Blue Energy - Studies on energy recovery and energy generation in CDLE devices

Optimizing methods and materials for maximizing energy recovery and energy generation in the Capacitive Double Layer Expansion cycle

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Abstract

The energy demand of human society is growing as technology evolves. Greenhouse gas emissions are at an all-time high. Humans have just begun exploring new sustainable energy sources such as solar, wind and nuclear fusion. One such source of energy is named blue energy which occurs at estuaries, regions where rivers flow into the sea and oceans. When salt water is mixed with fresh water, the energy of the system decreases in comparison to the sum of energies before mixing. That’s to say, some amount of free energy is lost due to mixing. The concept of blue energy is to harvest this free energy.

Capacitive Double Layer Expansion (CDLE) is a type of Capacitive Mixing technique which belongs to a family of technologies for harvesting this natural source of energy. CDLE makes use of a capacitive device. One of the major challenges while using these devices is loss of energy. This study is a practical approach that tries to dig deeper behind the causes and possible mitigation strategies for the loss of energy via different pathways.

The impacts of operational parameters on energy recovery and energy generation in a CDLE device have been evaluated. The impacts of a high dielectric coating (MnO₂) on energy generation (evolution of cell potential during mixing) have also been studied. A novel approach for minimizing the internal resistance of the cell has also been provided.

It was found that the optimization of various parts of the CDLE cycle had a significant effect on device performance. The novel cycle developed in this work boosted output electrical power and energy recovery post CAPMIX substantially.
Abstrakt


Capacitive Double Layer Expansion (CDLE) är en typ av kapacitiv blandningsteknik som tillhör en familj av tekniker för att skörda denna naturliga energikälla. CDLE använder sig av en kapacitiv apparat. En av de största utmaningarna när du använder dessa apparater är energiförlusten. Denna studie har ett praktiskt angrepsåtgärd som försöker gräva djupare bakom orsakerna och möjliga begränsningsstrategier för energiförlust via olika vägar.

Effekterna av driftsparametrar på energiåtervinning och energiproduktion i en CDLE-enhet har utvärderats. Effekterna av en hög dielektrisk beläggning (MnO2) på energiproduktion (utveckling av cellpotential under blandning) har också studerats. En ny metod för att minimera cellens inre motstånd har också tillhandahållits.

Det visade sig att optimeringen av olika delar av CDLE-cykeln hade en betydande effekt på enhetens prestanda. Den nya cykeln som utvecklats i detta arbete förstarkte den elektriska effekten och den energiåtervinning som följer CAPMIX kraftigt.
# Table of Contents

1. **Introduction** ............................................................................................................................. 1  
   1.1 Literature Survey.................................................................................................................. 2  
      1.1.1 EDL/Super Capacitor ................................................................................................ 2  
      1.1.2 Blue Energy .............................................................................................................. 3  
2. **Methodology** ............................................................................................................................ 9  
   2.1 Experimental Setup .............................................................................................................. 9  
      2.1.1 CDLE Cell ................................................................................................................... 10  
   2.2 Methods ............................................................................................................................. 11  
3. **Results & Discussions - Effects of process parameters on energy recovery from a CDLE device** ............................................................................................................................................ 14  
   3.1 Effects of electrolyte flow rate on energy recovery ....................................................... 14  
   3.2 Effects of charging time on energy recovery ................................................................. 17  
   3.3 Effects of applied potential on energy recovery............................................................. 19  
4. **Results & Discussions - Effects of process parameters on voltage gain during CDLE** ...... 24  
   4.1 Effects of fresh water flow rate on voltage gain during CDLE ........................................ 24  
   4.2 Effects of concentration gradient on voltage gain during CDLE ................................... 26  
   4.3 Voltage gain during CDLE at various charging voltages .............................................. 28  
5. **Results & Discussions - Synthesis of Nanostructured MnO$_2$ coating on ACC** .......... 30  
6. **Results & Discussions - A novel protocol for maximizing output power and energy recovery in a CDLE cycle** ............................................................................................................................ 35  
7. **Conclusions and recommendations** ....................................................................................... 37  
8. **References** ............................................................................................................................. 39
# List of figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 1.1</td>
<td>Typical CAPMIX process</td>
<td>5</td>
</tr>
<tr>
<td>Fig. 1.2</td>
<td>Typical current, voltage curves for a CAPMIX process. Red curves indicate discharging the device.</td>
<td>6</td>
</tr>
<tr>
<td>Fig. 2.1</td>
<td>Experimental setup. Blue lines represent water flow while orange lines represent flow of data.</td>
<td>9</td>
</tr>
<tr>
<td>Fig. 2.2</td>
<td>Front Panel of the experimental setup (LabVIEW interface)</td>
<td>10</td>
</tr>
<tr>
<td>Fig. 2.3</td>
<td>Blown up c/s view of the CDLE device. (1) ACC electrodes. (2) Cellulose Separator. (3) Graphite Current Collectors</td>
<td>11</td>
</tr>
<tr>
<td>Fig. 2.4</td>
<td>Experiments on effects of operational parameters for optimizing charge/discharge of the CDLE device.</td>
<td>11</td>
</tr>
<tr>
<td>Fig. 2.5</td>
<td>Experiments on process parameters for maximizing voltage gain</td>
<td>12</td>
</tr>
<tr>
<td>Fig. 2.6</td>
<td>Testing new electrode materials after process optimization</td>
<td>13</td>
</tr>
<tr>
<td>Fig. 3.1</td>
<td>Trend in energy efficiency as the flow rate of electrolyte through the ACC matrix is varied.</td>
<td>14</td>
</tr>
<tr>
<td>Fig. 3.2</td>
<td>Trend in Coulombic efficiency as flow rate of electrolyte through the ACC matrix is varied.</td>
<td>15</td>
</tr>
<tr>
<td>Fig. 3.3</td>
<td>Effects of flow rate on double layer capacitance.</td>
<td>16</td>
</tr>
<tr>
<td>Fig. 3.4</td>
<td>Optimization of charging time at the applied voltage and concentration.</td>
<td>17</td>
</tr>
<tr>
<td>Fig. 3.5</td>
<td>Typical charging Current (right axis) &amp; Voltage (left axis) curves divided into 3 arbitrary regions for a qualitative description of energy loss pathways.</td>
<td>18</td>
</tr>
<tr>
<td>Fig. 3.6</td>
<td>(a) Open circuit drop at the end of charging at various charging times depicting the balance between energy recovery and charge adsorption at 1000 s. (b) Difference between charge to voltage ratio during charging &amp; discharging.</td>
<td>18</td>
</tr>
<tr>
<td>Fig. 3.7</td>
<td>Variation in energy recovery as a function of applied potential.</td>
<td>19</td>
</tr>
<tr>
<td>Fig. 3.8</td>
<td>Comparison of input and output charge at various applied potentials.</td>
<td>20</td>
</tr>
<tr>
<td>Fig. 3.9</td>
<td>Measurement of standard electrode potential vs. Ag/AgCl electrode in 0.5 M NaCl.</td>
<td>21</td>
</tr>
<tr>
<td>Fig. 3.10</td>
<td>Standard ACC potential vs. SHE at various externally applied potentials</td>
<td>22</td>
</tr>
<tr>
<td>Fig. 4.1</td>
<td>Variation in Voltage gain with varying flow rates of fresh water.</td>
<td>24</td>
</tr>
<tr>
<td>Fig. 4.2</td>
<td>Volume of fresh water consumed during capacitive double layer expansion at various flow rates.</td>
<td>25</td>
</tr>
<tr>
<td>Fig. 4.3</td>
<td>Changes in voltage gain as the concentration of low salinity solution is changed.</td>
<td>26</td>
</tr>
</tbody>
</table>
Fig. 4.4 Better energy extraction with fresh water concentration of 10^{-4} M. Some amount of dissolved ions are better for CAPMIX

