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Wafer Enhanced Electrodeionization for Conversion of CO2 into Bicarbonate Feed for Algae Cultured Photobioreactors

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Table of Contents

Abstract

The world has acknowledged climate change as a global crisis that demands considerable attention, with one of the largest culprit being carbon emissions from industrial processing and power generation. While reduction in carbon emissions is the principal action towards mitigating the effects of climate change, scientists and engineers have given increased attention to alternative sources of energy as well as methods of carbon sequestration to coax traditional manufactory and industry into environmentally friendly and sustainable practices. One technology of this nature is the use of wafer-enhanced electrodeionization (WE-EDI) membranes to convert gaseous carbon dioxide (CO_2) from industrial flue gas into aqueous bicarbonate (HCO_3^-) to be used in enriched media to feed and grow *Chlamydomonas reinhardtii* algae in a photobioreactor. Studies have shown that this species of algae experience enhanced and controlled growth with soluble HCO_3^- as the sole or as an additional carbon source to air. Algae photobioreactors can then conduct various coveted conversions and recycling, such as bioethanol and biodiesel from waste water sources. In the following investigations, low concentrations of bicarbonate addition to algae media, up to 0.1mM, show a slight increase in algae growth and stabilization after 14 days. Higher concentrations past 0.1mM seem to stunt growth and delay the stabilization phase. With regards to investigations on the WE-EDI, while the system can successfully carry out the c conversion, the system suffered consistent failures with internal leaking, in which one of the liquid chambers would mix with the other. The most notable area involves highly acidic solution in the dilute chamber leaking into the positive electrode rinse chamber. This internal leaking will cause long term damage to the system's electrodes, which require buffer rinse solutions so as to prevent ion accumulation and corrosion. Regardless of this, carbon dioxide mix delivery tanks were also difficult to obtain, so investigation with gas delivery

into the WE-EDI was mostly unavailable. Ultimately, this report enumerates efforts to operate a WE-EDI system of this nature, the techniques learned, and provides conjecture and research as to the feasibility of this technology. This research will aid efforts to increase the viability of sustainable algal processes in industry such as this, and will hopefully inspire more widespread investigation and application of efficient and profitable flue gas scrubbing of carbon emissions in order to combat their globally destructive effects.

Bicarbonate Feed for Algae

Algae culturing has become a promising candidate for novel technologies in alternative and sustainable energy to rival conventional sources due to its rapid growth and biomass accumulation with low requirements of freshwater and energy. Harvested algae cultures can be extracted for triacylglycerols (TAGs) and converted into fatty-acyl methyl esters (FAMEs), commonly known as biodiesel compounds (Christi 2017). Cultures can also be fermented for ethanol, butanol, or methane for fuel sources and additives, as well as other bio-based chemical building blocks. One of the biggest applications of interest for algae is in wastewater treatment. While some argue that biofuel production alone through algae cultured bioreactors would not be energy positive (Pittman, Dean, & Olumayowa 2011) and therefore not economically feasible, pairing this with wastewater treatment may help, particularly with industrial brine water sources. Through this research, another utility of algae-based processing in the form of carbon sequestration from flue gas may further increase this technology's economic desirability.

While most autotrophs solely require CO_2 as their carbon source, other organisms such as algae can metabolize aqueous HCO_3^- as well. In fact, research has shown that HCO_3^- addition to CO_2 feed increases carbon storage and stability within algae cultures, suggesting an advantage to using HCO_3^- for algae-based industrial settings. Figure 1 shows results from (Gardner *et al*. 2012), demonstrating how HCO_3^- in media with 5% CO_2 bubbling affects cell growth, with and without air. The most notable effect of HCO_3^- addition is the stabilizing of culture cell count after 3 days. Furthermore, Figure 2 from (Gardner *et al*. 2012), plots Nile Red fluorescence for three algae samples over time. Nile Red fluorescence has become a reliable measure of TAG concentration (Chen *et al*. 2009). This shows how HCO_3^- addition yields the highest and most

stable accumulation of TAGs; even if sole addition of CO_2 yields a higher TAG accumulation at first, HCO_3^- added cultures catch up, surpass, and stabilize after 6 days. Such findings suggest more desirable conditions for algae based industrial processing, where culture density and product yield is more controllable.

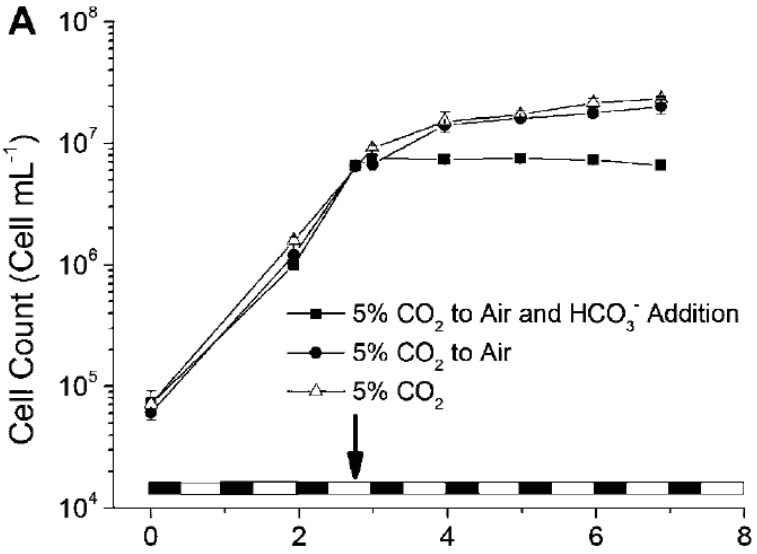

Figure 1. *C. reinhardtii* batch growth cell count over time with 5% CO_2 bubbling without air bubbling, with air bubbling, and with air bubbling paired with 50mM HCO_3^- addition. HCO_3^- addition stabilizes cell density after a period of growth. (Gardner *et al.* 2012).

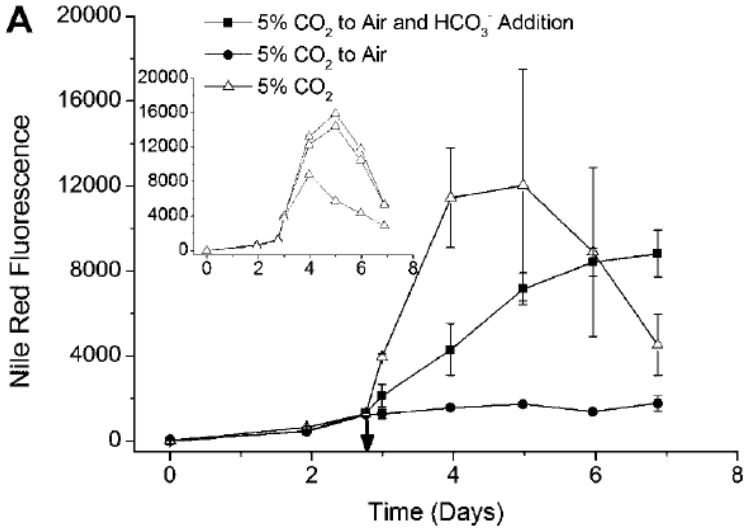

Figure 2. *C. reinhardtii* Nile Red Florescence (correlating to TAG accumulation) over time with samples referred to in Figure 1. HCO_3^- addition accumulates more TAG in the long run and stabilizes. (Gardner *et al.* 2012).

Materials and Methods

To confirm the effect of HCO_3^- addition towards enhanced algae growth, four 1L bottles sterilized in an MLS-3751L SANYO autoclave with Bold's Basal Media (BBM) were prepared with 0ml, 1ml, 2ml, and 3ml of 50mM sodium bicarbonate solution respectively. The bottles were sparged with laboratory house air sterilized through ArcroVent® 0.2µm PTFE filters and inoculated with 10% volume with stock *C. reinhardtii* algae in media (100ml per bottle). Due to the absence of a biosafety cabinet among the facilities, constant sterilization was maintained by spraying nitrile gloves with 70% ethanol, and using an open flame burning 95% ethanol to heat areas of potential contamination, for example the mouths of the media bottles when transferring inoculate from stock to experiment bottles, as well as aluminum foil coats around cotton plugs on the mouths of the bottles.

7mL samples were taken periodically throughout their growth cycles and 5ml of which were filtered through Whatman glass microfiber filters from GE Healthcare and placed in petri dishes covered in aluminum foil to enhance heat drying on both sides. The clean filters had previously been dried for at least 24 hours then tared using a Mettler Toledo AB104-5 analytical balance before dry weight was filtered through. The filters are then dried again to evaporate any remaining liquid for another 24 hours and weighed against the tare. The net weight is recorded and divided by the sample volume to give cell density. The results are given in Figure 3.

