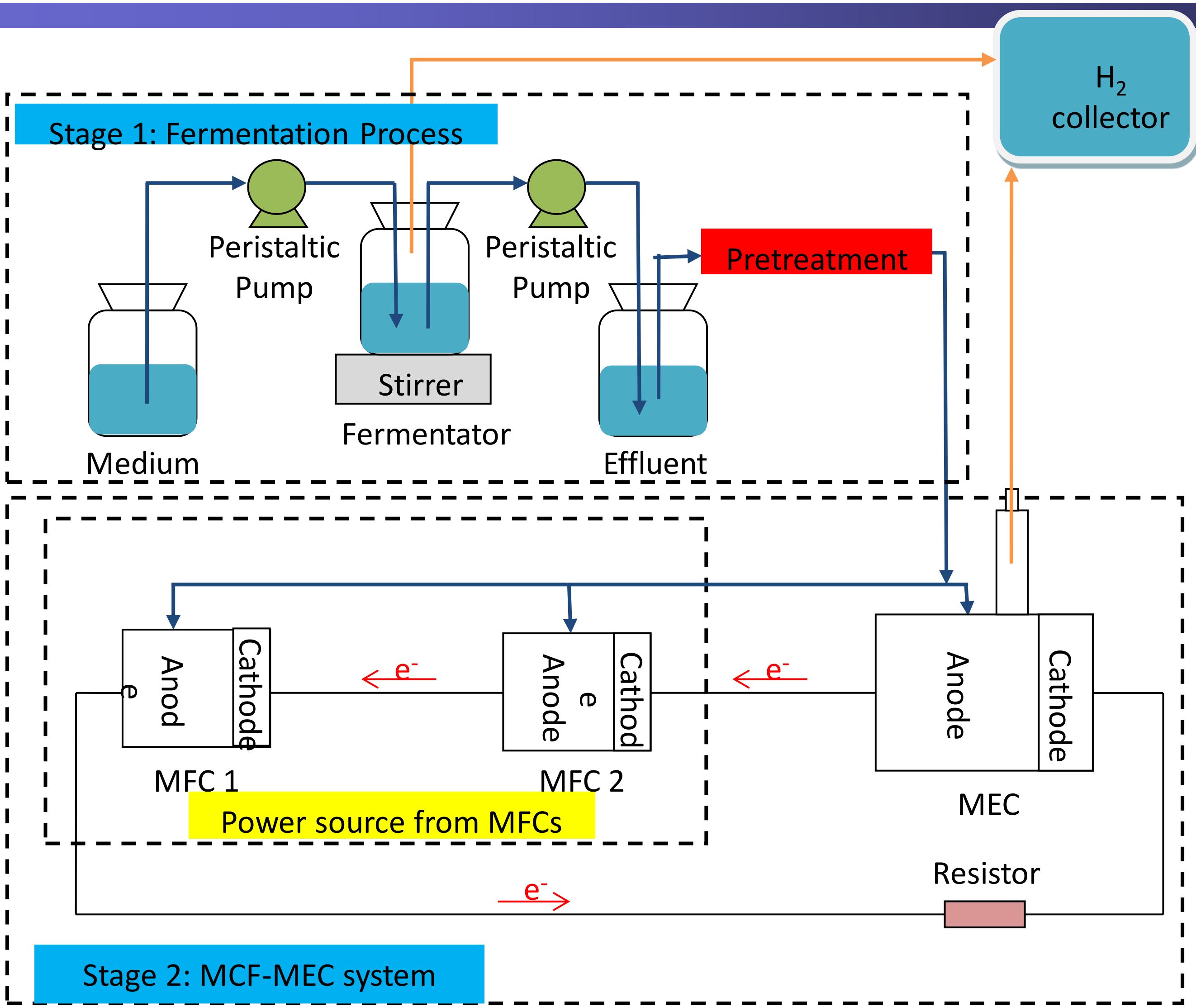
# DARK FERMENTATION-MICROBIAL FUEL CELL-MICROBIAL ELECTROLYSIS CELL HYDROGEN PRODUCTION PROCESS