Fig. 4.5 Dependence of voltage gain from CAPMIX on charging voltage

Fig. 4.6 (a) Dependence of DL capacitance & (b) Energy gain on applied potential

Fig. 5.1 MnO_2 nanorods growth process on ACC

Fig. 5.2 SEM analysis of MnO2 Nanorods on ACC

Fig. 5.3 CV curves for capacitance determination of (a) Plain ACC, (b) MnO2 NR’s on ACC

Fig. 5.4 GCD analysis for capacitance determination of (a) Plain ACC, (b) MnO2 NR’s on ACC

Fig. 5.5 8*8 cm2 electrode with MnO2 NRs on ACC

Table 1 Specific capacitance

Fig. 5.6 Voltage gain comparison between plain ACC and MnO2 NRs on ACC

Fig. 6.1 Novel operating protocol for maximizing output power and energy recovery

Fig. 6.2 The novel operation protocol utilizes sea water to maximize power output after a CAPMIX cycle.

Fig. 6.3 Improved energy recovery with the new operation protocol
1 Introduction

The human society still relies heavily on energy sources that should have been obsolete decades ago. Alternative technologies for producing electrical energy such as the photovoltaic effect were discovered as early as the mid-19th century. However, transition to such renewable sources of energy has been lethargic amidst kilos of evidence on the harmful effects of burning fossil fuels.

As the global economy grows, so does the energy demand. Primary energy consumption grew 2.9% in 2018 i.e. double its 10-year average. Out of the world’s total primary energy consumption of 13864.9 mtoe (million tonnes oil equivalent), 84.7% came from fossil fuels, 11.2% from nuclear and hydroelectricity while only 4.1% was produced from renewables. A majority of electrical power produced in 2018 came from coal at 38%, while renewables accounted for only 8.4 to 9.3%.

The growth of renewables although highest from the world fuel mix, hasn’t been enough to contain growing carbon emissions. To emphasize the gravity of this situation, tying carbon emission to 2015 levels would require a growth in renewables twice that observed in 2018 [1].

Just as one-third of the world’s food production is wasted, a major contributor to the global energy crisis is energy inefficiency. Roughly 8-15% of electrical energy is lost in transmission while machinery such as electric vehicles only convert 60% of the energy from the grid to mechanical work. This number drops substantially to 20% for gasoline powered cars.

The earth’s surface temperature has seen an unprecedented rise in the past 30 years. Globally averaged land and ocean surface temperature data show a 0.85 °C rise from 1880 to 2012. Ocean warming accounts for 90% of the energy accumulated from 1971 to 2010, which has direct effects on the water cycle by altering evaporation and precipitation, and thus affecting surface seawater salinity etc. Ocean acidity has risen by 26% since the beginning of the industrial era as a result of CO$_2$ uptake. Arctic sea-ice levels have been on a decline at a rate of 3.5 to 4.1% per decade in the last 30 years while the global mean sea level has risen by 0.19m in the 20th century.

These changes in climate have been linked to anthropogenic forcings such as Green House Gas emissions with a very high certainty. Growing economy and population have driven fossil fuel combustion leading to GHG emissions which have almost doubled since 1970, reaching a staggering 49 GtCO$_2$ eq/yr (GHG emissions are measured in CO$_2$ equivalent) in 2010, despite various mitigation policies [2].

These changes in climate have a clear impact on terrestrial ecosystems, livelihood, economy and food production across all continents. In the 21st century, climate change is expected to increase ill-health, loss of life and make living conditions poor. Changes in patterns of extreme events such as floods, draughts, heat waves, cyclones and wildfires have also been linked to human activities.
Thus, there is an urgent need for an efficient transition to renewable sources of energy and novel solutions to minimize free energy losses in equipment and machinery.

1.1 Literature Survey

Capacitors are high power density energy storage devices which are capable of providing high amounts of charge for short durations of time. Conceptualized in 1746 capacitors have quickly emerged as leading solutions in energy storage. They’re now stepping in the realm of energy generation and harvesting.

Capacitive Mixing (CAPMIX) is a sub category of technologies that makes use of charge storage phenomenon to harvest Blue energy. Capacitive Double Layer Expansion (CDLE) is a part of CAPMIX where in the dependence of charge to voltage ratio (Capacitance) on ionic concentration of the electrolyte is exploited for power production using an Electric Double Layer (EDL) capacitor.

The concept of energy storage in a capacitor can be best understood by looking into the workings of a parallel plate capacitor. It’s made up of 2 conducting parallel plates overlapping each other, separated by a thin layer of a dielectric material (insulator). An ideal dielectric material consists of polar molecules which can reorient themselves about their mean positions upon the application of an electric field.

When a potential difference is applied across the plates, charges of both polarity accumulate at the overlapping area of the plates. The electric field lines of these charges end at their respective counter charges on the other plate via the now re-oriented dielectric molecules. Thus, once the potential difference is removed, these charges hold each other via coulombic interaction resulting in effective storage of energy. In an ideal capacitor, these charges will hold each other indefinitely until they can flow elsewhere.

The charge holding scope of any capacitor is called its capacitance and is defined as the ratio of charge (Q) to voltage (V). The capacitance can also be estimated in terms of overlapping area (A), dielectric strength (σ) and plate separation (d) using the following relation,

\[ C = \frac{Q}{V} = \frac{\sigma A}{d} \]

1.1.1 EDL/Super Capacitor

The interfacial region between a solvated object (metal under potential) and the solvent (electrolyte) is generally known as the Double Layer. The properties of matter in this region are different than their bulk counterparts such as charge density. The modern double layer theory is a compilation of work put forward by various scientists.

Helmholtz first proposed this DL to be a compact structure close to the charged surface. Guoy-Chapman improved on the model by proposing that the ions are solvated and thus there exists a cloud of counter ions called a diffuse layer rather than a compact structure. The GC model though more sophisticated than Helmholtz, oversees important details such as ion size, and presence of co-ions.

The GCS model, after Otto Stern, presents a combination of Helmholtz and GC models. The double layer is made up of a compact inner layer (stern layer) of finite sized ions and a diffuse outer cloud of ions. Grahame, BDM contributed to the stern model by adding specifically adsorbed ions i.e. ions adsorbed on the electrode surface without a hydration shell and interaction of solvent molecules with the electrode in the stern layer respectively. These models are discussed in detail in section x.
The capacitance of an EDL capacitor is a result of both the double layer capacitance and the faradaic pseudo-capacitance which arises from specifically adsorbed ions. To store energy effectively, EDL/Super capacitors employ porous electrodes with very high surface areas. Thus, these capacitors have the characteristic high-power densities while maintaining energy density, and a recyclability higher than rechargeable batteries. Typical Electrostatic DL capacitors are derived from carbon based porous electrodes with highly conductive current collectors.