Result

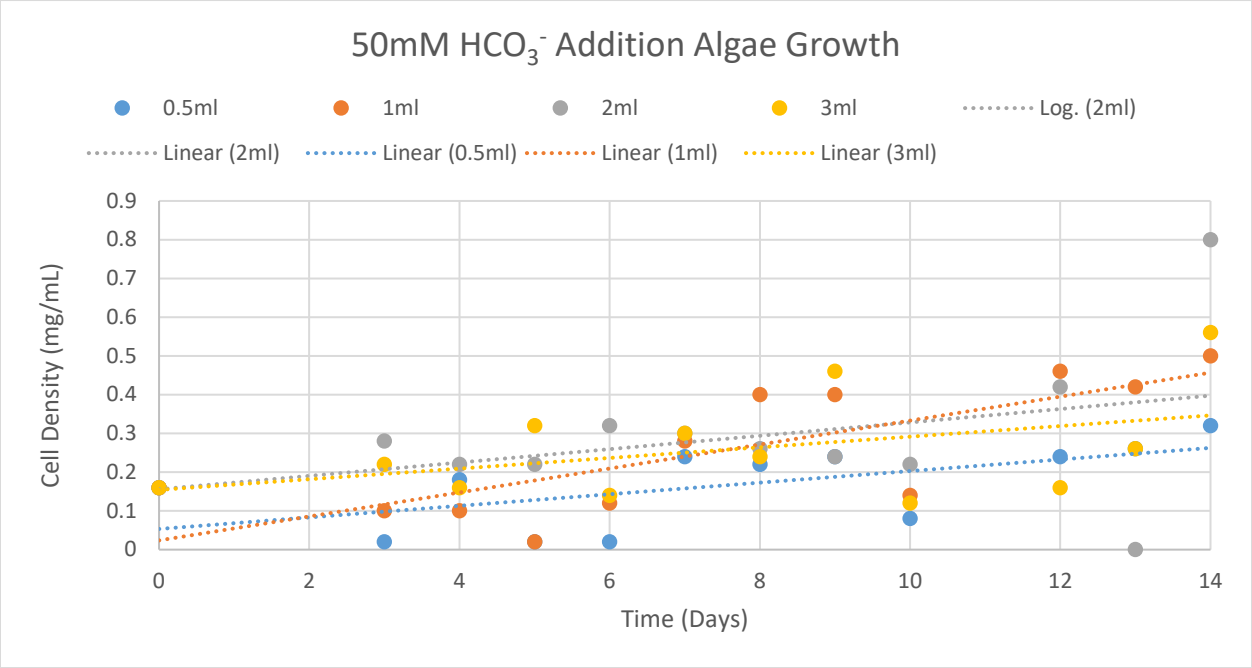

Figure 3. First growth experiment cell densities over 14 days of growth. Trendlines show general growth pattern.

The cell densities are plotted on the days since inoculation (Day 0). No conclusion can be made on these findings due to the sporadic nature of the data.

Conclusions

Unfortunately, no conclusion can be made in confidence due to the multiple discrepancies ignored. The individual data points are sporadic, in fact some of the points that show 0mg were actually recorded as negative, in which the tare of the dry tray was somehow heavier before the dry algae was filtered through. The expected leveling of dry weight at 3 days, as demonstrated in the results from (Gardner *et al.* 2012), also cannot be deduced. Though this may have been due to smaller culture sizing in their investigation.

The reasons for the flawed data could be attributed to inaccurate dry weight measurements at such low mass. Many typical analytic balances, like the one used, cannot accurately detect measurements lower than 10mg. For 5ml samples extracted from the growth bottles, the algae in the sample will ultimately reach no more than 2 or 3 mg. When concerned with measuring the weight during the growth period especially, higher accuracy is necessary; unless higher liquid samples are extracted from the growth bottles, accurate weight measurements may not be obtained. Extracted samples that are too large may disturb the culture's growth cycles, and lead to more discrepancies. Additionally, the fiber glass filters' weights may have changed slightly from absorption of water vapor in the air, even if the effort was made to prevent this with overnight drying and transport in dry containers. The expected stabilization of dry weight at 3 days was not deduced because samples were not even taken for the first three days, simply because the methods of this experiment would not have been accurate enough to notice to small differences in weight.

First Revisions

The experiment was refined. This time, 0, 0.5, 1, and 2ml 50mM sodium bicarbonate solution additions were added to four 1L BBM bottles in duplicate. The previous scale was replaced with a newer VWR Model 403B scale, in hopes of returning more confident data. The eight bottles were again sterilized and sparged with air through PTFE filters. Biosafety sterilization as well as data collection methods were repeated from the last experiment. The experimental setup is shown in Figure 4 and the results are given in Figure 5.

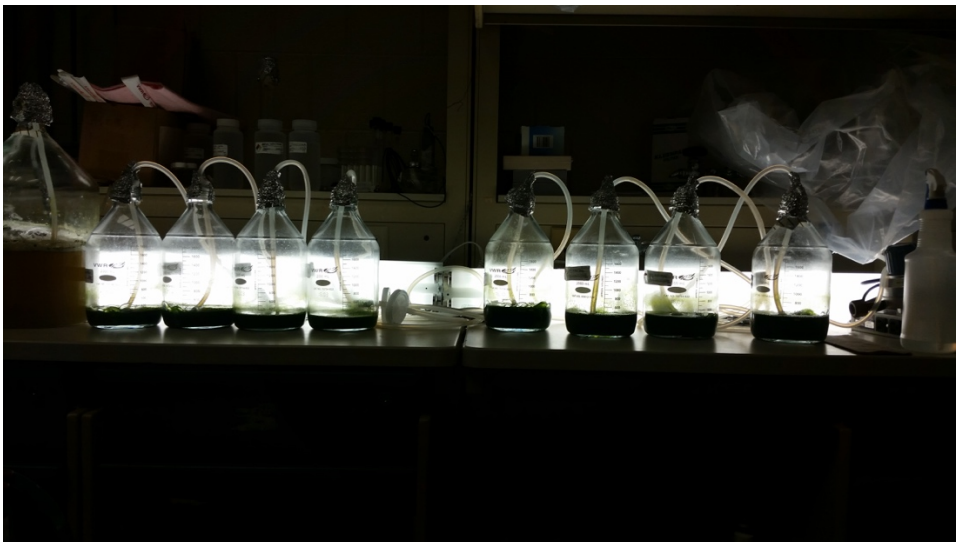

Figure 4: Algae growth bottles after 2 weeks. Here, the four bicarbonate concentrations are in duplicates. Air is sterilized through PTFE micro filters. Algae media seem to evaporate at different rates between bottles, which will create a likely source of error in the findings.

Results

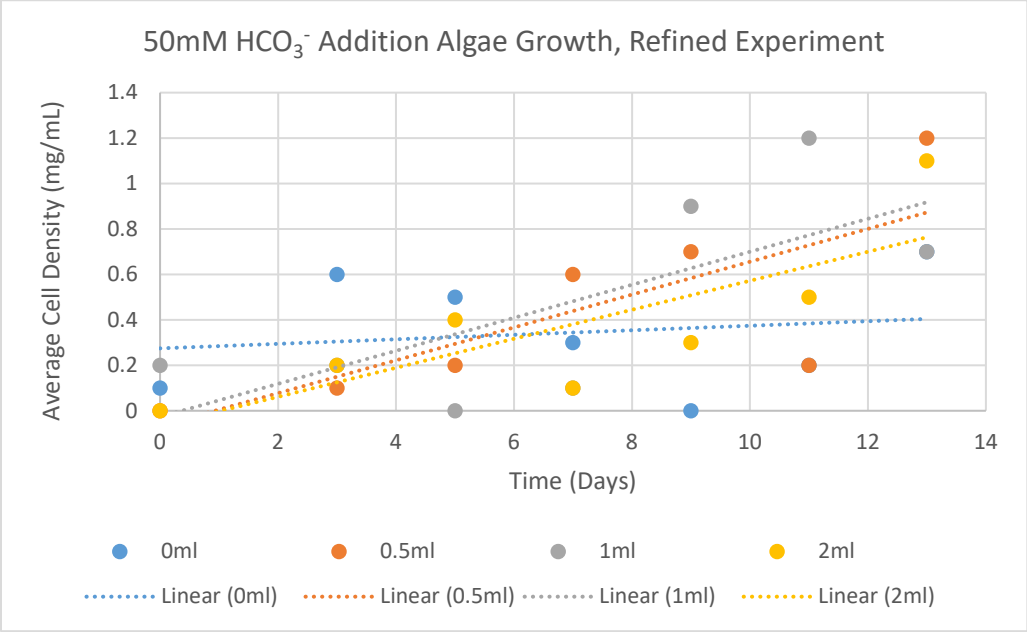

Figure 5. Second growth experiment cell densities over 14 days of growth. Trend lines show general growth pattern.

The cell densities are averaged between the duplicate bottles and plotted on the days since inoculation (Day 0). Again, no conclusion can be made on the relationship between HCO_3^- addition and algae growth from this data.

