Modeling and operation of scalable tubular microbial electrochemical technologies for the enhanced reduction of Co2 to liquid fuels

Researcher links UK-Russia workshop November 19th 2018

Iain Michie

Sustainable Environment Research Centre (SERC),
Faculty of Computing, Engineering and Science,
University of South Wales, Pontypridd,
Mid-Glamorgan, CF37 1DL, UK

Sustainable Environment Research Centre

- SERC is a multidisciplinary research centre, combining biology, chemistry, physics and engineering disciplines via a team with significant academic and industrial experience
- Focus on addressing major energy and environmental R&D challenges
- Emphasis on applied R&D, but with key areas of basic research
- Laboratory Facilities at Glyntaff (Pontypridd) and Baglan
- Current funders and projects including;



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Lifes-CO_2R - CO_2 reduction to formate

Project

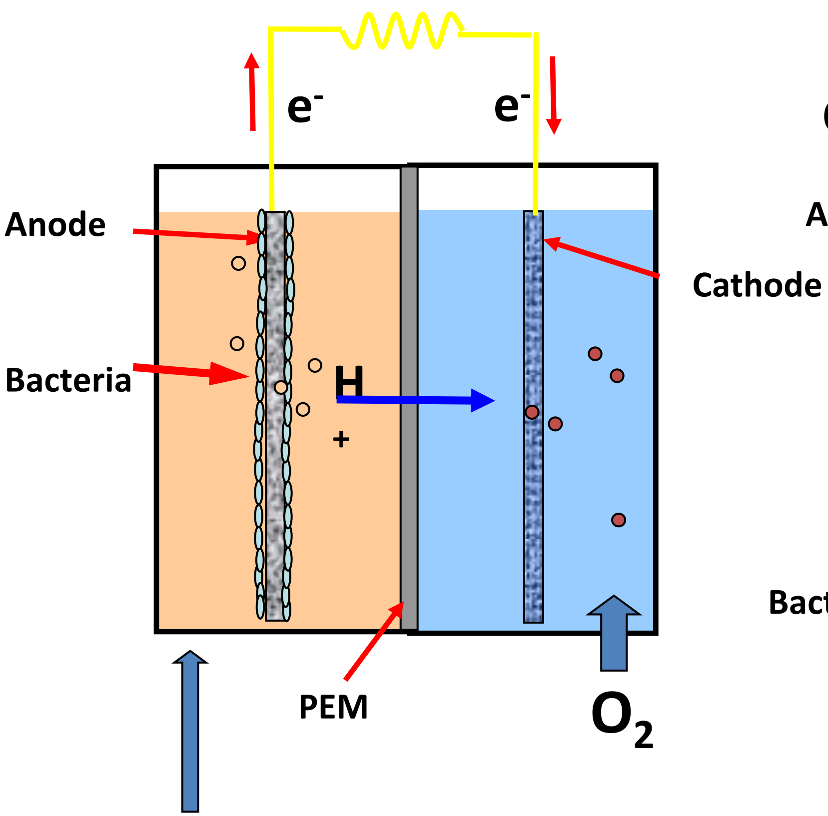
- Optimisation of **power** from relevant substrates
- Optimisation of cathodic systems for **CO_2 reduction to formate**
- Optimisation of **modular reactor configuration**, with attention to **materials and adsorption**
- Optimisation of **SimCell system** for **alkanes** from formate
- **Integration of SimCell and Microbial Electrochem Cells**, from simulation **to pilot**
- **Process integration** with **LCA** and **Policy Assessment**

Issues…

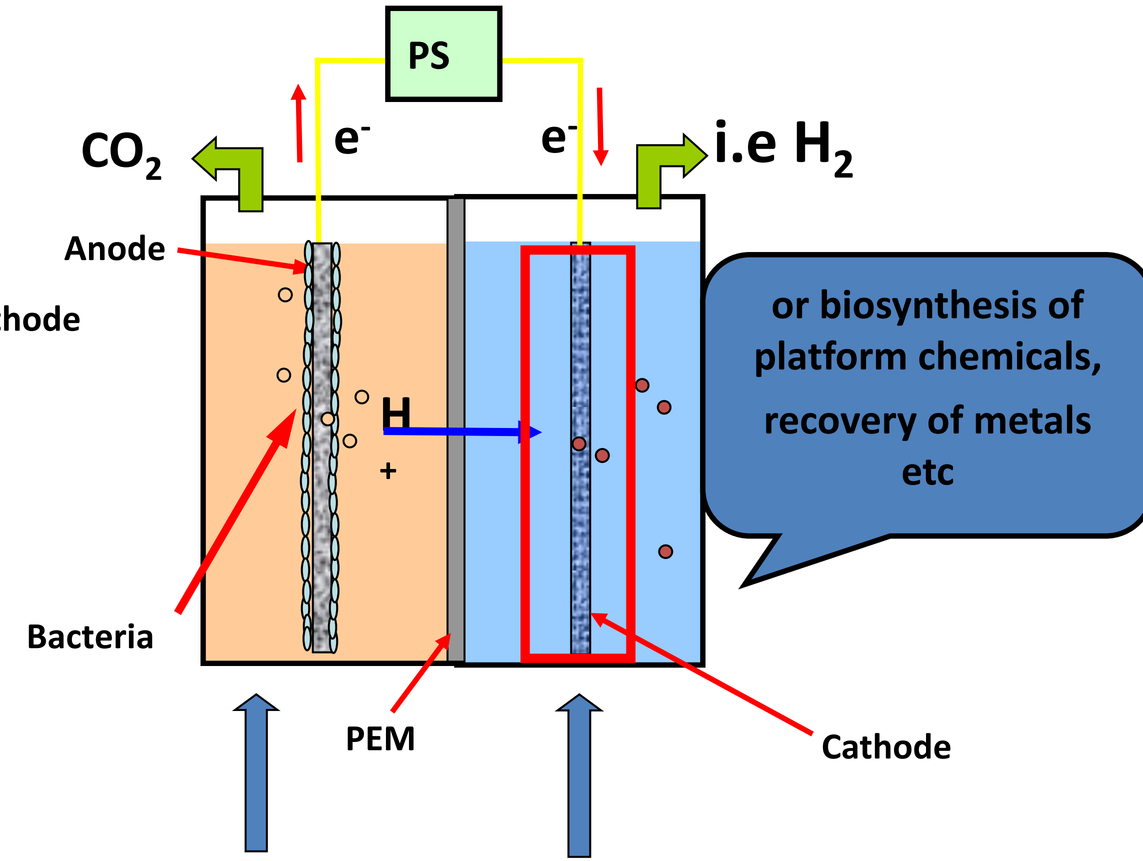
- Microbial rates and specificity
- Materials
- Reactor limitations
- Scale-up

Comparison of Microbial fuel cells and Microbial Electrolysis Cells

Microbial Fuel Cell (Spontaneous)

