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# ELECTROCHEMICAL ENERGY GENERATION FROM NATURAL AND SYNTHETIC SALINITY GRADIENTS USING REVERSE ELECTRODIALYSIS AND CAPACITIVE MIXING

A Dissertation in

Mechanical Engineering

by

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### ABSTRACT

Salinity gradient energy (SGE) technologies are emerging systems designed to recover energy from engineered and natural mixing processes. Two electricity producing SGE systems are reverse electrodialysis (RED) and capacitive mixing (CapMix). RED captures mixing energy using a series of ion exchange membranes that drive electrochemical reactions at redox electrodes. CapMix utilizes polarizable electrodes to store charge in the surfaces electric double layer (EDL). Energy generation can then occur when the EDL is expanded and compressed in different concentration solutions.

The use of themolytic salt solutions (e.g. ammonium bicarbonate–AmB) within a RED system is promising, as AmB can be regenerated using low-grade waste–heat (e.g. 40-60°C). One disadvantage to using AmB is the potential for gas bubbles (CO<sub>2</sub>, NH<sub>3</sub>) to form within the stack. Accumulation of bubbles can impede ion migration, and reduce system performance. The management and minimization of gaseous bubbles in RED flow fields is an important operational issue, and has not previously been addressed within RED literature. Flow field design with and without spacers in a RED stack was analyzed to determine how fluid flow and geometry effected the accumulation and removal of bubbles. In addition, the performance changes, in terms of power and resistance were measured in the presence of bubbles. Gaseous bubble accumulation was minimized using short vertically aligned channels, which resulted in a reduction in the amount of the membrane area which was restricted due to bubbles from ~20% to 7%. The stack power density improved by 12% when all gaseous bubbles were removed from the cell.

AmB-RED systems can potentially produce hydrogen or electrical energy through altering the cathodic reaction. With a kinetically favorable cathodic reaction (oxygen reduction reaction), the projected electrical energy generated by a single pass AmB–RED system approached 78 Wh per m<sup>-3</sup> (low concentrate). However, when RED was operated with the less kinetically favorable reaction (hydrogen evolution reaction), and hydrogen gas was harvested, the energy recovered increased by as much ~1.5 times to 118 Wh m<sup>-3</sup> (low concentrate). Indirect hydrogen production through coupling an RED stack with an external electrolysis system was only projected to achieve 35 Wh m<sup>-3</sup> (low concentrate) or a third of that produced through direct hydrogen generation. The flexibility of the RED architecture allows for the potential for simultaneous hydrogen and electricity production, whereas competing technologies such as PRO and CapMix only produce electricity.

Several approaches to generate electrical power using CapMix have recently been developed, but power densities have remained low. By immersing the capacitive electrodes in ionic fields generated by exoelectrogenic microorganisms in bioelectrochemical reactors, it was shown that energy capture using synthetic river and seawater could be increased ~65 times, and power generation ~46 times, when compared to controls (no ionic fields). Favorable electrochemical reactions due to microbial oxidation of organic matter, coupled to oxygen reduction at the cathode, created this ionic flow field that enabled more effective passive charging of the capacitive electrodes, and higher energy capture. This ionic-based approach is not limited to the use of river water-seawater solutions. Forced charging of the capacitive electrodes, using energy generated by the bioelectrochemical system and a thermolytic solution, further increased the maximum power density to 7 W m<sup>-2</sup> (capacitive electrode).

The amount of salinity gradient energy that can be obtained through capacitive-mixing based on double layer expansion (CDLE) also depends on the extent that the materials electric double layer (EDL) expands in a low concentration electrolyte (e.g. river water). I show here that the individual electrode rise potential, which is a measure of the EDL expansion process, significantly ( $P = 10^{-5}$ ) depends on the concentration of strong acid surface functional groups. Electrodes with a low concentration of strong acid functional groups (0.05 mmol g<sup>-1</sup>) resulted in a

positive–potential–rise of  $\Delta U_{+/-} = +59 \pm 4 \text{ mV}$  ( $\Delta U_{cell} = 16 \pm 0.7 \text{ mV}$ ) in synthetic river water, whereas activated carbons with high concentrations of strong acid groups (0.36 mmol g<sup>-1</sup>) produced a negative-potential-rise of  $\Delta U_{+/-} = -31 \pm 5 \text{ mV}$  ( $\Delta U_{cell} \sim -11 \pm 1 \text{ mV}$ ). Dissimilar electrodes, which coupled a negative electrode with a high concentration of strong acid groups with positive electrode with a low concentrations of strong acid groups, produced a whole cell potential rise which was 5.7 times greater than produced with similar electrodes (from 15 ± 0.2 to 89 ± 3 mV). Therefore, tuning the surface chemistry of known materials can be conducted through a variety of methods (oxidation, ammonia treatment, etc.) to more optimally extract energy through CapMix processes.

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# **Chapter 1**

### **General Introduction**

#### **1.1 Dissertation Broader Impact and Motivation**

With increasing importance placed on reducing greenhouse gas emissions, significant efforts to mitigate these issues have focused on large scale electrification [1, 2]. The success of this course has heavily depended on the development of new decarbonized sources of electricity, and reliable forms of energy storage. Furthermore, as natural resources (coal and oil) diminish, and atmospheric  $CO_2$  concentrations approach 400 ppm, the expansion of clean renewables is becoming both a national and global issue in order to divert the current trends associated with climate change (**Figure 1-1**) [1, 3-5].



**Figure 1-1:** (a) Anomalies in mean temperature ( $^{\circ}$ C) from 2010-2014 relative 1950-1954and (b) temperature change ( $^{\circ}$ C) over the last 5 years by region. Color bars below each image represent the temperature [6].

The same rising concerns surrounding energy and the environment have also lead scientists and engineers to notice a well-defined interrelationship between energy and water. This has encouraged the development of decentralized critical infrastructures (water and energy), so that as energy demands continue to rise our water supplies will not be affected. Studies conducted by the National Renewable Energy Lab (NREL) have estimated that in the United States, electricity production requires 190,000 million gallons of water per day, accounting for ~40% of the United States freshwater extraction [7]. Globally, nearly 15% of all water withdrawals (583 billion cubic meters), is used to produce energy, and 70% is used for food production and agriculture (**Figure 1-2**) [8]. In addition, the water and wastewater infrastructure consume energy. Nearly 4% of the United States energy is consumed during the treatment and transport of water, and 75% of this energy comes in the form of electricity. It is clear that both water and energy are uniquely linked and this directly promotes the development of energy producing technologies that require reduced amounts of water and low energy water treatment methods.



Sources: Shiklomanov (1993); UN FAO Aquastat database.

Figure 1-2: World water resources and human freshwater use [7]

Efforts to alleviate the water-energy nexus have focused on water reuse, and energy recovery. In the U.S., the industrial sector accounts for 1/3 (24.0 quadrillion Btu) of the total

energy consumed and it is estimated that 20-50% (4.8-12 quadrillion Btu) of the industrial energy input is lost to waste heat [9]. The energy consumption and waste heat released by industry will only continue to increase over the coming years if the price of natural gas remains low. Technological innovations that harvest a portion of this wasted energy will reduce energy demands at industrial sites, and by extension, the total water consumed during the production of that energy.

Electrochemical systems have the capability to transform our electrical grid, personal transportation sector, and water treatment facilities. However, in order to implement these sustainable technologies, system cost and performance needs to contend with current technologies. The focus of this dissertation is on the development of novel electrochemical-based systems to recover energy from industrial waste heat, wastewater, and estuarial salinity gradients. Each year, ~3.5 trillion kwh of energy is lost as waste heat[10], ~20 billion kwh of energy discharged in wastewater and 2.6 TW of power is released through reversible mixing processes at estuaries[11-13]. This promotes a strong need to develop systems that can harvest this energy. If a portion of this energy was captured, wastewater treatment facilities could become zero energy consumption processes and industrial sites could operate more efficiently.

#### **1.2 Dissertation Outline**

In order to increase renewable energy production, and harvest currently wasted free energy, two salinity gradient energy technologies were evaluated. In **Chapter 3**, I examined the role gaseous bubble formation plays in reducing ionic fluxes in an ammonium bicarbonate (AmB)–RED system. The main objectives of this work were to study the trapping of bubbles within a RED flow field, quantify the potential detriment to the system in terms of power production and electrochemical resistance, and to evaluate potential flow field designs that passively (without adding energy) aid in removing the formed gas bubbles. The results of this chapter are summarized in a manuscript by M.C. Hatzell, and B.E. Logan entitled "*Evaluation of Flow Fields on Bubble Removal and System Performance in an Ammonium Bicarbonate Reverse Electrodialysis Stack*" published in the Journal of Membrane Science. I conducted all experiments, analysis, modeling and prepared the first manuscript draft. Both co-authors aided with the final manuscript preparation.

In Chapter 4, I evaluated the performance of an AmB–RED system with different cathodic reactions (e.g. hydrogen evolution and oxygen reduction reaction), and low–cost catalysts. The main objectives of this study were to evaluate the potential for direct in-situ hydrogen production, in–direct hydrogen production with an electrolysis cell, and direct electricity production within a RED system. The results of this chapter are summarized in a manuscript by M. C. Hatzell, I.Ivanov, R.D. Cuisick, X. Zhu and B.E. Logan entitled "*Comparison of hydrogen production and electrical power generation for energy capture in closed-loop ammonium bicarbonate reverse electrodialysis systems*" published in the journal Physical Chemistry and Chemical Physics. I designed the experiments, performed all the analyses, and prepared the first manuscript draft. I.Ivanov aided with preparation of the cathodes, and all co-authors assisted with editing the final manuscript.

In **Chapter 5**, I examined the potential for capturing microbial fuel cell (MFC) ionic currents with a capacitive mixing (CapMix) cell. The main hypothesis of this study was that passive charging of the capacitive electrodes could be modulated through controlling the MFC electrical current. The results of this chapter were used in a manuscript by M.C. Hatzell, R.D. Cusick, and B.E. Logan entitled "*Capacitive Mixing Power Production from Salinity Gradient Energy Enhanced through Exoelectrogen-Generated Ionic Currents*" that was published in Energy and Environmental Science. I designed the experiments, performed all the analyses, and

prepared the first draft of the manuscript. All co-authors aided with the discussion and edited the manuscript.

In **Chapter 6**, I investigated the role surface chemistry has on reducing and expanding the operating potential window for capacitive mixing cells based on double layer expansion. The hypothesis of this study was that the type of surface functional groups (acidic and basic) could either reduce or improve the individual electrode potential rise during the electric double layer expansion process. This work resulted in a manuscript by M.C. Hatzell, M. Raju, V. J. Watson, A.C.T van Duin and B.E. Logan entitled "*The role of strong acid functional groups on capacitive mixing by double layer expansion*" that is currently being prepared to be submitted to a Journal. I designed the CapMix experiments, M. Raju performed the ReaxFF molecular simulations, and V. J. Watson characterized the materials. I prepared the first draft of the manuscript, and all co-authors were involved with the editing of the manuscript.

#### **1.3 Additional Research Publications**

The following list includes published research to which I contributed as a co-investigator, but will not be presented within this dissertation.

- M.C. Hatzell, X, Zhu, B. E. Logan "Simultaneous hydrogen production and waste-acid disposal in a Ammonium Bicarbonate Reverse Electrodialysis System," *In prep.*
- X. Zhu, W. Yang, M. C. Hatzell, and B. E. Logan, "Energy recovery from solutions with different salinities based on swelling and shrinking of hydrogels" ES&T, 2014. Submitted.
- 3. X. Zhu, M. C. Hatzell, and B. E. Logan, Microbial Reverse-Electrodialysis Electrolysis and Chemical-Production Cell for H2 Production and CO2 Sequestration, ES&T Letters (2014).
- F. Zhang, J.Liu, I. Ivanov, M.C. Hatzell, W. Yang, Y.Ahn, B.E. Logan, "Reference Electrode Placement Affects the Accuracy of Measurement in Microbial Electrochemical Systems," *Biotechnology and Bioengineering*. 2014.
- 5. X. Zhu, M.D. Yates, M. C. Hatzell, H.A. Rao, P.E. Saikaly, and B. E. Logan, "Microbial community composition is unaffected by anode potential. *Environmental Science and Technology*, (2014).
- Y. Ahn, M. C. Hatzell, F. Zhang, and B. E. Logan, "Different electrode configurations to optimize performance of multi-electrode microbial fuel cells for generating power or treating domestic wastewater," *Journal of Power Sources*, 249, 440-445 (2014).
- 7. R. D. Cusick, **M. C. Hatzell**, F. Zhang, and B. E. Logan, "Minimal RED cell pairs markedly improve electrode kinetics and power production in microbial reverse

electrodialysis cells," *Environmental Science and Technology*, 47(24): 14518-14524 (2013).

- 8. G. M. Geise, A. J. Curtis, **M. C. Hatzell**, H. A. Hickner, and B. E. Logan, ""Effect of salt concentration differences on membrane and reverse electrodialysis stack ionic resistances," *Environmental Science and Technology Letters*, (2013).
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## Chapter 2

### **Background and Literature Review**

#### 2.1 Salinity Gradient Energy- Blue Energy

When two different concentration solutions mix, the total entropy of the system increases. (**Figure 2-1**). A natural example of where this process takes place is at estuaries, where seawater (a high salt concentration solution) mixes with river water (a lower salt concentration solution). This entropy increase at estuaries is visible through the generation of heat; however, blue energy technologies aim to utilize this mixing process to create useable forms of energy such as electrical, mechanical, or chemical energy.



Figure 2-1: Mixing of a high and low concentration solution produces a mixture and releases energy

The entropy of mixing is given by:

$$S_i = -nR(x_1 ln x_1 + x_2 ln x_2)$$
 2-1

where  $\Delta S_i$  is the entropy of the solution, *n* is the number of moles,  $x_1$  is the mole fraction of component 1,  $x_2$  is the mole fraction of component 2, and *R* is the gas constant. The total increase

in entropy due to mixing can be estimated through calculating the entropy of the two initial solutions and the final mixture:

$$\Delta S_{total} = S_m - S_{HC} - S_{LC}$$
 2-2

where  $\Delta S_{total}$  is the change in entropy during solution mixing,  $S_m$  is the entropy of the mixture,  $S_{HC}$  is the entropy of the high concentration solution (e.g. seawater) and  $S_{LC}$  is the entropy of the low concentration solution (e.g. river water).

Considering the mixing process is reversible and isothermal, the change in Gibbs free energy can be used to calculate the energy. If the solutions are ideal, the enthalpy change is zero and the reversible work is equal to the entropy change multiplied by the temperature:

$$W = \Delta G = \Delta H - T \cdot \Delta S$$
 2-3

$$W = \Delta G = -T \cdot \Delta S \tag{2-4}$$

where  $\Delta G$  is the change in Gibbs free energy,  $\Delta H$  is the change in enthalpy, *T* is the temperature, and *W* is the reversible work. The Gibbs free energy for each solution can also be calculated if the chemical potential of each component is known, using:

$$G = \sum \mu_i \cdot n_i \tag{2-5}$$

where  $\mu_i$  is the chemical potential of component *i*, and  $n_i$  is the molar concentration of that component. Considering the mixing takes place at a constant pressure and potential, the chemical potential of a solution is reduced to:

$$\mu_i = \mu_i^0 + RT \ln(x_i) \tag{2-6}$$

where  $u_i^0$  is the standard potential of the mixture. Thus, the theoretical amount of energy obtainable through the mixing of two solutions is calculated using the Gibbs free energy is:

$$\Delta G_{mix} = G_{mix} - (G_{HC} - G_{LC})$$
 2-7

$$\Delta G_{mix} = -(n_{HC} + n_{LC})T\Delta s_{mix} + (n_{HC}T\Delta s_{HC} + n_{LC}T\Delta s_{LC})$$
2-8

where the Gibbs free energy ( $G_{HC}$  and  $G_{LC}$ ) can be thought of as the Gibbs free energy from any high and low concentration solution (e.g. seawater, river water, etc.). Typically, the free energy from mixing  $\Delta G_{mix}$  is reported in J/mol, as is the  $G_{HC}$ ,  $G_{LC}$ ,  $G_{mix}$ . Often equation 2-8 is reduced to:

$$\Delta G_{mix} = 2RT \left[ V_{LC} C_{LC} \ln \left( \frac{C_{LC}}{C_{mix}} \right) + V_{HC} C_{HC} \ln \left( \frac{C_{HC}}{C_{mix}} \right) \right]$$
 2-9

where  $C_{LC}$ ,  $C_{HC}$ , and  $C_{mix}$  are the concentration of the low concentrate (river water), high concentrate (seawater) and mixed solutions, and  $V_{HC}$  and  $V_{LC}$  are the volume of the high and low concentrate solutions[1-3]. Using 2-9, it has been estimated that mixing 1 m<sup>3</sup> of seawater with 1 m<sup>3</sup> of freshwater theoretically releases 1.4 MJ of energy [4, 5]. Alternatively, if the concentration of the solutions used during the mixing process are changed (e.g. 0.01 g/l and 50 g/l), nearly 3 MJ of energy can be obtained (**Figure 2-2**).



Figure 2-2: Energy released (Gibbs Free) from various high and low concentration solutions (Eqn. 2-9).

#### 2.2.1 Reverse Electrodialysis (RED)

In 1954, R.E. Pattle first noted that the energy lost when a pure solvent mixes with a solution may be an '*untapped*' source of energy [6]. This energy released he derived was from the osmotic pressure difference and the volume of solvent (PV). Pattle further hypothesized and confirmed that conversion of the salinity gradient energy could take place through the use of alternating acidic and basic membranes with flow of high and low concentration salt solutions in between the membranes. He showed that with 94 membranes, a 'hydroelectric pile' capable of generating 3.1 V or 15 mW was formed. This was the first demonstration of a reverse electrodialysis stack.

In 1976, Weinstein and Leitz extended Pattles idea of a hydroelectric pile, and developed a mathematical model to predict the capacity of the then termed 'Dialytic Battery' (**Figure 2-3**) [7]. Optimistic economic predictions, using an estimate of 1 \$/m<sup>2</sup> of membrane, revealed that the capital investment cost of a dialytic battery plant would be \$590 per kilowatt, which was economical when compared to the \$500 per kilowatt needed for hydroelectric power (based on 1976 estimates). These assessments resulted in the approximation that the cost of power could be as low as 0.97 cents per kilowatt-hour, making the technology competitive with the current rates (2-4 cents per kilowatt-hour). Conclusions emphasized the difficulties that may arise due to ecological impacts, limitations with domestic river flow within the United States, and the production of Chlorine at the anode. Since Pattles, Weinsteins and Leitz's early work, the upper limit on power estimates from estuaries have been refined to 980 GW[4, 8], and extensive research with RED has only taken place since 2005. RED is also currently being scaled up, and commercialized through the startup company 'RED stack' in the Netherlands[9].



Figure 2-3: Reverse Electrodialysis Stack with ionic and electronic fluxes displayed

#### 2.1.2 Pressure Retarded Osmosis (PRO)

During the energy crisis in the 1970s, R.S. Norman investigated the relationship between desalination and reverse desalination and stated that *"The reversal of any desalination process should, in theory, release energy*"[10]. Using a heuristic approach which related the entropy released through two volumes of water mixing, Norman calculated that when 1 m<sup>3</sup> of fresh water mixing with a large volume of sea water, 2.24 MW of power is produced. Norman then explored the use of a semi-impermeable membrane under a hydraulic pressure in conjunction with a water wheel and generator to convert the salinity gradient energy into mechanical and electrical energy (**Figure 2-4**). This was the first discussion of the technology now termed pressure retarded osmosis (PRO). Limitations of this technology were concluded to be the cost, materials lifetime, waste production (Brine), and system design.