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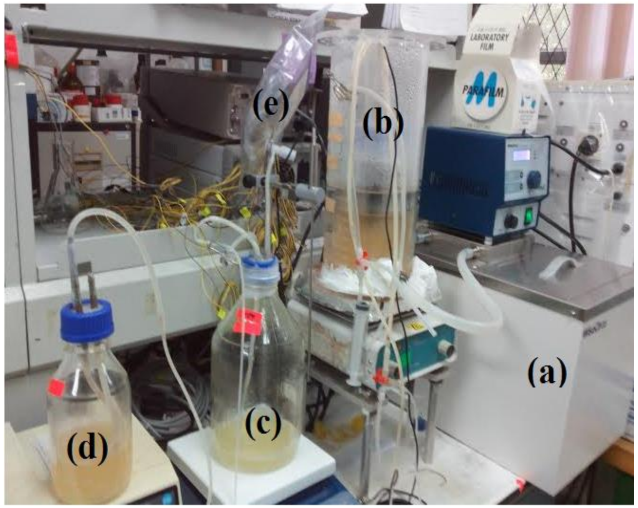



**Continuous Dark fermentation**

**Gas analysis**

- $H_2$ 6.81%
- $CO_2$ 93.19%

**Liquid effluent**

- Acetic acid 53%
- Lactic acid 35%

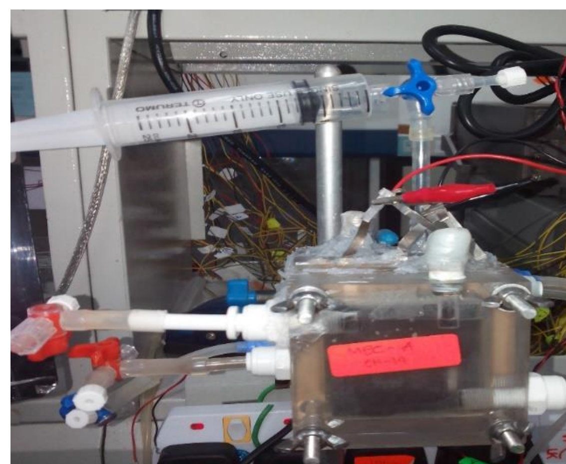
**Batch MFC-MEC**

**Gas analysis**

- $H_2$ 98.8%
- $CH_4$ 1.2%

**Coulombic efficiency 33%**

**COD Removal 82%**



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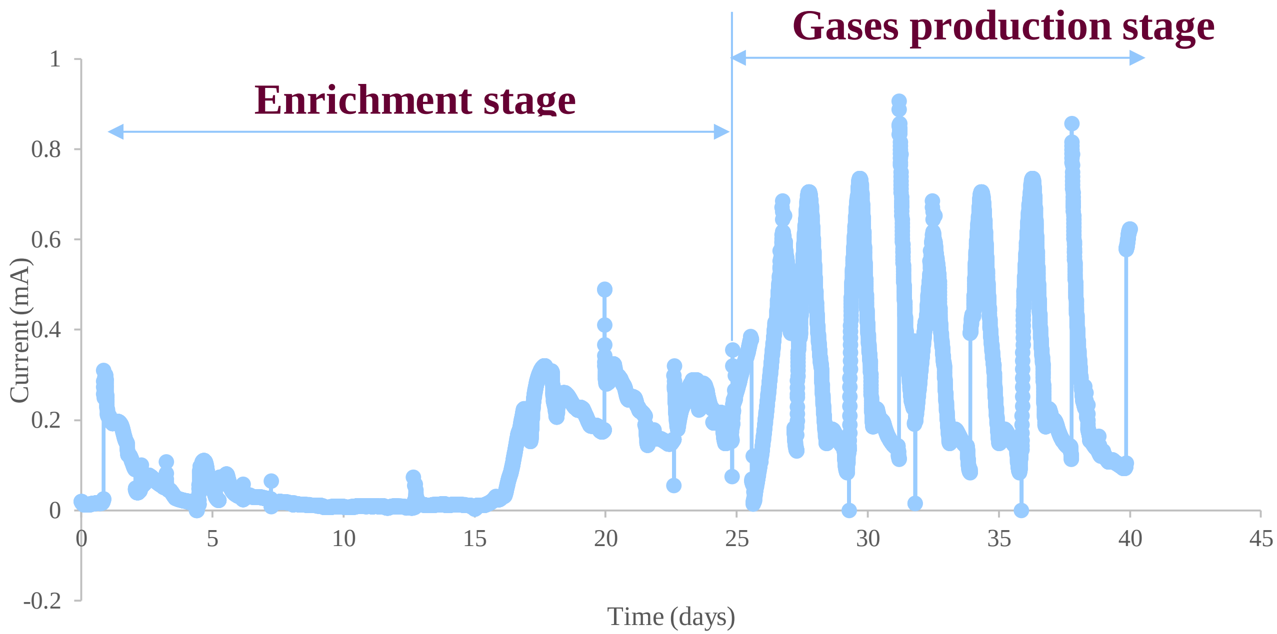
# DARK FERMENTATION-MICROBIAL FUEL CELL-MICROBIAL ELECTROLYSIS CELL HYDROGEN PRODUCTION PROCESS