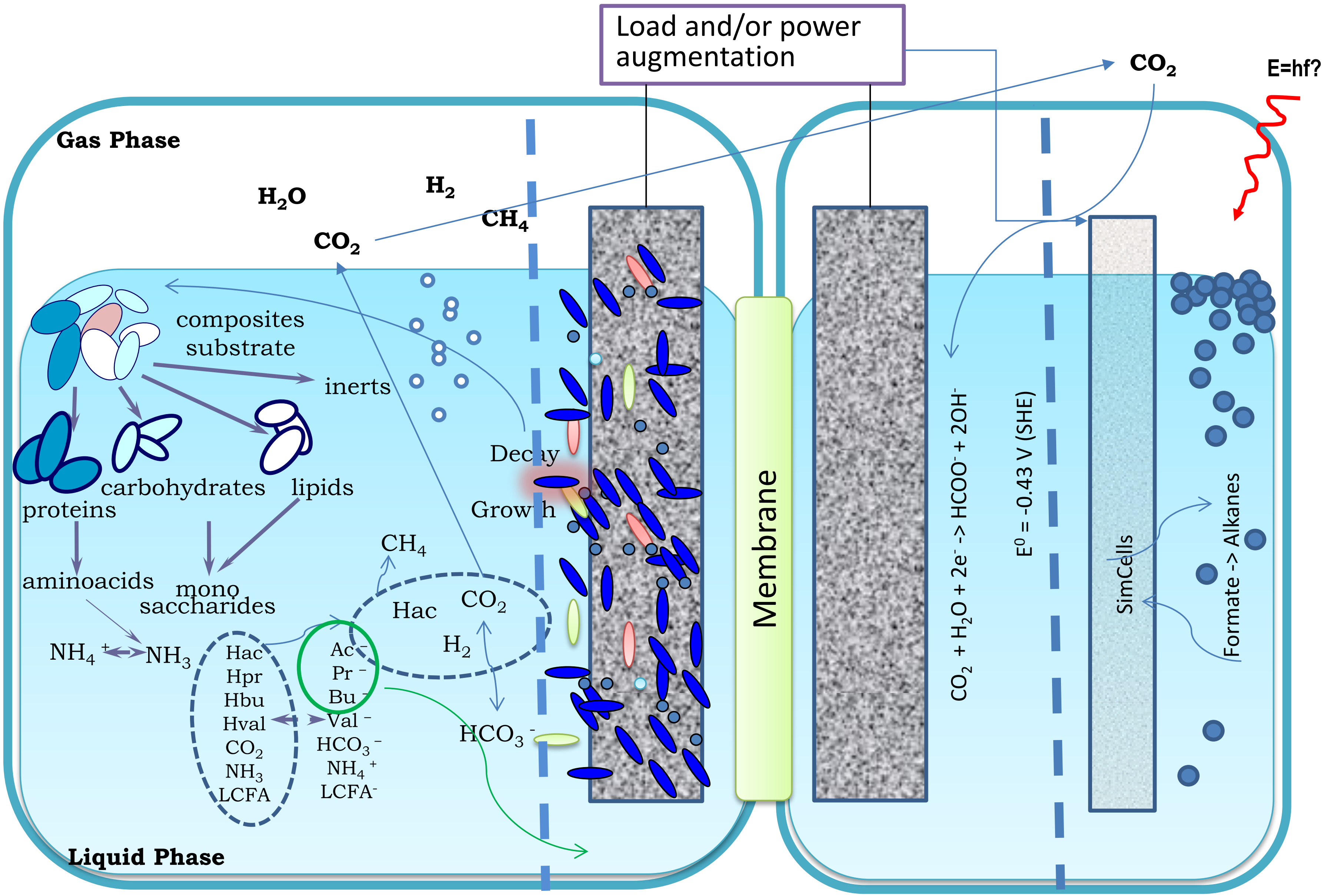


Microbial Electrolysis Cell (Non-spontaneous)



Wastewater flow into the anode

Wastewater flow into the anode/cathode?


Load and/or power augmentation
Gas Phase
H2O
H2
CH4
CO2
CO2
E=hf?
composites substrate
inerts
proteins
carbohydrates
lipids
aminoacids
mono saccharides
NH4+
NH3
Hac
Hpr
Hbu
Hval
CO2
NH3
LCFA
Ac-
Pr-
Bu-
Val-
HCO3-
NH4+
LCFA-
CH4
Hac
CO2
H2
HCO3-
Decay
Growth
Membrane
CO2 + H2O + 2e- -> HCOO- + 2OH-
E0 = -0.43 V (SHE)
SimCells
Formate -> Alkanes
Liquid Phase

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How can modeling help – MFC/MEC?

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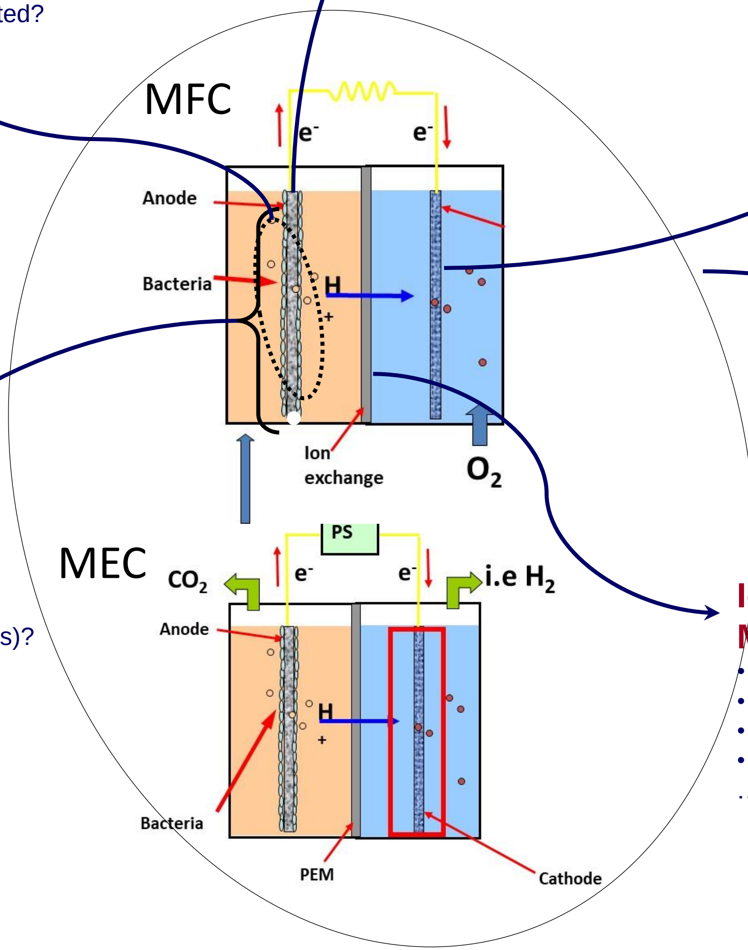
Electron Transport Mechanisms
• Which are the mechanisms?
• Which are dominant?
• How are they regulated?
…