PRO works under many of the same principals as osmosis. When a semi-impermeable membrane separates a concentrated (draw solution) from a dilute (feed solution), osmosis draws water (J=A $\pi$ ) from dilute side into the concentrated side (**Figure 2-5**). If a hydraulic head is applied to the concentrated solution, the flux (J) across the membrane is retarded, J=A ( $\pi$ –P) and

thus through changing the hydraulic head a set flux can be developed. As the dilute solution is transported into the draw chamber, this chamber will expand, and thus energy can be extracted through this expansion by a hydro–turbine.



Fig. 1. Diagram of an osmotic salination energy converter, to extract power from the natural flow of freshwater into the sea. See text for details of operation.

Figure 2-4: Pressure retarded osmosis first envisioned by R.S. Norman [10]



Figure 2-5: (a) Osmosis (b) Pressure Retarded Osmosis (C) Osmotic Equilibrium

A bulk of the research in PRO has focused on membrane development and scale up. Loeb and coworkers pioneered much of the early developments in PRO, and focused on analytical modeling and experimentation [11, 12]. Later PRO work set to establish the key criteria necessary for thermodynamic optimization and membrane development [13-15]. A Norwegian company (Statkraft) is currently working to develop a pilot plant with 1-2 MW capabilities[16].

#### 2.2.3 Capacitive Mixing (CapMix)

The third method for extracting energy from salinity gradients is termed capacitive mixing (CapMix). All of the salinity gradient energy technologies, as Norman noted, are the reverse of energy consuming desalting processes. RED is the reverse of electrodialysis, pressure retarded osmosis is the opposite of the most common form of desalination, reverse osmosis, and CapMix is the opposite of capacitive deionization. Doriano Brogioli first developed capacitive mixing in 2009 (**Figure 2-6**)[17]. In this seminal work, he proposed that the expansion and contraction of electric double layers through alternatively dipping capacitive electrodes into high and low concentration salt solution could serve as a way of extracting energy from salt gradients. Through this processes, he was able to extract 5  $\mu$ J per cycle, but estimated that because no membranes were necessary that this could become a cost competitive method for energy extraction with system improvement.

To date there are only a few publications (<50) on capacitive mixing technologies, and of the three methods for producing energy from salinity gradients, it produces the lowest power [18-21]. Yet the technology is regarded as nascent due to the potentially low cost and high durability of the electrodes. Since Doriano Brogioli's publication, two other methods of extracting energy through capacitive, or pseudo capacitive electrodes have emerged. The three methods are: capacitive mixing based on double layer expansion (CDLE), capacitive mixing based on a donnan potential (CDP), and battery mixing (BatMix). Each process is described in detail below.



Figure 2-6: Capacitive Mixing Device with activated carbon electrodes[17]

#### 2.3 Energy Generation and Conversion through Reverse Electrodialysis

RED operates through establishing a chemical potential gradient across series of alternating anion and cation selective membranes. When solutions of different chemical potentials (river and seawater) flow beside the membranes, a Donnan potential forms. With a large stacks of membranes, the potential generated is capable of driving current generation by forcing electrochemical redox reactions at electrodes located on either end of the stack. Recent studies have investigated the use of thermolytic salt solutions, such as ammonium bicarbonate (AmB) to potentially produce more energy through larger concentration gradients [22-27]. AmB can also be easily distilled using a waste-heat driven distillation column, and thus there is the potential to operate these system systems away from estuaries. Furthermore, due to the increased amount of energy lost at industrial sites, innovated solutions which capture waste heat is growing in demand.

In order for either RED to be applicable as an energy recovery, or waste heat conversion mechanism, system performance needs to improve. Currently, the RED stack performance, electrochemical reaction overpotentials, and system ohmic resistances (materials and solution) need to be addressed before RED can be sustainably implemented.

#### 2.3.1 RED Stack Performance

A reverse electrodialysis stack generates an electric potential due to the generation of a series of membrane potentials or Donnan potentials. The potential across each membrane is a function of the activity of the solutions on either side of the membrane (e.g. the concentration gradient), and typically is calculated through the Donnan equation:

$$E_{stack} = CP \frac{\alpha RT}{zF} \ln\left(\frac{a_{HC}}{a_{LC}}\right) \approx CP \frac{RT}{F} \ln\left(\frac{C_{HC}}{C_{LC}}\right)$$
2-10

where CP is the number of cell pairs,  $\alpha$  is the membrane permselectivity, *F* is faradays constant (96485 C mol<sup>-1</sup>), z is ion valence, *R* is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), *T* is temperature, and  $a_{HC}$ , and  $a_{LC}$  are the activity of the high and low concentration (e.g. sea and river water). Alternatively, if the activities of the solution are unknown, the solution concentrations ( $C_{HC}$  and  $C_{LC}$ ) can be used to approximate these activities. The power density from the stack can be obtained if through:

$$W = I^2 R_{load} = \frac{E^{0^2} R_{load}}{(R_{stack} + R_{load})^2}$$
2-11

where *I* is the current (A),  $R_{load}$  is the external load,  $R_{stack}$  is the resistance of the stack, and  $E^0$  is the open circuit voltage. Ultimately, as was demonstrated by Weinstein[28], the optimal operation load should be tuned based on the RED stack resistance (**Figure 2-7**). Often times, the external

resistance of the stack can be estimated based on the low concentration resistance, as this is much larger than the HC chamber resistance.



Figure 2-7: Power output as the river water concentration (low concentrate) and load resistance are changed (Eqn. 2-11).

#### 2.3.2 RED Electrodes Performance

The activation losses and can be approximated based on the Butler–Volmer equation:

$$\Delta U_{act,c} = U_{0,c} - U_c = \frac{RT}{\alpha_c F} \ln\left(\frac{i}{i_{0,c}}\right)$$
2-12

$$\Delta U_{act,a} = U_a - U_{0,a} = \frac{RT}{\alpha_a F} \ln\left(\frac{i}{i_{0,a}}\right)$$
2-13

where  $\Delta U_{act,c}$ , and  $\Delta U_{act,a}$  are the activation overpotential at the anode and cathode,  $U_{0,c}$ ,  $U_{0,a}$  are the equilibrium potentials,  $U_c$ , and  $U_a$  are the electrode overpotential,  $\alpha_c$  and  $\alpha_a$  are the charge
transfer coefficients, *i* is the current, and  $i_{o,a}$  and  $i_{0,c}$  are the exchange current density. For reverse electrodialysis systems, most electrodes have utilized precious metal catalyst to reduce kinetic limitations, yet low cost non precious metal catalysts are preferred.

To reduce electrode overpotentials various materials (catalysts) and electrolytes solutions (anolytes and catholytes) have been investigated. Early systems were designed around precipitating and dissolving electrode-electrolyte systems, and a recent study has proposed the use of capacitive electrodes [6, 29-31]. The main hindrance with these systems is the need for periodic current reversal in order to either maintain or discharge the electrodes. This can be done through switching the electrodes or feed solutions, though both methods are not easily scalable.

An extensive review of electrode reactions for RED systems recommended the use of inert electrodes submerged in NaCl-HCl supporting electrolytes that use reversible redox couples such as  $Fe^{2+}/Fe^{3+}$  and  $[Fe(CN)_6^{4-}/Fe(CN)_6^{3-}][32]$ . Homogenous charge transfer reactions (reactions where redox species can be oxidized and then reduced back into its original form) were deemed highly desirable as this enables recirculation of the anolyte and catholyte solutions in a closed loop. These redox couples reduce the overpotentials at the electrodes, but cannot be 100% contained within the electrode rinse chamber. Leakage through the membranes of the electrolyte would contaminate the feed solutions, and require redox couple solutions to be replenished. There is also a potential for damage of the membrane, which today is the most expensive part of the system.

In many other studies the stacks were fed high concentration solutions (seawater) as the anolyte and catholyte solutions [28, 30, 33], thereby relying on the water splitting reaction to drive current at each electrode. If the feed solution and electrolyte are the same, trace mixing is not an issue, and furthermore the overall system complexity is reduced. With sea/river water based RED systems, chlorine gas evolution at the anode has been noted as an important issue that

cannot easily be resolved. Chlorine is extremely toxic to the environment and membranes and thus it is not considered a viable option for sea/river based RED systems [30, 34-36].

Thermolytic solutions such as ammonium bicarbonate (AmB) are presently emerging as an alternative feed solution for closed-loop RED processes [15, 22, 24, 37]. With the new feed solution, chlorine gas evolution is no longer an issue, allowing AmB to potentially act as both the feed and electrolyte rinse solutions. Other issues, such as ammonium oxidization at the anode may persist as an issue, yet the overpotentials may be reduced.

Reaction	Reaction	Literature
Anode:	$H_2 O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$	[30, 38, 39]
	$2Cl^- \rightarrow Cl_2 + 2e^-$	[28, 30, 33]
	$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-$ $Fe^{2+} \rightarrow Fe^{3+} + e^-$	[25, 40, 41] [32]
Cathode	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	[28, 33, 36, 39]
	$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$	[25, 40, 41] [32]

Table 2-1: Electrode materials (catalyst and electrolytes) and reactions for REDs in literature

# 2.3.3 RED Ohmic Resistance

Ohmic losses refer to electrical resistances, which restrict the flow of ions in the electrolyte and the flow of electrons in the circuit. Ohms law is used to characterize these losses:

$$\Delta U_{ohmic} = iR_i = i(R_{ionic} + R_{electric} + R_{contact})$$
 2-14

where  $R_i$  is the resistance of the various system components (e.g. solution, membranes, electrical contacts etc.). With RED systems, the solution resistance dominates the system performance. The ionic resistance is comprised of the high and low concentrate solution resistance and the

membrane (AEM and CEM) resistance. The low concentration solution (e.g. river water) creates a very large resistance, and thus typically electrical resistances, contact resistance and the high concentrate resistance can be neglected. The ohmic losses can then be reduced to:

$$\Delta U_{ohmic} = i(R_{ionic}) = i(R_{AEM} + R_{CEM} + R_{LC})$$
2-15

where  $R_{AEM}$  and  $R_{CEM}$  are the membrane resistance and  $R_{LC}$  is the solution resistance. The solution resistance can be approximated by:

$$R_{LC} = \frac{t}{\Lambda_{LC} c_{LC}}$$
 2-16

where  $\Lambda_{LC}$  is the equivalent conductance,  $c_{LC}$  is the low concentrate concentration, and *t* is the compartment thickness. Increasing the low concentrate solution would provide an immediate reduction of ohmic resistance, but it would also decrease the open circuit potential of the cell, as the activity gradient increases (**Figure 2-8**). Thus, there is an important tradeoff between maintaining a concentration gradient, and decreasing the ohmic resistance of the cell.



**Figure 2-8**: Relationship between a cell pairs potential and resistance as the low concentration solution is varied (HC = 1 M) (a) NaCl (b) Ammonium Bicarbonate. The cell voltage is calculated using Eqn. (2-10), and the resistance is calculated using Eqn. (2-14).

The AEM and CEM membrane resistances have typically been thought to be minimal in comparison to the low concentrate chambers. However, recent findings have suggested that the membranes resistance is actually a larger percent (33-50%) of the total resistance[26]. Membranes are typically highly resistive when measured in a low concentration solution, and because of the RED system architecture, a portion of each membrane is always in contact with a low concentration solution. However, it is also evident that the membrane resistance is substantial portion of the overall resistance, and therefore efforts to mitigate this resistance will improve the overall performance of the RED system.

#### 2.2.4 RED System Operation

Flow through the RED cell pairs is dictated by the Navier–stokes equation, and ionic transport is governed by the Poisson- Nernst-Planck Equation:

$$\boldsymbol{N}_{i} = -D_{i} \nabla c_{i} - z_{i} u_{mob,i} F c_{i} \nabla \phi_{e} + c_{i} \boldsymbol{u}$$

$$2-17$$

where  $N_i$  is the total molar flux due to diffusion, migration, and convection,  $D_i$  the diffusivity of the charge ion,  $c_i$  the concentration,  $z_i$  the species charge number,  $u_{mob,I}$  the species mobility,  $\phi$ the electrolyte potential, u the fluid convection, and F faradays constant (96485 C·mol). The main operational parameter used to optimize the ionic flux is the system flow rate. Through increasing the stack flow rate, the transport (diffusion, electromigration and convection) is optimized. In addition, maintaining the concentration gradient aids in optimizing the electromigration term, and therefore total ion flux. However, as the flow rate is increased, there comes a point where the flux through the stack is no longer increased. Due to the high energy demands for pumping fluid, the lowest flow rate which produces the highest performance, should be used to optimize energy recovery.

### 2.4 Energy conversion and generation through Capacitive Mixing

### 2.4.1 Capacitive Mixing based on Double Layer Expansion

When an applied potential is placed across porous activated carbon electrodes submerged in an electrolyte solution, the tendency is for counter ions to adsorb onto corresponding positive and negative electrodes due to electrostatic forces. For salinity gradient energy generation, the ion  $Na^+$  is stored within the negative electrode and  $Cl^-$  ions are stored within the positive electrode. Brogioli proposed that if charged electrodes saturated with a salt solution come in contact with a fresh low concentration solution diffusion forces tend to dominate, drawing the ions previously trapped in the electric double layer within the carbon electrodes into the solution, thereby expanding the electric double layer[17]. This extraction of the double layer is equivalent to a force applied across a distance that shows that work is done through the movement of the salt ions.

Rica and coworkers and Brogioli recently described this phenomenon through electrochemical modeling based on Gouy-Chapman-Stern Theory [35, 36]. In these studies they described an electrostatic capacitor which is charged to a set voltage. The voltage can be described by

$$V_1 = \frac{Qd}{\varepsilon}$$
 2-18

where Q is the charge density, d is the distance between capacitor plates and  $\varepsilon$  is the electric permittivity of the dielectric medium. Thus, it can clearly be seen that as the distance between the two plates increases, the voltage must increase. To increase the distance between the plates work would need to be done to force the plate to the desired location. This mechanical work would increase the electrostatic forces, increasing the voltage. While capacitive mixing is not based on mechanically moving electrodes to increase the voltage, it the electric double layer is moved, which can be thought of as an electrolytic capacitor with one plate being the solid electrode and the other being the electric double layer.

From Gouy-Chapman-Stern theory, the distance d of the electric double layer is referred to as the Debeye length[42]. This is expressed through:

$$\lambda_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2Ce^2}}$$
 2-19

where,  $\varepsilon_r$ , and  $\varepsilon_o$  are the electric permittivity of the liquid and vacuum,  $k_b$  is the Boltzmann constant, *T* is the absolute temperature, *C* is the concentration, and *e* is the electron charge. Thus the Debeye length, or distance separating the two "plates", depends on the concentration of ions in the solution, and it can clearly be seen that as the concentration increases the double layer thickness decreases. Furthermore, the voltage across this diffuse portion of the double layer,  $\Delta V_D$ , and the voltage across the stern layer,  $\Delta V_{st}$ , can be written as:

$$\Delta V_D = -\frac{Q}{\frac{\varepsilon_r \varepsilon_0}{\lambda_D}}$$
 2-20

$$\Delta V_{st} = \frac{\frac{Q}{A}}{C_{st}}$$
2-21

From the above equations (Eqns. 2-20, 2-21) it can be seen that the voltage across the diffuse portion of double layer is a function of the Debeye length which is a function of ion concentration. In addition, it is clear that the voltage across the stern layer is inversely proportional to the stern layer capacitance. Two clear relations to concentration of solution are evident: (1) As the concentration of ions increases, the EDL, and  $V_D$  will decrease, and (2) As the concentration of ions decreases, the EDL and  $V_D$  will increase. This is also visible through the Gouy-Chapman-Stern model:

$$\varphi_H^0 = \frac{2RT}{zF} \sinh^{-1} \left( \frac{\sigma^d}{-\sqrt{8\epsilon_0 \epsilon_r C_H RT}} \right) + \frac{\sigma^0}{C_{st}}$$
 2-22

Thus, as the surface charge increases and concentration decreases, and the potential drop in the diffuse portion of the electric double layer increases (Figure 2-9) (Figure 2-10).



**Figure 2-9**: Potential of capacitive electrode surface depending on surface charge density and solution concentration (10 mM and 0.5 M) (Eqn. 2-22).



**Figure 2-10:** Electric double layer extraction and compression and relationship to Debeye length and voltage rise

Energy extraction from the CapMix cycle has been previously described in a similar way to typically heat engine processes [20, 43, 44], and most specifically the commonly known Stirling engine cycle. Instead of pressure, volume, and temperature changes, the cycle consists of voltage, charge, and chemical potential changes. From thermodynamic analysis of a heat engine, the change in internal energy is often written as Eqn. (2-23), which is analogous to Helmholtz free energy written as Eqn (2-24)[45]:

$$dF = \mu dN + \psi dQ \qquad 2-24$$

Therefore to extract significant usable energy from extraction and compression of the electric double layer it has been suggested that the cycle consist of two iso-u (constant chemical potential or concentration processes) and two constant-N or fixed charge.

A four-step process is used for extracting energy in the CapMix process (**Figure 2-11**). During step 1, the charge electrodes are brought into contact with a low concentrate solution, expanding the double layer and increasing the voltage. In step 2, the voltage is discharged in the low concentrate bringing the electrodes back to their original potentials while simultaneously extracting energy. Next, in open circuit, the low concentrate solution is replaced by a high concentration solution, which compresses the EDL, resulting in a decrease in potential. Finally, the electrodes are recharged back to their initial potentials (consuming energy). The areal integral of the exchanged charge and voltage provides you with the total energy extracted.



Figure 2-11: Four step energy extraction processes proposed for the CDLE method.

#### 2.4.2 Capacitive Mixing based on Donnan Potential (CDP)

Much of the same theory described for the CDLE method pertains to the CDP method. The major difference between the two techniques is the CDLE method must utilize an auxiliary power source such as secondary battery to initially charge the electrodes, while the CDP method relies on a generated membrane potential. CDP electrodes are coated with ion selective monomer, which selects for a counter-ion to adsorb onto a specific capacitive electrode. The two main advantages of the CDP method are that an external power source is not needed (although it can be used), and the capacitors leakage is reduced because co-ion transport out of the porous material no longer takes place[46]. However, the main negative of this process is the increased cost due to the need for ion exchange membranes.

Sales *et al.* first proposed the CDP method [46-48] with the aim being to develop a salinity gradient based technology that could operate with little auxiliary equipment (i.e. without pressure exchangers, turbines, redox solutions or secondary batteries), and called thee technology Auto Generative Capacitive Mixing (AGCM). The four steps for energy extraction through the CDP method are shown in **Figure 2-12**. During Step 1, the electrodes are exposed to a high concentration solution which generates a potential. This allows for each electrode to acquire a concentration of counter-ion which ultimately charges the electrodes. Next (Step 2) the high concentration solution is replaced by a low concentration solution that increases the potential due to the EDL sudden expansion. During step 3, the electrode are put in a closed circuit, and the flux of electrons causes a flux of ions, ultimately reversing the membrane potentials back to zero. Finally in step 4, the low concentrate solution is replaced by a high concentrate solution and the electrodes are maintained in open circuit. This causes the initial potential across each membrane to be regenerated, bring the potential back to its original state.



**Figure 2-12:** (A) Graphical summary on the cyclical process used to generate power from salinity gradient energy by regular (CDP) and forced CDP approaches. (B) The "voltage-charge window" (shown as the area within the blue or black quadrants) for the CDP and forced CDP approaches, where the energy extracted is represented by the size of the window.