# MICROBIAL ELECTROLYSIS CELL
# MAIN CHALLENGES & PROPOSED SOLUTIONS


**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

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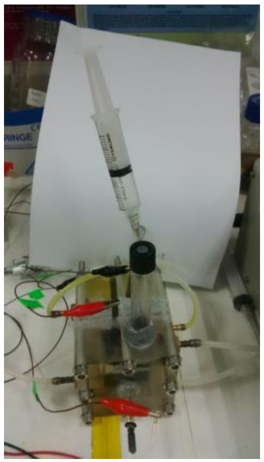
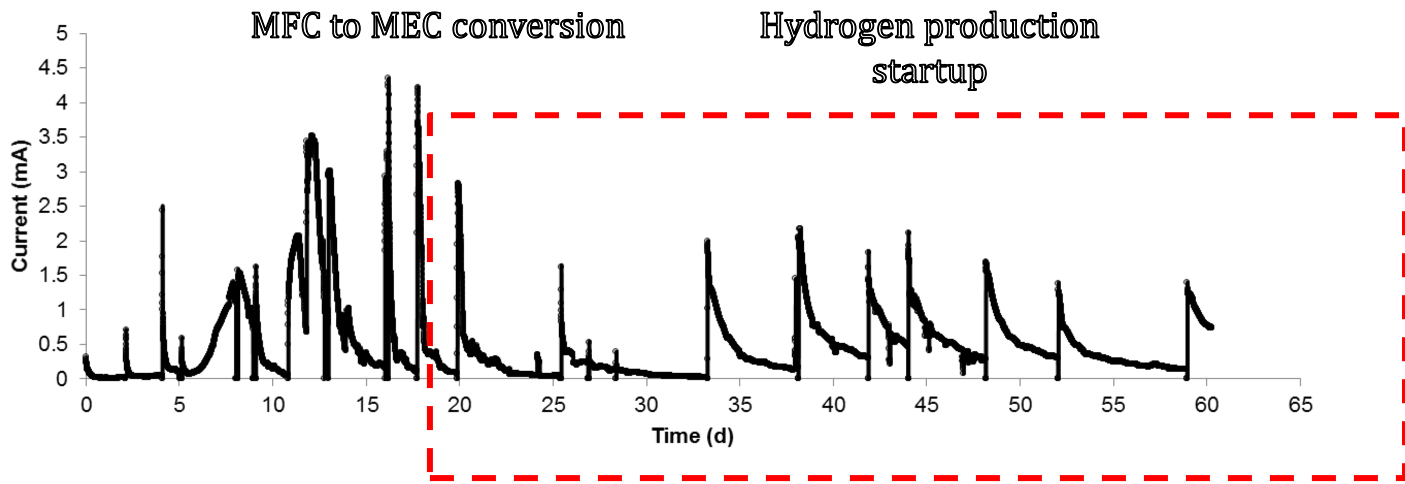
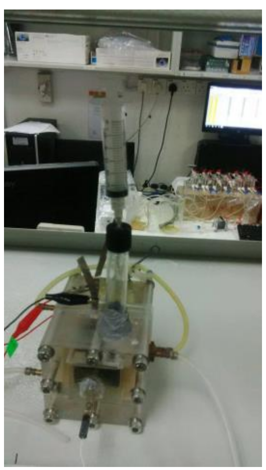
# MICROBIAL ELECTROLYSIS CELL BIOCATHODES

