Energy Harvesting from Salinity Gradient

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Abstract. Abstract: Energy harvesting from salt water received attention started back in 1970s’, but due to varying interests in the field and the growing potentials of other more promising sources, more work was required to fully establish it. This paper aims at identifying existing techniques of energy harvesting and the methodology involved determining an effective technique for small scale applications of the method. Capacitive deionization technique which involves electrochemical reaction was chosen for further analysis. The experiment was conducted to analyze factors affecting its performance including the electrode and the electrolyte. Combination electrode of carbon/aluminium, copper/aluminium and carbon/copper were selected and tested with different concentration of salty water. From the experiment, copper and aluminum electrodes were found to be the most effective among the rest. A DC-DC boost converter was used to step-up the voltage. Physical implementation of the circuit was done and the circuit was tested in which an input voltage of 1.022 V was boosted to 1.255 V. The efficiency of the boost converter was 38.17 % based on input power and output power obtained.

1. Introduction
Water is the most abundant resource in existence on Earth. 71 % of the Earth’s surface is covered in water, with the ocean holding 96.5 % of all the Earth’s water. With all the interest in renewable sources of energy being derived from the sun and wind, the extraction of energy of water never fully reached its full potential. A major method of harvesting the energy in water is by tapping in to the salinity differences of freshwater and salty water. The energy produced from mixing these two solvents produces significant electricity, with its effectiveness being determined mainly on the potential gradients.

Research on harvesting electricity using the concentration differences of freshwater and sea water has led to the coining of the term “Blue Energy” [1] to refer to the energy/power that is produced from harvesting sea water. The interest in energy harvesting reached a peak during the late 70’s as well as in recent times, corresponding on both instances, with lowered oil feed supply and security [2]. A significant research was carried by researchers at Massachusetts Institute of Technology (MIT) to develop a model to optimize the Pressure Retarded Osmosis system – the most common process for energy harvesting [3].

Energy or electricity produced from renewable energy sources have always fallen short in comparison to energy produced from non-renewable sources. This issue needs to be addressed if renewable energy (and more particularly Blue Energy) is to be deemed desirable to consumers as well as developers. One potential application of this technology is in in disaster affected areas (floods, earthquake), where there is little being done to ensure electricity generation. A portable extraction
mechanism for producing electricity needs to be researched, and a prototype development of harvesting energy from salty water can be utilized. Overall, there has been a recent spike in interest in energy harvesting from salty water for its potential. However, due to lack of information, and immature technology available, extensive research in the area needs attention.

This paper aims to review the implementation of the process of electricity production from salty water as well as to identify the possible implementation in Malaysia by reviewing the relevant researches in energy harvesting techniques.

2. Energy Harvesting Techniques

There are three major techniques in existence that are relatively effective on a large scale for energy harvesting from sea water which will be described.

2.1. Pressure Retarded Osmosis (PRO)

One method of energy harvesting from salty water is the process of Pressure Retarded Osmosis (PRO) which is best suited for a situation where river water meets the sea. According to [5, 6], PRO utilizes a semi permeable membrane which separates the river water (fresh water) from the sea water (salty water).

In PRO, there is not much large scale data related to how much electricity can be produced, but based on the research carried out by [4], it was shown that a power density between 0.11 – 1.22 W/m² was obtained. Two factors contributing to the amount of energy produced is the concentration of the solute and the type of membranes. The equation developed by Van’t Hoff for osmotic potential difference, is expressed by the activity of the salt in the two varying solutions [2].

\[ \Delta \pi = RT((\alpha_c - \alpha_d)) \]  

where \( \Delta \pi \) = osmotic potential difference; \( R \) = molar gas constant (8.314 m² kg s⁻² K⁻¹ mol⁻¹); \( T \) = temperature (°C); \( \alpha_c \) = activity of the salt in concentrated solution and \( \alpha_d \) = activity of the salt in diluted solution.

The exchange of salt activity between the two solutions is dependent on the type of membrane while the activity of the salt itself depend on its type and concentration. Studied has shown different performance of membrane in PRO and [7] reported that cellulose acetate membranes yield more favorable results in pressure retarded osmosis, with results of up to 2-5 W/m² being obtained. However, this is still far from the optimal value to achieve economic design. One PRO power generation pilot plant was built in Tofte, Norway in 2009 with 4 kW capacity. The targeted power density of the project is 5 W/m² with the type of membrane used. However, the actual performance of the plant can only generate roughly 1 W/m² [5], far lower than the target. The project was called off in 2014 due to the economic consideration. However, implementation of PRO as a complement in desalination water plant has a positive output. Maximum output power density can reach 13.5 W/m² which encourage its implementation.

2.2. Reverse Electrodialysis (RED)

In the concept describing the reverse electrodialysis (RED) process, Sodium (Na⁺) ions and Chlorine (Cl⁻) ions are placed in a compartment. The resulting chemical potential makes the ions transport through the membranes. For sodium ions, they move through the cation membrane toward the cathode and the chlorine ions move through the anion membrane toward the anode. The spontaneous process of ionic current is converted to electricity through red-ox reactions.