### 2.4.3 Capacitive Mixing using Battery Electrodes (BATMix)

With capacitive mixing based on battery electrodes, utilizes an anionic and cationic electrode to extract energy from a specific ionic liquid through faradaic like reactions. La Mantia et al. first proposed this approach, and used a battery electrode system with a  $Na_{2-x}$   $MN_5O_{10}$  cationic electrode and an Ag anionic electrode[49-53]. When the electrodes are submerged in the low concentration solution, there is the tendency for the ions to be removed from the electrode structure, and thus the battery is charged (step 1)**Figure 2-13**. Next, while in open circuit, the low concentrate is replaced by the high concentrate and the potential across the electrodes increases (Step 2). When the electrodes are placed in a closed circuit, the ions incorporate themselves back

into the electrodes the battery discharges (step 3). Finally, the high concentrate is replaced by the low concentrate solution, decreasing the cell potential (Step 4). The general equation and faradic potentials can be seen in the following table. Ultimately, energy is generated in a high concentration solution, which is the reverse of CapMix (CDP and CDLE).

Table 2-2: Battery electrode reactions and corresponding Nernst equations



Figure 2-13: Battery mixing four step cycle and potential versus charge plot.

### 2.5 Microbial Electrochemical Technologies (METs)

Microbial electrochemical technologies (METs) use bacteria to catalyze 'faradic-like' redox reactions at either an anode or cathode, and they can be used to generate either value added products (peroxide[54, 55], struvite[56], and hydrogen[54, 57]) or electricity[58]. These

bioelectrochemical systems may ultimately aid in alleviating the amount of grid-based energy that is needed to sustain wastewater treatment facilities. Today, nearly 4% of the energy produced is used to treat and transport water. Yet it has been estimated that nearly ~20 billion kwh of energy is discharged in wastewater each year [59, 60]. If this energy within the organic matter was harvested, through technologies (anaerobic digestion and METs), wastewater treatment plants might be able to operate as energy generation facilities, rather than energy consumers.

The most common MET investigated is the microbial fuel cell (MFC), which utilizes exoelectrogenic bacteria on the anode to oxidize organic matter, and platinum to reduce oxygen at the cathode, ultimately producing electricity [58, 61, 62]. The maximum potential generated using acetate as a fuel under standard conditions at the anode is:

$$CH_3CHOO^- + H_2O \rightarrow HCO_3^- + CO_2 + 8e^- + 8H^+$$
 (E<sub>0</sub>=-0.32 V) 2-25

Most MET studies have concluded that the bacteria responsible for releasing electrons extracellular to the electrode is *Geobacter sulfurreucens* [63], through the use of mediators, nanowires or direct contact [63-67]. MFCs are coupled to a range of reduction reactions, the most common as previously mentioned is oxygen reduction:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$
 (E<sub>0</sub>=-0.82 V) 2-26

Alternatively if hydrogen is the preferred energy product, an additional potential (~200-1000 mV) can be added to the cell, this is called a microbial electrolysis cell (**Figure 2-14**).

$$2e^- + 2H^+ \rightarrow H_2 \quad (E_0 = -0.414 \text{ V})$$
 2-27



**Figure 2-14:** Common microbial electrochemical technologies (METs), (a) Microbial fuel cell, and (b) microbial electrolysis cell with reactions labeled.

To date, the main challenge with scaling up MFCs has been with the cost of the cathode. However, recent work on the development of activated carbon cathodes has significantly reduced the overall cost of MFC cathodes, making MFCs more economically feasible [68, 69]. Another limitation with METs is the low power densities. Most power densities have remained on the order of (~1-2 W/m<sup>2</sup>-cathode), due to the high ohmic resistances and neutral pH operating conditions. However, significant improvements have been made to the power densities through coupling salinity gradient energy technologies, such as RED, with METs [22, 37, 70-73]. Cusick et al. was able to achieve power densities on the order of ~5 W/m<sup>2</sup> using organic matter and 2 W/m<sup>2</sup> using domestic wastewater, based on energy extracted from both substrates and salinity gradients. This demonstrated the tremendous potential that may be able to be achieved through coupling METs with salinity gradient energy technologies and further promotes the simultaneous investigation of both energy conversion techniques.

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# Chapter 3

# Evaluation of Flow Fields on Bubble Removal and System Performance in an Ammonium Bicarbonate Reverse Electrodialysis Stack

#### **3.1 Abstract**

Ammonium bicarbonate has recently been demonstrated to be an excellent thermolytic solution for energy generation in reverse electrodialysis (RED) stacks. However, operating RED stacks at room temperatures can promote gas bubble formation (CO<sub>2</sub>, NH<sub>3</sub>), which reduces performance. The management and minimization of bubbles formed in RED flow fields is an important operational issue which has yet to be addressed. Flow fields with and without spacers in RED stacks were analyzed to determine how both fluid flow and the accumulation and removal of bubbles affected performance. In the presence of a spacer, the membrane resistance increased by ~50  $\Omega$ . Without a spacer, the power density increased by 30% from 0.093 W m<sup>-2</sup> to 0.140 W m<sup>-2</sup>. Shorter channels reduced concentration polarization affects, and resulted in 8-23% higher short cut current density. Gas accumulation was minimized through the use of short vertically aligned channels, resulting in a reduction in the amount of the membrane area was covered by bubbles from ~20% to 7%, and a 12% increase in power density. As ammonium bicarbonate RED systems are scaled up, attention to channel aspect ratio, length, and channel alignment will enable more stable performance.

### **3.2 Introduction**

Developing renewable energy technologies capable of generating electricity is essential in order to meet rising global energy demands. Salinity gradient energy, which is based on extracting the free energy released from natural salinity gradients such as those where rivers flow into the sea, have been estimated to be capable of generating 1.9-2.6 TW [1-7]. Reverse electrodialysis (RED), a technology that can be used to harvest this energy and directly convert it to electrical energy, could be used to capture as much as 980 GW of this released energy [2]. In a RED system, stacks of alternating ion selective membranes are used to separate the high concentration solution (seawater) from the low concentrate (river water). This separation creates a gradient in chemical potential which generates a Donnan or membrane potential, producing an ionic flux through each alternating anion and cation exchange membrane. As the number of membranes is increased, the stack potential increases which drives electrochemical redox reactions at electrodes and ultimately electricity generation.

The majority of the resistive losses in RED are associated with the low concentrate chambers and the spacer thickness. To reduce these losses, RED stacks are designed to have thin flow compartments [5, 8, 9], and spacers that promote mixing and an even flow distribution. Removing the spacer completely has been shown to increase performance, and it reduces biofouling at the spacer-fluid interface [10]. Although spacer-less systems are preferred to reduce system complexity and cost [11], the majority of RED stacks have had spacers [11-13]. Spacer-less systems have been modeled [12], and experimentally investigated using 'ribboned' gaskets [14] and profiled membranes[15]. However, the effect non-uniform flow in spacer-less systems has on system resistance has not been studied experimentally.

Other resistances that reduce RED performance include the diffusion boundary layer resistance, membrane resistance, and the electric double layer resistance [16, 17]. Diffusion

boundary layers form at each solution-membrane interface, and grow along the direction of flow. This resistance typically can be reduced by high flow rates, short channels, and through the use of higher concentration solutions [18]. However, high flow rates can reduce the overall system energy recovery, often prompting hydrodynamic related losses through pressure drops, and cause ionic short circuiting [13]. In addition, low concentration solutions are required for power generation in RED systems.

The resistance of commercially available membranes (membrane resistance) has been studied independent of the RED stack in low and high concentration solutions [16, 19], and within a RED stack [20]. Results showed that in low concentration solutions, the membrane resistance increased dramatically. Likewise, the membrane resistance within the high concentration solution was shown to decrease with higher flow rates due to a reduction in concentration polarization effects. The final resistance is associated with the interfacial ionic charge transfer resistance through the electric double layer (electric double layer resistance) at the membrane interface. Due to the relatively insignificant thickness of this double layer in comparison to the diffusion boundary layer, this resistance is typically small.

While there is potential for sea/river water based RED systems, recent studies have tried to address the limitations through the use of synthetic thermolytic salts [21-23]. Thermolytic salts allow for more control of solution concentrations compared to those dictated by river and seawater concentrations. Using higher salt concentrations enhances osmotic pressure differences, and thus the amount of energy that can be produced. For example, the osmotic pressure difference between river and sea water (0.5 M) is limited to ~24 atm, or ~240 m equivalent pressure head [3]. For ammonium bicarbonate, higher concentrations (1 M to 1.5 M) can be created, producing hydraulic pressure heads equivalent to 380 m to 510 m. The use of ammonium bicarbonate also avoids the geographic constraints that are require for sea/river based RED systems (coastal

regions), and eliminates the need for energy intensive pretreatment processes. The high and low concentration thermolytic salt solutions can also be regenerated using waste heat in thermal distillation processes.

The fluid dynamics within reverse electrodialysis stacks play an important role in maintaining both optimal performance and extending material lifetimes. Thus, a better understanding of the flow distribution in both spacer and spacer-less stacks can improve system longevity and performance. To date, few laboratory studies have been conducted using ammonium bicarbonate in RED stacks [21-23], and the presence and consequences of the known gas composition intrinsic to thermolytic solutions (CO<sub>2</sub>, NH<sub>3</sub>) (Figure 3-2) has not yet been discussed. Furthermore, techniques for passive removal of gas bubbles through channel geometry have not been developed. In this study, we examined the effect channel geometry has on the system resistance, gaseous bubble removal, and evaluate the system performance in terms of the limiting current and peak power. Fluid flow was analyzed based on a 2-D CFD analysis to determine the best way to enhance bubble removal and enable more stable performance when using ammonium bicarbonate in RED stacks.

### **3.3 Materials and Methods**

#### **3.3.1 Reverse electrodialysis stack**

Electrolyte rinse chambers were made from two 2 cm long cylindrical chambers cut from a block of polycarbonate (Lexan, 18 mL empty bed volume). Silicon gaskets, used to separate the membranes and create a flow path across the membranes in the stack, were cut to contain a 2 cm<sup>2</sup> rectangular cross section that was ~1.3 mm wide (the gasket thickness). Tests were conducted without a spacer, except as noted where a strip of polyethylene mesh (2 cm  $\times$  0.5 cm) was fit into

the rectangular cross section (2 cm  $\times$  1 cm or 3 cm  $\times$  0.67 cm). The spacer was 1.1 mm thick and had 69% open area resulting in a maximum shadow of ~31%. Two cation exchange membranes, one anion exchange membrane (Selemion CMV and AMV, Asashi Glass, Japan) and two silicon gaskets were used to form a single cell pair stack. All membranes were equilibrated in an ammonium bicarbonate solution overnight prior to testing. High and low concentration solutions fed to the RED stack were 1.1 M and 0.011 M (salinity ratio of 100). The electrode rinse solution was a high concentrate ammonium bicarbonate solution (1.1 M). Two flow field channel aspect ratios were investigated (2  $\times$  1) and (3  $\times$  0.67) (Figure 3-1). In order to examine the effects of different channel alignments, these flow channels were designed to have either a vertical or a horizontal configuration. Co-current flow was used in all tests.

### 3.3.2 System performance

Electrochemical galvanostatic polarization was carried out using a potentiostat (VMP3 Multichannel Workstation, Biologic Science Instruments, USA) in a 30 °C constant temperature room. Current was scanned from 0 mA to 1.5 mA, and each current step was held long enough to arrive at a steady state whole stack potential (>15 min). Platinum mesh electrodes (projected area 7 cm<sup>2</sup>) were used as working and counter electrodes, with the stack potential monitored using Ag/AgCl reference electrodes (BASi, West Lafayette, IN) placed on either side of the stack. Stack current-voltage (polarization) curves were converted to power density, where power was normalized by the total membrane surface area (6 cm<sup>2</sup>), and current was normalized per 1 membrane (2 cm<sup>2</sup>). The slope of each current-voltage curve, obtained by a linear regression, was used to calculate the total internal resistance. The limiting current, estimated from the *x*-intercept using a linear fit of the polarization curve, represents the maximum electrical current able to be generated from the stack.

#### 3.3.3 Electrochemical impedance spectroscopy

Galvanostatic electrochemical impedance spectroscopy (GEIS) was performed using a potentiostat (VMP3 Multichannel Workstation, Biologic Science Instruments, USA). Current was set at 1.25 mA, and the frequency ranged from 1 MHz to 50 mHz, with a sinusoidal perturbation of 0.1 mA. Pt electrodes were used as both a counter and working electrodes. EIS was performed with and without the stack, with the difference used to remove the diffusion and solution resistances of the electrolyte rinse chambers. EIS spectra were analyzed using an equivalent circuit model (EC lab software) previously reported for RED stacks [17, 24, 25]. The resistances include:  $R_{m+s}$  the total membrane and solution resistance within the stack;  $R_{DL}$  and  $C_{DL}$ , the resistance and capacitance of the electric double layer; and  $R_{DBL}$ , and  $Q_{DBL}$ , the resistance and constant phase element associated with the diffusion boundary layer.

### 3.3.4 Gaseous bubble coverage

An ex-situ fluid flow analysis was performed with a high and low concentrate solution flowing on either side of a single membrane. Images of each flow field under both high and low flow rates were captured every five minutes for a half an hour to observe bubble formation. Membrane coverage by bubbles was estimated using the Adobe Photoshop CS6 extended measurement feature (Adobe Systems, USA), by calculating the ratio of number of pixels for the bubbles divided by the total number of pixels for the chamber.

### 3.3.5 Computational fluid dynamics analysis of varying channel length

The 2-D incompressible fluid flow analysis was conducted using the multiphysics 4.3a Fluid Dynamics module (COMSOL, Burlington, MA). Two inlet flow rates were investigated: a high flow rate of 2 mL min<sup>-1</sup> (18 mm s<sup>-1</sup>) and low flow rate of 0.5 mL min<sup>-1</sup> (4 mm s<sup>-1</sup>). The velocity and pressure profiles across each flow field were computed by solving the momentum and continuity equations:

$$\rho \left[ \frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u} \cdot (\nabla \boldsymbol{u}) \right] = -\nabla p + \mu \nabla^2 \boldsymbol{u}$$
3-1

$$\nabla \cdot u = 0 \tag{3-2}$$

where  $\mu$  is the kinematic viscosity (kg m<sup>-1</sup> s<sup>-1</sup>), *u* the velocity (m s<sup>-1</sup>),  $\rho$  the water density (kg m<sup>-3</sup>), and *p* the pressure (Pa). No-slip boundary conditions were assumed for all surfaces, and a parametric triangular mesh was fitted to the flow field. Additionally, simulations were run with a stagnant representative gaseous bubble present to investigate the effects the bubble had on the channels pressure and velocity profiles.

# **3.4 Results and Discussion**

### 3.4.1 Stack power density and polarization

Under high flow rate conditions, the vertically aligned channels performed better than the horizontal channels in terms of maximum power density. For the 2 cm channels, the maximum power density increased from 0.139 W m<sup>-2</sup>  $\pm$  0.002 in a horizontal alignment to 0.156 W m<sup>-2</sup>  $\pm$  0.0003 for the vertically aligned channel. Likewise, for the 3 cm channel the maximum power density increased from 0.125 W m<sup>-2</sup>  $\pm$  0.0008 to 0.143 W m<sup>-2</sup>  $\pm$  0.0003 (Figure 3-2). These results show that power density was increased by ~12% (2 cm channel) and 15% (3 cm channel) through aligning the channels in a vertical configuration. The short (2 cm) vertical channel

produced 14% more power than the longer vertical channel, indicating that short vertically aligned channels are preferable for high flow rates.

At low flow rates, vertical alignment again improved the power density. The 2 cm channel power density increased from 0.137 W m<sup>-2</sup>  $\pm$  0.002 to 0.154 W m<sup>-2</sup>  $\pm$  0.002, and the 3 cm channel power densities increased from 0.131 W m<sup>-2</sup>  $\pm$  0.001 to 0.154 W m<sup>-2</sup>  $\pm$  0.003 (Figure 3-3) The power densities for each channel were fairly similar under high and low flow rates in this spacer-less RED. As reported in literature studies, the performance typically increases with flow rate [26], indicating an additional resistance was present at 18 mm s<sup>-1</sup> which limited the performance.

Each power density curve can be split into two sections: the first portion where the stacks perform fairly similarly (low current); and a second portion where stack performance differs (high current). The transition point was defined when the power densities differed by more than 10%. At high flow rates this occurred at 4.5 A m<sup>-2</sup> and at low flow rates this transition was at 6.5 A m<sup>-2</sup>. At low current only small deviations in power density were observed. These were attributed solely to hydrodynamic differences between of each channel. For example, the 3 cm vertical channel performed the best at low current densities and low flow rates, indicating that the 3 cm vertical channel was the most optimal of these designs during conditions when ionic fluxes were low. At higher current densities where most of the deviation in power density was observed, it is expected that concentration polarization affects dominate. Therefore, the observed performance differences are in part due to the flow designs ability to maintain an even flow and mitigate concentration polarization effects.

The 2 cm horizontal channels produced 23% (18 mm s<sup>-1</sup>) and 8% (4 mm s<sup>-1</sup>) greater limiting current densities than the 3 cm horizontal channels at each flow rate (**Table 3-1**). In addition, the vertical 2 cm channels produced 6% (18 mm s<sup>-1</sup>) and 3% (4 mm s<sup>-1</sup>) greater limiting current then the 3 cm vertical channel. Therefore, although the peak power was significantly

inhibited by channel alignment at the high flow rates, the limiting current was increased through the use of a shorter channel.

### 3.4.2 Gaseous bubble accumulation within flow channels

During galvanostatic operation of the RED stack, the voltage output was not stable. Instead of a constant voltage output, voltage curves were step-like, showing sudden increases and decreases in the voltage over time (**Figure 3-4**). Bubbles in the stack were observed at the exit of the high concentrate stream. Thus, it was concluded that the intermittent voltage changes were due to the buildup and removal of bubbles within the channels. These bubbles would reduce performance by decreasing the active membrane surface area available for ion diffusion. The 2 cm and 3 cm horizontal channels produced fluctuating voltages, indicating that the horizontal channels did not operate as stably as vertical channels because of the persistence of bubbles on the membrane surfaces. It should be noted that while the horizontal channels were less stable, the channels average voltage remained similar to the vertical aligned channel with the same length.

Ex-situ experiments also showed significant bubble accumulation in the horizontal channels (**Figure A-5 and Figure A-6**). Bubbles accumulated along the top wall of all channels, and remained stagnant in corners and dead zones. The bubble coverage was calculated to be the highest in the 3 cm horizontal chamber, with maximum bubble membrane coverage of  $20\pm1\%$  of the membrane surface area (**Figure 3-5**). Changing the channel alignment from horizontal to vertical reduced the bubble coverage by ~60% (3 cm) and by 73% (2 cm) (**Figure A-56s**). Lower flow rates reduced the bubble coverage, likely due to the smaller volumes of water that passed through the channel during the given time period.

#### 3.4.3 System internal resistance

The diffusion boundary layer (DBL), double layer (DL), and solution and membrane ohmic (S+M) resistances were characterized using GEIS for each flow field. The solution and membrane resistance accounted for 58-85% of the total resistance ( $60 \pm 16 \Omega$ ). The solution resistance remained the same in each test; and thus the observed differences in  $R_{s+m}$  were attributed to changes in the membrane resistance. The membrane resistance is a function solution concentration, decreasing non-linearly in high concentration solutions [17]. This decrease in membrane resistance with increasing concentration was evident when a single membrane was tested using ammonium bicarbonate (**Figure A1**). However, with the spacer-less RED stack as the flow rate decreased the total ohmic resistance at lower flow rates is due to the longer hydraulic retention time which increases solution conductivity in the low concentrate. However, bubble accumulation, membrane deformation, and possibly ionic leakage at higher flow rates may also contribute.