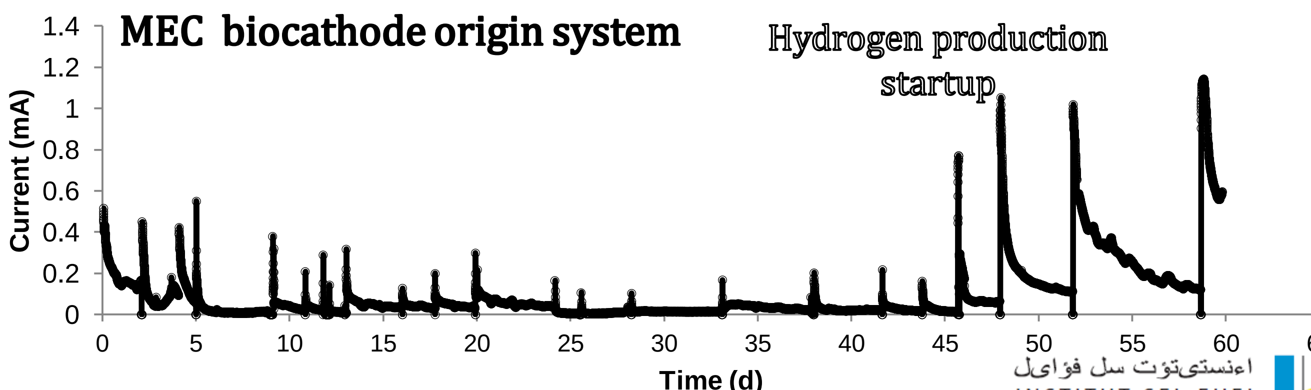
- **"Biocathode" is a cathode that employs electrochemically-active microbes as catalysts to reduce either oxygen in microbial fuel cells (MFCs) or protons in microbial electrolysis cells (MECs).**
- **Microbial catalysts of biocathodes have several advantages over inorganic catalysts like Pt**
  - **Inexpensive**
  - **Sustainable**
  - **Resistant to sulfide poisoning.**