Conclusions

Unfortunately, the results are again not found in confidence because almost none of the previous errors were addressed, such as liquid samples being too small for accurate weight measurement, fiber glass filters not maintaining constant mass before and after liquid filtration, and discrepancies in measurement from the analytic balance. In fact, many of the data points of this trial were worse than the first. Many points had a far lower weight showing than their tare, resulting in negative cell densities; these were eliminated. Also, any average cell densities recorded above that were 0 were the result of both bottles showing a negative cell density.

Second Revisions

A third experiment of this nature was conducted, this time using a novel, non-invasive biomass scanner called the BugEye® 200 from BugLab. The scanner can take biomass readings from the outside of bottles. The advantages of this instrument are obvious. Firstly, data can be taken more frequently, perhaps every day or twice a day. Secondly, use of the noninvasive scanner can lower the chance of contamination and bypass the need for accuracy with dry weight measurements. (Chioccioli *et al.* 2014) explores the complications with measuring cell density with small samples, as well as small inaccuracies between optical density (OD) and dry weight measurements when growth conditions are changed, though also cite that these inaccuracies can sometimes be inconsequential. In any matter, optical density (OD) measurements from this

scanner will hopefully provide higher accuracy in algae growth measurements, particularly for the initial 3-day growth phase.

Bugunit Calibration

To use the BugEye scanner, the arbitrary units of the scanner, called Bugunits, must be converted into typical, translatable units, such as cell density or, for this experiment's purposes, optical density (OD). In order to do this, a 1L 0ml 50mM bicarbonate BBM algae growth was conducted with the BugEye to continuously record biomass in "raw Bugunits". Offline samples of 5ml were physically taken using similar techniques to prevent contamination described in the first growth experiment. Of these samples, three 0.5mL samples were analyzed in a DU800 spectrophotometer from Beckman Coulter, using a media blank extracted from the bottle before inoculation. Absorbance was measured at 685nm, per recommendations from (Rodrigues *et al.* 2011); however (Chioccioli *et al.* 2014) conducted absorbance measurements at 750nm in order to exclude absorbance by pigments like chlorophyll and carotenoids. Regardless, 685nm is used here. The three samples' measured ODs were averaged and recorded at that sample's raw Bugunit to make a calibration curve. Simultaneously, 1ml of the extracted sample was used in attempt to create a dry weight vs. Bugunit calibration curve to match the one for OD. 1ml of the sample was centrifuged, the media was extracted to prevent the salts in the media from corrupting the dry weight measurement, and the pellet was resuspended in DI-water. The sample is pipetted onto a Mettler Toledo MJ33 heated dry weight scale, which evaporated the water holding the suspended pellet at around 100°C. However, again likely due to the sample weights being too small for the scale to read, as has been noticed multiple times throughout these experiments, no useful dry weight measurements were taken during the BugEye calibration.

Instead, the OD vs. Bugunit calibration, results shown in Table 1 and Figure 6, were used to continue the experiment.

Table 1. Bugunit Calibration for C. Reinhardtii

Sample	*OD 1*	*OD 2*	*OD 3*	*Average OD 685nm*	*Stdv*	*Raw Bugunit*
Blank				0.0022		0.29
0	0.0232	0.0232	0.0212	0.0225	0.0012	0.92
1	0.0568	0.0727	0.0655	0.0650	0.0080	0.96
2	0.1330	0.1339	0.1264	0.1311	0.0041	1.40
3	0.2639	0.2677	0.2504	0.2607	0.0091	1.95
4	0.4750	0.4885	0.4747	0.4794	0.0079	2.42
5	0.6569	0.6613	0.6502	0.6561	0.0056	2.90
6	0.8510	0.9355	0.8850	0.8905	0.0425	3.40
7	1.0558	1.1949	0.9453	1.0653	0.1251	3.60
8	1.1400	1.1327	1.1661	1.1463	0.0176	3.77
11	1.7074	1.7463	1.7496	1.7344	0.0235	5.57
12	2.1098	2.0235	2.0407	2.0580	0.0457	8.30
13	2.3220	2.2447	2.3020	2.2896	0.0401	9.95
14	2.2714	2.2852	2.2528	2.2698	0.0163	11.83

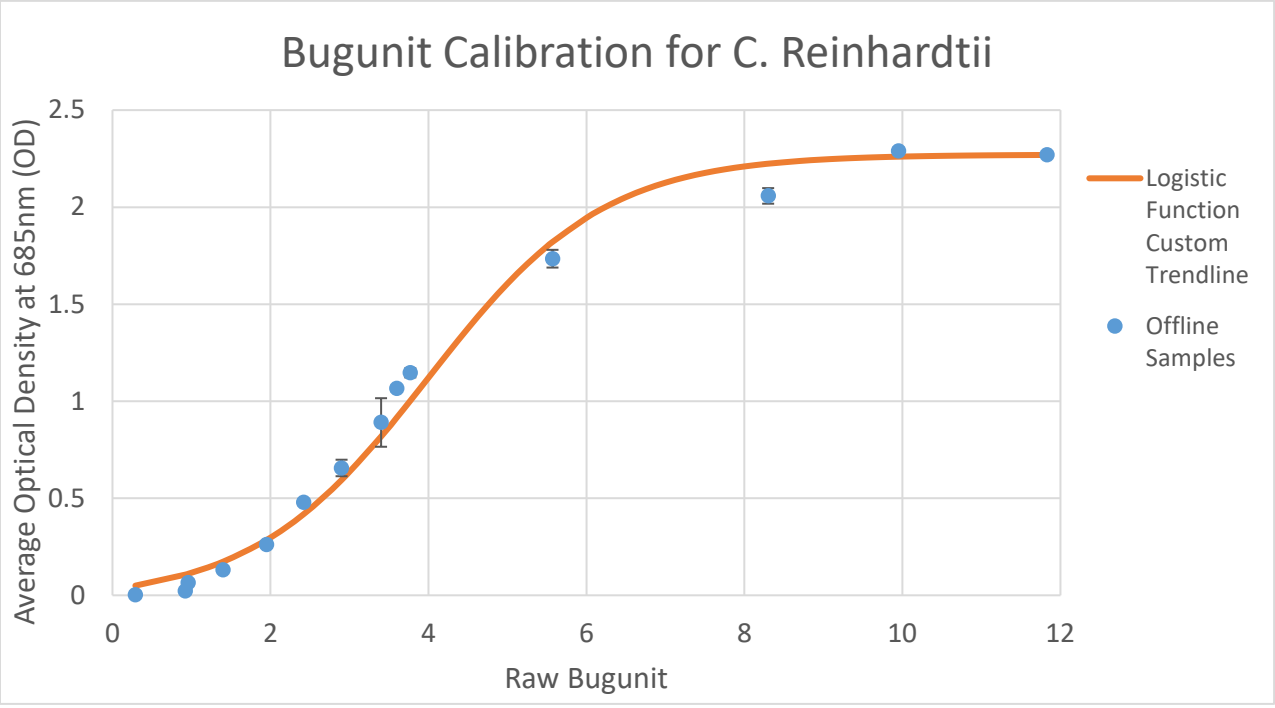

Figure 6. Bugunit Calibration Curve fitted with logistic function custom trendline.

The scatter of the points in the calibration graph above are reminiscent of a logistic growth function. Because this regression tool is not available in Microsoft Excel, the regression was done manually using the standard form:

$$f(x) = \frac{L}{1 + e^{-k(x_0 - x)}}$$

And constants:

L = 2.3

x_0 = 4

k = 0.9

Visually, this regression looks decent. Coefficients of correlation (such as the r^2 value) for logistic functions are not common; some, like the McFadden pseudo-r^2 value (Hu, Shao, & Palta, 2006) exist and can be calculated, but this is not conducted in this report. MATLAB can also be used to find computer based regressions, this was not conducted at this time.

Using this calibration, the second growth experiment with HCO_3^- levels 0-2ml described in the second algae growth experiment, is repeated, this time taking non-invasive biomass scans with the BugEye. The Bugunits are converted to OD using the calibration curve equation and shown in Figure 7.

