## Supplemental Information

### *1.0 Calculation of proton concentration using changes in pH and hydrogen measurements:*

Change in proton concentration can be written as:

$$\Delta[H^+] = \left[m_{[H^+],cat}\right] t_0 + \left[m_{[H^+],cat}\right] t_{end}$$

Based on the Henderson-Hasselbalch equation, the pH change in a cathode can be described by the following equation:

$$pH_{cat} = pK_a + \log_{10}\frac{\left[K_2HPO_4^-\right]_{ini} + \Delta[H^+]}{\left[KH_2PO_4^-\right]_{ini} - \Delta[H^+]}$$

The *$\Delta[H^+]$* can be calculated from this equation, since the other parameters are known or measured experimentally. Subtracting this number of moles (consumed from the cathode buffer solution, *$\Delta[H^+]$*) from the total moles of protons required for hydrogen production (using experimental volume of hydrogen produced), one can obtain the moles of protons transferred to the cathode from the anode. This is used to calculate the rate of proton transfer.

### *2.0 Table of MEC experimental conditions:*

| Flow rate, mL/min | Organic Loading Rate (OLR) | Concentration, g/L |
|---:|---:|---:|
| *0.3* | *0.85* | *0.026* |
| 1 | 3 | 0.026 |
| *2* | *5.85* | *0.026* |
| *3.6* | *10* | *0.026* |
| | | |
| 0.3 | 10 | 0.3 |
| 3.6 | 100 | 0.26 |
| 0.3 | 100 | 3.0 |
| | | |
| 0.188 | 20 | 1.0 |
| *3.6* | *20* | *0.05* |

*Table S1. Experimental conditions under which MEC was tested for assessment of proton transfer rate. EIS studies were conducted for some of the conditions as highlighted in blue.*

### *3.0 Cell potential during EIS experiments.*

The EIS experiments were conducted at a fixed anode potential of -0.2V. This condition resulted in a different cell potential (Anode potential – cathode potential). These values are listed in Table S1 below.

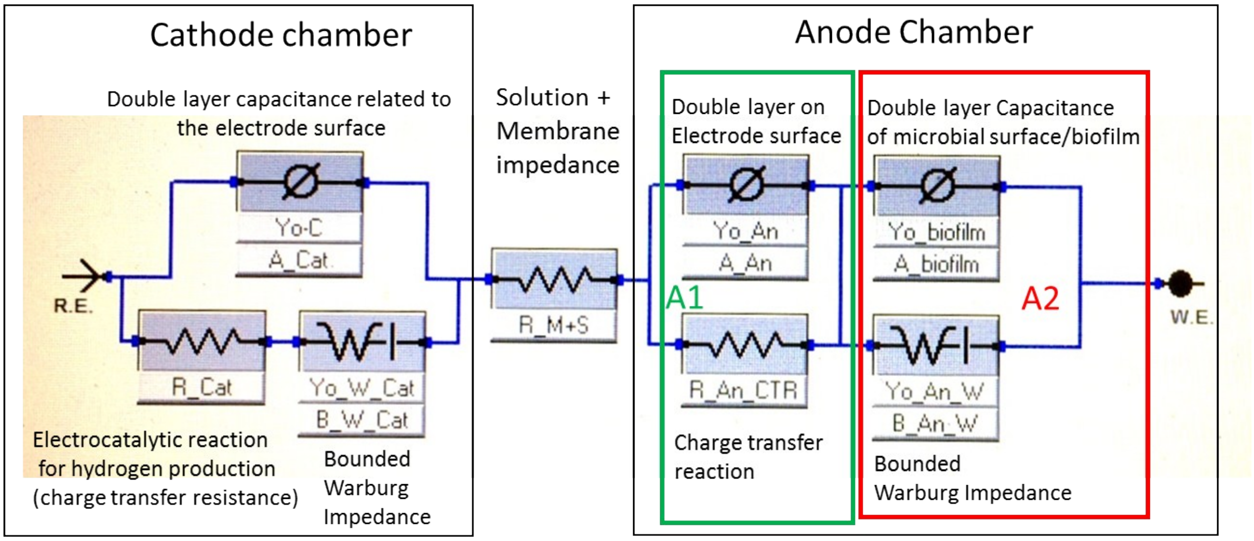
| Run # | Flow rate, mL/min | Organic Loading Rate | Cell Potential, V |
|---|---|---|---|
| 1 | 0.3 | 0.85 | 0.78 |
| 2 | 2 | 2 | 0.65 |
| 3 | 3.6 | 10 | 0.77 |
| 4 | 3.6 | 20 | 1.1 |

Table S2. Cell potential reached at the end of experiments.