The most common type of electrodes are carbon based, such as, Activated Carbon, Carbon-fibre cloths, Carbon Aerogels, Graphene, Carbon Nanotubes, etc with surface areas in the range of 1000 m²/g.

An electrolyte fluid acts as a bridge between the 1st electrode and the 2nd (+, -). It does so by acting as an intermediate counter electrode (-, +) to the ACC electrodes, the physical state (liquid) of the electrolyte thus enables the use of porosity as the overlapping area between plates (parallel plate capacitor, \( C \propto S.A. \)).

Commonly a solution, the electrolyte is made up of a solvent and a solute that dissolves and dissociates into cations and anions. The electrolyte is stable under a specific range of temperatures and voltages. Thus, the type of electrolyte being used determines the supercapacitor’s operating temperature, voltage, ESR (Equivalent Series Resistance) and Capacitance. The limitations on energy over which the electrolyte molecules decompose are called breakdown voltage and temperature, for e.g. water molecules split at 1.23 V. Depending on the solvent, supercapacitor electrolytes can be classified as Aqueous and Organic. Aqueous electrolytes provide a higher power density in contrast with organic electrolytes’ higher energy density.

A thin separator made of a porous insulating material is used between the 2 capacitor electrodes to prevent short circuit. Thus, EDL capacitors store energy in the form of charged electrodes and ions.

1.1.2 Blue Energy

Amidst negative impacts of carbon emissions and growing energy demands, there’s an unprecedented need to find new methods of producing renewable energy. One such renewable source of energy possible to harvest is blue energy. At estuaries, where rivers meet the sea, the mixing of fresh water and sea water proceeds thereby increasing entropy of the system and reducing free energy. Blue energy is an umbrella of technologies aimed at harvesting the thermal energy of mixing. Theoretically, each cubic meter of river water flowing into the sea releases around 2.3 MJ of energy, some of which can be harvested. Considering all estuaries in the world, blue energy has a global potential of ~2.5 TW [3]. Pressure retarded osmosis, Reverse Electrodialysis, Capacitive Mixing, Capacitive Donnan potential & Mixing entropy batteries are some key technologies available to harvest energy from salinity differences.

1.1.2.1 Pressure Retarded Osmosis –

Water flows from a region of low solute concentration to a region of high solute concentration. Osmotic pressure is the pressure required to stop the mixing between a solution and its pure solvent across a semi permeable membrane. For deionizing water via reverse osmosis, a
pressure is applied to instigate flow of water across a semi permeable membrane. The membrane stops salt from passing through. As a result, fresh water is collected on the other side of it. The osmotic pressure difference between sea water and river water is equivalent to a dam with a hydrostatic head of 231 m [4]. Filtered fresh water and sea water are filled into modules separated by a semi permeable membrane. The fresh water with a lower concentration of salt flows through into the salt water chamber. This flow increases the pressure of sea water which can used drive a turbine and produce electrical power [5, 6].

1.1.2.2 Reverse electro-dialysis (RED) –

Reverse electro-dialysis makes use of anion and cation exchange membranes to harvest energy from salinity differences without the use of external power. The idea was first proposed by R.E. Pattle in the 1950s. A stack consisting of these membranes arranged alternatively are connected in series. Sea water and fresh water are pumped into these stacks. Due to the difference in concentration and ion selectivity of the CEM and AEM an electric potential is generated which can be converted to current using an electrochemical redox couple [7].

1.1.2.3 Capacitive Donnan Potential –

CDP is a combination of CAPMIX and ion exchange membranes. It makes use of Anion and Cation exchange membranes placed in front of 2 carbon electrodes. Due to the selectivity of these membranes and the concentration difference between the electrodes and the main chamber separated by the ion selective membranes, a Donnan potential is established which drives an ionic current. A cell voltage increment is observed when the solution in the spacer channel is switched due to EDL formation in the electrode matrix. This charge stored in the electrodes drives an electronic current in the external circuit thus harvesting power from salinity differences.

1.1.2.4 Mixing Entropy Batteries –

An electrochemical cell is used to store charge in the electrode material’s bulk crystal. The mixing entropy battery uses an Na$_2$Mn$_5$O$_{10}$ electrode which interacts with Na$^+$ ions and an Ag/AgCl reference electrode which interacts with Cl$^-$ ions. The equilibrium potential between the 2 electrodes depends on the concentration of the electrolyte. This potential is higher in sea water than fresh water. Thus, the cell after being submerged in fresh water (to remove Na$^+$ & Cl$^-$ ions) is flushed with sea water to capture Na$^+$ & Cl$^-$ thus producing electrical power [8].

1.1.2.5 Capacitive Double Layer Expansion –

This technique makes use of an EDL capacitor described above to harvest electrical energy from difference in salinity between 2 solutions. The pair of ACC electrodes are charged in sea water. A double layer is formed at the electrode/electrolyte interface. The electrostatic forces from the electrode create a region of higher ionic concentration close to it while diffusive forces work to equalize this increased concentration of ions. The electrostatic effect from the electrode is completely screened by the ions present in the double layer such that there are no
forces acting on the bulk solution. The relationship between charge density and potential are as follows,

\[ \psi = \frac{2k_B T}{e} \sinh^{-1} \frac{\sigma}{\sqrt{8cN_A e_0 \varepsilon r k_B T}} \]

Where,

\( k_B \) is the Boltzmann constant, \( T \) is absolute temperature, \( e \) is the electronic charge, \( C \) is ionic strength of the electrolyte, \( N_A \) is Avogadro constant, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon \) is dielectric constant of water.

Thus, the potential is higher at lower concentrations if other parameters are kept same. Fig. 1 presents the typical operating protocol for a CAPMIX cycle.

The following describes the operation and working principle behind capacitive mixing,

The CDLE device chamber is flushed with sea water with a typical ionic concentration of 0.5 M NaCl.

An external power supply or a battery is connected to the electrodes and the device is charged. At this point the device capacitance is given by,

\[ C_D = \frac{\partial \sigma^0}{\partial \psi} = \frac{\varepsilon \varepsilon_0}{\lambda_D} \cos \frac{\psi m z_i e}{2k_B T} \]

Where,
C_D is the diffuse layer capacitance, \( \sigma^0 \) is the charge density in the double layer, \( \psi \) is the voltage drop over the diffuse layer which is equal to the voltage rise on the metal side \( \psi^m \), \( \varepsilon_0 \) is the permittivity of the medium (water in this case), \( z_i \) is the valence of the \( i^{th} \) ion (=1 for a monovalent electrolyte like NaCl), \( e \) is the elementary charge, \( k_B \) is the Boltzmann constant, \( T \) is the temperature in kelvin, & \( \lambda_D \) is as follows,

\[
\lambda_D = \left( \frac{k_B \varepsilon_0 e}{2N_A c z^2 e^2} \right)^{1/2}
\]

Here, \( N_A \) is Avogadro’s constant, \( c \) is electrolyte concentration in M.

Since the concentration of sea water is higher than fresh water, the device capacitance is higher than in the subsequent cycle steps.

After charging to the applied voltage, the device is put in an open circuit and the electrode chamber is flushed with fresh water. The capacitance according to the equations presented above decreases while the voltage of the device increases. According to, \( E = \frac{1}{2} CV^2 \), the energy stored in the device is now higher than before. From the viewpoint of Guouy chapman model, in fresh water, due to a lower concentration of ions, the diffusive forces are higher than in sea water which results in the diffuse cloud of ions forming the double layer to expand away from the electrode.