Results

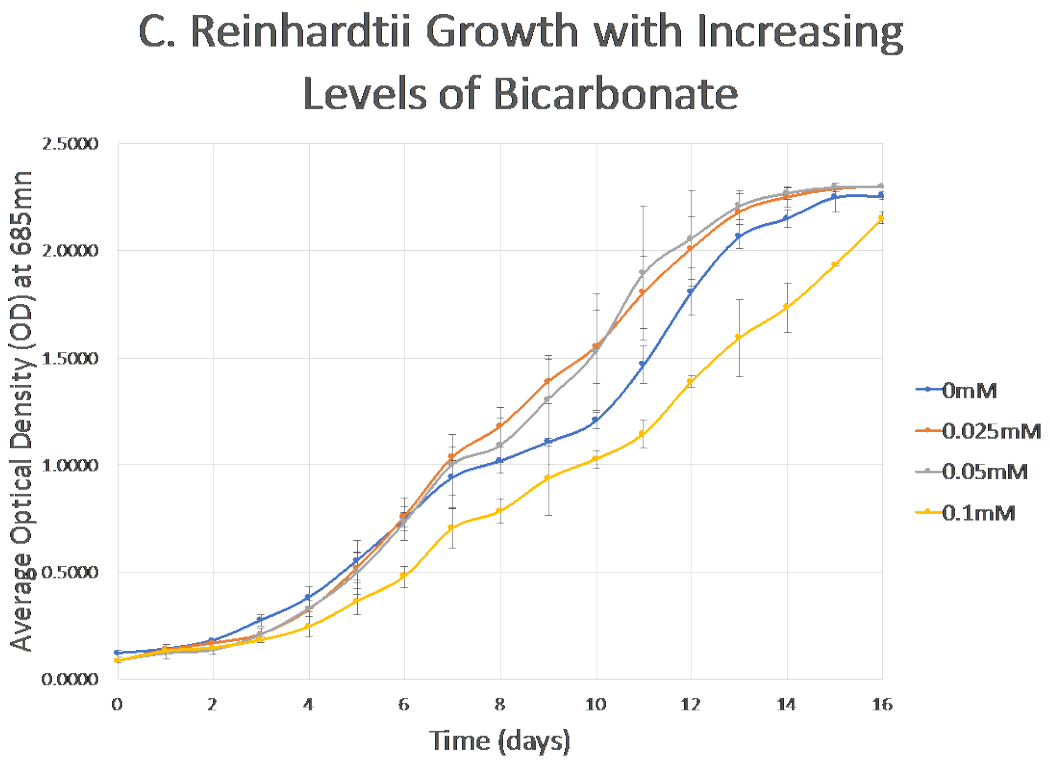

Figure 7. Third growth experiment sample optical densities at 685nm over 16 days of growth. Error bars show standard deviation between duplicate samples. HCO_3^- addition shows slight increase in algae growth and stabilization until 0.1mM, where growth seems to become stunted.

The confidence of these curves in comparison to the last two growth experiments has increased. With duplicate bottles, standard deviation error bars can be provided. Accordingly, small HCO_3^- addition to algae media slightly increases algae growth, up until 0.1mM (2ml/L of media), where growth seems to become slower and stunted.

Conclusions

(Gardner *et al.* 2013) observed that algae cells supplemented with HCO_3^- shed their flagella and formed membrane bound, incompletely divided cells that immobilized cells but increased size. They also conclude that cultures with bicarbonate exhibit more carbon storage.

A discussion of complications for this type of experiment would include noting that biological systems do not behave quite as consistently as is preferred for scientific study. Media evaporation between bottles also occurred at varying rates, so this inconsistency will skew results as well. It is also possible that the BugEye scanner could have been old or faulty; however, this should not matter if it is calibrated with the organism. At that point, changes in the scanners values will result and correspond in the same pattern of growth.

Future experiments may try increasing or decreasing media volumes, to see if the magnitude of growth rate changes, with correlating concentrations of $NaHCO_3$. As with any scientific investigation, the solution to suspicious data is deliberate repetition.

Wafer-Enhanced Electrodeionization

WE-EDI is a membrane separation process in which an electric current drives ion separation between solutions. Typical WE-EDI systems involve a cathode and anode, bipolar membranes to separate protons and hydroxyl ions, cation or anion exchange membranes to facilitate to flow of current, and one or more ion exchange resin wafers (Alvarado 2014). EDI systems can have multiple chambers as well. Figure 8 show EDI cells from (Datta *et al* 2013), the latter an extension of the former, in which CO_2 is stripped from flue gas, and routed into a purified form for sequestration. The WE-EDI setup to be for this research is shown in Figure 9. As an inspiration of the (Datta *et al* 2013) systems, the only difference in the current setup is that the HCO_3^-, which is an intermediary flowing out of the basic chamber into the acidic chamber in the former, is allowed to accumulate in the basic chamber for analysis in the latter.

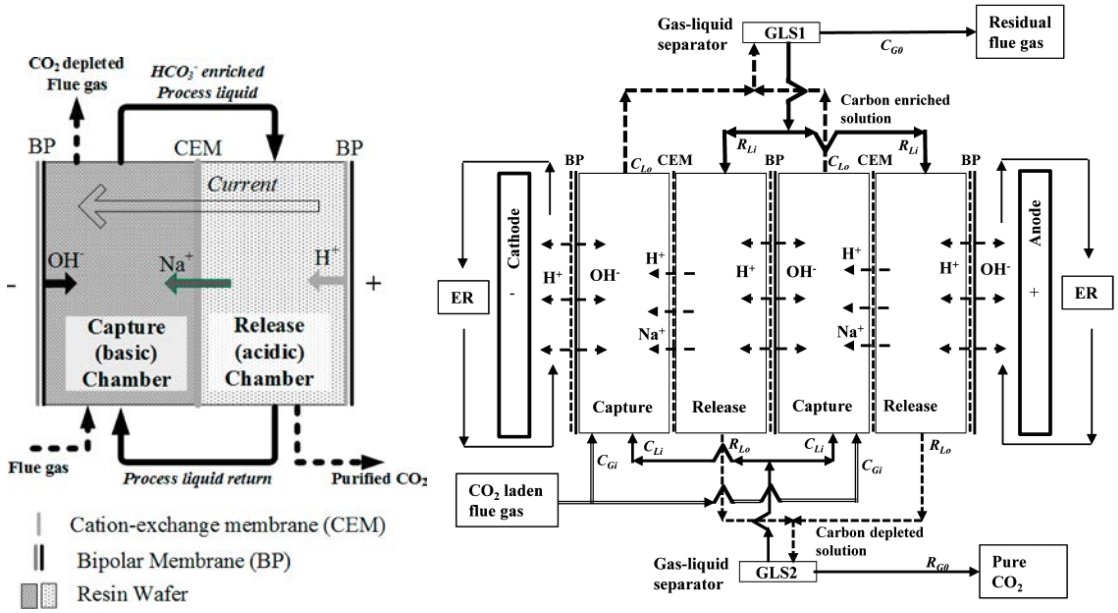

Figure 8. (a) Single cell of a WE-EDI, used for CO_2 capture and (b) a multi-cell system WE-EDI with gas liquid separators for gasous CO_2 recovery. HCO_3^- is cycled in and out of chambers. Source claims up to 200 cells can be used for commercial-scale WE-EDIs. "CO_2 concentrations are represented as CLi = capture liquid inlet, CLo = capture liquid outlet, RLi = release liquid inlet, RLo = release liquid outlet, CGi = capture gas inlet, CGo = capture gas outlet, RGo = release gas outlet (recovered CO2). BP: bipolar membrane. CEM: cation-exchange membrane. ER: electrode rinse solution. GLS: gas−liquid separator. (Datta *et al* 2013)

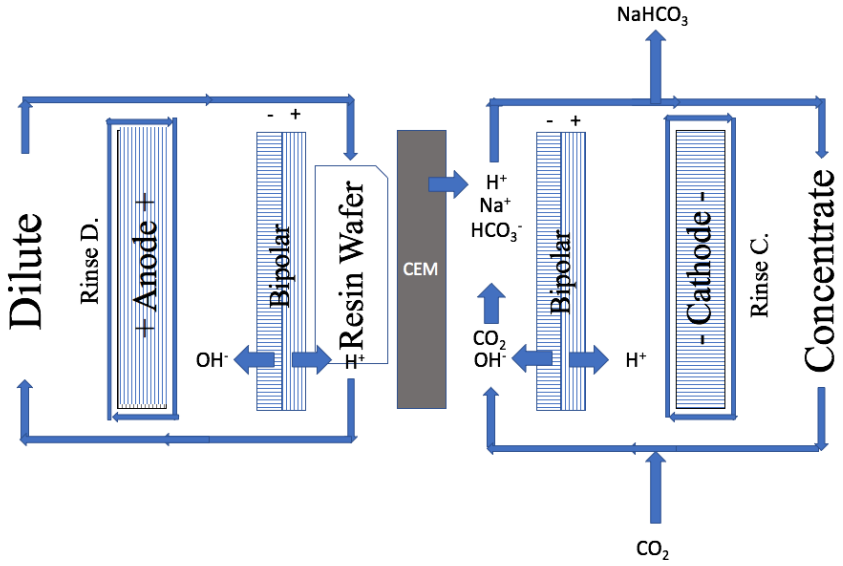

Figure 9. Initial WE-EDI setup. The bipolar membranes only split water molecules, creating alternating acidic and basic chambers. The alkaline chamber of the concentrate will provide favorable conditions for the conversion of CO_2 into HCO_3^-. (Author created.)