The diffusion boundary layer resistances within the horizontal channels at high flow rates was on average 12  $\Omega$  greater than those for the vertical channels. However, at low flow rates the vertical channels R<sub>DBL</sub> increased by 850% (16.5  $\Omega$ ) and 275% (15  $\Omega$ ) (**Figure 3-6b**). The diffusion boundary layer resistance at low flow rates accounted for ~35% of the total internal resistance. Thus, even though the membrane and solution resistance dominated, the diffusion boundary layer effects were substantial. Ultimately, the power remained quite similar at both high and low flow rates because the decrease in membrane resistance was balanced by the increase in diffusion boundary layer resistance.

### **3.4.4 Effect of a spacer**

Adding the woven spacer into the flow fields between the membranes decreased the maximum power density from on average by 33% at 18 mm s<sup>-1</sup> (from 0.141 W m<sup>-2</sup> ±0.012 to 0.106 W m<sup>-2</sup> ±0.016), and by 49% at low flow rates (from 0.139 W m<sup>-2</sup> ±0.010 to 0.093 W m<sup>-2</sup> ±0.017) (**Figure A-3 and Figure A-4**). The decrease in performance is a result of the increased resistance produced at the membrane-spacer interface, known as the shadow effect [9]. Shadow effect is caused by the spacers being non-conductive and thus impeding any ionic conduction through the membrane in contact with the spacer. The spacer increased the solution and membrane resistance on average by ~39 ± 12  $\Omega$  (high flow rates) and ~52 ± 7  $\Omega$  (low flow rates) when compared to the spacer-less system (**Figure 3-6**). With the spacer, the membrane resistance by 21  $\Omega$  at 18 mm s<sup>-1</sup> in the spacer-less stack. In addition the diffusion boundary layer resistance at high flow rates doubled from ~8 ± 5  $\Omega$  without a spacer, to 16 ± 8  $\Omega$  with a spacer. This indicated that although a more uniform flow is produced with a spacer, resulting in less dead zones, concentration polarization affects are equally present in both spacer and spacer-less systems.

### 3.4.5 Flow field analysis using computational fluid dynamics

CFD revealed highly non-uniform flow distributions for high flow rate conditions (18 mm s<sup>-1</sup>) (**Figure 3-7**). The linear flow rates calculated within the channels ranged from 1 to 18 mm s<sup>-1</sup>, with the highest volume flow rates maintained in the manifolds and the center of the channel. The imbalance in the flow across the membrane surface led to the presence of dead zones that reduced system performance through the production of inactive membrane surfaces.

Flow fields with longer channels had a more uniform flow field which may explain the more optimal performance during open circuit voltage, although dead zones were still present at the corners (**Figure 3-8**).

The pressure drop for each channel without a spacer was minimal (0.92 Pa, 2 cm horizontal; 0.46 Pa, 2 cm vertical; 0.73 Pa, 3 cm horizontal; 0.38 Pa, 3 cm vertical), with a major portion of the pressure drop in each channel taking place in the manifold region. With the addition of the stagnant gas bubble (**Figure 3-7**) the non-uniformity in the flow was further accentuated, and the linear velocity within each channel increased significantly. The pressure drop across each channel only marginally increased for each channel (0.96 Pa, 2 cm horizontal; 0.48 Pa, 2 cm vertical; 0.74 Pa, 3 cm horizontal) except for the 3 cm vertical channel which nearly doubled (0.65 Pa). Under low flow conditions (**Figure 3-8**), nearly uniform flows were predicted even without a spacer, with a minimal pressure drop of 0.01 to 0.05 Pa with and without a stagnant bubble. Low flow conditions are preferable in larger-scale RED stacks due to the low input energy needed for the flow, as energy losses due to pumping through the stack can consume  $\sim 25$  % of the gross energy production [13].

This CFD analysis demonstrated that the performance differences within the various flow fields is due to flow non-uniformities and dead zones. The hydraulic losses can be neglected because of the low pressure drops. Non-uniform flows can accentuate concentration polarization effects at the membrane surface and increase the membrane resistances compared to spacer-less designs, whereas the shadow effect increases the membrane resistance in spacer based designs. Dead zones cause a significant decrease in performance and promote the accumulation of bubbles, reducing the active membrane area available for ion diffusion.

# **3.5** Conclusions

Fluid flow within RED channels is crucial for optimal performance. Channel alignment was shown here to be necessary to remove bubbles that accumulated within the membrane stack with ammonium bicarbonate solutions. In addition, reorienting the channels from horizontal to vertical alignment decreased the total membrane area covered by gaseous bubbles from 20 to 7%. Channel length was important for achieving high current densities, and reducing the length by 1 cm increased the limiting current density by 23% and power density by 14%. Spacer-less RED stacks had ohmic resistances that were ~50  $\Omega$  lower than those with spacers. However, non-uniform flow limits the use of spacer-less systems to low flow rate conditions because the membrane resistance was shown to increase by 21  $\Omega$  as the flow rate was increased from 4 mm s<sup>-1</sup> to 18 mm s<sup>-1</sup>.

	$18 \text{ mm} \cdot \text{s}^{-1}$	$4 \text{ mm} \cdot \text{s}^{-1}$
2 cm horizontal	11.1	12.0
2 cm vertical	10.2	9.9
3 cm horizontal	9	11.1
3 cm vertical	9.6	9.6

**Table 3-1**: Extrapolated limiting current density from polarization curves ( $A \cdot m^{-2}$ ).


Figure 3-1: Reverse electrodialysis stack and four flow field designs.



**Figure 3-2:** Performance data for high flow rates (a) stack polarization (b) stack power density (normalized per membrane area).



**Figure 3-3:** Performance data for low flow rates (a) stack polarization (b) stack power density (normalized per membrane area).



**Figure 3-4:** Steady state stack voltage for four flow fields with a set current (1 mA) applied to adjacent electrodes.



Figure 3-5: Maximum membrane bubble coverage for high and low flow rates.



**Figure 3-6**:Internal resistances, RDBL- diffusion boundary layer, RDL- double layer, Rs+msolution and membrane ohmic resistance, Slope- the total resistance based on using the slope of the polarization curve in stack with and without spacer (a) 18 mm s-1 (b) 4 mm



**Figure 3-7:** CFD analysis at high flow rate (a) with no bubble obstructions, and (b) with a gas bubble present.



**Figure 3-8:** CFD analysis at low flow rate (a) with no bubble obstructions, and (b) with a gas bubble present.

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## **Chapter 4**

# Comparison of Hydrogen Production and Electrical Power Generation for Energy Capture in Closed-Loop Ammonium Bicarbonate Reverse Electrodialysis Systems

## 4.1. Abstract

Currently, there is an enormous amount of energy available from salinity gradients, which could be used for clean hydrogen production. Through the use of a favorable oxygen reduction reaction (ORR) cathode, the projected electrical energy generated by a single pass ammonium bicarbonate reverse electrodialysis (RED) system approached 78 Wh m<sup>-3</sup>. However, if RED is operated with the less favorable (higher overpotential) hydrogen evolution electrode and hydrogen gas is harvested, the energy recovered increases by as much ~1.5× to 118 Wh m<sup>-3</sup>. Indirect hydrogen production through coupling an RED stack with an external electrolysis system was only projected to achieve 35 Wh m<sup>-3</sup> or ~ 1/3 of that produced through direct hydrogen generation.

## 4.2. Introduction

The development of novel decarbonized methods of renewable energy generation has become increasingly important as atmospheric CO<sub>2</sub> concentrations approach 400 ppm [1-3]. Estuarial salinity gradient energy, released when river and seawater mix, represents nearly 1.9 TW of unexploited clean energy [4-13]. The primary technologies capable of capturing this energy are pressure retarded osmosis (PRO), reverse electrodialysis (RED) and capacitive mixing (CapMix) [14-16]. Each technology has a unique approach for energy conversion, but the usable energy produced has been limited to electrical energy. The use of RED uniquely enables continuous and direct electrical current generation that could be used to produce a variety of products such as hydrogen gas.

Within a RED stack, series of ion exchange (anion and cation selective) membranes separate solutions with different chemical potentials (e.g. river water and seawater). This concentration gradient allows a Donnan or membrane potential to form at each membrane interface. By increasing the number of membranes, the overall potential rises, driving electrochemical reactions and current generation at the surrounding electrodes. In most RED studies, reversible redox couples (e.g.  $Fe^{2+}/Fe_3^+$  or  $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ ) are used to reduce the number of membranes needed to overcome the electrode reaction overpotentials[6, 17]. Alternatives are precipitating/dissolving electrodes [16, 18, 19], gas (H<sub>2</sub>/O<sub>2</sub>/Cl<sub>2</sub>) generating electrodes [8, 18-23] and capacitive electrodes [24]. Many of these reactions are either unfavorable and consume energy, or are impractical for large scale systems.

Two electrodes which may present unique opportunities for energy production using RED are oxygen reduction, and hydrogen evolution. The oxygen reduction reaction (ORR) could enable current production without consumption of significant amounts of energy (low overpotential). The use of a passive air breathing cathode system would avoid energy needed for solution aeration using dissolved oxygen or catholyte regeneration. Only one RED system has been operated with an ORR cathode, but a thorough evaluation of the electrode overpotentials was not conducted [19]. Cathodes based on the hydrogen evolution reaction (HER) have been considered to be disadvantageous for RED systems due to high overpotentials. However, if the hydrogen gas generated is harvested, there is a possibility for energy production that has not been previously recognized. Hydrogen gas has primarily been viewed as a waste gas produced during

electricity generation in RED systems, but RED has never been intentionally used or optimized as a method for renewable hydrogen gas production.

The potential for energy capture using either oxygen reduction or hydrogen evolution was investigated here using ammonium bicarbonate (AmB) solutions. Thermolytic solutions such as AmB have recently been examined as a method to enable energy production from salinity gradients in closed-loop systems [9, 25-28]. AmB is an excellent chemical for creating salinity gradients from waste heat because it has a low temperature decomposition point, which allows it to be distilled to  $CO_2$  and  $NH_4$  to form high and low concentration solutions that can be used for salinity gradient energy production. AmB has an additional advantage compared to NaCl solutions because its use reduces electrode overpotentials for both HER and ORR [26, 27]. Thus, AmB may make these reactions more favorable for energy production than previously achieved using river water and seawater in RED systems. Energy production using an AmB solution was examined under five general scenarios: 1) simultaneous electrical and hydrogen generation with an HER cathode operated at the limiting current; 2) electricity generation with an ORR cathode operated at the limiting current; 3) simultaneous electrical and hydrogen generation at an HER cathode operated at the peak power; 4) electricity generation with an ORR cathode operated at peak power; and 5) indirect hydrogen generation using an ORR based RED to power a separate water electrolysis cell. For direct hydrogen gas production, the use of a non-precious metal catalyst (MoB) and a bifunctional electrocatalyst (Pt/Ir) was also examined.

#### 4.3 Materials and Methods

## 4.3.1 Reverse electrodialysis Stack

A 20 cell pair RED stack was constructed by modifying a commercially available electrodialysis stack (PCCell, Heusweiler Germany). This unit has a total active membrane area of 0.87 m<sup>2</sup>, a projected surface area of 207 cm<sup>2</sup>, and each cell pair was 0.5 mm thick. The anolyte volume was 80 mL, and the anode was titanium mesh coated with Platinum/Iridium (Ti Pt/Ir) with a projected area of 207 cm<sup>2</sup>. The system was modified to use two different cathode endplates. One was completely sealed and used for the HER reaction for hydrogen gas production, while the other one contained an open area to enable passive oxygen diffusion to an ORR cathode (**Figure 4-1**). The exposed area with the open endplate was ~175 cm<sup>2</sup>. Anolyte and catholyte solutions (1 M AmB) were each recycled separately at 100 mL min<sup>-1</sup>. The 10 L high concentration solution (1.5 M AmB) was continuously recycled through the stack, while the 2 L of low concentrate solution (1.5 M AmB) was continuously recycled through the stack, while the stack, while the 2 liters of low concentrate solution (distilled water) was used in a single pass mode (400 mL min<sup>-1</sup>).

## 4.3.2 Cathodes

Three different cathodes where used: Platinum and carbon (Pt/C) on carbon cloth for both ORR and HER; and Pt/Ir on titanium or molybdenum boride and carbon (MoB/C) on carbon cloth for only HER. The Pt/C cathode was wet proofed carbon cloth (type B, E-TeK) coated with carbon black, Pt (0.5 mg-Pt cm<sup>-2</sup>), and a Nafion binder on the water side, and 4 layers of polytetrafluoroethlyene (PTFE) on the air side to prevent water leakage out and to allow passive

oxygen delivery for ORR tests [29]. During HER tests the PTFE layer was placed against the solid endplate. The two other cathode catalysts, MoB and Pt/Ir were examined as alternatives to Pt for HER. Mo-based catalysts such as  $MoS_x$ ,  $Mo_2C$  and MoB have shown activity for HER, but  $MoS_x$  is not stable at higher pH. Preliminary electrochemical tests in our lab with AmB have revealed a higher activity with MoB than  $Mo_2C$  (data not shown), which might be due to the lack of electrochemical activation for MoB at higher pH [30, 31]. Thus MoB was tested here as a possible alternative to Pt, with performance compared to the commercially available electrode provided with the test cell (mixed catalyst Pt/Ir on titanium)[32]. The molybdenum-based MoB cathode was prepared in a similar manner to the Pt cathode, but with a higher catalyst loading (5 mg-MoB cm<sup>-2</sup>), and no PTFE layers. Currently the commercial cost of MoB is 5 \$•g<sup>-1</sup>, whereas for Pt it is 45 \$•g<sup>-1</sup>. Therefore, the higher loading of MoB did make the final cost similar to Pt, but no precious metals were used. In addition, the loading and application of the MoB cathode were not optimized here.

### 4.3.3 Performance data

Galvanostatic polarization was performed with a multi-channel potentiostat (model 1470E, Solatron Analytical, Hampshire, England), and current was scanned from 0 to 300 mA at 1 mA sec<sup>-1</sup>. Ag/AgCl reference electrodes (BASi, West Lafayette, IN) were placed on either side of the stack in the anolyte and catholyte. Anode, cathode, stack and whole cell potentials were recorded during each sweep. Five to ten polarization curves were recorded to ensure reproducible results. The whole cell power density was calculated as

$$P_{cell} = \frac{U_{cell} \cdot I_{cell}}{A_{mem}}$$

$$4-1$$

where  $P_{cell}$  is the electrodes power density (W·m<sup>-2</sup>),  $U_{cell}$  is whole cell voltage (V),  $I_{cell}$  is the whole cell current (A), and  $A_{mem}$  is the cross sectional area of all the membranes (m<sup>2</sup>). The stack power density,  $P_{stack}$ , which excluded electrode overpotential, was calculated using Eqn 1., but the stack voltage (U<sub>stack</sub>) was used instead of the whole cell. The stack voltage was recorded using reference electrodes located on either side of the stack. The difference (P<sub>stack</sub>-P<sub>cell</sub>) was calculated in order to calculate the power consumed at the electrodes.

#### 4.3.4 Determination of the potential for electrical power generation or hydrogen generation

Energy production from electrical power generation or hydrogen gas production was evaluated under five cases (**Table 4-1**). For cases 1-4, (**Figure 4-2**) the electrical energy generated with various cathodes (ORR and HER) was determined through dividing the electrode peak power density by the volume flow rate, as

$$E_{e^-} = \frac{P_{cell}}{Q} \tag{4-2}$$

where  $E_{e}$  is the electrical energy harvested (Wh m<sup>-3</sup>), and Q the volume flow rate (m<sup>3</sup> h<sup>-1</sup>)

For case 1 & 3 the theoretical moles of hydrogen generated was calculated using the using

$$n_{H_2} = \frac{I \cdot 3600}{zF} \eta \tag{4-3}$$

where  $n_{H2}$  is the (moles H<sub>2</sub> h<sup>-1</sup>), *I* the current (A), 3600 a conversion factor (seconds per hour), *z* the equivalent electrons per mole of hydrogen, F is Faradays constant (96485 C mol-e<sup>-1</sup>), and  $\Box$  is an conversion efficiency factor (to account for hydrogen gas losses relative to current generation) which was set at 80% [33]. The moles of hydrogen gas were converted to hydrogen energy based on the heating value of hydrogen gas, as

$$E_{H_2} = \frac{n_{H_2} \cdot \Delta H_{H_2}}{Q} (0.277)$$
 4-4

where  $E_{H2}$  is the energy (Wh m<sup>-3</sup>),  $\Delta H_{H2}$  is the high heating value of hydrogen (286 kJ mol<sup>-1</sup>), and 0.277 is a conversion factor from kJ to Wh.

To calculate the indirect (ex situ) hydrogen generation by a coupled RED-water electrolysis system (Case 5), the current corresponding to the RED voltage necessary to drive water electrolysis at 2 V was chosen (**Figure 4-2, point 4**). This current at 2 V corresponds to the maximum electrical current which would be supplied to the electrolysis system from the RED system. Current was converted to the theoretical moles of hydrogen gas that could be produced using equation 3, and to energy using equation 4-4. The electrolysis efficiency was assumed to be 80% [33].

As RED systems are scaled up in size, and the number of membranes is increased, the fraction of energy consumed at the electrodes is expected to decrease. To capture this scenario, the electrode overpotential were neglected and the stack performance data (power and current) were used to estimate possible electrical power and hydrogen energy production.

## 4.3.5 Energy extracted through batch testing

To verify that energy predictions based on the smaller number of cells were reasonable, additional batch tests with a 20 cell pair RED with either an ORR or HER cathode were conducted. During these tests, 10 L of high and low concentration solutions were constantly recycled through the stack, and the electrodes were maintained near the limiting current operating using a 2  $\Omega$  resistor, or the peak power operating point with a 10  $\Omega$  resistor. The resulting current through the external circuit was used to calculate the total electrical energy generated during the hour-long test as

$$E_{e^-} = \frac{\int_0^t P_{cell} \cdot dt}{v}$$
 4-5

where  $P_{cell}$  is the power of the cell, and v is the volume of solution mixed. The potential hydrogen energy was estimated using eqn 4-3 and 4-4, assuming cathodic recoveries of 70% or 90%."

### 4.4 Results and Discussion

#### 4.4.1 Electrical power generation with oxygen reduction

The maximum power density produced with an ORR cathode was greater than that obtained with the HER cathode (Figure 4-3). With 20 cell pairs, the peak power density with ORR reached 0.18 W m<sup>-2</sup>, whereas with the HER the peak power density was 0.13 W m<sup>-2</sup> (33%) difference). These values are significantly lower than those typically reported in the literature for RED stacks (~0.6 W W  $m^{-2}$  / 50 cell pair[34]) because both the electrode overpotentials were included here in the total power. The stack power density (calculated using reference electrodes) approached 0.45 W m<sup>-2</sup>, which is similar to other RED stack power densities (Figure B-1) [17]. With 20 cell pairs, the reduction in power due to the electrodes was 61% with the ORR cathode, and 70% with the HER electrode. This difference was further increased to 70% (ORR) and 75% (HER) with 15 cell pairs, and to 89% (ORR) and 93% with 10 cell pairs (HER). There was a linear relationship observed between the difference in power measured between the stack and electrodes, and the cell pair number. As the number of cell pairs increases, this difference is essentially eliminated. It is estimated based on a linear regression of the data here that the difference between the stack and electrodes would be removed with ~40 cell pairs (80 membranes) with the ORR electrode. With an HER electrode, this difference is not eliminated until ~52 cell pairs (104 membranes).