The circuit is closed again to harvest the produced energy.

![Fig. 1.2 Typical current, voltage curves for a CAPMIX process. Red curves indicate discharging the device.](image-url)
The cycle in fig. 1.1 was first introduced by Brogioli as a proof of concept in [9]. Using the Gouy chapman model, the charge distribution close to the electrode surface and the evolution of cell voltage with a change in concentration were explained. It was shown that the cycle could extract an amount of work done equal to,

\[ W = - \int \psi dQ \]

Where, \( W \) is the work done, \( \psi \) is cell potential & \( Q \) is stored charge.

After the proof of concepts, subsequent lab scale prototypes built by various groups saw an improvement in the maximum power output of CDLE devices [10]. To gain new insights into the dynamics of capacitive double layer expansion and capacitive mixing for energy generation from salinity gradients, thermodynamic descriptions of the system have been studied [11-13]. Here, the performance of a ‘blue engine’ consisting of a pair of electrodes dipped in a monovalent electrolyte were investigated by calculating the Helmholtz potential \( F(T, V, N, Q) \) of a half cell with a volume \( V \), at temperature \( T \), containing charge \( Q \). The system has \( N \) counter ions and \( N \) co-ions for charge neutrality. Keeping the temperature and \( V \) constant the function can be simplified to \( F(N, Q) \). In more recent work, several Maxwell-like relationships have been identified in the view presented above. Mathematical modelling on the relationship of work performed by the blue energy cycle to the changes in concentration and potential have been presented.

These dynamics are closely related to the ion transport and solution exchange mechanisms taking place inside the chamber when mixing occurs. To study these dynamics in detail, various models of ion transport and adsorption in porous and membrane electrodes have been created and tested. These also consider the electro-diffusion of ions in pores and how it’s affected by the change in salinity gradients arising from adsorption and desorption of salt occurring to and from these pores [14-16].

Several electro kinetic and electrochemical models have also been employed for explaining the observed potential evolution of different electrode materials in a CAPMIX cycle [17].

Since CAPMIX is an emerging technique a lot of work explaining the concept and various dynamics involved in the technique has been carried out. There exists a gap on how to optimize energy recovery and generation in a CDLE device. The studies carried out in this thesis are aimed at presenting a practical approach for making the application of this technique feasible at the lab scale. The following are the objectives for bridging this gap.

### 1.1.2.6 Objectives

- To build an experimental rig for the purpose of controlling, monitoring the CDLE device in real time and to facilitate data collection.
- To test the effects of process parameters during charging/discharging on the energy recovery performance of a CDLE device.
• To test the effects of process parameters during the open circuit step on the potential evolution arising from capacitive double layer expansion.
• To test the effects of activated carbon electrodes coated with a high di-electric constant, nanostructured material on potential evolution in CDLE.
• To further optimize energy recovery by altering the cycle originally proposed by D. Brogioli.
2 Methodology

2.1 Experimental Setup

A simple circuit was designed to test the CDLE device and principle using a PeakTech 3210 DC power supply, a Keithley 2110 DMM & a load resistance of 1.5 ohms. An Arduino equipped with a relay shield was used to control the circuit states namely, (a) Charging, in which, relay 1 is on while relay 2 is off. (b) Open circuit in which, both relays are off and (c) Discharge, in which, relay 1 is off while relay 2 is on.

The Keithley 2110 DMM was used for voltage and current measurements as shown in Fig.1. These measurement and control devices were interfaced to a PC via LabView. LabVIEW allows for in-situ data processing and provides real time monitoring capabilities for Voltage, Current & Power curves. The LabVIEW front panel and back end program can be found in Fig. 2 & 3 respectively. Voltage, Current measurements were taken by the DMM every second, transmitted to the PC via a USB connection where by LabVIEW coalesced arrays used for displaying curves in real time. An Arduino interfaced with LabVIEW was used for controlling the circuit from the front panel.

A peristaltic pump was used for controlling the flow of electrolyte to the cell. The experiments were operated in continuous mode i.e. the input and output reservoirs were separate and formed an open loop.
2.1.1 CDLE Cell

The EDL capacitor in use for producing blue energy via CAPMIX is a sandwich constructed of graphite current collectors, Activated Carbon Cloth (ACC) electrodes and a thin cellulose separator in an acrylic housing. The electrolyte i.e. sea water/fresh water, flows continuously to and from the chamber via a peristaltic pump. The device is 17 x 17 x 1.73 cm with a chamber volume of 37 cm³. The maximum electrode sizes the device can house is 100 cm². Typically, 64 cm² square electrodes are used with tolerances left to prevent cloth fibers from short circuiting around the separator. The electrode
stack can consist of 3 electrodes per side with a surface area of 1200 m²/g, separated by a porous cellulose sheet of thickness 200 µm. All electrical connections are made to flat graphite current collectors. These plates have high conductivity and make an even contact with the whole electrode face area.

![Fig. 2.3 Blown up c/s view of the CDLE device. (1) ACC electrodes. (2) Cellulose Separator. (3) Graphite Current Collectors.]

2.2 Methods

The operation of a CDLE device for the purpose of CAPMIX involves a few key physical parameters. The typical CAPMIX cycle was divided into parts, namely, charging/discharging & expansion. Evaluation of these subparts lead to the identification of parameters affecting them. Once identified, the effects of these parameters on device performance were investigated in the order presented below.

![Fig. 2.4 Experiments on effects of operational parameters for optimizing charge/discharge of the CDLE device.]

The operational parameters used during charging and discharging the CDLE device were optimized experimentally. The energy recovery of the charge storage device was optimized by determining experimentally how the parameters, namely, (a) Flow Rate of electrolyte, (b) Charging time, & (c) Applied potential effect device performance. Fig. 1 shows the sub-parts of the cycle that were optimized. After optimization of these experimental parameters and maximizing energy recovery, parameters effecting voltage gain were optimized. A typical sub-cycle is shown in Fig. 2.

The investigation of the effects of process parameters on cycle performance consisted of data collection and subsequent analysis. The measurement setup allowed for the collection of cell voltage & current curves. These curves were later used for deriving other characteristics such as Charge (Coulombs), Electric power (Watts), Energy (Joules) & Capacitance (Farads).

These derived values were plotted. The analysis of these plots revealed characteristic information about the effect of the parameter being tested on the device performance such as energy recover, energy generation etc.

After testing the effects of operational parameters on voltage gain, a novel protocol for maximizing energy recovery and minimizing the effects of increased internal resistance after a CAPMIX cycle was developed and presented.