Four chambers are run at constant flow rate, the dilute (D) and concentration (C) chambers with 2000ppm NaCl and the rinse dilute (RD) and concentrate chambers (RC) with 4.2% by volume Na_2SO_4. The purpose of the rinse chambers is to prevent salt accumulation and corrosion of the electrodes (Ho *et al*. 2010). The chambers are separated by bipolar membranes (BPMs) and a cation exchange membrane (CEM). The function of the BPMs is to split hydrogen and hydroxyl ions in the flowing water streams, creating alternating charge polarity and providing a better driving force for the current. More importantly, the BPMs allow the accumulation of hydroxyl ions in the concentrate chamber, which will drive the conversion of gas soluble CO_2 into HCO_3^- in solution; this "pH swing" between chambers facilities a more effective conversion of HCO_3^- in the C chamber (Datta *et al.* 2013). The purpose of the CEM is to allow the constant flow of Na^+ ions across the system to help maintain current. The resin wafer is a 2mm thick pressed composite surface composed of anion and cation exchange resins, sugar, and polymer for

binding. The purpose of the wafer in the WE-EDI system is to prevent uneven ion flow distributions, referred to as ion leakage, between chambers. This subsequently increases the overall efficiency of the system (Datta *et. al* 2013). The wafer's anion to cation resin ratio, selectivity, as well as the amount and type of polymer have the most notable effects on ion transport in the WE-EDI system, while thickness and capacity have lower effects. Previous investigation has found the optimal composition for general use of a resin wafer to be 2.3:2.3:1:1.5 parts cation resin, anion resin, polyethylene, and sucrose, respectively (Ho *et al.* 2010). CO_2 will be bubbled to mix in the C chamber. Studies have shown that low gas flow rate paired with low liquid flow rates through the WE-EDI increases CO_2 uptake (Datta *et al.* 2013). Current will be held constant through continuous runs.

Research by (Moss 1973) provides a benchmark for what pH in the C chamber is desired, about a pH = 9. At this alkalinity, the concentration of HCO_3^- will reach viable levels to incorporate into algal media.

Materials and Methods

Wafer Fabrication Method

Resin wafers were fabricated by hand mixing 23g of Amberlite IRA-400 (Cl^-) anion resin, 23g of Amberlite IR-120 (Na^+) cation resin, 15g of sucrose, and 10g of polyethylene. A pressing plate for use in a Carver hydraulic press was cleaned. Parchment paper was cut out to shape in the press plate to ease the removal of the wafer after heated pressing. Five small cups (around 25ml) of wafer mix were then further mixed in a Flacktek Sppedmixer DAC150SP at 300rpm for 5 seconds, then placed on the parchment paper like cookies on a cookie sheet. The mounds were then pressed to spread evenly onto the plate. It should be noted that not more than five cups of the mix should be put in the press plate, so as to not overfill the plate. Doing so will result in a wafer that is too thick, around 3mm, when the desired thickness from this recipe is 2mm. A wafer that is too thick may result in internal leaking of the EDI by swelling the plates, which are cut to 2mm in thickness. Internal leaking, amount other failures, will invalidate the results of any EDI trial. The lid of the plate was then carefully put in place, and the plate was placed in the Carver press that had been heated to 250°C. The lever raised the plate until an applied load of 10,000psi was reached. The pressure was watched for a few minutes to raise the pressure back up as it dips a bit. The wafer is allowed to be pressed for 90min. As the wafer heats, the polyethylene melts and becomes a binding agent between the resins. After which, the plate was lowered and cooled with high pressure air for 20min. Using the screw latches, the lid of the plate was screwed off, and the plate was then removed and soaked in DI water for at least 24 hours, this is to dissolve the sugar in the wafer and create pores to allow ion flow through solution. Thus, changing sugar concentration in the wafer will change the wafer's porosity. Figure 10 shows the finished wafer before soaking and storage

Figure 10. Resin wafer made of cation resin, anion resin, sugar, and polyethylene. The sugar is dissolved in a DI water soak for 24h prior to using the wafer in operation, allowing pores to form for solution to pass and aid in ion exchange.

Bicarbonate Titration

In an attempt to more precisely measure HCO_3^- concentration in the concentration chamber, a titration was conducted using the method described by (Hach Company 2017), involving a double titration with phenolphthalein and Bromescrol green-methyl red (BGMR) indicator, which is specified for solutions of mixed carbonate (CO_3^{2-}) and HCO_3^-. However, when tested with HCO_3^- solution standards, the concentrations found by this method gave results that differed by a factor of 2. So, Hach method was bypassed for a more traditional method, which was a custom calibration of the indicator solution. Three 50ml sodium HCO_3^- samples were prepared at 1000, 1500, and 2000mg/L concentrations in DI water, three more of these were repeated in

2000ppm Na^+ ion NaCl solution (5.04g/L NaCl). This NaCl concentration will be what the is run through the C chamber in the EDI, and where the HCO_3^- conversion will take place. For an anticipated HCO_3^- concentration of 1000-2000mg/L, a sample of 10ml from the C chamber will be taken during EDI trials, as was recommended in the Hach Company method, therefore the titration calibration also regarded titrant volume for a 10ml sample, diluted to 50ml with DI-water. Phenolphthalein was initially added to discern the presence of other ions. For these samples, the phenolphthalein alkalinity (PA) was near 0. According to the Hach method, for PAs less than half of the total alkalinity (TA) of the sample, the HCO_3^- alkalinity is equal to the total alkalinity; in effect, the PA can therefore be ignored for the purposes of the calibration. Before the BGMR indicator was added, a drop of sodium thiosulfate is added to remove Cl ions, which in concentrations above 3.5mg/L will cause the indicator to turn the solution yellow and render it unusable for titrating HCO_3^- alkalinity. After sodium thiosulfate addition, the solutions are then continued to be titrated with 0.02N sodium sulfate.

The results of this calibration are shown below in Table 2 and Figure 11, in which the actual concentration of the samples is plotted versus the respective amount of titrant necessary just to turn the solution from green to red – in actuality, the indicator before titration looks more blue than green. Because the process solution in the EDI will be NaCl, this calibration is plotted in Figure 11. pH and conductivity are also recorded in order to parallel sample measurements during EDI operation, and may be useful in comparing EDI samples to HCO_3^- concentration.

Table 2. Bromescrol Green Methyl Red Indicator Calibration for HCO_3^-

	Mass [mg]	*Water [ml]*	*Conc. [mg/L]*	*Actual [mg/L]*	*pH*	*Cond [uS/cm]*	*Sample [ml]*	*Phenol [ml]*	*BGMR [ml]*
Water	0	50	0	0	6.35	1.37	0		
	50	50	1000	1000	8.21	1015	10	0.5	5
	74	50	1500	1480	8.26	1600	10	0.3	8.1
	102	50	2000	2040	8.16	2180	10	0.4	11.4
						mS/cm			
NaCl	0	50	0	0	6.61	9.85	0		
	49	50	1000	980	7.93	10.75	10	0.3	5.7
	76	50	1500	1520	7.9	11.17	10	0.3	8.8
	98	50	2000	1960	7.97	11.54	10	0.2	11.75

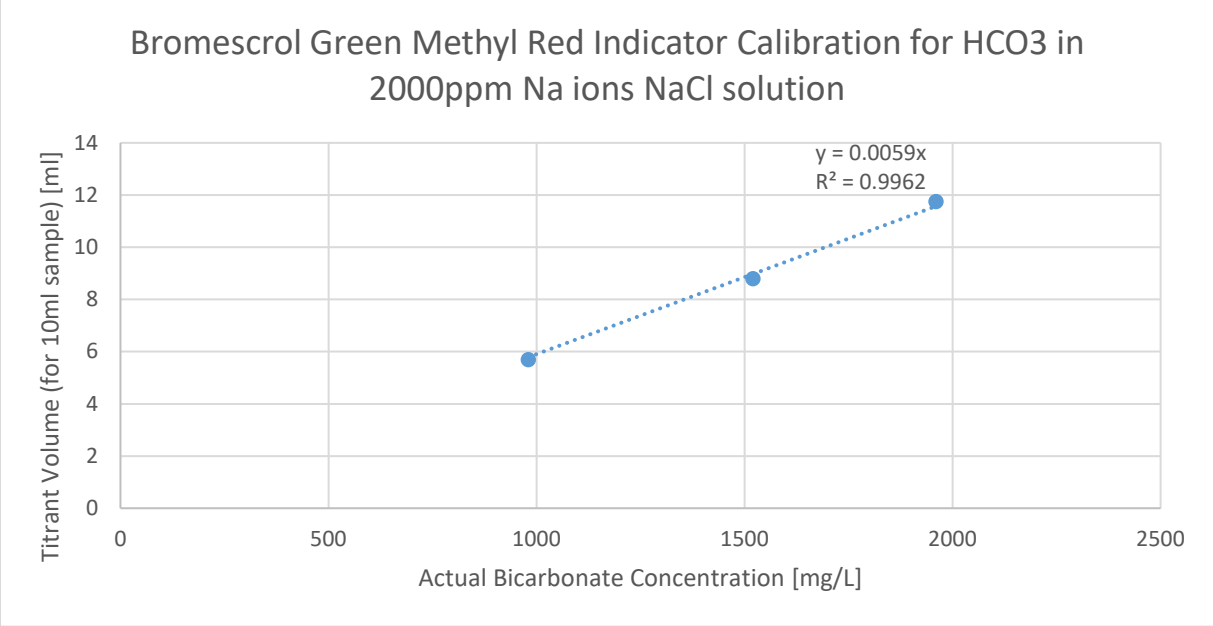

Figure 11. BGMR indicator calibration for HCO_3^- titration. Trendline can be used confidently for HCO_3^- concentration measurement within operational goals.