Anode
• Materials
•Design
• Electrode kinetics
• Biological/biochemical processes
…

Cathode
• Materials
•Design
• Electrode kinetics
…



Modelling
Bottlenecks identification
• Testing of hypotheses
• Sensitivity analysis

Control
• Optimisation
•Scale-up

Integration & Operation
• Feeding strategy
•Flow rate
• Start-up procedures
…

Microbial Activity
• Which microbial activities (species)?
• Kinetic or energetic regulation?
• What are the regulatory rules?
• Role of microbial ecology
• Effects of the biofilm structure
…

Ion Exchange Membrane
• Materials
• Anion, cation selectivity
• Effect on coulombic efficiency
• Needed at all?
…

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Optimisation and Actuation

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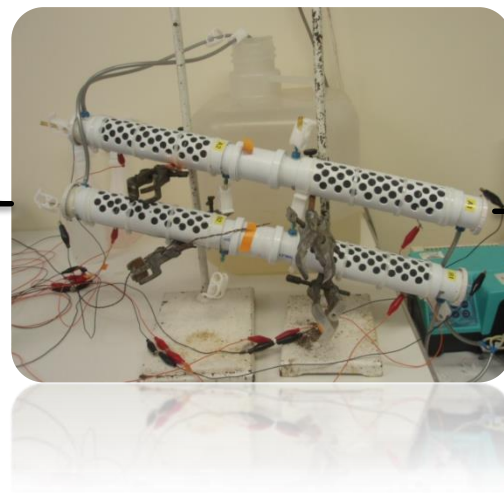
Complex interaction of co-dependent factors will drive performance

- Substrate characteristics, dilution rate, organic loading rate, nutrients
- Flow characteristics
- Inoculums and inoculation regimes
- pH buffering and dosing
- Conductivity of all phases/internal impedance
- Stack connectivity
- Temperature/Side reaction suppression
- Current sourcing from biocatalyst



MFC/BES

- Biocatalyst concentration, ecology and activity
- Biocatalyst retention, electron transfer and mass transfer
- Functional expression
- Inhibition and reaction kinetics
- Cell potentials and internal losses
- Current flow-paths, voltage reversal and power quality
- Conversion and COD removal efficiency
- Metabolism, function selection and competition

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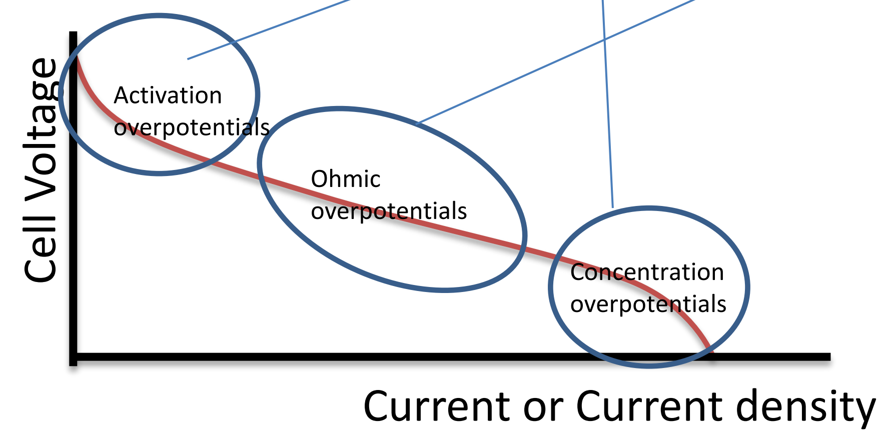
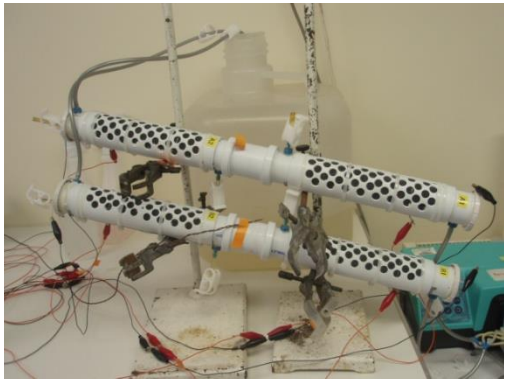
Design and scale-up: Implications for control

$$V_{cell} = V_e - \sum \eta_a - \left|\sum \eta_c\right| - IR$$

- Limitation on geometry and relationship to ohmic losses
- Modularization of some type
- Efficiently getting complex substrate to and removing products from microbial populations
- Hydraulic and gas diffusion sealing
- Cost effectiveness: substrates, products/ functions, CAPEX and OPEX





Continuous Operation of MFCs using Sucrose

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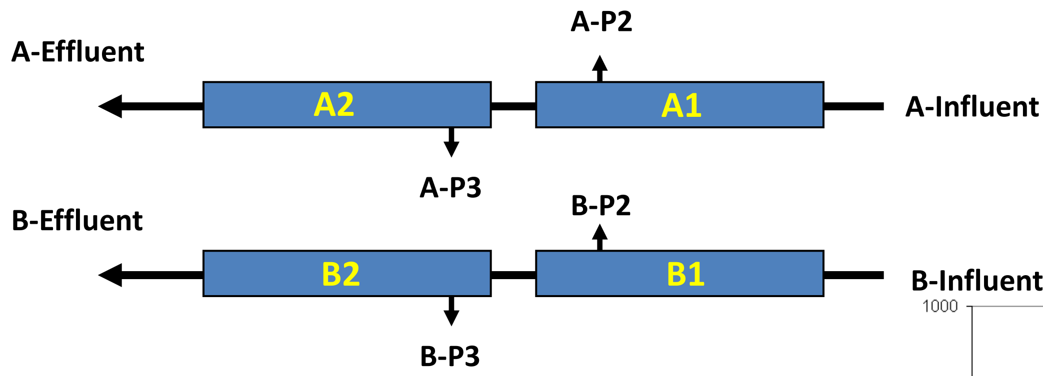
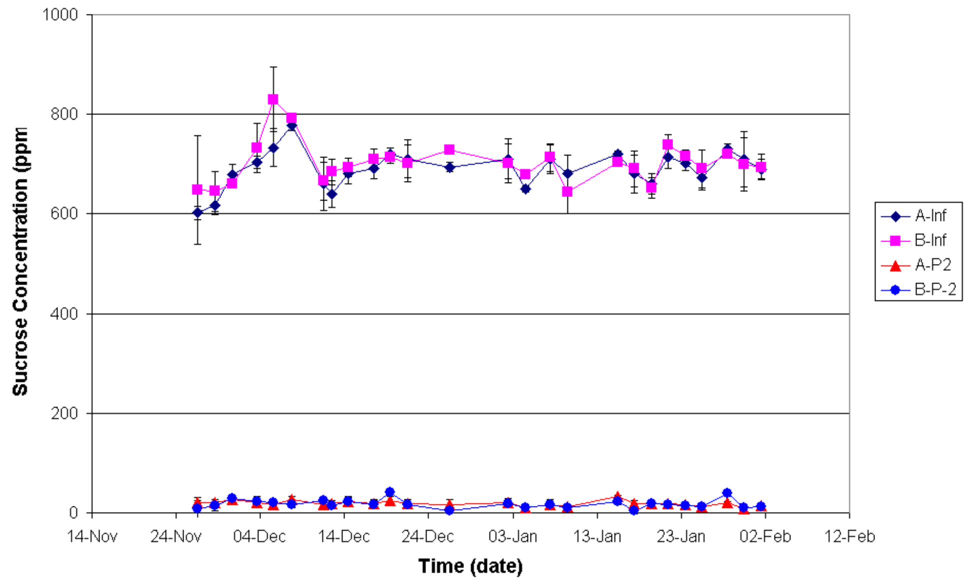
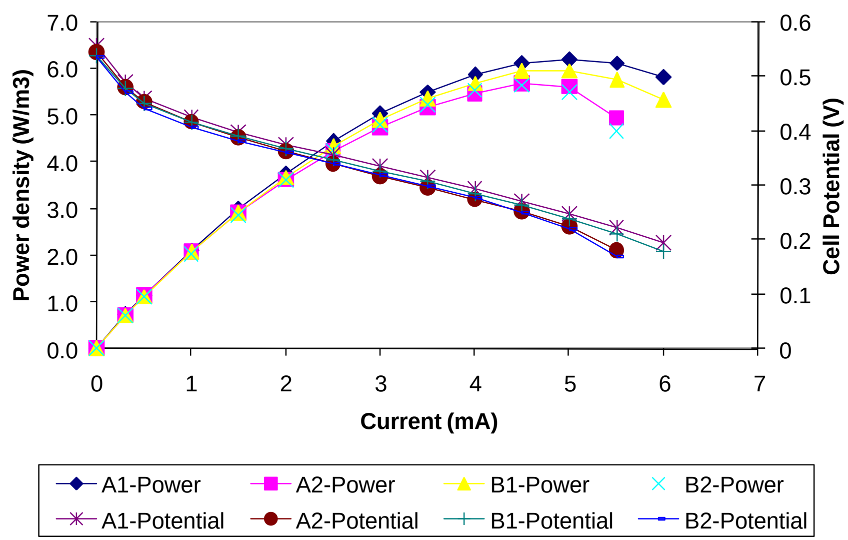