# CONVERSION OF MFC TO MEC SYSTEM & IN-SITU ENRICHMENT





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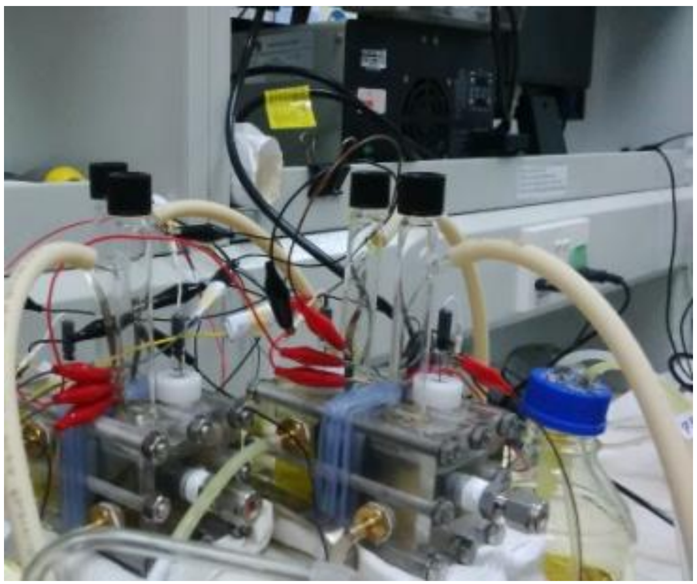
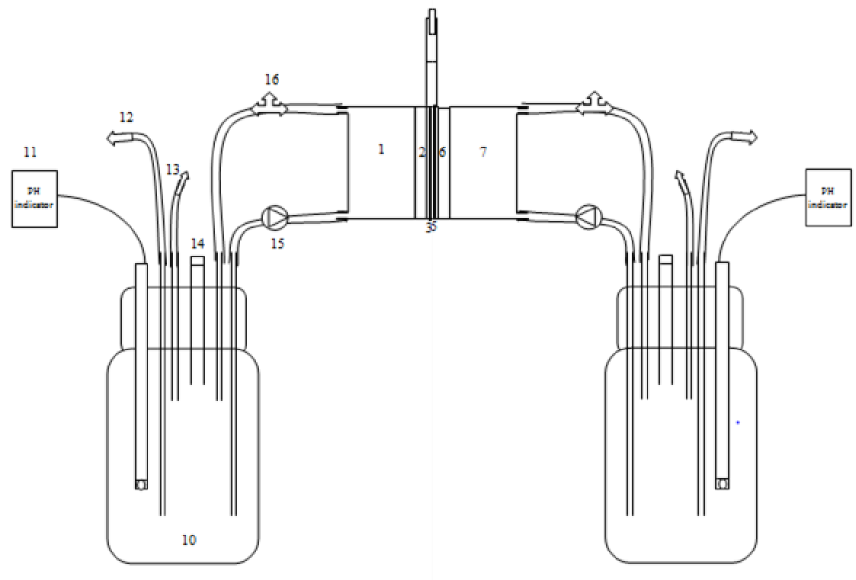
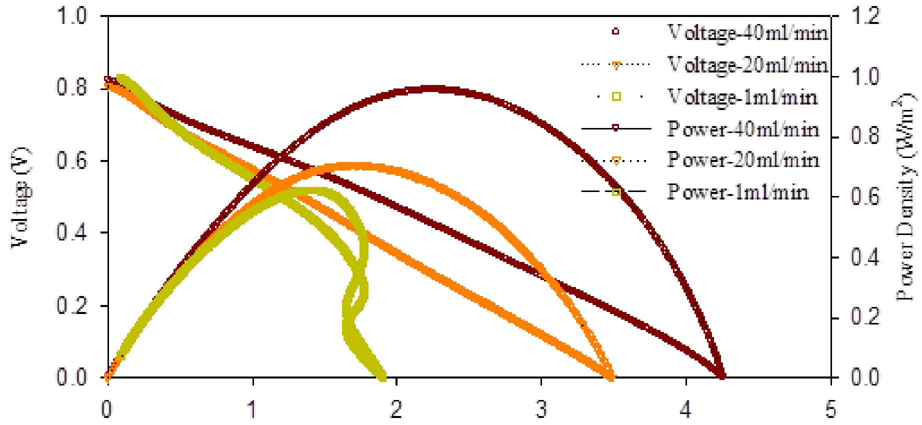
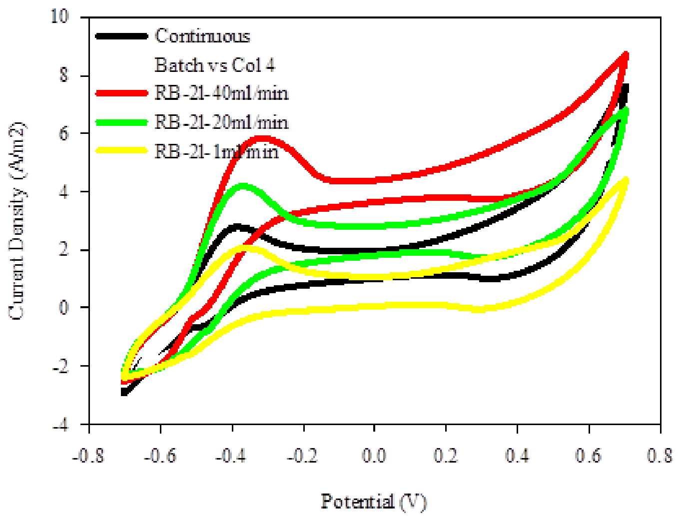
# RECIRCULATED BATCH MICROBIAL ELECTROLYSIS CELL

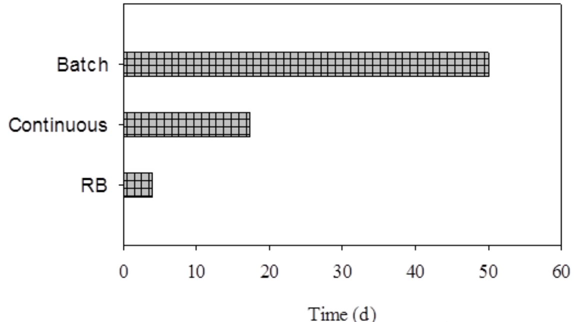




# RECIRCULATED BATCH MICROBIAL ELECTROLYSIS CELL




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.**

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Terima kasih

Thank you

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