Another particular note to make about the utility of the BGMR indicator solution lies with its reactivity with chlorine ions. The indicator solution can be used to test for ion leakage through the CEM, as only sodium cations are allowed through. Ion leakage may be caused by faulty or torn membranes or by internal leakage.

Initial Trials

The configuration of the plates within the EDI are shown in Figure 12. This orientation insured that each solution stayed in its respective chamber. Neosepta bipolar membranes and standard cation exchange membranes from Ameridia were used. The C side had the negative electrode, therefore the cation side of the BPMs would need to face towards the negative electrode to maintain the desired ion separation. The HCO_3^- conversion was therefore conducted in the C chamber, as the orientation of the BPMs created an increasingly alkaline chamber. Chamber plates were cut out of polyethylene, and a plastic mesh was placed to enhance mixing. Separating the C and D chamber was the cation exchange membrane, which would only allow the flow of Na^+ and H^+ ions, as well as allow for current to flow through the EDI's potential difference. The wafer was placed in the D chamber. The D side electrode was positive, so the BPM cation side had to face away, in the same direction as the other BPM. The plates were carefully pressed and screwed in place. The spouts were connected with Mity-Flex rubber tubing to their respective bottles, whose caps had to be drilled through to fit the tubes. The inlet tubing was routed through Mity-Flex peristaltic pumps and into the inlets of the EDI. The outlets are routed directly back to the bottles in such a way as to be convenient to remove and test for flow rates. The EDI is run with water initially to test for flowrates and internal leaking. Flow rates were tested by dripping the outlet into a 20ml graduated cylinder for 15 seconds. The liquid level is then divided by 15 seconds. Gas delivery was conducted at 2psig into the C bottle and vented out into a vent hood. The gas tank composition as 15% by volume CO_2 balanced with nitrogen, to simulate the upper range of industrial flue gas emissions. However, for the initial EDI trials, gas delivery was not implemented. This was due to complications in ordering the gas as a custom mixture.

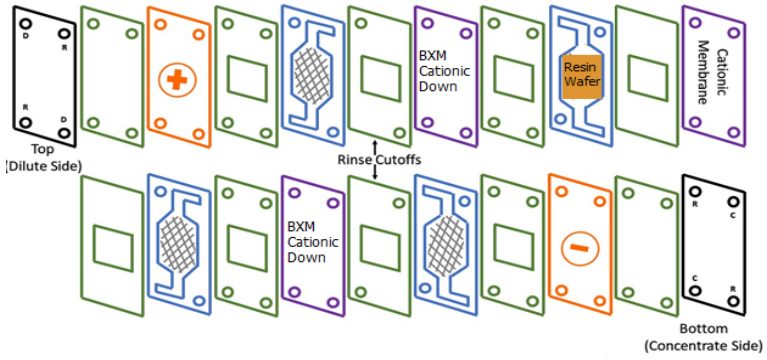

Figure 12. EDI plate configuration. Plates are aligned to make rinse flows isolated, dilute and concentrate flows bypass into their own chambers.

Results

The results of the first 6 EDI trials were mystifying. A typical set of results from these trials is shown in Table 3 and Figure 13.

Table 3: EDI Trial 6

	Time (h)	*Flow Rate (ml/15s)*	*(ccm)*	*pH*	*Conductivity (mS/cm)*	*Voltage (V)*	*Current (A)*
D	0	18	72	5.32	9.02	9.18	0.2
RD		18	72	2.60	37.70		
C		18	72	9.48	9.05		
RC		18	72	11.62	38.80		
D	3	18.5	74	2.51	9.08	8.27	0.2
RD		18	72	1.56	38.60		
C		18.5	74	11.57	10.41		
RC		18.5	74	12.00			
D	6	17.5	70	2.01	10.22	7.62	0.2
RD		18	72	1.27	39.70		
C		18	72	11.96	12.61		
RC		18	72	12.53	48.50		
D	24	17.5	70	1.48	9.83	7.53	0.18
RD		16	64	0.76	44.00		
C		18	72	11.07	9.81		
RC		19.5	78	12.6	79.20		

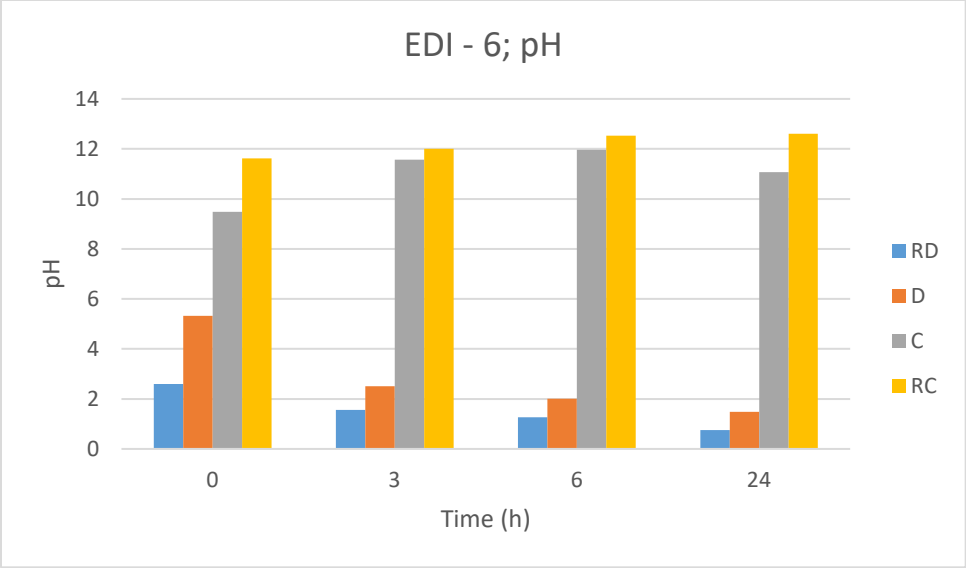

Figure 13(a). Typical EDI pH over 24h of operation. D/C chambers were 2000ppm Na^+ ions, rinse chambers 4wt% Na_2SO_4. Chamber volumes were 500ml. Flow rates were around 70ccm. Current was held constant at 0.2A.

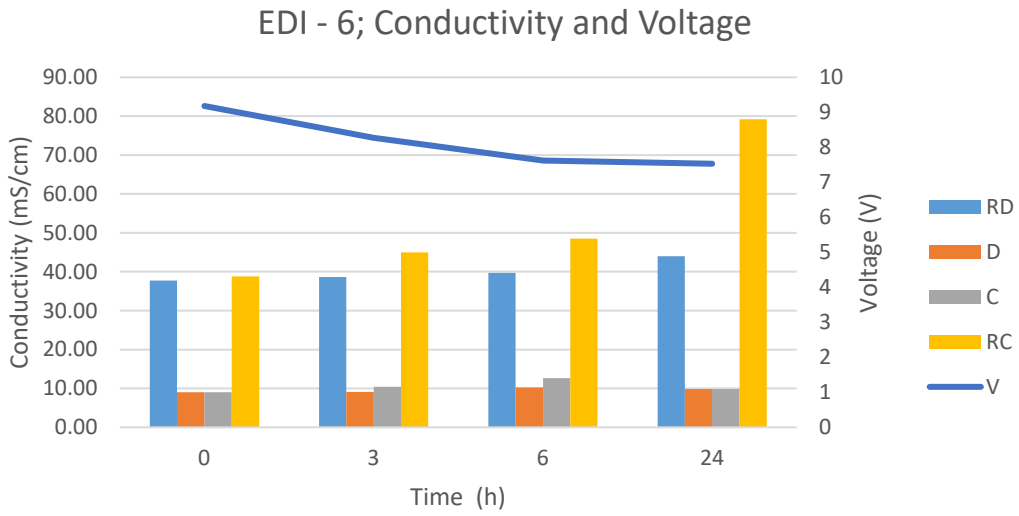

Figure 13(b). Typical EDI pH over 24h of operation. D/C chambers were 2000ppm Na^+ ions, rinse chambers 4wt% Na_2SO_4. Chamber volumes were 500ml. Flow rates were around 70ccm. Current was held constant at 0.2A.

At the onset of this EDI – 6, multiple issues and errors in the experiment setup were found to be causing this unusual behavior. One of the major issues was that the BPMs were flipped the wrong way. This incorrect orientation allowed accumulation of hydroxide ions in the RC chamber as well as protons in the RD chamber. While the D and C chambers still became more

acidic and basic respectively, as desired, prolonged exposure of the electrodes to the high acidity and alkalinity environments could lead to long term damage and instability of the system as a whole. The correct orientation would have the rough surface of the bipolar side being the cationic side, and therefore would need to face the negative electrode, toward the C chamber.