Tubular Concept development



- Sucrose (sugar) as the feed
  - Fermentable
  - At different concentrations
- HRT: 13.6 hr, pH 7.0, ~20°C
- Duplicated
- Able to get similar power from each module
- Able to replicate



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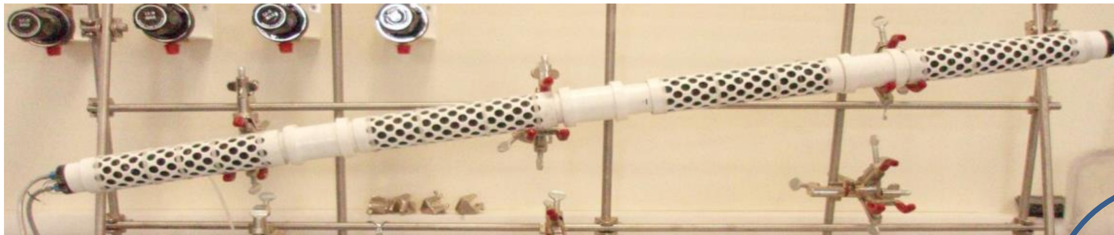
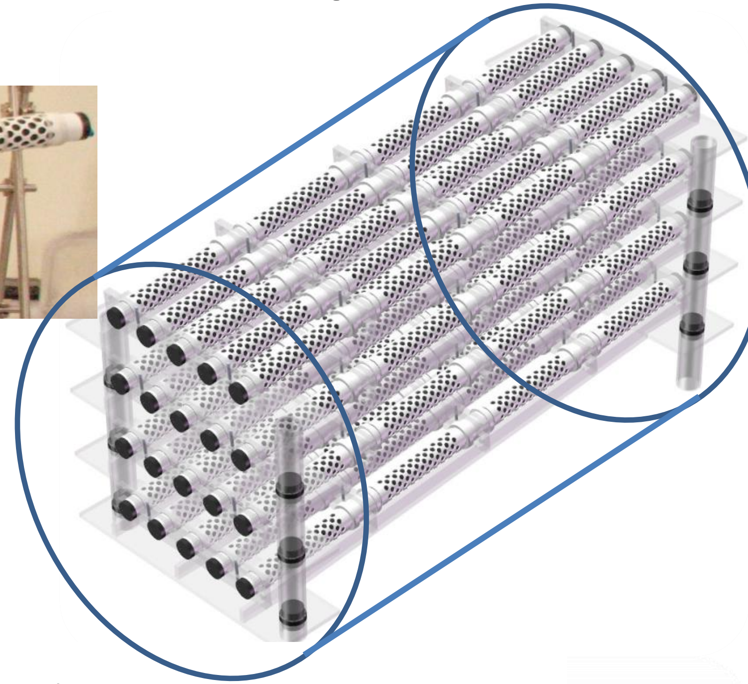
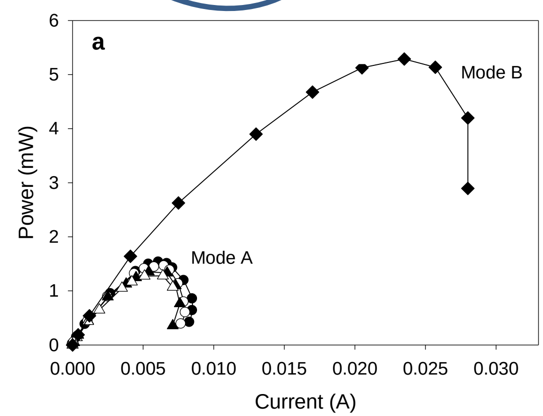
Replicating reactors – scale up





- Twice doubling its scale to 1 Lt
- Power recovery and COD removal comparable
- Power recovery and organic removal could be maximized by extending length
- Could simultaneously control effluent quality and power, facilitating scale-up.