After optimization of process parameters for charging/discharging, voltage gain and development of a new operating protocol for maximizing output power and energy recovery, new electrode materials with a high dielectric constant were grown and tested in the CAPMIX cycle (Fig. 3).
Fig. 2.6 Testing new electrode materials after process optimization
3 Results & Discussions - Effects of process parameters on energy recovery from a CDLE device

3.1 Effects of electrolyte flow rate on energy recovery

Experiments were carried out to optimize the flow rate of feed solution through the supercapacitor. The prototype CDI device is of a flow through configuration, meaning, that the feed solution/electrolyte flows perpendicular to the electrode matrix through the anode to the cathode or vice versa. The activated carbon electrodes are materials comprising of micro, meso and macro pores. On addition to adsorption sites, the macropores also serve as pathways for the flow of electrolyte from where the exchange of salt and ions with the micropores takes place via diffusion [15]. Thus, assuming that variations in flow rate would affect the concentration gradients and availability of ions for adsorption/desorption to and from micro/macropore EDL’s, experiments were conducted to gain insights into the effects of such variation on charging/discharging efficiency of the CDLE device. At higher flow rates, a higher volume of solution is exchanged improving the kinetics for adsorption/desorption of ions. As adsorption/desorption occurs, the concentration of counter ions in micropores, where transport is diffusion dominated increases/decreases. Simultaneously, the concentration in macropores decreases/increases. Decreased concentration in macro pores affects kinetics of adsorption and places limitations on diffusion. For efficient charging and discharging, this difference in counter-ion concentration between macro & micropores should be maintained close to its maxima. A higher rate of fresh electrolyte replacing old solution should aid in this process.

![Fig. 3.1 Trend in energy efficiency as the flow rate of electrolyte through the ACC matrix is varied. Standard deviation was calculated from 2 data sets.](image-url)
Previous studies on flow rate have shown a positive influence of increasing flow rates for a particular current load on desalination performance [18]. However, in this study, negative effects arising from very high flow rates have also been studied.

Fig. 1 shows the trend in energy recovery as flow rate of the electrolyte flowing through the electrodes is varied. Contrary to the assumptions used for motivating the experiment, data shows diminishing energy recovery with increasing flow rates. These results have been derived by integrating power curves measured during charging and discharging. To isolate the cause of the observed drop in Fig. 1, coulombic efficiency derived from current curves measured during charging/discharging is plotted in Fig. 2.

![Fig. 1 Trend in energy recovery as flow rate of the electrolyte flowing through the electrodes is varied.](image)

The coulombic efficiency i.e. the percentage of input charge that was recovered across the load during discharging falls almost linearly with increasing electrolyte flow rates. This trend establishes a correlation between charge leakage and volume of the electrolyte exchanged or velocity of flow/drift velocity of ions. The decrease in the percentage of input energy recovered can in part be explained by increasing charge leakages.

Flow through electrodes have been shown to overcome mass transfer limitations vs. flow by electrodes in various electrochemical techniques such as microbial fuel cells, electrochemical disinfection & CDI [19-22]. More extreme pH fluctuations in flow through CDI in comparison to flow by CDI have been observed. These pH fluctuations may arise from faradaic or non-faradaic processes. Increased H₂O₂ production and faster dissolved oxygen decay rates have also been observed [23, 24]. These observations can be used to support a correlation between flow of electrolyte and electron transfer processes and how flow of electrolyte has direct consequences on the kinetics of these processes by modifying mass transfer rates and number of available sites. An increase in flow rate should achieve the same effects, explaining the

![Fig. 2 Trend in Coulombic efficiency as flow rate of electrolyte through the ACC matrix is varied. Standard deviation was calculated from 2 data sets.](image)
higher charge leakages observed in Fig. 2. However, these conclusions are speculations at best and a more complete treatment which includes investigation of effluent water is required to establish their validity.

Another possible reason for the observed behavior of charge efficiency could be an increase in ionic leakages due to forces arising from convection. In the macropores which are pathways for flow, at higher flow rates forces from the motion of ions and water molecules could overcome the forces of electrostatic attraction that hold the ions in the double layer.

An important feature of effects of flow rates was observed in comparing capacitance values at different flow rates as plotted in Fig. 3. The values were derived by taking the ratio of charge (area under the current curve) and change in voltage between $t_0$ (Open Circuit Potential after charging) & $t_{\text{final}}$ (Potential after discharging). These can be linked to changes in flow profile as a result of change in flow velocity. It is believed that higher flow velocities will modify the dynamics of fluid flow inside the cell. The decreasing capacitance in Fig. 3 is a result of turbulent flow giving rise to a higher number of dead zones in the ACC matrix making ion exchange poor in such regions, decreasing the number of active sites for adsorption, thus decreasing capacitance.

![Capacitance variation w.r.t electrolyte flow rate](image)

**Fig. 3.3 Effects of flow rate on double layer capacitance. Standard deviations calculated from a min. of 2 data sets.**

On the basis of the results obtained in this study, it can be concluded that flow rate of electrolyte should be high enough to kinetically facilitate adsorption of ions in the double layer (charging) for a particular current load while also being low enough so as not to promote unwanted charge transfer processes, dead zones and charge leakages due to convection in the ACC matrix.
3.2 Effects of charging time on energy recovery

Experiments were conducted to find optimal time of charging for the CDLE device. As an external potential is applied across the device, current flows to the electrodes and ions of opposite polarity are absorbed. As ionic population in the double layer builds up towards its maximum capacity at a given voltage, the current gradually drops. This drop in current directly indicates a drop in the rate of adsorption of counter ions. If the charging time is lower than its optimal value, the double layer formation will be incomplete while if the charging time is longer that this optimal value, current consuming processes will continue to occur even after complete formation of the double layer. Thus, charging time is a crucial parameter to optimize for minimizing energy loss and maximizing energy recovery from a CDLE device.

![Energy efficiency as a function of charging time](image)

*Fig. 3.4 Optimization of charging time at the applied voltage and concentration. Standard deviations calculated from a minimum of 2 data sets.*

Fig. 4 depicts energy recovery derived from power measurements during charging and discharging. The energy recovery almost follows a Gaussian trend with the highest recovery observed for a charging time of 16 min (1000 s). The energy recovery falls as the charging time is deviated from this point. There are 2 pathways of energy loss that have been identified, namely, (i) Heat loss via resistive elements in the circuit and the CDLE device structure, (ii) Charge leakages at the electrode/electrolyte interface owing to faradaic reactions.

Analyzing the current charge/discharge curves can reveal useful information for a qualitative description of energy loss. For such a description, since the energy loss pathways are charge related, the current curve can be divided into 3 arbitrary regions as shown in fig. 5.
The 1st region constitutes the beginning of charging when the cell voltage is minimum while the current values are maximum. Power dissipated as heat over resistive elements given by \( P = I^2R \) (ohm’s law) is dominant in this region of the charging cycle. Towards the end of charging, the voltage of the CDLE device begins saturating while the current decays before settling at a finite minimum value. This is the 3rd region of charging where resistive losses are low and charge leakage dominates. It is assumed that the charging process is most efficient in the 2nd region. The optimal charging time is thus a fine balance between the 3 and for the particular experimental conditions used in this study was found to be \textbf{1000s}. This claim is further supported by Fig. 6(a) which depicts the open circuit drop as a function of charging time. Open circuit drop is the sudden drop in potential when device is switched to open circuit (power is disconnected). This drop saturates after the 1000 s mark, confirming optimum balance between charge adsorption and energy recovery. Fig. 6(b) is a comparison between charge to voltage ratio between input and output for various charging times. The input ratio increases linearly with time while the output ratio saturates. The increasing difference between them is an indication of charge leakages.
3.3 Effects of applied potential on energy recovery

Applied potential, charging voltage or operating voltage is one of the key limitations in modern supercapacitors. It refers to the external battery/supply potential that is used for charging these devices. When the applied potential is exceeded above a rated value, electrolyte breakdown occurs. In the CDLE device, sea water breaks down at 1.2 V. This process consumes electrons from the electrode and thus results in energy loss. However, other electron transfer processes can also result in energy loss via charge leakage. According to ohm’s law, energy lost as heat is also directly proportional to applied potential. Thus, an electrical analysis of the CDLE device at various applied potentials was carried out to select an optimal voltage for maximum energy recovery.