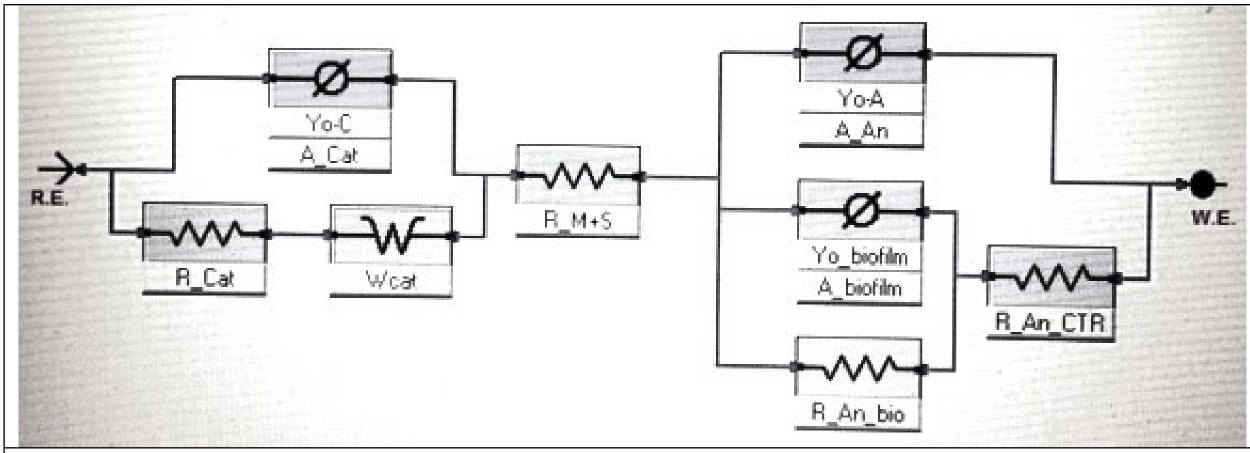
### *4.0 EIS models*

In order to fit the impedance spectra, the following models were examined. The first model (A) was used for the MEC analysis, since it fit the data the best and was most relevant in terms of physical representation of the system. The other models (B & C) did not fit the data as well as the first model, as evidenced by goodness of fit which was higher than 0.0001. The lower the parameters, the better the data fitting.

A



B



*C*

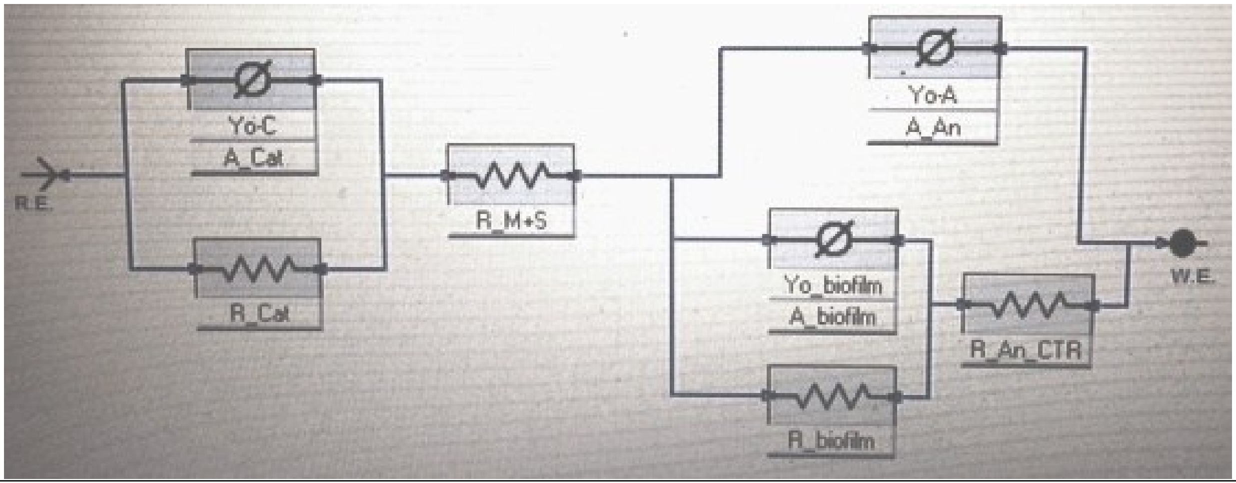


*Figure S1. Equivalent circuit model used for analysis of impedance spectra. The circuit shown in A includes components for bioelectrochemical reaction at the anode, Warburg diffusion in the anode, capacitive impedance due to double layer formed on the electrode and the biofilm surface, solution and membrane resistance, electrochemical reaction at the cathode, diffusion of reactants/products in cathode and the capacitive impedance due to the double layer at the cathode surface. Alternate equivalent circuit models explored to fit the data are shown in sections B and C. These latter models did not provide a better fit than the model shown in section A.*

## *5.0 Charge transfer by cations vs. protons.*

Figure shows distribution of charge transferred by protons vs. cations other than protons. At low loading rates, most of the charge is transferred by cations, but as the loading increases, the contribution of proton transfer to charge transfer increases.