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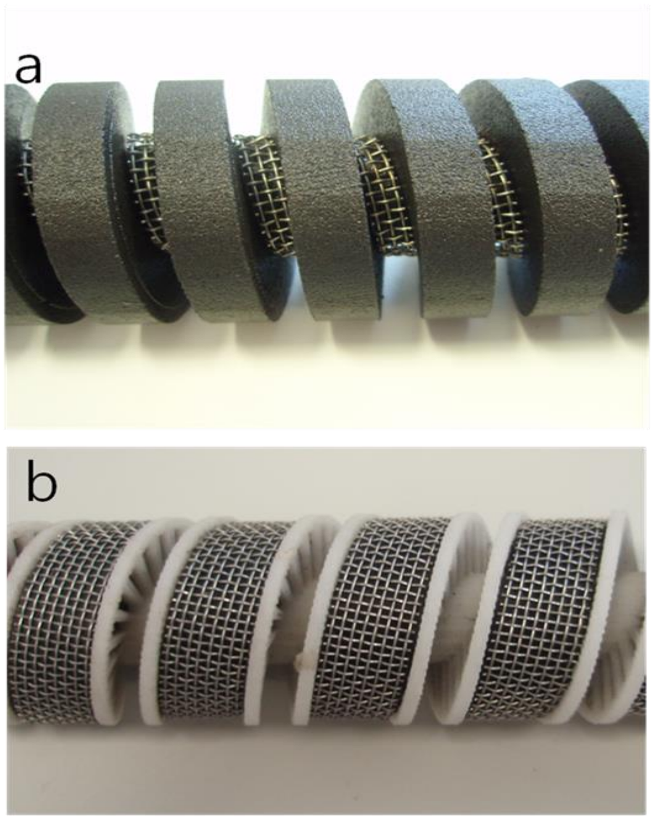
Scaling the anode performance

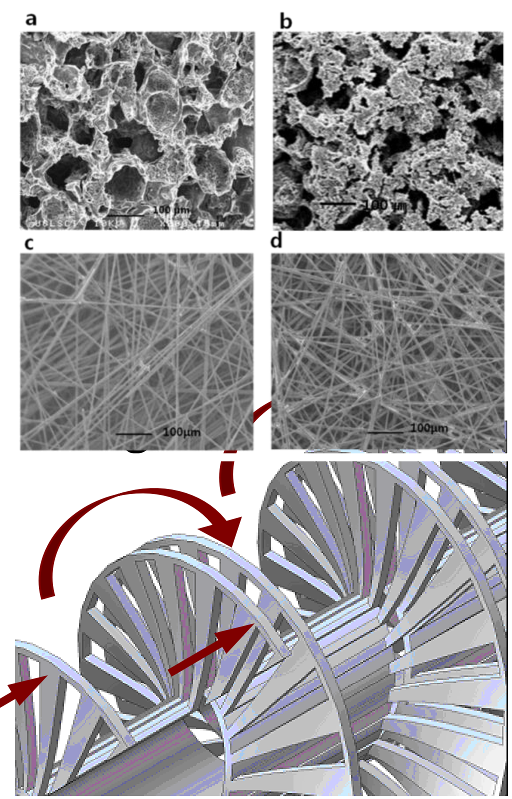
Volume of single tube (empty bed) = 1.5 L;
Power density = 30W/m^3 have been seen;
Length = 1 m;
Number of Anodes per meter = 5

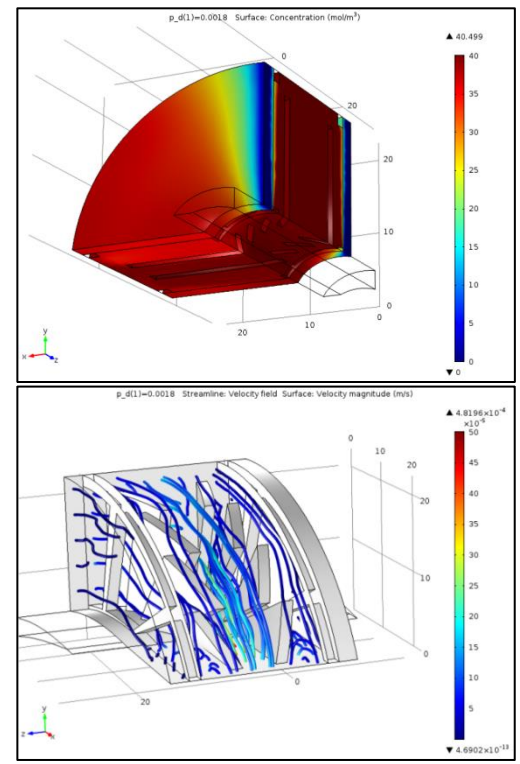
Volume of single tube (empty bed) = 0.88 L;
Power density = 6.1 W/m^3;
Length = 1 m;
Number of Anodes per meter = 4

Materials, design and mixing

- Biocatalyst to substrate contact involves economics as much as performance.
- HRT affects inhibitory products, flow velocities, mixing /mass transfer
- Turbulence and the flow direction affect performance.
- Materials are set, but biofilm, sloghing, even internal impedance conceivably affected.







Kim, J.R., H. Boghani, N. Amini, I. K. Aguey-Zinsou, Michie, R. M. Dinsdale, A. J. Guwy, X. Guo, G. C. Premier. 2012. Porous anodes with helical flow pathways in bioelectrochemical systems: The effects of fluid dynamics and operating regimes. Journal of Power Sources.

Enhancing mass transport in helical electrodes

- Fluid flow in free and porous medium (Stokes-Brinkmann equations)

$$\frac{\rho}{\varepsilon_p}\left(\mathbf{u}\cdot\nabla\frac{\mathbf{u}}{\varepsilon_p}\right) = \nabla\cdot\left[-p\mathbf{I} + \frac{\mu}{\varepsilon_p}(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2\mu}{3\varepsilon_p}(\nabla\cdot\mathbf{u})\mathbf{I}\right] - \frac{\mu}{\kappa_{br}}\mathbf{u}$$

$$\rho\nabla\cdot\mathbf{u} = 0$$

- Mass transport of diluted chemical species (Fick's law for diffusive term)

$$\nabla\cdot(-D_j\nabla c_j) + \mathbf{u}\cdot\nabla c_j = R_j$$

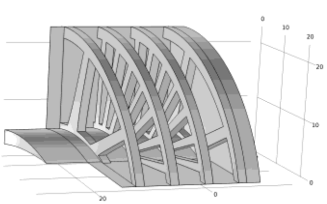
$$\mathbf{N}_i = -D_j\nabla c_j + \mathbf{u}c_j$$

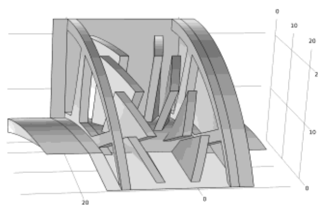
- Acetate degradation according to monod kinetics

$$R^{s}_{ac} = \frac{R^{s}_{ac,max}\cdot c_{ac}}{K^{s}_{ac} + c_{ac}}$$

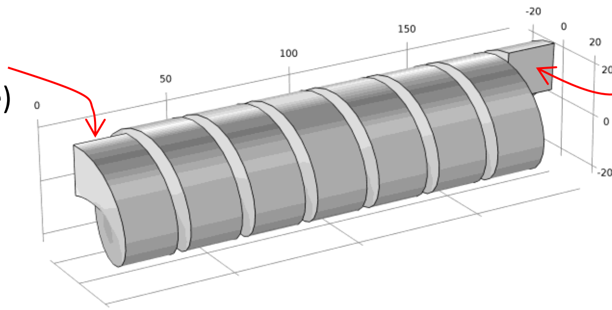
- Mixing ratio

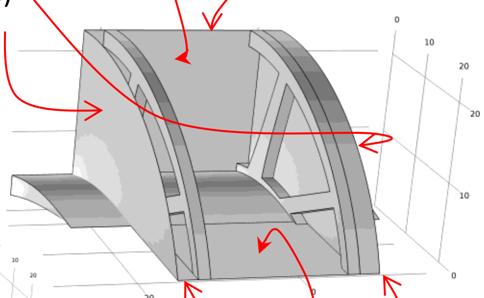
$$S_{outlet} = \frac{\sum_{i=1}^{n}(c_i - c_{av})^2 \ at\ outlet}{\sum_{i=1}^{n}(c_i - c_{av})^2 \ at\ inlet}$$