![Energy recovery at various applied potentials](image)

Fig. 3.7 Variation in energy recovery as a function of applied potential. Standard deviations calculated from a minimum of 2 data sets.

The derived energy recovery values are plotted in Fig. 7. Highest energy recovery of 38 % was achieved with a low applied potential of 200 mV closely followed by 36 % at 600 mV. Since capacitance of a double layer capacitor is proportional to voltage according to the Gouy - Chapman theory [25-31],

\[
C_D = \frac{\partial \sigma}{\partial \psi} = \frac{\varepsilon \varepsilon_0}{\lambda_D} \cos h \frac{\psi^m z e}{2 k_B T}
\]

(1)

Where, \(C_D\) is diffuse layer capacitance & \(\psi^m\) is the potential on electrode side. Previous studies have shown that a higher capacitance results in higher energy production from CAPMIX. An applied potential of 600 mV is thus recommended, providing a balance between energy loss via mentioned pathways and energy production from capacitive mixing.
To gain better insights into which energy loss mechanism is the major contributor to the observed difference in energy recovery values, a comparison of input charge to output charge is plotted in Fig. 8.

![Comparison between input & output charge at various applied potentials](image)

*Fig. 3.8 Comparison of input and output charge at various applied potentials.*

The difference between input and output charge rises as the applied potential is increased. This divergence in the charge curves points towards higher charge leakages when the voltage is increased. Charge leakages are caused due to faradaic reactions at the electrode electrolyte interface, the rates of which are potential energy dependent.

To further investigate the nature and possibility of these faradaic reactions, the potential of 3M HCL treated ACC electrodes was measured in open circuit & at various applied potentials vs. an Ag/AgCl electrode and later converted to Standard Hydrogen Electrode values. The standard electrode potential $E^0$ of Ag/AgCl is 0.230 V against SHE. A measurement setup (Fig. 9) was built for these measurements and the results are plotted in Fig. 10. Redox reactions are electron transfer processes that occur via oxidation at the anode and reduction at the cathode.

At the anode, several oxidation reactions are possible, namely, oxidation of the carbon electrode which occurs at 0.21 V/SHE, oxidation of Cl$^-$ to free chlorine at 1.36 V/SHE, further reactions involving byproducts and oxidation of water resulting in oxygen evolution at 1.23 V/SHE [32, 33].

Anodic oxidation reactions –

\[
C + H_2O \rightarrow C = O + 2H^+ + 2e^- \quad @ \ 0.21 \text{ V/SHE}
\]

\[
C + H_2O \rightarrow C - OH + H^+ + e^- 
\]

\[
C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- 
\]
\[2Cl^- \rightarrow Cl_2 + 2e^- \quad @ 1.36 \text{ V/SHE}\]

\[2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad @ 1.23 \text{ V/SHE}\]

Dissolved oxygen in water is a result of diffusion from the atmosphere. As a result, at the cathode, oxygen reduction reactions occur via two pathways, reduction to H\textsubscript{2}O\textsubscript{2} at 0.69 V/SHE and reduction of H\textsubscript{2}O\textsubscript{2} to H\textsubscript{2}O at 1.78 V/SHE.

Cathodic reduction reactions –

\[O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad @ -0.69 \text{ V/SHE}\]

\[H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad @ 1.78 \text{ V/SHE}\]

\[C + H_2O + e^- \rightarrow C - H + OH^-\]

Due to OCP of ACC & non-neutral pH at the electrode/electrolyte interface resulting from an adsorption of H+ and OH- ions, ORR is thermodynamically promoted and becomes unavoidable even at operating voltages lower than the standard redox potential of O\textsubscript{2} [2]. Previous studies have reported finding H\textsubscript{2}O\textsubscript{2} following a decay in DO content for charging voltages as low as 0.5 V [34]. A considerable amount of hydrogen peroxide (0.047 ± 0.009 mg) present at an applied voltage of 0.6 V, which increased with increasing applied voltage has also been reported.

As seen from Fig. 10, the resting potential of 3 M HCL treated ACC is 0.4702 V/SHE making carbon oxidation feasible at the anode even without the application of an external potential. The highest potential used for optimizing the charging/discharging process of CDLE was 1 V,
which translates to the anode being at 0.877 V/SHE and cathode being at -0.123 V/SHE. Comparing these values to the standard potential of cathodic reduction reactions found in literature, it’s clear that no redox reactions are possible other than carbon oxidation. This explanation is further supported by the low extrema of the difference between input and output charges observed in Fig. 8 and it can be concluded that charge leakages only hold a small stake in energy loss.

![Electrode potential vs. SHE at various applied voltages](image)

*Fig. 3.10 Standard ACC potential vs. SHE at various externally applied potentials*

The major contributor to poor recovery at higher voltages seems to be energy lost as heat over resistive elements. When power is applied to the CDLE device at the beginning of the charging cycle, the voltage drop across the electrodes is low and thus a major part of the applied voltage drops over ohmic resistive elements in the circuit. As charging proceeds, the voltage drop across the device electrodes increases & current drawn by the device reduces, thereby reducing the voltage drop and heat loss over these parasitic resistances w.r.t. time.

\( \frac{dI}{dt} \) is the rate of current decay as charging proceeds,

Which should be followed by the rate of decay of heat loss over ‘R’ as \( I^2R \).

In the above experiments, the charging time was kept constant.

Thus, for a given voltage, the energy leaving the power supply can be given by,

\[
E_{\text{supplied}} = \sum_{n=t_0}^{t_f} P_n = \sum_{n=t_0}^{t_f} I_n \cdot V
\]

where, \( t_0 \) denotes beginning of charging & \( t_n \) denotes the end,
The energy lost in an ohmic element of resistance R as heat at an instant,

\[ E_n^{heat} = I_n v \cdot 1 \]

where, \( v = I_n R \), is the voltage drop over the resistive element,

And, Energy reaching the CDLE device at time t,

\[ E_{CDLE}^t = E^{supplied} - E^{heat} = I_t(V - v) \cdot 1 \]

Also,

\[ V \propto v \]

Therefore, heat loss increases and energy recovery decreases as applied potential is increased.
4 Results & Discussions - Effects of process parameters on voltage gain during CDLE

4.1 Effects of fresh water flow rate on voltage gain during CDLE

![Graph showing the variation in voltage gain with varying flow rates of fresh water.](image)

Fig. 4.1 Variation in Voltage gain with varying flow rates of fresh water. Standard deviations calculated from a minimum of 2 data sets.