The anode potentials were the same in all tests, ranging from 0.9 - 1.0 V versus NHE, and therefore differences between the power densities were due to cathode performance (**Figure 4-3**). At low current densities ( $(-1 \text{ A m}^{-2})$ ) the cathode potentials differed by (-200 mV). However, at higher current densities ( $(-10 \text{ A m}^{-2})$ ) this difference increased to nearly 700 mV. This reduction in cathode overpotential by 700 mV accounts for the extra (-10 cell pairs), or 20 membranes needed for the RED with a HER cathode. With the price of ion exchange membranes limiting practical implementation of large scale RED systems, reducing the number of membranes needed through reducing electrode overpotentials will likely improve the economic and technical feasibility of RED systems.

## 4.4.2 Evaluating energy generation through H<sub>2</sub> production versus O<sub>2</sub> reduction

The energy extracted per m<sup>3</sup> of low concentrate solution was extrapolated from peak power and the limiting current operating points (**Figure 4-3**). The greatest energy extraction was attained with the highest number of cell pairs (20), and through hydrogen gas generation (Figure 4-4). With 20 cell pairs the expected maximum energy extracted through hydrogen gas and electricity production at the systems limiting current was -10.6 Wh m<sup>-3</sup> (with 95% of that energy coming through hydrogen). If a HER based RED was operated at the peak power position, 9.39 Wh m<sup>-3</sup> would be generated, with 4.63 Wh m<sup>-3</sup> obtained through electricity and 4.75 Wh m<sup>-3</sup> from hydrogen. With the RED operated with the low overpotential cathode (ORR RED), only 2.8 (limiting current) to -6.5 Wh m<sup>-3</sup> (peak power) of electrical energy was generated (**Figure 4-3**). This was 28% more electrical energy than produced with the HER RED, but overall 36% less energy than produced through hydrogen. However, the total energy extracted through each system would remain similar, as the H<sub>2</sub> would eventually need to be converted to electricity through a fuel cell which typically operates with 50-80% energy efficiency. In order to estimate the energy that could be extracted using a stack with a larger number of cell pairs which incorporated either the ORR or HER cathode, a linear regression was applied to the plots in **Figure 4-4**. For a 100 cell pair stack, 53 Wh m<sup>-3</sup> (R<sup>2</sup>=0.97) was projected to be attainable through direct hydrogen generation, with only 17 Wh m<sup>-3</sup> (R<sup>2</sup>=0.99) through indirect hydrogen generation (electricity generation followed by water electrolysis). In terms of electrical energy generation, 44 Wh m<sup>-3</sup> (R<sup>2</sup>=0.98) was obtained through the use of an ORR cathode and 33 Wh m<sup>-3</sup> (R<sup>2</sup>=0.99) from an HER cathode.

The stack performance data (peak power and limiting current values), which eliminates the impact of electrode overpotentials, were also used to estimate the maximum electrical and hydrogen energy attainable from RED systems (**Figure 4-5**). This was evaluated because with larger systems the potential losses at the electrodes become negligible. With 100 cell pairs ~118 Wh m<sup>-3</sup> (R<sup>2</sup>=0.96) may be obtainable through hydrogen generation (approaching PRO) and only ~78 Wh m<sup>-3</sup> (R<sup>2</sup>=0.99) from electricity. Furthermore, the potential for indirect hydrogen generation was ~3 times less than direct hydrogen production, only producing ~35 Wh m<sup>-3</sup> (R<sup>2</sup>=0.97).

Batch recycle tests conducted with 10 L of low concentrate showed that significantly more energy could be generated through hydrogen production with the cathode operated near the limiting current (**Figure 4-6**). In addition, with a low concentration recycle, the potential energy extracted assuming a cathodic recovery of 70% approached 25 Wh m<sup>-3</sup>. This was an increase in  $\sim$ 135% when compared to performance predicted with a 20 cell pair HER-RED stack with no recycle. One difference observed between the batch recycle tests and the predictions based on the performance data was a slight decrease in electrical energy extracted at the peak power position, than at the limiting current. This was likely due to the fact that a fixed resistance had to be used during the batch recycle tests, and thus as the system resistance changed (was reduced), the cell would approach the peak power position.

#### 4.4.3 Evaluation of low cost catalyst for hydrogen evolution

When MoB was used as the cathode catalyst instead of Pt, the limiting current density decreased from 10 A m<sup>-2</sup> to 8 A m<sup>-2</sup> (**Figure 4-7**). When the current collector was changed from a carbon cloth to titanium, and the catalyst was Pt/Ir, current density was further decreased to 7 A m<sup>-2</sup>. This was due to the ~150 mV difference between the MoB cathode and the Pt cathode (**Figure 4-7**), and the nearly 500 mV difference between the Pt and the Ti (Pt/Ir).

With these alternative catalysts, the energy captured through hydrogen from the various cathodes decreased from to 10.2 Wh m<sup>-3</sup> with MoB, and to 8.9 Wh m<sup>-3</sup> with Ti (Pt/Ir), compared to 12.6 Wh m<sup>-3</sup> with Pt. If these results are extrapolated to 100 cell pairs, the projected energy extracted through the MoB and Ti (Pt/Ir) electrodes was ~56 Wh m<sup>-3</sup> and 35 Wh m<sup>-3</sup> (**Figure B-**2). Thus, the MoB electrode only produced 16 % less energy than the Pt, making it a potentially viable alternative to hydrogen generation.

The main advantage of using RED for renewable hydrogen gas production, is the higher value product (i.e. self-powered H<sub>2</sub> gas generation) [35]. Today, 10-11 million metric tons of hydrogen are produced each year in the United States [36] with a majority of this hydrogen used at industrial sites. With the average price of this hydrogen around \$10/kg this represents a market value of nearly \$150 billion. Last year in the United States, industrial sites used 980 billion kWh of electricity [37], which on average cost \$0.1/kWh, accounting for a market value of \$98 billion. While both electricity and hydrogen production are large markets, renewable technologies which are capble of directly producing hydrogen are limited. Thus, RED may be able to better compete with other renewables in the energy sector, through direct hydrogen production.

### 4.5 Conclusions

To date, hydrogen generation in RED systems has been avoided due to high overpotentials which cause a reduction in the electrical power generation. However, if hydrogen gas can be recovered, a hydrogen generating RED can produce ~118 Wh m<sup>-3</sup>, or  $1.5 \times$  more energy than that derived solely through electricity. The value of the combined product is also estimated to have an ~27% greater value than electricity alone. Furthermore, this hydrogen gas production is carbon neutral and can be produced without any electrical grid based energy. For renewable electricity generation, the ORR cathodic reaction was shown to reduce overpotentials by as much as 700 mV, and electrical energy generation was increased by ~40% compared to a RED stack with HER. The MoB catalyst shows significant promise as low cost HER catalyst in this RED system, with overpotentials that were only ~0.1 V greater than Pt in the AmB electrolyte.

**Table 4-1:** Different cathode reaction (and catalysts) for energy production from AmB RED. The operating point with which the energy (hydrogen or electricity) was estimated from is also listed.

	Cathode	Cathode	Operating point
	Reaction	Catalyst	from Figure 2
Case 1: Direct			
Hydrogen and		Pt,MoB, Pt/Ir	Limiting Current (Point 1)
Electricity	ΠΕΚ		
generation			
Case 2: Electricity	ODD	Pt,MoB, Pt/Ir	Limiting Current (Point 2)
generation	OKK		
Case 3: Direct			
Hydrogen and	LIED	Pt	Peak Power (Point 3)
Electricity	ΠΕΚ		
generation			
Case 4: Electrical		D+	Pault Down (Doint 4)
Energy	ORR	Ρl	Peak Power (Point 4)
Generation			
Case 5: Indirect	ORR	Dt	Current at 2V (Point 5)
Hydrogen	Coupled with	Γl	Current at 2V (Follit 3)
Generation	Electrolysis		



**Figure 4-1:** Hydrogen generation from a RED stack. (a) Indirect generation through coupling an RED with an ORR cathode with an external electrolysis system. (b) Direct hydrogen generation through a HER cathode.



**Figure 4-2:** Polarization curve demonstrating four cases discussed (1) the limiting current which was used for estimating the potential hydrogen generated through direct hydrogen production (2) the current corresponding to 2V needed for indirect hydrogen production



**Figure 4-3:** (a) Power density plots for 10, 15 and 20 cell pair RED with Pt air breathing (ORR) cathode and Pt no air cathode (HER) electrodes. (b) Cathode electrode potential for RED with air breathing (ORR) Pt cathode and no air (HER) Pt cathode.



**Figure 4-4:** Direct hydrogen, indirect hydrogen and electrical energy production estimates including electrode overpotentials present with an ORR and HER pt cathode. Based on RED electrode performance data with no stack recycle.



**Figure 4-5:** Direct hydrogen, indirect hydrogen and electrical energy production estimates excluding electrode overpotentials. Based on RED stack performance data.



**Figure 4-6:** Direct hydrogen, indirect hydrogen and electrical energy production predicted based on batch testing with an ORR and HER Pt cathode. Stack feed solutions were recycled.



**Figure 4-7:** A comparison of Pt, MoB and Pt/Ir mixture cathodes in terms of a) whole cell power density, and (b) cathode potentials.

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## Chapter 5

# Capacitive Mixing Power Production from Salinity Gradient Energy Enhanced through Exoelectrogen-Generated Ionic Currents

## 5.1 Abstract

Several approaches to generate electrical power directly from salinity gradient energy using capacitive electrodes have recently been developed, but power densities have remained low. By immersing the capacitive electrodes in ionic fields generated by exoelectrogenic microorganisms in bioelectrochemical reactors, we found that energy capture using synthetic river and seawater could be increased ~65 times, and power generation ~46 times. Favorable electrochemical reactions due to microbial oxidation of organic matter, coupled to oxygen reduction at the cathode, created an ionic flow field that enabled more effective passive charging of the capacitive electrodes and higher energy capture. This ionic-based approach is not limited to the use of river water-seawater solutions. It can also be applied in industrial settings, as demonstrated using thermolytic solutions that can be used to capture waste heat energy as salinity gradient energy. Forced charging of the capacitive electrodes, using energy generated by the bioelectrochemical system and a thermolytic solution, further increased the maximum power density to 7 W m<sup>-2</sup> (capacitive electrode).
## **5.2 Introduction**

Harnessing the entropic energy released when river and seawater mix could globally provide ~1 terrawatt of renewable power[1]. To capture this energy, three main processes have been used: pressure retarded osmosis (PRO)[2], reverse electrodialysis (RED)[3], and capacitive mixing (CapMix)[4]. These three processes are based on reversing three common approaches used to desalinate water, which are reverse osmosis, electrodialysis, and capacitive deionization. Industrial scale PRO and RED applications have been limited primarily due to relatively high energy requirements for river water and seawater pretreatment, high costs of membranes, and reduced lifetimes due to fouling [1, 5-7]. The CapMix approach to extract salinity gradient energy is based on controlled ion transfer to and from capacitive or battery electrodes. Suitable materials for energy generation using battery electrodes have not sufficiently advanced as precious metals (e.g. Ag) can be required [8]. In contrast, capacitive electrodes can be made from materials that are both renewable and inexpensive (such as activated carbon), and they can have longer lifetimes than battery electrodes[4, 9, 10].

CapMix energy is captured by cycles of charging and discharging capacitive electrodes with seawater and river water. The energy can be captured with these capacitive electrodes two different ways: either through changes in membrane potentials due to ion concentration gradients [9, 11-13]; or through work done by expansion of the electric double layer. For energy recovery based on changes in the membrane potentials (also called Donnan potentials), the capacitive electrodes are coated with ion exchange polymers that allow only selective charge transfer (anions or cations) to each of the electrodes. Energy captured using this capacitive Donnan potential (CDP) approach requires cycles that consist of four separate steps (**Figure 5-1**). Initially, under open circuit conditions, the capacitive electrodes are polarized using a high concentrate solution (seawater) due to the generation of a membrane potential at each electrode (Step 1). Next, the capacitive electrodes are connected to an external load that allows the flow of electrical current through a circuit, and ionic current in the electrolyte (Step 2). Once the capacitive electrodes are fully charged (voltage U = 0), the circuit is again opened (no current) and a low concentrate solution (river water) is introduced, reversing the polarity of each membrane potential (Step 3). The electrodes are then connected to an external load and discharged, creating an electrical current in the opposite direction (Step 4). The net energy that is extracted is defined by the voltage window produced by the membrane potential (Figure C-1). This four-step CDP cycle results in spontaneous energy generation, and therefore the process does not require any electrical input energy. However, the potential energy, *E*, that can be recovered is limited as only a relatively small voltage (<100 mV) can be produced by the membrane).

To increase the amount of energy recovered from this four-step cycle, an external power supply is used in Step 2 to increase the charge loaded onto the membrane-coated electrodes (called forced CDP) (**Figure 5-1**). While the use of the power source requires additional energy to be put into the system, the forced charging step increases the size of the voltage window. As long as there is no substantial charge leakage [14] (i.e. coulombic losses during the charging step), the current extracted in step 4 (at a higher voltage) enables increased energy recovery, as shown by the larger voltage window (Figure 5-1). Thus, the peak power density that can be obtained using forced CDP has been increased to an average of 200 mW per square meter of electrode area [14], compared to 20-40 mW m<sup>-2</sup> using (passive) CDP [9, 11] However, even these higher power densities for forced CDP are still well below those reported for RED (0.95-1.2 W m<sup>-2</sup>-membrane area) [15, 16] or PRO (1-10 W m<sup>-2</sup>-membrane area)[17, 18]. Thus, this technology will not be useful for energy generation until power densities can be substantially improved.

One approach recently used to increase energy recovery from salinity gradients using RED was incorporating the RED stack of membranes into a bioelectrochemical system, such a

microbial fuel cell (MFC). The combination of these two technologies enabled significant improvements in performance for both technologies [19-21]. The RED process was improved because the reactions at the MFC electrodes were thermodynamically favorable, thereby avoiding energy losses needed to overcome unfavorable reactions usually occurring with RED alone. The MFC process was improved due to the reduced electrode overpotentials that resulted from the ionic current that was driven by the RED stack[20, 22]. The combination of these two technologies thus created a more effective means to harvest both free energy associated with the salinity gradients, as well as energy in a domestic wastewater (2-3 kWh per m<sup>3</sup> of wastewater [23]). The success in combining salinity gradient and bioelectrochemical technologies suggested that it might be possible to improve performance of the other salinity gradient energy technologies by using MFCs.

A new method was developed here to increase CDP performance by placing the capacitive electrodes into the ionic field generated in a bioelectrochemical system (**Figure 5-2**). When exoelectrogenic bacteria oxidize organic matter and release electrons to the anode in a bioelectrochemical system such as an MFC, ions (protons) are released into the electrolyte, and protons are consumed at the cathode [24]. In order to maintain electroneutrality, an electric field drives ionic currents in the solution either through the motion of protons or by transport of other ionic species [19, 20, 25]. It was reasoned that immersion of capacitive electrodes into this ionic field could enhance charging of these capacitive electrodes, and enable increased power densities captured through the CapMix process. The combined process could then be used capture energy both from salinity gradients and organic matter in wastewater with the MFC.

The energy and power produced from both the CDP, and combined CDP-MFC process, was examined here to show that ionic fluxes from the MFC could improve the CapMix process. In addition to tests using synthetic seawater and river water solutions (NaCl), the potential use of recyclable thermolytic salts (ammonium bicarbonate, AmB) was also examined. Capacitive

energy extraction so far has only been investigated using NaCl solutions, which would limit applications to coastal regions. The use of thermolytic solutions enables closed loop operation using waste heat, with conventional distillation processes for solution regeneration. Industrial waste heat accounts for between 20-50% of industrial energy input[26], and capturing this energy using AmB would allow for power generation at industrial sites where it could readily be used. Both conventional CDP and forced CDP processes were investigated for improving performance of CapMix systems with AmB and NaCl solutions.

### **5.3 Materials and Methods**

## 5.3.1 Capacitive mixing microbial fuel cell design

The combined CapMix and MFC system, called a capacitive mixing microbial fuel cell (CMFC), consisted of three chambers: anolyte, CapMix, and catholyte (**Figure 5-2**). The three chambers were separated from each other using two anion exchange membranes (AEMs). The use of the membranes allowed the solutions used for the two different processes to remain separated, while maintaining an ionic connection needed for the MFC. The anolyte chamber was created from a 4 cm Lexan cube that had a 28 mL cylindrical chamber cut out. The CapMix (middle chamber) and catholyte chambers consisted of a 2 cm Lexan cube, each 14 mL with the same diameter cylindrical chambers. Brush anodes (manufactured by Mill-Rose, Mentor, OH) were made from graphite fibers twisted between two titanium wires. Anodes were heat treated and enriched in single chamber MFCs, as previously described (26). When enrichment was complete the anode was transferred to the CMFC anolyte chamber. The anolyte solution used in all tests was a 50 mM phosphate buffer, 1 g  $l^{-1}$  sodium acetate and trace vitamins and minerals.

Cathodes were made using wet proofed carbon cloth (type B, E-TeK) which was coated with carbon black, platinum (0.5 mg-Pt cm<sup>-2</sup>) and a NAFION® 117 (Aldrich) binder on the water side[27]. The air side had 4 layers of polytetrafluoroethlyene (PTFE) coatings which acted as diffusion layers two allow oxygen diffusion to the catalyst, and to prevent water leakage[28]. The catholyte solution consisted of the high concentrate saline solution, which was either 500 mM NaCl or NH<sub>4</sub>HCO<sub>3</sub> as indicated.

The capacitive electrodes were made using 90 wt.% YP-50F activated carbon (Kuraray Chemical Company, USA), 5 wt.% polytetrafluorethylene as a binder, and 5 wt.% carbon black (100% compressed; Alfa Aesar, USA) to increase electrode electrical conductivity. The resultant slurry was rolled and cut into square electrodes with an area of 1 cm<sup>2</sup> and an approximate weight of 15 mg. During electrochemical characterization tests, the electrodes were placed on non-corrosive current collectors made of graphite foil. A polyvinylidene fluoride (PVDF) membrane separator with a mesh width of 100 nm (Durapore<sup>®</sup>; Merck Millipore, Germany) was used as the separator between the two electrodes. The entire cell was compressed between two PTFE plates with clips.

For CapMix tests the capacitive electrodes were hot pressed onto a current collector (SS mesh Type 316, McMaster-Carr). One coating of an anion exchange polymer (polysulfone polymer with quaternary ammonium groups) [29] was put onto one capacitive film electrode, and one coating of cation exchange polymer (NAFION® 117) polymer was put onto the other one. Both electrode were dried overnight prior to use. These capacitive electrodes were placed on either side of the central CapMix chamber (2 cm apart). The capacitive electrode with the anion coating was placed against the AEM membrane|anolyte interface, with the membrane coated capacitive electrode side facing the water side. The capacitive electrode with the cation coating was placed near the membrane|catholyte interface, with the membrane coated facing the water side of the CapMix chamber.

### 5.3.2 Ex situ capacitive electrode electrochemical characterization

The capacitive electrodes were electrochemically characterized in a symmetrical two electrode set-up (**Figure C-1**). Cyclic voltammetry (CV) studies of the capacitive electrodes were performed using the two-electrode setup [30, 31]. CVs were run at different scan rates (2, 5, 10, 20, 50, 100 mV s<sup>-1</sup>) in the different aqueous media used here to assess their performance (Fig. 1s). From these CVs, the specific gravimetric  $C_{sp}$  was obtained using

$$C_{sp} = \frac{2}{\Delta U} \cdot \frac{\int i dU}{v \cdot m}$$
 5-1

where  $\Delta U$  is the width of the voltage scan, *i* is the discharge current, *U* is the voltage, *v* is the scan rate, and *m* is the mass of carbon in one electrode.