A second major issue is the evidence of internal leaking in the system. In this particular trial, it was noticed that 300ml of solution from the D bottle leaked through some unsealed part of the EDI into the RD bottle. This leaking of highly acidic D into RD could also be causing the hyper acidification of this chamber in parallel to the incorrectly facing BPMs.

Through delegation with others at the University, it was understood that one technique to reduce the effects of internal leaking is to only tighten the EDI just enough to press the gaskets and plates together, and not as tightly as possible. While one would expect making the plates as tight as possible would prevent leaking, the case is the contrary. Excessive tightening of the plates can cause the edges of the EDI plates to pinch inward, creating gaps in the center of the system, and therefore paths for solution to leak and mix.

A third major issue involved the gas regulator losing control and maxing delivery pressure. This drained the gas tank overnight during EDI – 5. Because this was a specialty gas, a custom mixture of 15% CO_2, the tank was not available to be readily replaced, and in fact took months to obtain until the allocated time to this research had ended. In its absence, EDI trials were continued anyway without gas delivery and HCO_3^- titration, beginning at the onset of EDI – 6.

One minor issue with the setup involved the concentrations of the solutions. The rinse solutions, RD and RC, initially contained 13.54g/L of Na2SO4 in DI water, or 1.4 wt%. This was revised to 42.36g/L, or 4.2 wt%. The process solutions, D and C, initially contained 20g/L of NaCl in DI water. This was revised 5.04g/L NaCl, equivalent to 2000ppm Na^+ ions. These revisions were made at the onset of EDI – 6, shown above.

A second minor issue involved not maintaining constant current throughout the system through the instrumentation. As current is the driving force of this system, it's important to maintain it constant to continuously drive ion separation at a constant rate. This issue was rectified at the onset of EDI – 6, shown above.

A third minor issue involved not maintaining constant liquid flow rates, likely due to rubber tubing becoming pinched, or pressure drops through the EDI cell.

A fourth minor issue involved liquid and gas flow rates that were too fast. As recommended by the findings in (Datta *et al.* 2011), small liquid flow rate and gas delivery rate will lead to higher absorption of CO_2 in solution and higher efficiency in HCO_3^- conversion.

A fifth minor issue, as mentioned in the wafer fabrication procedure, involved creating and using a wafer that was too thick and/or not cut to a close enough shape to fit in the D chamber plate. This could have contributed to internal leaking as well.

First Revisions

Some of these errors in the process were rectified in the next trial. The BPMs were flipped with correct orientation, cationic side facing the negative electrode. The assembly procedure was revised to tighten only as much as necessary, in hopes that internal flow will be eliminated. Constant current was maintained. Additionally, data was taken while the solutions were static in their bottles, after 5min of flow through the EDI before introducing a current, and right as current is introduced, the 0 hour data was taken 5min thereafter. The aim was to try to catch the sources of operational error; namely, internal leakage. The results are shown in Table 4 and Figure 14.

Table 4: EDI Trial 7. Corrected BPM Orientation and Assembly

	Time (h)	*Flow Rate (ml/15s)*	*(ccm)*	*pH*	*Conductivity (mS/cm)*	*Voltage (V)*	*Current (A)*
D	Before flow or elect.	0	0	6.30	9.88	0	0
RD		0	0	9.62	41.80		
C		0	0	6.47	9.84		
RC		0	0	9.68	42.00		
D	5min flow no elect.	18	72	3.33	9.50	0	0
RD		17.5	70	9.47	40.00		
C		18	72	6.24	9.56		
RC		18.5	74	9.26	40.30		
D	0min flow + electricity	19	76	2.25	9.91	9.5	0.2
RD		18	72	9.06	40.80		
C		18.5	74	11.24	10.10		
RC		18	72	9.76	40.70		
D	0	17.5	70	1.85	10.63	9	0.2
RD	0	18.5	74	9.08	39.70		
C	0	18	72	11.54	10.52		
RC	0	18	72	9.65	40.20		
D	3	18	72	1.07	17.15	7.28	0.2
RD	3	18	72	3.15	38.3		
C	3	18	72	12.24	15.82		
RC	3	18	72	9.83	40.7		

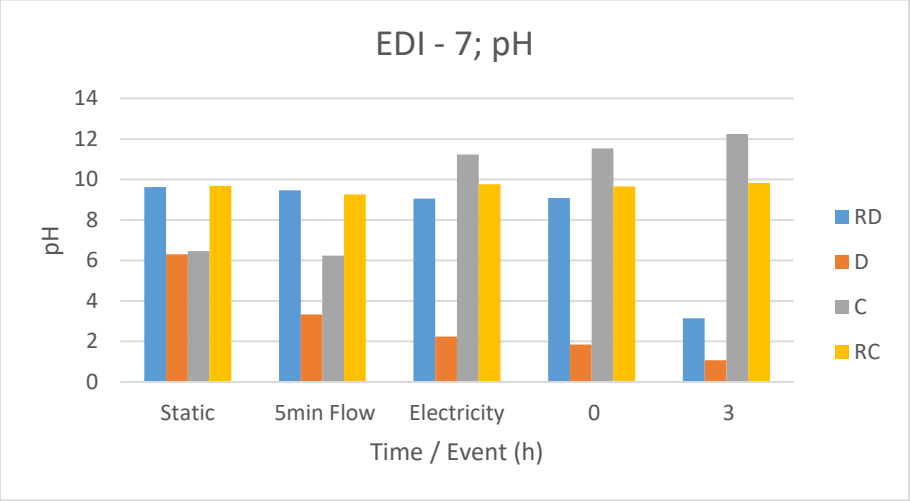

Figure 14(a). EDI Trial 7, pH measurements while static, after 5min of flow, after electricity introduced, 5min thereafter, and 3h after. D/C chambers were 2000ppm Na^+ ions, rinse chambers 4wt% Na_2SO_4. Chamber volumes were 500ml. Flow rates were around 72ccm. Current was held constant at 0.2A. Sharp decrease in RD pH at 3h indicative of acidic D leaking internal into RD.

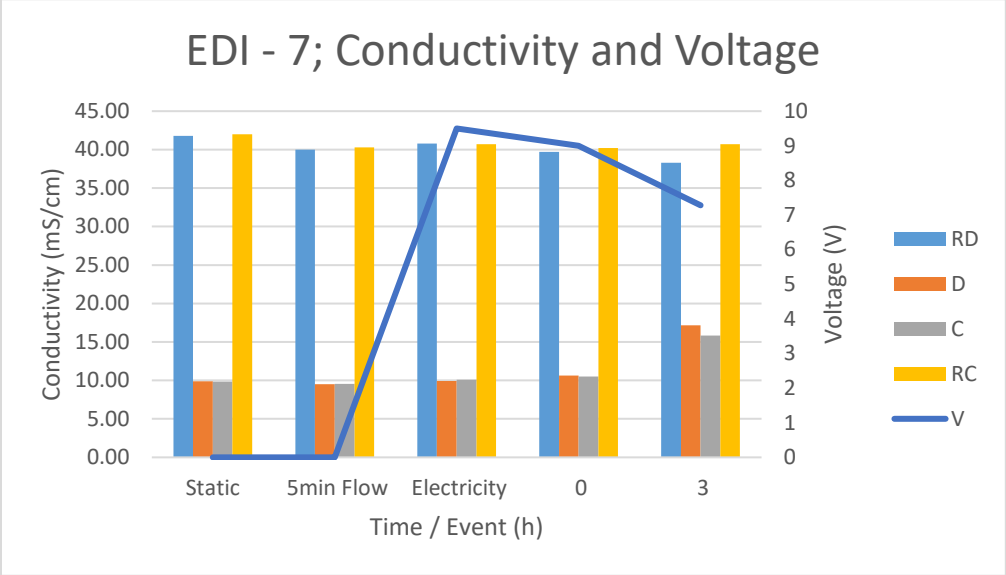

Figure 14(b). EDI Trial 7, conductivity and voltage while static, after 5min of flow, after electricity introduced, 5min thereafter, and 3h after. D/C chambers were 2000ppm Na^+ ions, rinse chambers 4wt% Na_2SO_4. Chamber volumes were 500ml. Flow rates were around 72ccm. Current was held constant at 0.2A. Accumulation of ions, per increasing conductivity, shows that ions are flowing and separating through the membranes.

These results show behavior more consistent with the understanding of the EDI. At the onset, the RC and RD solutions as well as the C and D solutions had the same pH and conductivities

respectively, as expected. However, an interesting phenomenon occurs after 5min. The D chamber immediately starts to become acidic, as well as losing ions to the C chamber, without the need of a current. This could be the result of a phenomenon known as reverse electrodialysis. In this case, the anions in the D chamber can pass through the CEM spontaneously, without current, due to a diffusion potential between the chambers. The diffusion potential could be a result of the small differences in flow rate between the chambers, making their steady state concentrations differ. In any case, spontaneous diffusion over enough time should return the concentrations back to equilibrium. This enumerates the need for the current in the first place, to maintain the membrane selectivity for a continuous process. The effect of this reverse eletrodialysis should not be so drastic, particularly after only 5min of flow, so this behavior may be explained by another process error, even if the outcome is desired. It's also possible that extraneous voltage on the membranes may cause this exaggerated reverse electrodialysis, allowing a higher volume of unlike ions to spontaneously bypass the membrane that's become weaker by excessive voltage.