Fresh water sources all over the world are diminishing. Entropic energy production via controlled mixing of solutions with different concentrations then is a double-edged sword. Thus, optimizing this process is of utmost importance. As discussed in previous sections, varying the flow rate of electrolyte through the CDLE device has major impacts on its performance. Primed with this information, experiments were conducted to analyze the effects of fresh water flow rate on the voltage gain in the CAPMIX process. The charging/discharging of the device was carried out with the optimized parameters from the previous section. After formation of the double layer, the power supply is disconnected and the electrode chamber is flushed with an NaCl solution of a concentration lower than that used for charging. This solution of lower salt concentration is referred to as fresh water. In this particular study the fresh solution used is De-ionized water. The flow rate of this fresh water was varied between 3 to 78 ml/min. The effects on voltage gain from this variation are plotted in Fig. 1. A gaussian trend is observed with the highest voltage gain of 165 mV resulting from a flow rate of 18 ml/min. As the flow rate is increased the voltage gain decays. Fresh water flowing into the ACC matrix will give rise to turbulence. This turbulence causes dead zones which is believed to reduce the total surface participating in capacitive mixing. This results in a lower voltage gain at higher flow rates. The volume of fresh water consumed to reach a stable voltage after capacitive double layer expansion at different flow rates is presented in Fig. 2. Volume of fresh water consumed rises linearly before exponentially increasing between 60 to 78 ml/min. In
conclusion, it was found that flow rate during CDLE has major implications on the amount of energy produced and volume of fresh water consumed.

Fig. 4.2 Volume of fresh water consumed during capacitive double layer expansion at various flow rates. Standard deviations calculated from a minimum of 2 data sets.
4.2 Effects of concentration gradient on voltage gain during CDLE

![Graph showing voltage gain as a function of difference in salinity](image)

Fig. 4.3 Changes in voltage gain as the concentration of low salinity solution is changed. Standard deviations calculated from a minimum of 2 data sets.

A simplified picture of energy production from capacitive double layer expansion considers a traditional parallel plate capacitor, the capacitance of which is given by,

\[ C = \frac{\sigma A}{d} \]

Where, A is the overlapping areas between the plates & d is the distance between them,

When the chamber is flushed with a solution of lower salt concentration, the diffusive forces force the ionic layer away from the electrolyte. In other words, ‘d’ increases and ‘C’ decreases. Capacitance is also defined as the ratio of charge to voltage.

\[ C = \frac{Q}{V} \]

The mixing is done in open circuit, i.e. no charge exchange takes during the process and Q remains constant, resulting in a decrease in ‘C’ which in evidently raises ‘V’ to maintain the above equation.

Since the energy stored in a capacitive system is given by,

\[ E = \frac{CV^2}{2} \]

The total energy of the system after fresh water flushing increases. The Gouy Chapman model can be employed to describe the same logic for an EDL capacitor. The ionic distribution next to a charged surface dipped in an electrolyte depends on the concentration of the solution and the charge stored on the surface. The electrostatic interaction from the charged surface extends to a distance ‘\( \lambda_D \)’ in the solution called the Debye length which is around 0.4 nm for sea water (0.5 M) and is given by [25-31].
\[ \lambda_D = \left( \frac{K_B T \varepsilon_0 \varepsilon}{2N_A z e^2} \right)^{\frac{1}{2}} \]

Where,

c is the ionic strength of the solution in mol/m³

The above equation states that Debye length increases as the concentration of electrolyte is decreased. The relationship between capacitance and Debye length is as follows,

\[ C_D = \frac{\partial \sigma^0}{\partial \psi} = \frac{\varepsilon \varepsilon_0}{\lambda_D} \cos \frac{\psi m z e}{2k_B T} \]

The charge – voltage relationship is as follows,

\[ \sigma^m = (8k_B T \varepsilon \varepsilon_0 N_A c)^{1/2} \sinh \frac{\psi m z e}{2k_B T} \]

As a result, the energy stored in the CDLE device increases proportionally to the difference in concentration ‘c’ of the electrolytes being mixed, i.e.,

\[ \Delta V \propto \Delta \lambda_D \]

&

\[ \Delta E \propto \Delta \lambda_D \]

Experiments were conducted to analyze this change in voltage gain for fresh water samples of different ionic strengths against sea water (0.5 M NaCl). The results are plotted in Fig. 1. Highest voltage gain of ~160 mV was observed when the mixing solution being used was DI water with an approximate ionic strength of 10⁻⁶ M followed by ~100 mV with 10⁻⁴ M. The ionic strength was converted from resistivity values (15 MΩ.cm). However, since the internal resistance in inversely proportional to ionic strength of the electrolyte, it was found that better energy extraction is achieved when mixing samples are 10⁻⁴ in comparison to DI water as shown in Fig. 2.

![Fig. 4.4 Better energy extraction with fresh water concentration of 10⁻⁴ M. Some amount of dissolved ions are better for CAPMIX.](image)
4.3 Voltage gain during CDLE at various charging voltages

The ionic interface next to a charged object is a result of electrostatic forces attracting counter ions towards the surface and diffusive forces acting against it. Experiments were conducted to analyze the effects of charging voltage on voltage gain from capacitive double layer expansion to get insights into the upscaling potential of this technology. Fig. 1 shows a saturation of voltage rise at applied potentials of 600 & 800 mV after which the voltage gain from CDLE drops. Higher magnitude of electrostatic forces acting at higher voltages could be a cause for decreased voltage gain. However, since the double layer capacitance of a CDLE device also rises with voltage, an analysis of stored energy after expansion becomes necessary.

\[ C_D = \frac{\partial \sigma^0}{\partial \psi} = \frac{\varepsilon \varepsilon_0}{\lambda_D} \cos h \frac{\psi m z_i e}{2 k_B T} \]

![Fig. 4.5 Dependence of voltage gain from CAPMIX on charging voltage](image)

![Fig. 4.6 (a) Dependence of DL capacitance & (b) Energy gain on applied potential](image)
Fig. 2 & 3 show the variation in capacitance & a comparison between energy stored before and after double layer expansion with a fresh water concentration of $10^{-4}$ M NaCl. Thus, a lower voltage gain isn’t necessarily a sign of lower energy gain in practical applications. Energy production from the CAPMIX process upscales with capacitance which can be increased by high dielectric coatings or increasing the size and thus the surface area of the device.
5 Results & Discussions - Synthesis of Nanostructured MnO$_2$ coating on ACC

Following past observations of voltage gain dependence on capacitance during CAPMIX, a nanostructured coating of a high dielectric material was grown on activated carbon cloth to serve as electrodes in the CDLE device. Synthesis of MnO$_2$ coating was achieved following previous studies found in the literature [35]. The research followed describes a binder free process of synthesizing MnO$_2$ nanowires through a hydrothermal route using a precursor of potassium permanganate (KMnO$_4$) in DI water. The samples grown in the literature were 1.5*1.5 cm. In this study the process has been optimized for mass production and potential for upscaling has been determined. Electrodes of 64 cm$^2$ have been grown.

The growth process is presented in fig. 1. The grown layer was analyzed under a Zeiss SEM and results are presented in Fig.2. The average length of nanorods was 2-10 µm and width in the nanometer scale giving an average aspect ratio of 1:50.

Electrochemical analysis of the MnO$_2$ coated ACC electrodes was carries out on a Gamry electrochemical workstation. Cyclic Voltammetry and Galvanostatic charge discharge techniques were used to determine specific capacitance. The results are plotted in Fig. 3.

![Fig. 5.1 MnO$_2$ nanorods growth process on ACC](image-url)
Fig. 5.2 SEM analysis of MnO₂ Nanorods on ACC
The CV & GCD reveal useful information about the sample’s current & voltage response. An electrochemical cell with a Pt (platinum) counter electrode and an Ag/AgCl reference electrode was used in 0.5 M NaCl. The area under the current curve is the charge that flows in and out of the electrode. The potential window measured with respect to the reference electrode can be used in conjunction with charge that flowed in one half cycle (assuming symmetrical distribution between positive and negative half cycles) to determine capacitance. Mass/Area of the working electrode is then used to calculate specific capacitance according to,

\[ C_{\text{specific}} = \frac{Q}{2Vx} \]

Where,

Q is total charge flowing in and out of the device during the duration of the test,
V is potential window for CV and change in potential for GCD,
x is mass or area.