## 5.3.3 MFC system performance

Whole cell polarization curves were conducted without capacitive electrodes present, with both high and low concentration solutions tested in CapMix experiments. Galvanostatic polarization curves were obtained using a Biologic Potentiostat (VMP3 Multichannel Workstation, Biologic Science Instruments, USA). Current was stepped between 0 mA to 9 mA (1 mA steps), and held for 10 minutes until steady state conditions were obtained (**Figure C-2**). Ag·AgCl<sup>-1</sup> reference electrodes (BASi, West Lafayette, IN) were placed in the anolyte, CapMix and catholyte chambers to monitor electrode and membrane potentials, and to calculate the whole cell potential. Both power and current density for the MFC were normalized against the total cathode area (7 cm<sup>2</sup>).

#### **5.3.4** Capacitive mixing performance

The CapMix (middle chamber) and MFC (end chambers) were operated separately without any electrical connections between the two systems (**Figure 5-2**). The MFC was operated by connecting the brush anode to the air breathing oxygen reduction cathode through an external load (controlled by the galvanostat). Likewise, the two capacitive electrodes within the CapMix chamber were connected to each other through a separate external load. Energy obtained through the MFC circuit was due to the oxidation of organic matter (acetate), while energy harvested through the CapMix circuit was due to mixing energy.

The MFC was operated under constant current conditions between 1-5 mA (galvanostatically), which was chosen to ensure that the MFC potential was positive when both the high and low concentration solution was present within the CapMix chamber. Separate tests using a constant load (resistor) were also conducted to demonstrate that the use of the galvanostic operation for these tests did not produce different results than those under typical MFC operation with a constant load (**Figure 5-3** and **Figure C-3**). Substrate removal in the MFC was not monitored. While the MFC electrodes were maintained in a constant discharge mode using the galvanostat, the capacitive electrodes were repeatedly cycled through the four step CDP energy extraction process. Briefly, in Step 1, capacitive electrodes were polarized in the high concentration solution (NaCl or AmB) under open circuit conditions (**Figure C-4**). In Step 2 the capacitive electrodes were connected to a 10  $\Omega$  external resistance for 5 minutes, until the current through the circuit approached zero (**Figure C-4a**). In Step 3, the capacitive electrodes were again disconnected (open circuit), and the high concentration solution was replaced by the low concentration solution (10 mM NaCl or AmB) (**Figure C-4c**). After the electrode polarity switched due to the reversal of the membrane potential, in Step 4 the capacitive electrodes were

discharged through a 100  $\Omega$  resistor for 20 minutes (**Figure C-4d**). This cycle was repeated 5-10 times to ensure repeatability.

Voltages were converted to power density, and power density and current density were plotted versus time to evaluate the CapMix system performance using P = (UI)/A where here U is the voltage, I is the current, and A is the area of one biased electrode (1 cm<sup>2</sup>). Individual cycles were analyzed from the voltage and charge accumulation, with the energy extracted from each cycle calculated using the integral:

$$W = \frac{-\oint_C \Delta U dq}{m}$$
 5-2

where  $\Delta U$  is the change in voltage, dq is the change in charge stored in the capacitors, and m is the mass of one electrode.

# 5.3.5 Forced capacitive mixing performance

Forced charge CDP experiments were conducted using the MFC as the power source. All forced charge CDP tests used 500 mM and 10 mM AmB as the high and low concentrate solutions in the CapMix chamber, and 500 mM AmB as the catholtye in the MFC. The same four step process described for CDP operation was used (**Figure 5-1a**), except that during step 2 the MFC electrodes were connected to the capacitive electrodes (**Figure 5-1b**). The MFC electrodes were connected to the capacitive and current was monitored by measuring the voltage drop across a 10  $\Omega$  resistor. Next, the MFC and capacitive electrodes were disconnected and the CapMix chamber was flushed with the low concentrate solution, reversing the membrane potential (Step 3). The capacitive electrodes were then discharged through an 800  $\Omega$  resistor for 1 hour to reduce the charge leakage (Step 4). During this time, the MFC electrodes were connected to a 10  $\Omega$  resistor. After 1 hour, the capacitors were left in open circuit, and the low concentrate

was replaced with a high concentrate. The cycle was repeated multiple times to ensure repeatability.

### 5.4 Results and Discussion

#### 5.4.1 Evaluating the effect of MFC current on CapMix

To demonstrate enhancement on CapMix by MFC ionic currents, the capacitive electrodes were cycled multiple times through the four-step energy extraction process with the MFC current set at 2 or 4 mA using NaCl solutions. The capacitive electrodes were charged for five minutes (10  $\Omega$  external resistance) in high concentration solution, and discharged for 20 minutes (100  $\Omega$  resistor) in low concentration solution. At 2 mA, the peak voltage was 114 ± 4 mV (n=3), producing a maximum power density of  $232 \pm 18$  mW m<sup>-2</sup> (average of  $44 \pm 4$  mW m<sup>-</sup> <sup>2</sup>) (Figure 5-3). This is a 2.3× increase in voltage, and 24× increase in maximum power compared to controls with no enhanced ionic current (35  $\pm$  0 mV and 9.6  $\pm$  0.3 mW m<sup>-2</sup>; average of  $0.013\pm0.001$  mW m<sup>-2</sup>, n=4). The low power density for the capacitive electrodes in the absence of the ionic current was consistent with previous reports (Table 5-1). When the MFC current was increased toward the limiting current that could be produced by this reactor (~4 mA), the peak power increased to 448  $\pm$  67 mW m<sup>-2</sup> (77  $\pm$  24 mW m<sup>-2</sup> average), which was 11× more power than that previously obtained in CDP tests (no forced charging), and  $46 \times$  that achieved with the same capacitive electrodes and no induced ionic current (Table C-1). Multiple CapMix cycles were possible because the length for a full CapMix cycle (~ 30 min) was substantially less than that needed for a single MFC fed-batch cycle (16-18 hrs). A higher current might have further increased power densities produced by the CDP, but this was not possible with NaCl due to having reached the limiting current density (limited by internal resistance). The reason for the

increased performance of the CapMix process combined with the MFC could only have been due to the ionic currents. Further background on possible reasons for this increase is provided in the Supporting Information.

### 5.4.2 Evaluating the effect of MFC current on CapMix energy extraction

The energy extracted by CDP charging was calculated from the area inside the voltage versus charge accumulation curve over each cycle (**Figure 5-4**) Energy recovery with MFC operation was  $59 \pm 10 \text{ mJ g}^{-1} \text{ cycle}^{-1} (2 \text{ mA}) \text{ or } 175 \pm 16 \text{ mJ g}^{-1} \text{ cycle}^{-1} (4 \text{ mA})$ , compared to only  $2.7 \pm 0.1 \text{ mJ g}^{-1} \text{ cycle}^{-1}$  for controls (no ionic current) (**Figure 5-4**). The energy that can be extracted from the capacitive electrodes in the presence of an MFC with a constant discharge of 2 mA is equivalent to nearly 19 cycles from the CDP process without an MFC. When the MFC was operated at 4 mA the energy extracted in one cycle was comparable to nearly 60 cycles without the MFC. In addition to this energy extracted by the capacitive electrodes, ~200 - 300 mJ cycle<sup>-1</sup> was extracted from organic matter using the MFC over its complete cycle.

### 5.4.3 Effect of CapMix on Microbial Fuel Cell Performance

The operation of the three-chamber MFC allowed for greater peak power densities than achievable in a single chamber MFC (**Figure C-2**), however, the voltage and power fluctuated during the CDP four step process (**Figure 5-5** and **Figure 5-6**). In particular, the performance decreased during Steps 2 and 3 due to the addition of a large resistance (low concentrate chamber). The MFCs operational power at 4 mA decreased from  $1.41 \pm 0.03$  W m<sup>-2</sup> (cathode) to  $0.44\pm0.09$  W m<sup>-2</sup> (cathode) when the high concentration was replaced by the low concentration (NaCl). When the MFC was operated at 2 mA, the MFC power decreased from  $1.03 \pm 0.01$  W m<sup>-</sup>

<sup>2</sup> (cathode) to 0.71  $\pm$ 0.05 W m<sup>-2</sup> (cathode) (**Figure 5-5b**). The intermittent addition of the low concentration solution was therefore detrimental to the MFC operation, but necessary for CapMix power production. One way to reduce this resistance would be to design the system to have a thinner CapMix chamber.

### 5.4.4 Capacitive mixing with thermolytic salts

The performance of the CapMix electrodes was further examined using AmB high and low concentration solutions in the middle CapMix chamber, and a high concentration of AmB in the cathode chamber. The switch to AmB as the electrolyte did not significantly alter the capacitance of the electrodes compared to NaCl, with ~80-90 F g<sup>-1</sup> obtained for both electrolytes based on cyclic voltammetry tests (5 mV sec<sup>-1</sup> scan rate) (**Figure C-1**). The use of AmB reduced cathodic resistance, increasing the systems limiting current (5 mA). At this higher current, the energy captured increased to 314 ±27 mJ g<sup>-1</sup> cycle<sup>-1</sup> (**Figure 5-6**), which was ~6× more than that previously obtained using CDP. The increased limiting current with AmB compared to NaCl was due to the reduced overpotential of the cathode (**Figure C-2**) because ammonium functions as a proton shuttle, which improves oxygen reduction. The cathode potential was therefore ~200 mV higher at current densities in AmB than in NaCl.

Power densities for the CapMix electrodes with CDP charging using AmB reached 942  $\pm$  100 mW m<sup>-2</sup> (average 301  $\pm$  87 mW m<sup>-2</sup>), which approached levels previously obtained using only PRO, RED, or forced CDP processes. AmB increased the overall energy extracted through the CDP process relative to NaCl solutions. At a current of 4 mA, 244  $\pm$  30 mJ g<sup>-1</sup> cycle<sup>-1</sup> was extracted using AmB, compared to 175  $\pm$  16 mJ g<sup>-1</sup> cycle<sup>-1</sup> using NaCl. The advantage of the CapMix process compared to RED is that this power is extracted using only a pair of membranes, although the four-step charging cycle is more complex than that needed for RED operation. The

advantage of CapMix compared to PRO may be that membrane fouling is reduced, as water does not need to flow through the membrane as it does in PRO.

## 5.4.5 Forced charged CapMix using the MFC

Power generation and energy extraction using the CapMix process was further examined using the MFC to directly charge the CDP electrodes in AmB. This forced charge method avoided the need for an external power source, as the power was provided directly by the MFC. To force charge the CapMix electrodes, the MFC anode was connected by a wire to the anioncoated capacitive electrode, and the cathode was connected to the cation-coated capacitive electrode. Forced charging increased the potential of the capacitive electrodes to ~0.65 V after five minutes, which allowed increased energy extraction from the capacitive discharge process. The peak voltage increased from ~0.1 V to ~0.85 V (**Figure 5-7a**), and peak power densities increased  $8.5 \times$  to  $7.6 \pm 0.1$  W m<sup>-2</sup> (0.67  $\pm$  0.08 W m<sup>-2</sup>, averaged over the discharge curve) compared to non-forced conditions (**Figure 5-5b**). The energy extracted from the CapMix process increased 47× to 14,900  $\pm$  400 mJ g<sup>-1</sup> cycle<sup>-1</sup>.

Power densities were further increased to 20 W m<sup>-2</sup> (capacitive electrode) when the discharge external load was reduced. However, at this lower external load the high rate of discharge caused an increase in leakage current, which reduced the net energy recovered (**Figure C-7**). The charge obtained through the discharge was due solely to initially invested charge from the MFC, and not from the CapMix process. When the charged capacitive electrodes were exposed to the low concentrate, the voltage increased from 0.5 V to nearly 0.75 V. However, when connected to an external load, the voltage of the capacitive electrodes immediately decreased to a voltage below that of the initial charge (0.5 V). Further optimization of materials

and membranes to reduce charge leakage could therefore improve power densities using this approach.

# **5.5 Conclusions**

Capacitive and battery-type electrode approaches offer novel methods for producing electrical power using naturally-occurring (seawater/river water) or engineered (thermolytic solution) salinity gradients. The use of an ionically driven current represents a new approach in the development of these technologies as it substantially increased power densities from ~10 mW  $m^{-2}$  to ~500 mW  $m^{-2}$  with NaCl, and ~900 mW  $m^{-2}$  using thermolytic salts. The direct use of the MFC electrodes to force charge the capacitive electrodes increased power densities further to ~7 W  $m^{-2}$ . The combination of the bioelectrochemical and capacitive mixing processes could enable simultaneous wastewater treatment and provide a new method of power generation and energy recovery at either coastal or industrial sites.



**Figure 5-1:** (a) The four step process for capacitive mixing based on a membrane potential with open circuit and closed circuit condition and ion flux indicated. The individual steps (1 through 4) are explained in the text. Negatively charged ions move through the anion exchange membrane (AEM) to charge the anode, while the positively charged ions (yellow) travel through the cation exchange membrane (CEM) to charge the cathode. Note the circuit is opened when changing out the solutions from high to low concentration. The plug shown in step 2 indicates energy can be input into the system during a forced CDP charging step, while the light bulb indicates that energy is extracted in this step 4. (b) Voltage versus charge plot for the four step process, with each step and membrane potentials indicated. The work done over the four-step cycle is represented by the area enclosed by the blue outline (referred to here as the voltage window). In the forced charge mode, this area can be expanded to increase energy recovery.



**Figure 5-2:** a)CMFC showing reactor components and electrode reactions. Note that the MFC and the capacitive electrodes are operated using two separate electrical circuits. The solution in the CapMix middle chamber is changed using the four step cycle (see details in Fig 1a) while the MFC operation over that period of time is continuous. b) Energy extracted from CDP (smaller blue lined area), compared to higher energy that can be extract using the CDP placed into the MFC (red lines), and energy recovered forced charge CDP approach in an MFC (grey lines).



**Figure 5-3:** Capacitive mixing chamber performance with the MFC operated at constant current at 2 mA or 4 mA, compared to CapMix alone. (a) Voltages produced during the four step charging-discharging CapMix process; and (b) power density produced (normalized per  $m^2$  of one capacitive electrode).



**Figure 5-4:** Energy extracted from CapMix and CapMix-MFC system is defined as the area inside the voltage-charge cycle.



**Figure 5-5:** Performance of the MFC during the four-step CapMix cycles: (a) voltage and (b) power density (normalized per m2 of MFC cathode).



**Figure 5-6:** Total energy extracted with the MFC set at different fixed currents using high (500 mM) and low (10 mM) concentration solutions of ammonium bicarbonate (AmB) or sodium chloride (NaCl) in the CapMix chamber. Energy extracted was normalized per gram of capacitive electrode.



**Figure 5-7:** Performance of the capacitive electrodes with forced charging using the MFC: (a) capacitive electrode voltage; and (b) power densities (normalized to a single capacitive electrode area).

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# Chapter 6

# Role of surface functionality on electric double layer expansion process during capacitive mixing

# 6.1 Abstract

The amount of salinity gradient energy that can be obtained through capacitive-mixing based on double layer expansion (CDLE) depends on the extent the materials electric double layer (EDL) is altered in a low concentration electrolyte (e.g. river water). We show here that the individual electrode rise potential, which is a measure of the EDL perturbation process, significantly ( $P = 10^{-5}$ ) depends on the concentration of strong acid surface functional groups. Electrodes with a low concentration of strong acid functional groups (0.05 mmol  $g^{-1}$ ) resulted in a positive-potential-rise of  $\Delta U_{+/-} = +59 \pm 4 \text{ mV}$  ( $\Delta U_{cell} = 16 \pm 0.7 \text{ mV}$ ) in synthetic river water, and activated carbons with a high concentration of strong acid groups (0.36 mmol  $g^{-1}$ ) produced a negative-potential-rise of  $\Delta U_{\pm} = -31 \pm 5 \text{ mV}$  ( $\Delta U_{cell} = -11 \pm 1 \text{ mV}$ ). Dissimilar electrodes, which coupled a negative electrode with a high concentration of strong acid groups with positive electrode with a low concentration of strong acid groups, produced a whole cell potential rise which was  $5.7 \times$  greater than that produced with similar electrodes (from  $15\pm0.2$  to  $89\pm3$  mV). ReaxFF reactive force field molecular dynamics and metadynamics simulations show that the EDL expands within a low concentration solution if the carbon lacks strong acid functional groups producing a positive-potential-rise, and the EDL compresses when the electrode has a high concentration of strong acid functional groups producing a negative-potential-rise. This dissimilar behavior with strong acid functional groups provides an effective tool to maximize energy generation from CDLE.

### **6.2 Introduction**

Globally, between 0.8-2.6 TW of power exists at estuaries through the natural mixing of sea and river water.[1, 2] Capacitive mixing based on double layer expansion (CDLE), is an electricity–producing salinity gradient energy (SGE) technology that can harvest mixing energy using capacitive electrodes. Current competing pilot phase SGE technologies, pressure retarded osmosis (PRO) and reverse electrodialysis (RED), require the use of membranes, which increases capital costs [2-13]. CDLE utilizes only low cost activated carbon electrodes, potentially making CDLE the most sustainable conversion technique available for extracting energy from natural mixing processes[14-21].

CDLE is the reverse of an emerging desalting technique termed capacitive deionization (CDI)[22-26]. CDI consumes energy to extract ions from a concentrated solution using supercapacitor–based electrodes, while CDLE produces electrical energy from the mixing of a concentrated and less-concentrated solution. Energy extraction with CDLE takes place through four-steps (**Figure 6-1**). Initially, electrodes are placed in a 'seawater solution' and either charged without a power supply (zero charging), or charged using a power supply (force charging) [15-17, 27, 28] (step 1). The zero charging method is favored because this alleviates the need for an initial investment of energy into the system, and minimizes charge leakage. Once this surface charge is established, the electrodes are placed in open circuit (no external load), and river water displaces the seawater solution. The change in concentration results in a perturbation of the electric double layer (EDL) on each electrode. The change in the EDL thickness, measured based on the Debye length ( $\lambda$ ), increases the potential drop through the diffuse portion of the EDL

 $[\varphi_{EDL}^{\pm} = f(\lambda)]$ , elevating the whole cell potential ( $\varphi_{cell}$ ) (step 2). The capacitive electrodes are then discharged (at the higher potential), and energy is harvested through an external circuit (step 3). The cycle is completed when seawater displaces the river water under open circuit (fixed surface charge) conditions, compressing the EDL (step 4)[15].

The EDL expansion and material capacitance (*C*) dictate how much energy is generated during the CDLE process  $[E_{CDLE} = \frac{1}{2}C(2\varphi_{EDL})^2]$ . From the Poisson-Boltzmann equation and the Gouy–Chapman–Stern (GCS) model, the potential distribution in the diffuse portion of the EDL is:

$$\varphi_{EDL} = \frac{2k_b T}{e} \sinh^{-1} \left( \frac{\sigma}{\sqrt{8C_s N_A \epsilon_0 \epsilon_r k_b T}} \right)$$
6-1

where  $k_b$  is the Boltzmann constant, *T* the temperature, *e* the electron charge,  $\sigma$  the surface charge density,  $C_s$  the concentration,  $N_A$  Avogadro's constant,  $\varepsilon_0$  the electric constant, and  $\varepsilon_r$  the relative dielectric constant. The potential distribution ( $\varphi_{EDL}$ ) increases, as the surface charge density ( $\sigma$ ) increases and the solution concentration decreases. During 'zero–charging', the material properties dictate the surface charge density, whereas with 'force–charging' the external power supply provides the surface charge density. Methods that increase the activated carbon's intrinsic charge density are needed in order to capture a significant amount of energy through the 'zero–charging' method.