The rinse chambers, with considerable concentration of buffer salt, should maintain their pH levels, which is the case in the first few minutes of this trial. However, by 3 hours, the pH of RD plummets. This is paired with observation of 100ml of D solution leaking into RD. Internal leaking remained an issue, possibly due to warping of the EDI apparatus plates from long term overtightening. The RC chamber did not seem to leak by 3 hours, however it may be prone to leaking after a longer time duration.

Second Revision

At the onset of the ninth EDI trial, the experiment apparatus was changed to fix the remaining few errors identified from previous experiments. New Mity-Flex pumps were introduced that would allow for flowrates as slow as 5-10ccm. The voltage on the EDI was reduced below 7V, this reduced the current as a consequence. Solution compositions and volumes were carried over from previous experiments. Unfortunately, the gas tanks still had not become available at this point in time, so gas delivery was still not introduced. The focus of this trial was to track the source of the internal leaking from D into RD, or elsewhere in the system. The results from EDI – 9 are shown in Table 5 and Figure 15.

Table 5. EDI – 9. Corrected Liquid Flow Rate

	Time (h)	*Flow Rate (ml/15s)*	*ccm*	*pH*	*Conductivity (mS/cm)*	*Voltage (V)*	*Current (A)*
D	0	2.5	10	1.72	9.71	6.86	0.07
RD	0	2.5	10	6.63	36.30		
C	0	2.5	10	11.58	9.57		
RC	0	3	12	8.46	36.80		
D	3	2.5	10	1.12	13.64	5.43	0.07
RD	3	2.5	10	6.85	36.80		
C	3	2.5	10	12.15	13.03		
RC	3	2.5	10	9.48	36.30		
D	6	2.5	10	1.02	17.38	5.33	0.07
RD	6	2.5	10	9.86	39.60		
C	6	2.5	10	12.25	16.00		
RC	6	2.5	10	10.03	40.10		
D	24	2.5	10	0.88	20.60	5.22	0.07
RD	24	2.5	10	2.8	36.20		
C	24	3	12	12.45	18.16		
RC	24	2.5	10	9.94	36.50		

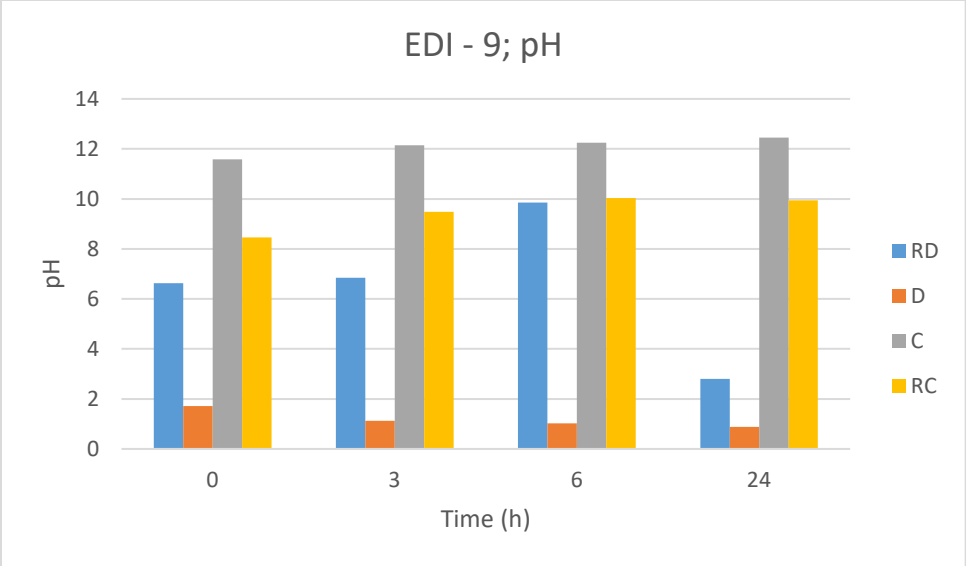

Figure 15(a): EDI Trial 9, pH over 24h of operation. D/C chambers were 2000ppm Na^+ ions, rinse chambers 4wt% Na_2SO_4. Chamber volumes were 500ml. Flow rates were around 10ccm. Current was held constant at 0.07A. Rinse chambers mysteriously do not hve matching pHs but have matching conductivities.

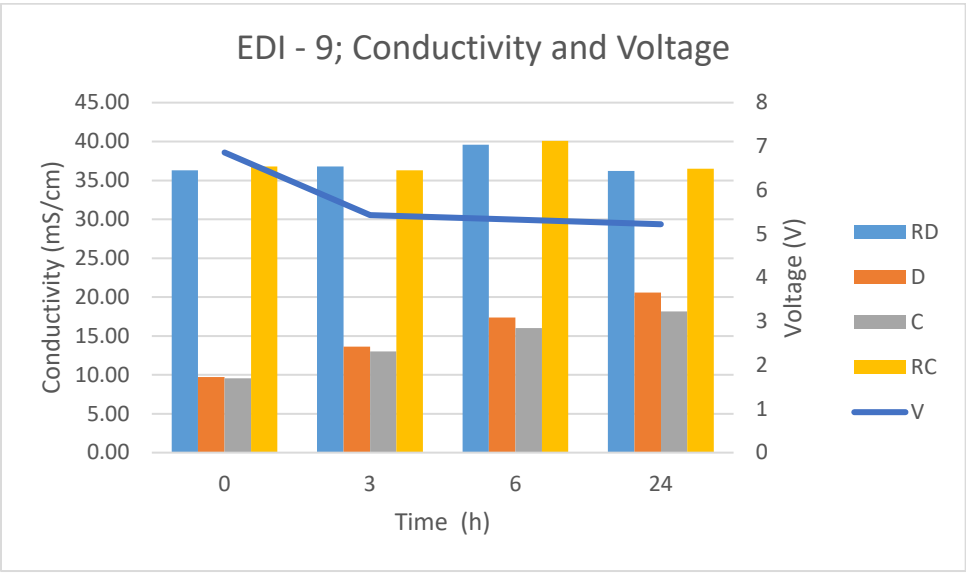

Figure 15(b): EDI Trial 9, conductivity and voltage over 24h of operation. D/C chambers were 2000ppm Na^+ ions, rinse chambers 4wt% Na_2SO_4. Chamber volumes were 500ml. Flow rates were around 10ccm. Current was held constant at 0.07A. Accumulation of ions, per increasing conductivity, shows that ions are flowing and separating through the membranes.

The behavior seen from this trial does not differ much from the previous trial, with the exception of RD having a lower pH than RC. The pH is suspiciously the level of the NaCl solution, so it's likely that D solution was accidentally poured into the RD bottle, however, the correct pH occurs

in RD at 6 hours, on par with RC. In this case, the pH probe may be at fault, or the solutions were not well mixed to identify all ions present. Regardless, the same internal leaking occurred from acidic D into RD, dipping the pH of RC after 24h. Another interesting observation is the stabilization of voltage across the EDI after 24 hours. This is also seen in EDI – 6. Unfortunately, the parallels between these trials, again, cannot be made in confidence due to the faults of the respective experiments, with the former being far worse than the latter. A second observation is in regards to the changes in conductivity over time. For EDI – 6 and EDI – 9, both the C and D seem to accumulate ions, as per their increasing conductivities.

Conclusions

With regards to HCO_3^- supplementation in algae growth media, minute amounts $NaHCO_3$, up to 0.05mM can increase *C. reinhardtii* growth rate as well as reach the stabilization stage faster in this investigation. However, a threshold seems to exist, where too much HCO_3^- stunts growth and delays the stabilization stage. In order to better incorporate algae packing into bioreactors, stable, predictable, and controllable growth and storage is preferred in order to lower replacement frequency and better account for production.

With regards to operating and analyzing performance of a WE-EDI to convert CO_2 into HCO_3^- solution, the theory behind the operation has been hitherto developed (Datta *et al.* 2013). As a result of this investigation, the WE-EDI cell does conduct HCO_3^- production, quantified by titration; however, successful operation with gas delivery was not managed due to complications in ordered specialty CO_2, as well as internal leakage due to overtightening of cell plates being the major culprit of operational failure. Regardless, the EDI cell can manage with internal leaking,

for a short time. Long term exposure to highly ionic solution leaking around electrodes will damage the precious metal electrodes, and lead to inefficiency of the system. The techniques accumulated in the making of this report may provide a foundation for novice investigators towards successful research into electrodeionization systems. Further work is necessary in order to increase the feasibility of this technology's utility.

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