Model Set-up





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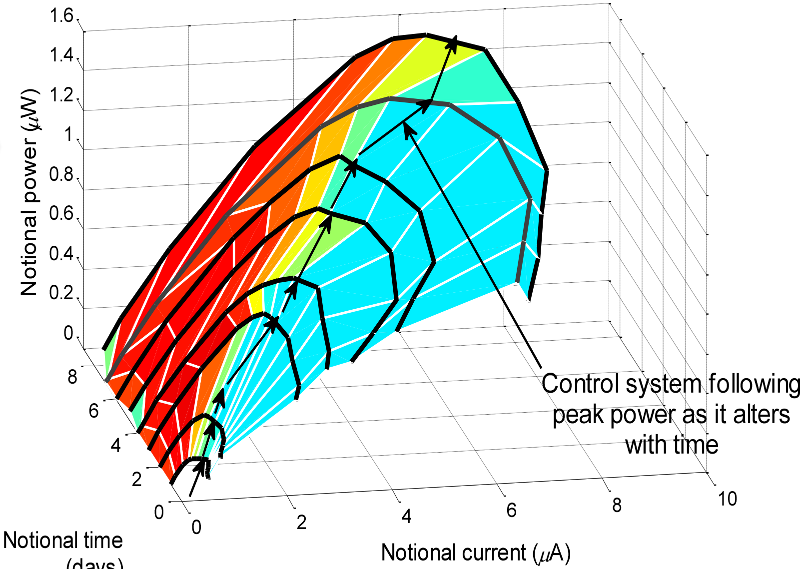
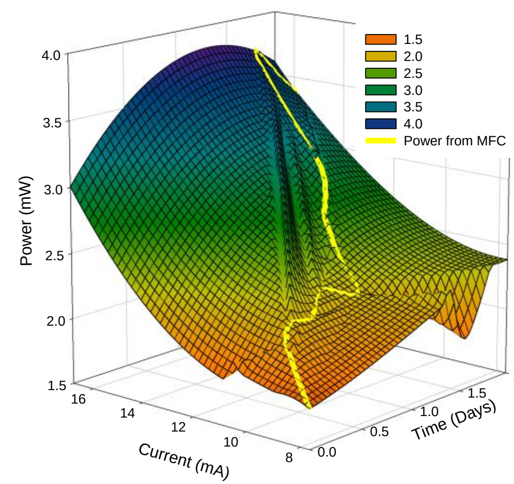
Control as a mechanism to improve metabolic processes

Maximum power point tracking (mppt)



We postulated – that it was possible to enhance the power generated by an MFC/BES by:

- Tracking the peak power to achieve impedence matching - load and internal impedances equal
- And... maintaining a persistent increasing electrical loading pressure on electrogens -
- So altering biofilm ecology for high performing electrogens.



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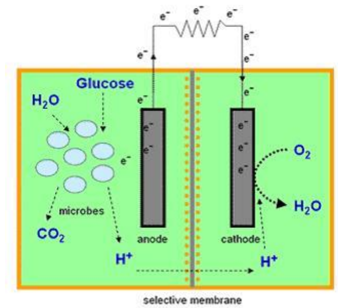
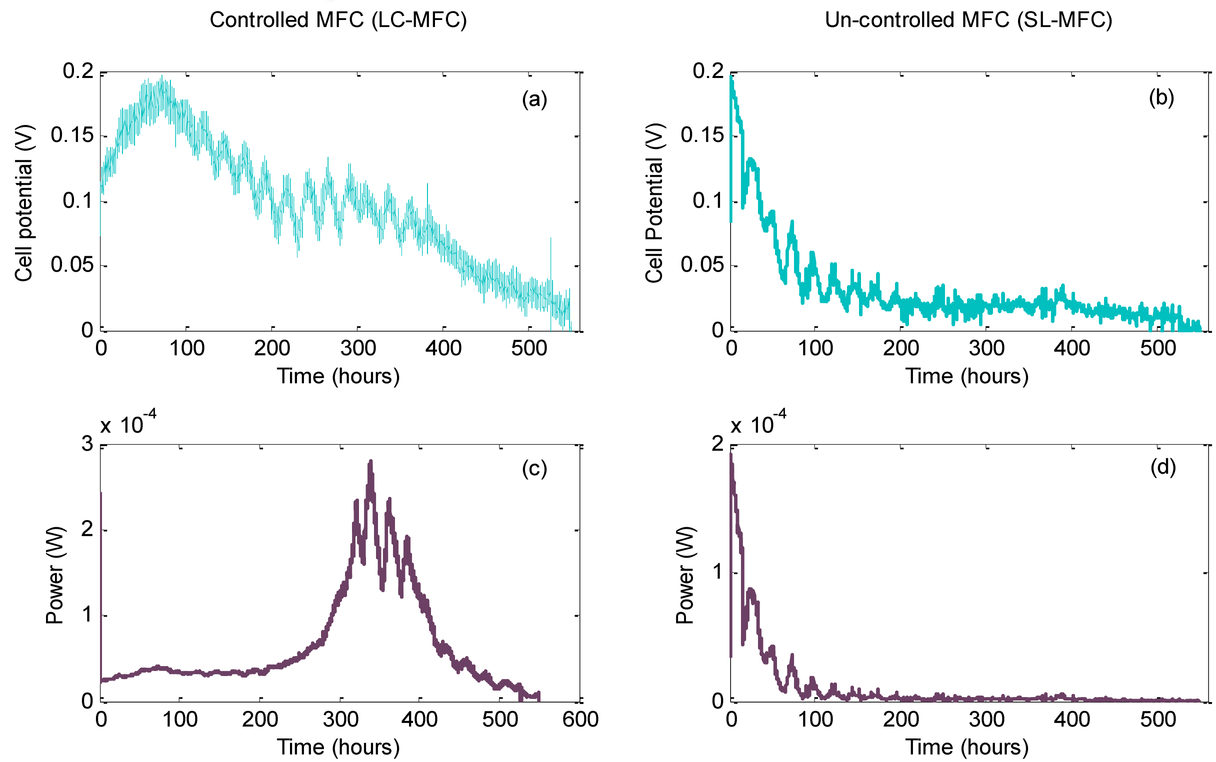
Control as a means to improve performance

Higher coulombic efficiencies
Higher cell potentials



- MPPT is beneficial to BES
- The control strategy imposes selection pressures
- Favouring electrogenic behaviour
- 5 times more energy as electricity from the controlled MFC



Premier GC, Kim JR, Michie I, Dinsdale R, Guwy A. 2011. Automatic control of load increases power and efficiency in a microbial fuel cell. Journal of Power Sources 196:2013-2019.