From the GCS model, an individual electrode operated with sea and river water at the electrode's spontaneous potential could approach  $\varphi_{EDL}\approx60-90 \text{ mV}$  ( $\varphi_{Cell}=2\varphi_{EDL}$ ). In practice, individual electrodes have approached the theoretical predictions, but the whole cell potential has not. The whole cell potential has remained low, typically between  $\varphi_{Cell}\approx-30$  to 30 mV [15-18]. This is because each individual electrode's rise potential is similar if the electrodes (positive and negative) have the same material properties. To avoid this, dissimilar materials (materials with

different properties) are often paired together to make a whole cell. Ideally, the greatest whole cell potential rise occurs when one electrode decreases in potential ( $\Delta \varphi^{\pm} < 0$ ) and the other increases in potential ( $\Delta \varphi^{\pm} > 0$ ) when exposed to a low concentrate solution. Through matching dissimilar electrodes, the whole cell potential has approached  $\varphi_{Cell} \approx 100 \text{ mV}[15]$ . Many carbons have been characterized in CDLE cells, yet the defining characteristic that promotes the directional rise potential differences has yet to be explained.

The objective of this study was to investigate the effect that surface functionality has on the voltage rise (energy generation phase) during a CDLE cycle. It was hypothesized that the type of surface functional group is an important factor for promoting either an electrode potential rise or fall when solutions are switched. To examine this effect, different activated carbons (ACs) made from various precursor materials (coconut, phenolic resins, bituminous coals, hardwood, and peat) were evaluated based on potentiometric titrations to quantify the concentration of acidic surface functional groups[29]. The materials were further characterized in terms of electrochemical (capacitance) and physical (pore size distribution, and total surface area) properties. The voltage rise ( $\Delta \varphi^{\pm} > 0$ ) or fall ( $\Delta \varphi^{\pm} < 0$ ) of each individual electrode was determined at the materials spontaneous potential. Dissimilar configurations with varying surface chemistry were examined as an effective means to expand the voltage rise of the capacitive electrodes during a 'zero charging' CDLE process. Furthermore, the use of an oxidation treatment method, which increased the carbons concentration of strong acid groups, was demonstrated to be an effective means for generating dissimilar electrodes with high capacitance materials.

### 6.3.1 Capacitive Mixing System

The CDLE device was manufactured from antistatic clear cast acrylic (McMasterCarr, IL). The endplates  $(5.1 \times 5.1 \times 0.95 \text{ cm})$  and a middle chamber  $(5.1 \times 5.1 \times 0.25 \text{ cm})$  were machined. Each endplate had a 0.64 cm hole drilled and tapped so that a polypropylene tube fitting (0.64 cm tube OD × 0.64 cm male pipe) could be screwed into the endplate. Fine extruded graphite rods (0.64 cm diameter, Graphitestore.com, Inc.) were fitted into the polypropylene tube fitting, and sealed using Loctite epoxy (McMasterCarr, IL). The graphite rods served as the current collector for the capacitive electrodes. The middle chamber was hollowed out and this served as the flow cell (empty bed volume ~2 mL). Tube fittings were glued to the top and bottom of the middle chamber, allowing for flow into and out of the cell. A reference electrode (Ag/AgCl +0.205 versus SHE) (BASi, West Lafayette, IN) was placed in the middle chamber to measure individual electrode potentials.

## 6.3.2 Electrode preparation, treatment, and characterization:

Capacitive electrodes were prepared from commercially available activated carbon (AC) powders. The ACs used were: a peat based AC, (SX+) (Norit, USA), a coconut shell based AC, (YP50) (Kuraray Chemical, Japan), a phenolic resin based AC, (RP-20) (Kurraray Chemical, Japan), a bituminous coal carbon, (BC)(Carbon Resources, USA, and a hardwood sample (HRD) (MeadWestvaco, USA). To produce a highly acidic carbon, YP50 was oxidized (YP50 ox) using 0.5 M Nitric acid (Sigma–Aldrich, St. Louis MO) for 12 hours.

Capacitive electrodes were prepared through combining the powder AC with 10 wt% polyvinylidene fluoride (PVDF) (Sigma–Aldrich, St. Louis MO). The mixture was homogenized with a sonifier in 2 mL of dimethylformamide (DMF) (Sigma–Aldrich, St. Louis MO), and the slurry was cast onto the graphite rod (~3.2 mg cm<sup>-2</sup>). Electrodes were dried overnight, washed with ethanol, and then soaked in 0.5 M sodium chloride before use in the CDLE system.

Cyclic voltammagrams (CVs) of each electrode were collected using a potentiostat (Biologic VMP-3, USA). The electrodes were scanned from 0 to 0.5 V at 2, 5, 10, 20, 50 and 100 mV sec<sup>-1</sup>, and the capacitance calculated by:

$$C_{sp} = \frac{2}{\Delta U} \cdot \frac{\int i dU}{v \cdot m}$$
 6-2

where  $\Delta U$  is the width of the voltage scan, *i* the discharge current, *U* the voltage, *v* the scan rate, and *m* the mass of carbon on one electrode. Electrodes were characterized in terms of the surface area, pore volume distributions, and surface functional groups as previously described[29]

### **6.3.3 Spontaneous Potential Measurements**

The spontaneous potential of each electrode was obtained through stepping the whole cell voltage from 0 to 1 V at 0.2 V increments, where each voltage was held constant for 10 minutes to ensure steady conditions. The positive, negative, and whole cell voltage was monitored with Ag/AgCl reference electrodes. Step voltages were run three times to ensure repeatability. The potential of the individual electrodes measured at 0 V corresponded to the electrode's spontaneous potential.

### 6.3.4 Gouy-Chapman-Stern Model

Using the GCS theory (Eq 6-1), the individual electrode potentials in different solutions ( $\varphi_{river/sea}^{\pm}$ ), and resulting individual electrode potential rise/fall ( $\Delta \varphi^{\pm} = \varphi_{river}^{\pm} - \varphi_{sea}^{\pm}$ ) can be estimated.[14] Calculating the resulting potential rise/fall for various base potentials produces a curve which is used to evaluate the CDLE performance.[15] This vanishing point (point where the potential rise is expected to be zero), differs based on solution concentration and the material properties of the activated carbons. Here, we estimate that the vanishing point should take place near the material's point of zero charge (PZC), and therefore it can be obtained from the potentiometric titration data ().

# 6.3.5 Capacitive Mixing Performance

Capacitive mixing cycle testing was conducted to look at the potential rise when solutions were changed. In all tests a 0.5 M NaCl solution was used as the high concentration (e.g., seawater), and 0.011 M solution was used as the low concentration (river water) solution. The flow rate was maintained at 5 mL min<sup>-1</sup> using a peristaltic pump (Cole Parmer, IL) when solutions were flushed through the cell. During energy extraction tests, the high concentration solution was flushed through the cell while the electrodes were connected to a 10  $\Omega$  resistor and charged to ~0.0 V. The load was removed, and the low concentration solution was flushed through the potential rise reached a plateau, the electrodes were discharged through a 100  $\Omega$  resistor until the whole cell reached ~0.0 V. A high concentration solution was flushed through the cell, and this cycle was repeated for five cycles to ensure repeatability.

#### 6.3.6 ReaxFF reactive force field method

A detailed description of the ReaxFF reactive force field method is given in van Duin *et al.*[30] and Chenoweth *et al.*[31]. In the ReaxFF reactive force field, the total (system) energy is given by

$$E_{system} = E_{bond} + E_{val} + E_{tors} + E_{over} + E_{under} + E_{lp} + E_{vdwaals} + E_{coulomb}$$
 6-3

The terms in Eq. (1) include bond energies  $(E_{bond})$ , valence-angle energies  $(E_{val})$ , torsion-angle energies  $(E_{tors})$ , the energy to penalize over-coordination of atoms  $(E_{over})$ , the energy to stabilize under-coordination of atoms  $(E_{under})$ , lone-pair energies  $(E_{lp})$ , and terms to handle non-bonded Coulomb  $(E_{coulomb})$  and van der Waals  $(E_{vdwaals})$  interactions.

ReaxFF employs a bond order/bond energy relationship, which allows for bond formation and bond dissociation during molecular dynamics (MD) simulations. The bond orders obtained from inter-atomic distances are updated at every MD or energy minimization step. All connectivity dependent interactions (*e.g.*, valence-angle and torsion-angle energies) are bondorder dependent and therefore energies and forces associated with these terms go to zero upon bond dissociation[32]. ReaxFF calculates non-bonded interactions (van der Waals and Coulomb) between every atom pair, irrespective of their connectivity and excessive short-range non-bonded interactions are avoided by incorporating a shielding term in these interactions.

The ReaxFF force field uses the same general and O/H ReaxFF parameters as employed in a number of previous ReaxFF descriptions, including proteins, alcohols and organic acids, inorganic acids, phosphates, zincoxides, iron-oxides, copper-oxides, aluminium, silica and aluminosilicates, thus allowing straightforward transferability to multicomponent liquids and mixed metal-oxide materials. The ReaxFF force field employed in this study uses the same C/H/O parameters in Rahaman *et al[33, 34]*. to describe graphene-water/graphene oxide-water interactions and the same Cl/O/H parameters in Rahaman *et al.* to describe chlorine-water interactions.

### **6.3.7** Theoretical methods

ReaxFF MD simulations have been employed to calculate the change in EDL thickness during capacitive-mixing while changing from a high to low concentration electrolyte to investigate the dissimilar (positive vs. negative) potential rise at electrodes, with low and high concentrations of strong acid functional groups. The ReaxFF reactive force field implementation in the ADF computational chemistry package was used for these calculations. All MD simulations were performed in the canonical (NPT) ensemble, with a time step of 0.25 fs using the Berendsen thermostat with a coupling time constant of 100 fs, and Berendsen barostat with a coupling time constant of 500 fs to control temperature and pressure of the entire system.

We simulated pristine graphene (PG) sheets to model electrodes with low concentration of strong acid functional groups, and graphene oxide (GO) sheets to model electrodes with high concentration of strong acid functional groups as shown in Figure S2. The atomic structure of GO sheets used in our simulations have been obtained from MD studies by Bagri *et al.* In our simulations we used periodic slabs with dimensions 43.35 Å x 40.04 Å parallel to the surface to describe the electrodes. Water molecules, potassium, and chlorine atoms were placed in random configurations between the electrodes separated by 16 Å to represent the 2.4 M KCl solution which was used as a representative high concentration solution in all simulations. The system was energy minimized with convergence criterion of 0.25 kcal/Å and equilibrated in in the canonical (NPT) ensemble for 50 ps at 300K. We performed MD simulations on the equilibrium configuration for 50 ps at 300K to calculate the EDL thickness at the electrodes for the high concentration electrolyte case. The potassium and chlorine ions not part of the EDL at the electrodes were removed manually to simulate the change from a high to low concentration electrolyte. The resulting 0.9 M KCl solution was used as a representative low concentration solution in all simulations. We then perform MD simulations for 100 ps at 300K to quantify EDL thickness for the low concentration electrolyte case. In these simulations the equilibration time was 50 ps and the subsequent production run was 50 ps.

### 6.4 Results and Discussion

#### 6.4.1 Evaluation of electrode potential rise

With the addition of a low concentration solution (e.g., river water), the whole cell voltage rise ( $\Delta \varphi_{cell} = \Delta \varphi^+ - \Delta \varphi^-$ ) for all 'similar' configuration AC electrodes (made from the same materials) increased by ±15 mV (**Figure D-3**). The hardwood sample potential decreased, while all other samples had increased potentials. The individual electrode rise potentials (positive  $\Delta \varphi^+$  and negative  $\Delta \varphi^-$ ) both increased or decreased together. The SX+ produced the largest positive and negative electrode rise ( $\Delta \varphi^+ = 63 \pm 1.7 \ mV$ ;  $\Delta \varphi^- = 47 \pm 1.5 \ mV$ ), and the HRD sample had the largest positive and negative electrode fall ( $\Delta \varphi^+ = -37 \pm 4 \ mV$ ;  $\Delta \varphi^- = -21 \pm 4 \ mV$ ). The carbon materials had spontaneous base potentials ( $\varphi_0$ ), ranging from -0.085 to -0.023 mV versus SHE (0.120 to 0.182 mV versus Ag/AgCl). These base potentials are similar to those previously reported in literature.[15] There was a significant correlation (P= 10<sup>-5</sup>) between the concentration of surface strong acid groups (pKa < 8) and the electrode potential rise (**Figure 6-2**). There was no correlation between the rise/fall potential magnitude and the spontaneous base potential.

The PZC for the SX+ and HRD differed by ~5 pH units or nearly 300 mV (**Figure D-1**). The GCS curves for HRD and SX+ are formed through using the PZC as the vanishing point  $(\Delta \varphi^{\pm} = 0)$  (**Figure 6-2**). Both the positive and negative electrode rise/fall potentials for SX+ and HRD were in good agreement with those predicted using the GCS theory. When similar electrodes are used for CDLE, to establish a large potential difference between individual electrodes, the electrodes need to be pushed away from their spontaneous base potentials, along the same GCS curve (**Figure D-4**). With dissimilar electrodes (with different PZC) the system is able to operate on two GCS curves, which promotes a potential difference between each individual electrode even at the spontaneous base potential. Furthermore, when one electrode's spontaneous base potential is greater than the PZC, and the other electrode's spontaneous base potential is below the PZC (as is the case with SX+ and HRD), it is expected that one electrode will rise and one electrode will fall as the solutions are altered, which is desired.

### 6.4.2 CDLE performance with dissimilar electrodes (SX+/HRD)

The benefits of using dissimilar electrodes was demonstrated through coupling the SX+ carbon material (low acid content) with the HRD (high acid content). Using the SX+ as the positive electrode and the HRD as the negative electrode, the whole cell potential rise reached 86  $\pm$  1.7 mV (**Figure 6-3**). This increase was due to the individual electrode rise or fall potentials  $(\Delta \varphi_{SX+}^+ = 68 \pm 1.7 \text{ mV and} \Delta \varphi_{HRD}^- = -21 \pm 4 \text{ mV})$  (**Figure 6-3**). When the electrodes were reversed ( $\varphi^+$ =HRD and  $\varphi^-$ =SX+) the whole cell voltage decreased to  $-84 \pm 4$  mV. This difference in whole cell potential rise was due to  $\Delta \varphi_{cell} = \Delta \varphi^+ - \Delta \varphi^-$ . To obtain a positive whole cell voltage, the positive-electrode-rise must be greater than the negative-electrode-rise ( $\Delta \varphi^+ > \Delta \varphi^-$ ). To maximize $\Delta \varphi_{cell}$ , the negative electrode should contain strong acid groups, and the positive electrodes should have minimal strong acid groups. When the SX+ and HRD electrodes were operated with similar (SX+/SX+ or HRD/HRD) positive and negative electrodes,

the potential rise was minimal ( $\Delta \varphi_{SX+|SX+} = 16 \pm 0.7 \ mV$ ;  $\Delta \varphi_{HRD|HRD} = -11 \pm 1 \ mV$  HRD) (Figure 6-3c). Again, the low voltage rise was attributed to the similar rise and fall potential associated with each cell's positive and negative electrodes (Figure 6-3d).

# 6.4.3 Surface chemistry

The different rise-potential measurements between the two carbons were due to the different surface functionalities. The strong acid functional groups measured for the HRD sample were primarily oxygen containing acids (e.g. phenolic, carboxylic, and lactonic) (**Figure D-5 & 6**).[29] Surface functional groups can act as a source of surface charge, as the functional groups can undergo dissociation or protonation.[35] From the potentiometric titrations, the HRD sample has the largest quantity of strong acid surface functional groups around the operating electrolyte's pH (e.g. pH=7), whereas SX+ has the lowest concentration of functional groups at pH=7. The groups that could potentially dissociate or protonate at pH 7 most likely are the carboxylic acid groups. Due to the increased concentration of OH<sup>-</sup> at the surface, the functionalized surface may have an increased propensity to perform best as a negative electrode. Different treatment methods, which increase the concentration of positive surface functional groups at the positive electrode, may also increase the potential rise.

### 6.4.4 Theoretical results- Evaluation of EDL thickness

We modelled dissimilar electrodes using pristine graphene (PG) and graphene oxide (GO) sheets in the MD simulations. PG and GO sheets were examined as cathodes in our simulations by assigning a net charge of 0.1e per atom, or anodes by assigning –0.1e per atom at
the electrodes. The formation of an EDL at the electrodes for the case where PG is the cathode and GO is the anode, in the high concentration electrolyte case, is shown in Figure 6-4. The ions that, are not part of the capacitance or Stern layer (not adsorbed to the electrode) were removed manually to simulate the change from high to low concentration electrolyte (Figure 6-4b). At equilibration, we observed that the EDL thickness at the PG electrode increased when changing from a high to low concentration electrolyte irrespective of whether PG was the cathode or anode. The EDL thickness increased by  $0.11\pm0.05$  Å when PG was cathode, and  $0.10\pm0.05$  Å when PG was the anode. The GO electrode showed the converse behaviour, where the EDL thickness decreased on going from a high to low concentration electrolyte, with the direction of this response (but not the magnitude) independent of whether GO was simulated as the cathode or anode in the cell. The EDL thickness decreased by 0.10±0.06 Å when GO was the cathode, and decreased by 0.17±0.05 Å when GO was the anode. The EDL expansion at PG gave rise to the positive potential rise, and the EDL compression at GO produced the negative potential rise during the CDLE cycle. These simulation results are in agreement with the experimental observations that electrodes with low concentration of strong acid functional groups showed a positive potential rise, and electrodes with high concentration of strong acid functional groups showed a negative potential rise during CDLE cycle, irrespective of whether they were the cathode or anode in the cell.

To investigate the origins of the dissimilar EDL changes at the PG and GO electrodes we performed metadynamics simulations to investigate the free-energy surface (landscape) of ions with the separation of ions from the electrode and solvation of ions in water as the collective variables. Metadynamics was performed using version 1.3 of PLUMED (called using a "fix" routine from lammps). Technical details are listed in the Supporting Information (SI). **Figure 6-4c** and **Figure 6-4d** shows the free-energy surface (FES) of chlorine ions near the PG electrode for the high concentration electrolyte and low concentration cases respectively when PG is the

cathode in the cell. From these two figures, we can observe that upon changing from the high to low concentration electrolyte, the position of minimum free-energy of the chlorine ion moved farther away from the PG electrode (x-axis), and that its coordination with water increased from 3 to 5 (y-axis). In the high concentration electrolyte the minimum free energy of the chlorine ion is at a separation of 2.51 Å from the PG electrode and in the low concentration electrolyte this increases to a value of 2.59 Å. This suggests that in the low concentration electrolyte, because of the absence of surrounding ions, the chlorine ions were stabilized by moving further into solution and coordinating with more water molecules. This resulted in an EDL expansion, which would produce a positive potential rise at electrodes having a low concentration of strong acid functional groups. Figure 6-4E and Figure 6-4F shows the FES of potassium ions near the GO electrode for the high and low concentration cases, with GO as the anode. When changing from the high to the low concentration electrolyte, the position of minimum free-energy of the potassium ion moved closer to the GO electrode (x-axis), and its coordination with water remained around 3 (y-axis). In the high concentration electrolyte the minimum free energy of the potassium ion is at a separation of 2.73 Å from the GO electrode and in the low concentration electrolyte this decreases to a value of 2.65 Å. At the GO electrode, ion coordination with surface oxygens was also considered as a collective variable since the surface oxygen atoms could provide part of the solvation shell for the potassium ions near the GO electrode. We can note from Figure D-7 that in the low concentration electrolyte the potassium ion moves closer to the electrode and at the same time its coordination with surface oxygens has decreased slightly from 2.9 to 2.7 (y-axis). Figure 6-4G and Figure 6-4H shows the FES of potassium ions near the GO electrode as a function of coordination with surface oxygens (x-axis) and coordination with water (y-axis). In the high concentration electrolyte the free-energy minimum was produced when potassium was coordinated with 3 water and 3 surface oxygens. In the low concentration electrolyte the potassium ion has closely spaced free-energy basins at (3,3) as well as (2,4) with a barrier of 1.27

kcal mol<sup>-1</sup> between the basins. This suggests that in the low concentration electrolyte the potassium ion can move closer to the electrode and preserve its total coordination of 6. This would produce an EDL compression and thereby a negative potential rise at electrodes with high concentration of strong acid functional groups. The strong acid functional groups on the electrodes can provide part of the solvation shell of the adsorbing ion and in their presence the adsorbing ion moves closer to the electrode in the low concentration electrolyte producing a negative potential rise. In the absence of strong acid functional groups the adsorbing ion moves away from the electrode in the low concentration electrolyte to increase its solvation in water producing a positive potential rise. This gives rise to the opposite potential rise trends on electrodes with low and high concentration of strong acid function groups.