Table 1 presents these results for a 1.5*1.5 cm^2 sample.

The selection of scan rates is done on the basis of the electrode structure. A lower scan rate is better suited to analyze microporous structures where transport of ions is diffusion dominated.
The time scale of diffusion dictates the adsorption of ions into these pores and thus is a crucial parameter for selection of scan rate to ensure proper charging. The peak current values from the CV curve can be used to determine current density for a GCD scan.

![Figure 5.5 8*8 cm² electrode with MnO₂ NRs on ACC](image)

Table 1 Specific capacitance

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacitance (F/g) CV</th>
<th>Capacitance (F/cm²) GCD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 mV/s</td>
<td>10 mV/s</td>
</tr>
<tr>
<td>ACC</td>
<td>62.27</td>
<td>13.24</td>
</tr>
<tr>
<td>MnO₂ NRs on ACC</td>
<td>67.675</td>
<td>10.26</td>
</tr>
</tbody>
</table>

![Figure 5.6 Voltage gain comparison between plain ACC and MnO₂ NRs on ACC.](image)

These electrodes were further tested in the CDLE device for analyzing the effects of a high dielectric coating on energy production from capacitive mixing. The voltage gain values of 10⁻
M and 10\(^{-6}\) M NaCl against sea water (0.5 M) are plotted in Fig. 6. The performance wasn’t affected by the presence of MnO\(_2\) NRs. Further studies are required to determine the reason behind these observations and are left as future work.
6 Results & Discussions - A novel protocol for maximizing output power and energy recovery in a CDLE cycle

A major drawback of harvesting entropic energy via capacitive mixing is the subsequent rise in internal resistance of the cell due to the lower conductivity of the electrolyte following mixing. This rise in internal resistance depends on the concentration of fresh water being used for mixing and results in a serious loss of power at the output. According to Jacobi’s law, to maximize the electrical power of a source with a finite resistance, the load resistance should be as close as possible to the internal resistance of the source. However, this maximum power is still a function of the source resistance [36]. To improve the electrical power further, decreasing the resistance of the source remains as the only option. To achieve a minimal source resistance for energy recovery from the CDLE device a novel operating protocol was developed, Fig. 1.

![Fig. 6.1 Novel operating protocol for maximizing output power and energy recovery](image)

Fresh water is introduced to the electrode chamber after charging double layers in sea water. As the diffuse ionic cloud next to the electrode interface expands as a result of diffusive forces, the voltage of the CDLE device rises. Once all the sea water is replaced by fresh water and the voltage is at its peak value, the energy stored in the device becomes higher than its previous state as discussed in the introduction section. The energy stored in the device can now be harvested. However, due to the low conductivity of the electrolyte in step 4 the output power greatly suffers. This loss of power can be mitigated by flushing the chamber with an electrolyte of high concentration at the instant the device starts discharging. This prevents the loss of voltage gained from CDLE and at the same time maximizes output power and energy recovery. CDLE cycles run using this new operating protocol are presented in Fig. 2.
Using the alternate protocol following step 5 in fig. 1, the power was boosted 7-fold from 0.01 W after flushing the chamber with fresh water to 0.07 W after flushing with sea water at the beginning of discharge. The reduction in IR of the CDLE cell resulted in a more than 200% boost in current. The energy recovery was also improved dramatically and a comparison with the normal operating protocol is plotted in fig. 3. An improvement of ~13% was observed.
7 Conclusions and recommendations

Current trends and past advances in the field of blue energy were surveyed. A CDLE device was constructed using porous carbon electrodes. Parameters affecting various parts of the CDLE cycle such as charging/discharging & expansion (voltage gain) were identified. These parameters were systematically tested following the methodology mentioned in Chapter 3. It was found that operation parameters such as flow rate of the electrolyte, charging time & applied potential have a great impact on energy recovery in a CDLE device. After optimizing energy recovery, the effects of operation parameters relating to double layer expansion (potential rise) such as flow rate of fresh water solution, concentration of fresh water solution and applied potential (base potential) were tested. It was found that these parameters greatly influenced the evolution of potential during mixing.

Once energy recovery and generation were optimized, nanorods of a high dielectric material were grown on activated carbon electrodes in attempts of increasing the capacitance. The structures were grown successfully as observed from the SEM analysis. However, the increase in capacitance wasn’t as expected. Thus, the effects of a high dielectric coating on voltage gain during CDLE can’t be assessed from these results.

One of the main drawbacks of the CDLE cycle i.e. the subsequent rise in the internal resistance of the cell following mixing with a low salinity solution was tackled by developing a new protocol which involves flushing the cell again with sea water after expansion. Following this 2nd mixing step it was found that the electrical power could be boosted several times owing to a drop in the cell’s IR.

Thus, the objectives of the study were successfully achieved.

To further improve energy recovery, the resistance of the system can be improved. Multiple strategies could be implemented to different parts of the system. The internal resistance of any EDL capacitor is a function of the type of electrolyte being used, resistivity of the electrode material and the contact resistance between current collectors and electrodes. Since the application (blue energy) places constraints on the type of electrolytes being used (sea water, fresh water), the remaining two options to mitigate internal resistance are decreasing the contact resistance and improving the resistivity of the electrode materials. The contact resistance between current collectors and the ACC matrix can be reduced by growing Carbon Nanotubes on the surface of these current collectors to increase the surface area of contact. Since the total resistance is also a function of length, a grid like structure of a highly conductive material protruding outwards can be a useful solution. A 2nd strategy can be implemented to reduce resistive losses outside the device i.e. in the circuit. A specialized PCB can be designed and manufactured for this purpose.

Since only the diffuse part of EDL participates in expansion, the electrode materials can be modified to increase the proportion of charge stored in the diffuse layer vs. the IHP (inner Helmholtz plane). This can be achieved by reducing the number of surface groups or modification of the contact angle to further improve hydrophilicity.
Analyzing the MnO$_2$ coating under an SEM revealed high density of rods, a high aspect ratio and a high overall material loading. However, the flakes of NRs that were attached to the ACC fiber were heavy and thus easily fell off under forces of convection from flowing water. Thus, it can be concluded that the binding of the coating requires improvement. A simple way of doing so would be increasing the density of surface groups on ACC by treating with stronger acids such as 6M HNO$_3$ instead of 3M HCL.

The electrical circuit used in this study doesn’t provide means for storing the generated energy. Since the optimum operating voltage for the particular device architecture is 600 mV, a boost convertor of proper specifications can be used for transferring the generated energy to another supercapacitor.

A pilot plant at an accessible estuary can be built. The electrodes can be submerged in sea water while the kinetic energy of the river can be used during the expansion steps to displace sea water from the chamber, hence saving on electrical cost of pumping.

A lot of problems exist for making Blue energy via CDLE a feasible technology for energy production. However, these problems have practical solutions. From this study, Blue energy via CDLE seems to have the potential for carrying forward the future of electrical energy generation from sustainable sources.
8 References

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