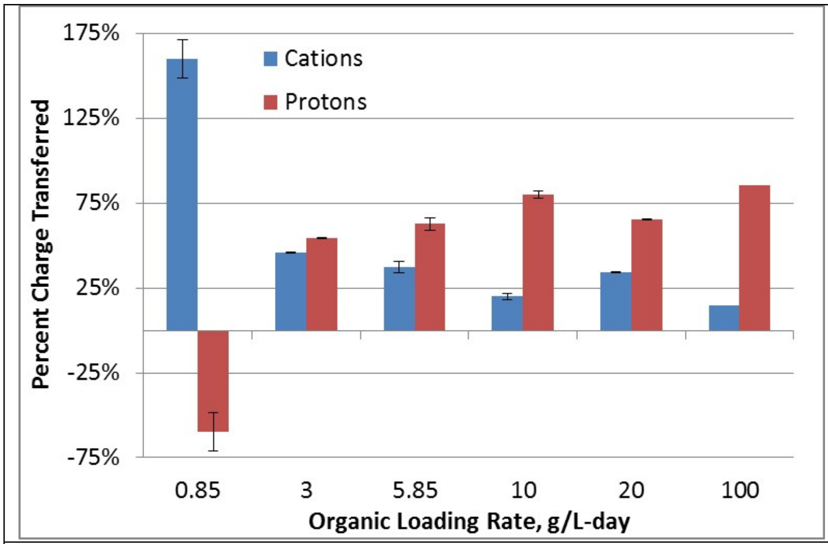


Figure S2. Distribution of charge transferred by protons vs. other cations, during production of hydrogen in MEC.

*6.0 Effect of run time on hydrogen productivity.*

In addition to the effect of proton availability in the cathode, the run time also affects the measured hydrogen productivity during a batch run. The production of hydrogen is highest at the start of the experiment when the cathode pH is lowest. As time progresses, the hydrogen productivity drops and approaches the productivity possible using the protons transferred from the anode to the cathode. The difference of the measured hydrogen productivity vs. that derived using Equation 15 for all the experiments was plotted in Figure S3. This differential productivity drops as time progresses as expected, proving that the cathode supplies the excess protons needed for higher hydrogen productivity, above what is predicted by Equation 15.

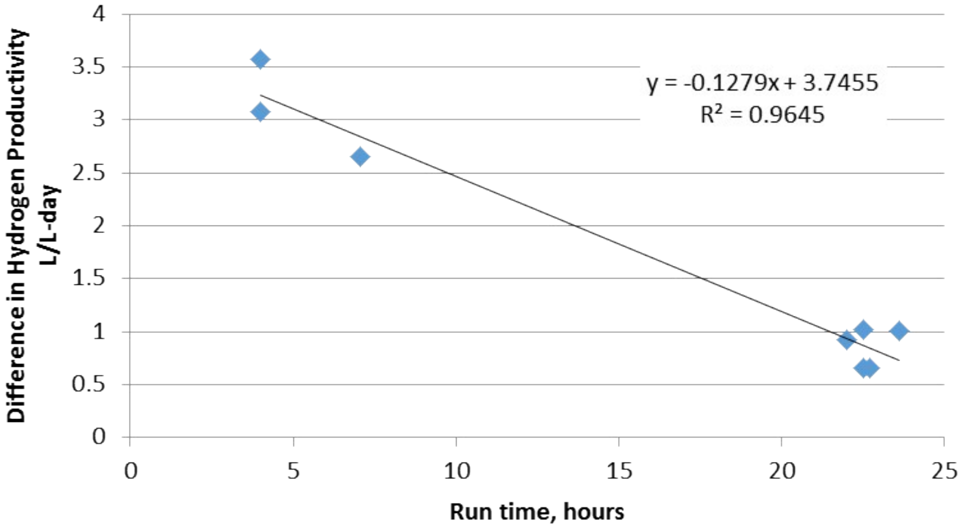


*Figure S3. Effect of run time on hydrogen productivity during a batch run.*