### 6.4.5 Establishing dissimilar electrodes through oxidation

Using the oxidized negative electrode (YP50 ox) with a non-oxidized positive electrode (YP50) increased the whole cell potential from  $12 \pm 1 \text{ mV}$  to  $53 \pm 1.7 \text{ mV}$  (Figure 6-5a). This increase was due to the directional differences between the individual electrode rise potentials  $(\Delta \varphi_{YP50}^+ = 46 \pm 2 \text{ mV} \text{ and } \Delta \varphi_{YP500x}^- = -6 \pm 0.5 \text{ mV})$  (Figure D-8 & 9). The use of this dissimilar configuration produced a whole cell potential rise which was 3-10× greater than that obtained using either of the similar-electrode configurations (YP50/YP50 or YP500x/YP500x).

Treating activated carbons to alter surface functional groups may be more preferable than choosing dissimilar materials, because this allows more control over material properties (e.g. exact functional groups, pore distribution, surface area etc.). YP50 is a typical activated carbon used for supercapacitor work, because it has high surface area, large concentration of micropores, and consequently high capacitance (**Figure 6-5b**). This indicates that the addition of functionality through surface treatments, such as oxidization processes, is preferable to ensure high

capacitances (**Figure D-10**). Based on the energy equation  $[E_{CDLE} = \frac{1}{2}C(2\varphi_{EDL})^2]$ , if the voltage rise acquired through treatment methods can approach that of dissimilar materials, increasing the capacitance by 2× will double the amount of energy extracted from a CDLE cycle.

### **6.5** Conclusions

CDLE represents a clean, cheap, and potentially sustainable method for extracting energy from salinity gradients. Dissimilar electrodes increased the potential rise by 5.7×, and the concentration of strong acid surface functional groups was shown to strongly correlate with both the direction and magnitude of the individual electrode potential rise/fall. Based on analysis of the concentration of strong acid groups on the different carbons, it was determined that optimal performance is obtained when the negative electrode has a high concentration of strong acid groups, while the positive electrode had few strong acid groups. ReaxFF simulations revealed that the rise and fall potential of individual electrodes is attributed to the EDL expanding or compressing in the low concentration solution (e.g. river water). Additional chemical treatments can be completed to tune the type of functionality and the ideal concentration of acidic or basic functionality to improve the potential rise of both the positive and negative electrodes.



**Figure 6-1:** (a) Four step capacitive mixing based on double layer expansion process. Step 1: electrodes charged in seawater. Step 2: under open circuit, river water replaces seawater solution, causing the EDL to expand (generating energy). Step 3: electrodes discharged at a higher potential (energy harvesting). Step 4: under open circuit, seawater replaces river water, compressing the EDL. (b) Typical voltage response curve during a CDLE cycle with river water steps (2- EDL expansion and 3- Discharge) shaded in light blue, and seawater steps (4- EDL compression and 1- Charge shaded in dark blue.



**Figure 6-2:** (a) Individual electrode  $(\Delta \varphi^{\pm})$  potential rise as a function of the concentration of strong acid surface functional groups for various activated carbons, and (b) experimentally observed rise potentials for SX+ and HRD (red and black symbols) plotted along the predicted GCS curves which are shifted around each materials point of zero charge (PZC). Also indicated is the materials spontaneous base potential ( $\varphi_{HRD,0}$  and  $\varphi_{SX+,0}$ ).



**Figure 6-3:** (a) Whole cell ( $\varphi_{cell}$ ) and (b) individual electrode ( $\varphi_{HRD/SX+}^{\pm}$ ) potentials for asymmetrical CDLE operation using SX+ and HRD activated carbons. (C) Whole cell ( $\varphi_{cell}$ ) and (d) individual electrode potentials ( $\varphi_{SX+/SX+}^{\pm}$  and  $\varphi_{HRD/HRD}^{\pm}$ ) for a symmetrical CDLE operation using SX+ and HRD. Blue shaded area indicates when seawater was present in the cell (step 1&4), and red shading indicates when river water was present.



**Figure 6-4:** Snapshot from a MD simulation showing the electric double layer (EDL) in the (a) high concentration electrolyte and (b) low concentration electrolyte; the water molecules are not shown explicitly. Free-energy surface (FES) for adsorption of chlorine ion on the pristine graphene (PG) electrode as a function of separation from the electrode and coordination with water for the (c) high concentration electrolyte and (d) low concentration electrolyte when PG is the cathode in the cell. Free-energy surface (FES) for adsorption of potassium ion on the graphene oxide (GO) electrode as a function of separation from the electrode and coordination electrolyte and (f) low concentration electrolyte when GO is the anode in the cell. The arrows indicate the direction of shift of free-energy basins when changing from high to low concentration electrolyte. Free-energy surface (FES) for adsorption of potassium ion on the graphene oxide (GO) electrode as a function of shift of free-energy basins when changing from high to low concentration electrolyte. Free-energy surface (FES) for adsorption of potassium ion on the graphene oxide (GO) electrode as a function with surface oxygens and coordination with water for the (g) high concentration electrolyte and (h) low concentration electrolyte when GO is the anode in the cell.



**Figure 6-5:** (a) CDLE cycle with dissimilar electrode YP50/YP50 ox, and YP50 ox/YP50, light blue shaded region indicates river water CDLE steps (2 and 3) and dark blue shaded region indicates seawater steps (1 and 4). (b) Cyclic voltammagram for dissimilar electrodes SX+/HRD and YP50/YP50 ox.

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# Appendix A

### **Supporting Information for Chapter 3**



**Figure A-1 :** Membrane resistance at different flow rates in high (1 M) and low concentration (0.011 M) ammonium bicarbonate.



**Figure A- 2:** Carbon dioxide vapor concentration in solution, and the bubble point temperature at various ammonium bicarbonate concentrations.



**Figure A- 3:** Performance data for high, 2 ml min–1 flow rates with spacer (a) stack polarization (b) stack power density (normalized per membrane area).



**Figure A- 4:** Performance data for high, 0.5 ml min–1 flow rates with spacer (a) stack polarization (b) stack power density (normalized per membrane area).



**Figure A- 5:** Gaseous bubble coverage during high flow rates (a) 2 cm horizontal, (b) 2 cm vertical (c) 3 cm horizontal (d) 3 cm vertical.



**Figure A- 6:** Gaseous bubble coverage during low flow rates (a) 2 cm horizontal, (b) 2 cm vertical (c) 3 cm horizontal (d) 3 cm vertical.

# Appendix B

# **Supporting Information for Chapter 4**



Figure B-1: Reverse electrodialysis stack performance for 10, 15 and 20 cell pair.



Figure B- 2: Evaluation of energy extracted through hydrogen evolution reacting electrodes.



**Figure B- 3:** Reverse electrodialysis system performance with AmB, acidic and basic electrolytes (anolyte/catholytes).



**Figure B- 4:** Individual electrode potentials with AmB analytes, basic analyte, acidic catholyte, and AmB catholyte with the stack operated at 600 mL min<sup>-1</sup>.



**Figure B- 5:** Energy consumed by electrode overpotential for hydrogen and oxygen evolution as a function of solution pH. Whole cell activation overpotentials indicated at two operating points (pH 7 and cathode=pH 2; anode=pH 12)



Figure B- 6: Speciation of ammonium bicarbonate with as a function of the solution pH.



**Figure B-7**: Effect of flow rate on gas evolving (O2/H2) electrodes with ammonium bicarbonate and waste acid catholyte.



Figure B- 8: Gas composition collected from catholyte headspace.



**Figure B- 9:** Polarization and power density curves for an AmB–RED stack as (a & b) low concentration conductivity (concentration) is altered, and (c &d) number of cell pairs (CP) is altered. Results are from a RED stack operated at 600 mL min<sup>-1</sup>, and each membrane was 207  $cm^2$ .



**Figure B- 10:** Component resistance break downs based on cells total resistance from polarization curves with (a) different cell pairs, (b) different flow rates and (c) different concentration gradients.



**Figure B- 11:** Polarization and power density curves for an AmB–RED stack as (a & b) flow rate.

#### Appendix C

#### **Supporting Information for Chapter 5**

### 1. Increased ion transport to capacitive electrodes

Ion transport is dictated by the Nernst-Planck-Poisson (NPP) model. Thus, the ion flux is due to ion concentration gradients (diffusion) and potential gradients (electromigration). Previous capacitive deionization models (the opposite process to CapMix) have described a simplified approach to calculate these fluxes[1]. The transport of ions due to the electrostatic driving forces is calculated through

$$J_{charge} = \mathbf{k} \cdot \mathbf{c} \cdot \Delta \phi_{mtl} \tag{Eq. 1s}$$

where  $J_{charge}$  is the ion flux (mol m<sup>-2</sup> s<sup>-1</sup>), k is the mass transfer coefficient, c is the ion concentration in the solution, and  $\Delta \phi_{mtl}$  voltage gradient divided by the thermal voltage (V<sub>T</sub>=RT F<sup>-1</sup>). Likewise, ion transport in an electrochemical system such as the MFC can be estimated if the current passing through the external circuit is known as:

$$J_{cur} = \frac{i}{AnF}$$
(Eq. 2s)

where  $J_{cur}$  is the ionic current induced by the electrical current (i), A is the cross sectional area, n is the (mol  $e^- \cdot mol^{-1}$ ), and F is faradays constant. Thus, for a pure CDP process, the flux of ions may be dictated by  $J_{charge}$ , and for the CMFC flux is approximated by  $J_{charge}+J_{cur}$  (Fig 5s).

While this approximation for electromigration plays a significant role in the enhanced voltage, concentration gradients also may be important. For CDP, while there is no need for an external power supply, the voltage window remains limited by the membrane potential which is a function of the concentration gradient across the membrane

$$\Delta \phi_{\rm mem} = \ln \left( \frac{c_{\rm sp}}{c_{\rm e}} \right) \tag{Eq. 3s}$$

where  $c_{sp}$  is the concentration in the spacer, and  $c_e$  is the concentration in the electrode. Based on equation 5, slight changes in the high and low concentrate in either the spacer or electrode can significantly reduce the established membrane potential (Fig 6s). Because the voltage window is inherently small, obtaining the theoretically maximum voltage is necessary for useful energy extraction, and thus establishing concentration gradients across the membrane quickly is important. Previous theoretical work showed that in practice the observed voltages can be 50% less than the theoretical limit [2]. This reduction was attributed in part to charge leakage, and to insufficient flow at the electrode/spacer interface which reduced the concentration difference. Thus, another reason for the enhanced voltages from the capacitive electrodes produced in the MFC may be due to the creation of a rapidly established concentration gradient across the membrane.



**Figure C- 1:** (a) Cyclic voltammetry of film electrodes within high concentration (500 mM) sodium chloride and ammonium bicarbonate solutions (b) Capacitance versus scan rate obtained from cyclic voltammetry at various scan rates with inset displaying the two electrode assembly used.



**Figure C- 2:** Steady state whole cell power density for three chamber microbial fuel capacitive mixing system when CapMix chamber contains high and low concentration solutions and (b) individual electrode potentials.



Figure C- 3: Potential and power density over successive cycles with MFC operated under constant load (resistance) conditions.



**Figure C- 4:** CMFC system (not drawn to scale) with MFC electrodes in a constant state of discharge and CapMix chamber undergoing the four step process for energy extraction. Ion fluxes are indicated by blue and white arrows.


**Figure C- 5:** Evaluation of flux into capacitive electrodes as result of a generated Donnan (membrane) potential and ionic currents induced by the MFC.



Figure C- 6: Donnan (membrane) potential generated with various high and low concentration NaCl solutions.



**Figure C- 7:** Forced charge from MFC performance data (discharge through 100 ohm resistance) (a) capacitor voltage and (b) power densities.



**Figure C- 8:** One dimensional transport model displaying role of diffusion and electromigration of ions into the capacitive electrodes.

# Appendix D

# **Supporting Information for Chapter 6**

# **Potentiometric Titration**

The potentiometric titrations of the acidic (HRD) and low acidic (SX+) carbons display the charge at the surface of the carbon at various pHs ((a) Charge versus pH from potentiometric titrations for SX+ and HRD samples, with PZC indicated.**Figure D- 1**). The point of zero charge indicates the pH where the charge density at the carbon's surface is zero. This point is displayed in Figure S2. The electrode potential at zero charge can be calculated based on the Nernst equation,  $E = E^0 - 0.059pH$ . Because the point of zero charge differs by ~4.7 pH units, the potential of zero charge for the two electrodes should therefore be shifted by ~270 mV. This information can be used to determine the vanishing point for the GCS curves.



**Figure D- 1:** (a) Charge versus pH from potentiometric titrations for SX+ and HRD samples, with PZC indicated.



**Figure D- 2:** Snapshot of the simulation cell from a molecular dynamics run with pristine graphene as the cathode and graphene oxide as the anode in the cell.

#### **Metadynamics**

We used the May 5th, 2012 version of the lammps software package[3] and version 1.3 of PLUMED[4] for the metadynamics calculations. Metadynamics simulations were performed to calculate the free-energy surface (FES) of ion adsorption/desorption to the electrode surface. For most adsorbates, the vertical distance of adsorbate to the surface (z) is expected to be a reasonable collective variable that distinguishes the adsorbed and desorbed states. However computing the adsorption FES as a function of z alone is not always reliable. When the adsorbate is charged, its binding to the surface involves displacement of the surface layer of water molecules and desolvation of its coordination shell. Therefore, a reliable description of the free energy landscape associated with ion adsorption requires explicit consideration of its desolvation as part of the reaction coordinate. We therefore consider the coordination number of the adsorbing ion with surrounding water molecules (s) as a second collective variable in our calculations. The two collective variables, the separation of ion from the electrode along the z direction (z) and solvation of ion in water (s), are defined as

$$z = z_{ion} - z_{electrode} \tag{1}$$

and

$$s = \sum_{i \in ion} \sum_{j \in O_{water}} s_{ij} \tag{2}$$

respectively. Here  $z_{ion}$  is the *z* coordinate of the adsorbing ion,  $z_{electrode}$  is the average *z* coordinate of the electrode and

$$s_{ij} = \begin{cases} 1 & \text{for } r_{ij} \le 0\\ \frac{1 - (\frac{r_{ij}}{r_0})^6}{1 - (\frac{r_{ij}}{r_0})^{12}} & \text{for } r_{ij} \ge 0 \end{cases}$$
(3)

where  $r_{ij} = |r_i - r_j| - d_0$  and  $d_0$ ,  $r_0$  is set to 3.05 Å and 0.2 Å respectively. For ion adsorption on the graphene oxide (GO) electrode we also consider the coordination of adsorbing ion with surface oxygens as a collective variable as defined in equations (2) and (3) with O<sub>water</sub> replaced by O<sub>surface</sub>. This is important since near the GO electrode the surface oxygens can provide part of the solvation shell for the adsorbing ions. A hill height of 0.10 kcal/mol and width of 0.35 Å were used, and hills were added every 100 timesteps. FES's were reconstructed from the Gaussian bias potentials added during the metadynamics trajectory.



**Figure D- 3:** (a) Whole cell potential rise during CDLE cycle, and (b) Individual electrode ( $\varphi^+$ ) and ( $\varphi^-$ ) potential rise and fall for various activated carbon materials.

#### Gouy-Chapman-Stern Model for similar and dissimilar electrodes

All carbons when submerged in an electrolyte have display some potential, unless the pH of the electrolyte corresponds to the point of zero charge. This excess surface charge creates the potential, termed the spontaneous potential, which is displayed as a red star in **Figure D- 4**a. If the electrodes are not charged, then the potential difference between the positive and negative electrodes will be minimal, resulting in only a small potential rise. When electrodes are charged, the individual electrodes will be pushed away from the spontaneous potential, to establish the applied potential. This can promote charge leakage. If the two electrodes have different PZC, then a potential difference will naturally exist between the two electrodes at their spontaneous potential (**Figure D- 3**b). Here the green line indicates the spontaneous potential of the individual electrodes, and the red square and white circle represent the positive and negative electrode potentials at the cells spontaneous potential.



**Figure D- 4:** (a) individual electrode movement around the spontaneous potential for symmetric electrodes (b) individual electrode movement around spontaneous potential for asymmetric electrodes.



**Figure D- 5:** (a) Total oxygen functional groups for each precursor material, and (b) type of functional group.



**Figure D- 6:** Potentiometric titration curves for tested carbons (a) pH range from 4 to 10 (b) zoomed in selection (pH from 5 to 8).



**Figure D- 7:** Free-energy surface (FES) for adsorption of potassium ion on the graphene oxide (GO) electrode as a function of separation from the electrode and coordination with surface oxygens for the (a) high concentration electrolyte and (b) low concentration electrolyte when GO is the anode in the cell. The arrows indicate the direction of shift of free-energy basins when changing from high to low concentration electrolyte.



**Figure D- 8:** (a) Whole cell and (b) individual cell potentials asymmetric (SX+ (Positive)/HRD (Negative)) and (HRD (Positive)/ SX+ (Negative)) configurations.



**Figure D- 9:** (a) Whole cell and (b) individual cell potentials for symmetric CDLE operation using YP50 and YP50 ox activated carbons. (C) Whole cell and (d) individual electrode potentials for an asymmetric (YP50 (Positive)/YP50 ox (Negative)) and (YP50 ox (Positive)/YP50(Negative)) configurations.



**Figure D- 10:** (a) Capacitance of various activated carbons as a function of CV scan rate and (b) cyclic voltammagram at 2 mV/sec.



**Figure D- 11:** Voltage profile through the electric double layer during an expansion and compression process.

# VITA

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- 2. <u>M.C. Hatzell</u>, Y. Kim, and B. E. Logan, "Powering microbial electrolysis cells by capacitor circuits charged using microbial fuel cell," *Journal of Power Sources*, 229, 198-202 (2013).
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- 5. <u>M.C. Hatzell</u>, Roland D Cusick, and Bruce Logan, "Capacitive Mixing Power Production from Salinity Gradient Energy Enhanced through Exoelectrogen-Generated Ionic Currents," *Energy & Environmental Science* DOI: 10.1039/C3EE43823F (2014).
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