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Controlling MFCs in stacks

- **The issues**
  - Power quality is low (voltage). Reversals have been noted when stacking (Oh & Logan, 2007; Ieropoulous et al, 2009)
  - Large stacks with variable OLR, pH etc will be difficult to equilibrate.
- Connectivity and control were considered (Fig 1) to improve the cell stability compared to Fig 2.
- Causing an imbalance in the stack by supplying 2mM Ac to MFC1&3 and 0.5 mM to MFC2 – could investigate stability/reversal.

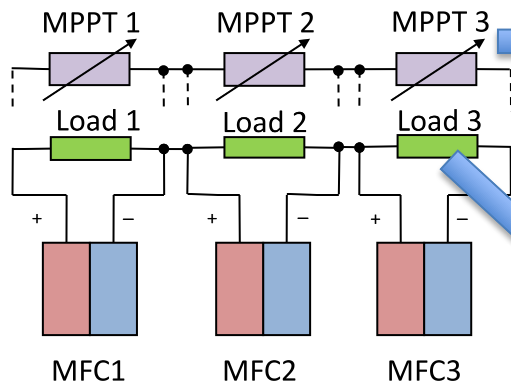
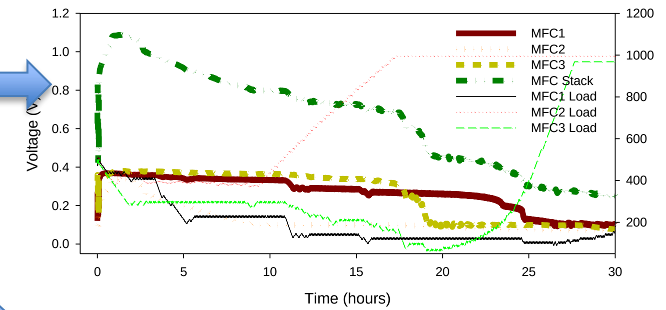
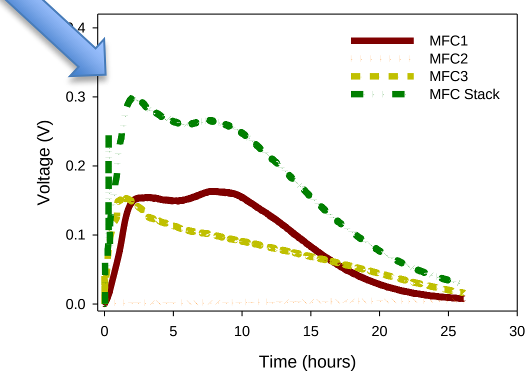


Fig 1 – Series/parallel and Controlled





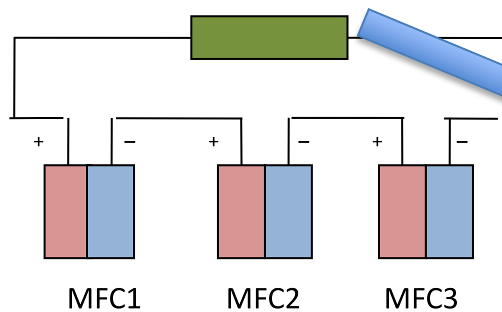
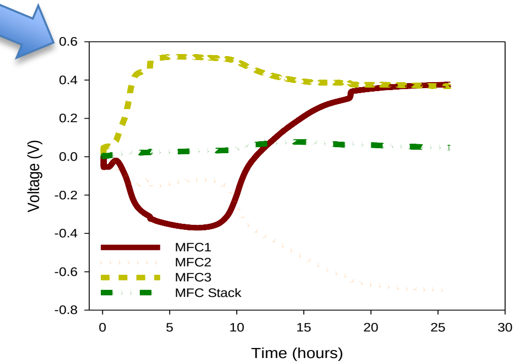


Fig 2 – Without control



Boghani, H. C., Papaharalabos, G., Fradler, K., Michie, I., Dinsdale, R. M., Guwy, A. J., Ieropoulos, I., Greenman, J., and Premier, G. C. (2014) Controlling for peak power extraction from microbial fuel cells can increase stack potential and avoid cell reversal, *Journal of Power Sources*.

Comsol - Modeling Tubular MFC

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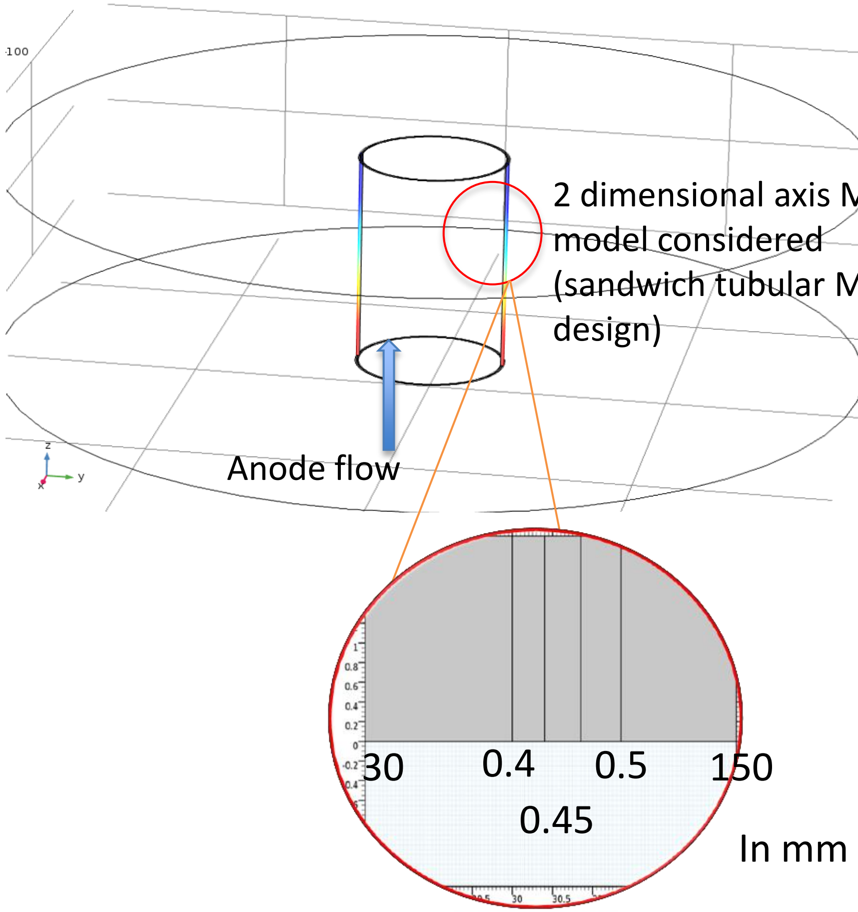
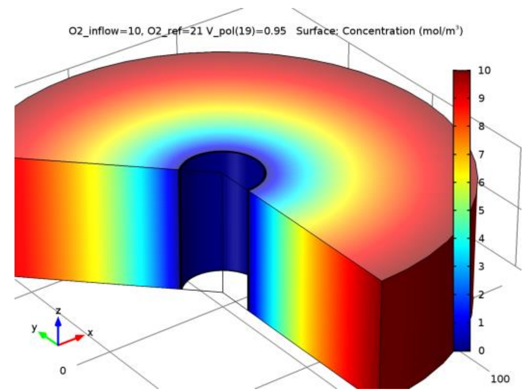
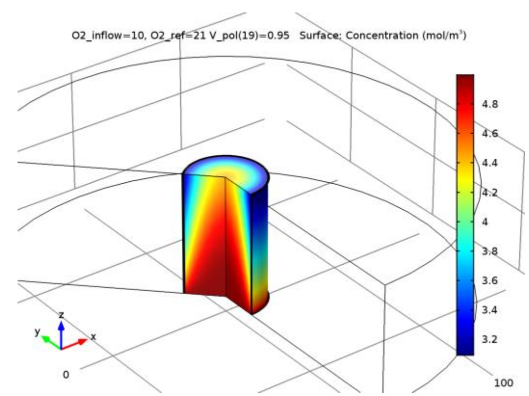
Finite element analysis to help understand BES



anolyte-anode-IEM-air cathode



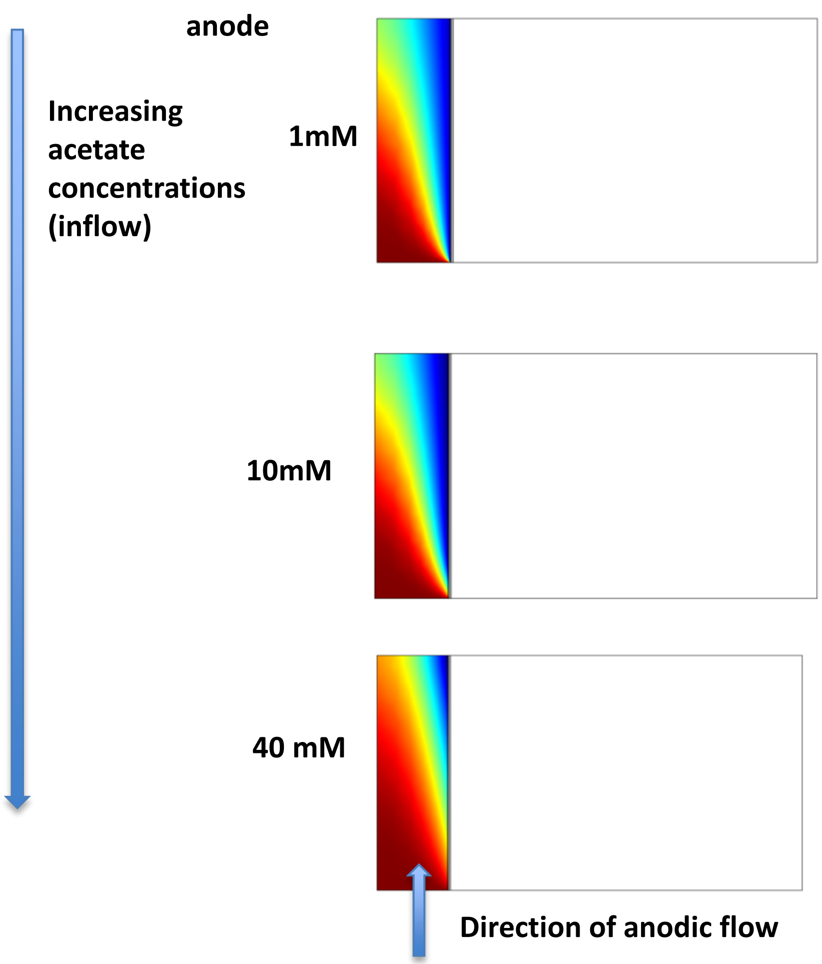
Concentration of Oxygen around the Cathode



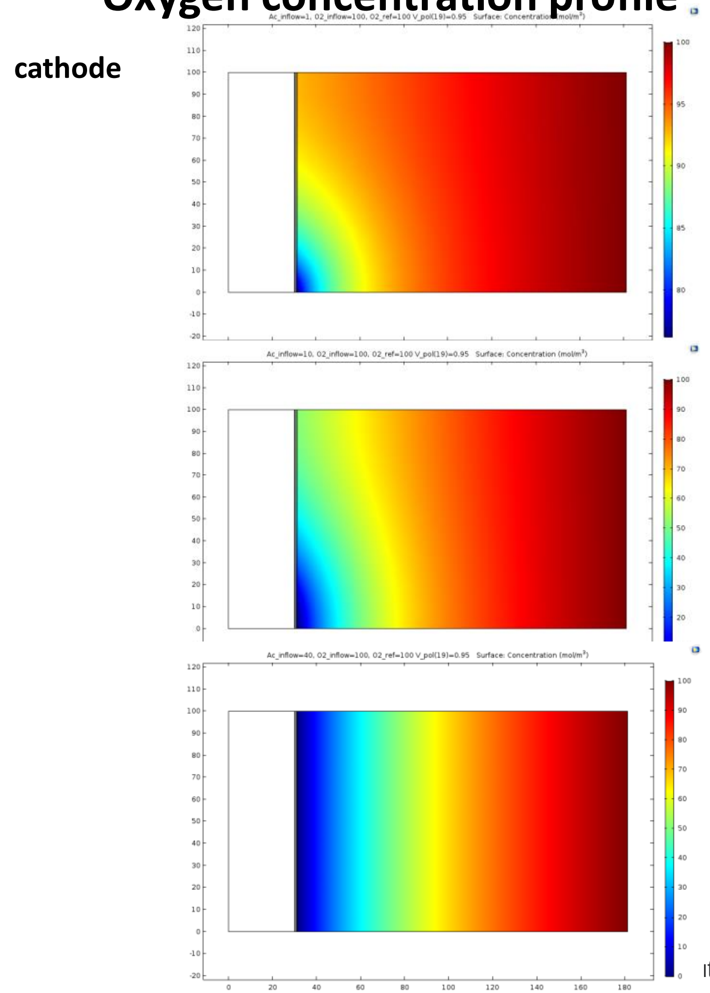
Concentration of Acetate in anode chamber

Modeling MFCs

Acetate concentration profile due to flow



Oxygen concentration profile



CONCLUSIONS

- Control and design strategies to enhance system performance
- Mechanistic models allow for the interpretation of interactions and behaviors in BES.
- BES models can be used for preliminary scale-up design and feasibility studies.
- Use in the design and validation of scaled integrated BES for the production of chemicals from CO_2

Thank you!

Any questions