Based on the experimental data, in a typical scenario of freshwater and sea water mixing, the RED process yields a power density of 0.41 W/m², while in more concentrated mixtures, such as brine and concentrated fresh water, a power density of 1.2 W/m² is achieved. A pilot plant located at Afsluitdijk, the Netherlands is operating to harvests salinity gradient power through RED by a company called RedStack. The plant production forecast is 50 kW blue-energy per hour, and targeted to produce 200
kW per plant in future. As mentioned by Schaetzle and Buisman [12], the RedStack engineers must overcome challenges in implementing RED technology in the real environment as opposed to.

2.3. Capacitive Deionisation
Capacitive Deionisation or CDI is the newest method of energy production from water desalination using porous carbon electrodes. According to [11], the salt ions (NaCl) are removed from salty or brackish water when it is passed through porous carbon electrodes, where these ions are temporarily stored in the electrodes, thus causing them to be charged. Once this is done, the solution in the cell is altered by fresh water in an open circuit. This enables the stored charge to remain constant, and since the concentration of the solution has changed, it causes a greater amount of voltage to be stored. The surplus charge stored can then be tapped by discharging the cell. To describe further of how the process functions, two “super-capacitor” electrodes are connected and then placed in salt water. The difference in concentration gradients cause the electrodes to charge. Each electrode is also connected to a pole of an external capacitor in the circuit. This capacitor should operate at a low overvoltage and its capacity should be considerably greater than the capacity of the flow cell [11]. During operation, while the external capacitor gains charge of the flow cell during flow of salty water in the solution (ocean), the external capacitor will gain charge again as fresh water flows through the cell making the current direction switch (opposite). The processes of events that take place in the flow cell that affect the electrodes shall be discussed.

Once in contact with salt water (more concentrate), it causes the electrons to move through the circuit (external) causing one electrode to be positive and the other, negative. At the same time, within the porous electrodes, the electrostatic double layer develops where the electrodes in the layer itself hold charge. Formation of this layer continues to vary when it is placed back in fresh water which causes it to expand ($V_{cell}$ initially small becomes equal to $V_o$) thus resulting in an increase in cell potential $V_{cell}$ more than $V_o$ causing the flow of electrons to reverse, re-charging the external capacitor. Throughout the experiments conducted, [6] achieved $V_o$ of between 0.3 V – 0.7 V, as the variation in charge stored depended on the salinity gradients. This was where carbon electrodes were used and in a fixed salinity concentration. If the initial solution had exceeding salinity and was then placed in fresh water or if the system was considerably larger (industrial scale) it would yield much higher voltages. In capacitive deionization, it does not incorporate membranes unlike the other two techniques which eliminates the limitation due to the membrane itself especially the cost and risk of fouling phenomena. Even though it is relatively new, it has the potential to produce more as it grows bigger. It is even more suitable for small scale or portable energy harvesting.

3. Experimental Setup and Procedure
This section describes the experimental set up and procedure conducted. Experiments were carried out to analyze varying concentrations of salt water and their effect on the electrodes as well as the amount of voltage/current that can be generated from electrochemical reaction. Different type of electrode material was tested. The experiment was conducted for a single cell and followed by a series connected cell.

Figure 1 shows a single cell with activated carbon as the electrode and Figure 2 shows the series connected cells to get accumulated output voltage. The dimensions of electrodes (rod) were:

- Aluminium: 150 mm × 75 mm × 0.5 mm
- Copper: 125 mm × 50 mm × 0.5 mm
- Carbon: 50 mm × 0.5 mm

For carbon electrode, both rods and powdered activated carbon was used in the experiment. The powdered material increases the surface area and should be able to produce more energy due to the electrochemical reaction.
Figure 1. Side view of the cell using powdered activated carbon electrode

Figure 2. Set up of experiment for series connected cell

The salty solution to represent seawater is prepared by dissolving particular amount of salt into water to obtain required concentration. The pair of electrodes is immersed into the solute accordingly and the reading was recorded at 5 minutes interval. Redox reaction of aluminium electrode and carbon electrode when immersed into the salt water occurs according to the following chemical reaction:

$$4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3$$

(2)

The open circuit voltage is measured using multimeter, where the load is disconnected. In measuring the current, a 100-ohm resistance is used and connected between the two terminals. The anode and cathode must not have touched and must be checked before the measurement. This is important to avoid short circuit and ensure the reliability of the data measured. Multiple cells can be connected in series to increase the voltage or connected in parallel to increase the current as shown in Figure 2.

4. Result and Discussion

This section focuses on the results of the experiments carried out on varying concentrations of salt water and their effect on the electrodes as well as the amount of voltage/current that can be generated from electrolysis. Two sets of experiments were carried out at varying concentrations of salt water to identify if increasing salinity effects power generation, with 3 different sets of electrodes used. The electrodes used were aluminium, copper and carbon. The first set of experiment uses 1.150 M concentration while the second set of experiment uses a concentrated solution which is 2.875 M. Figure 3 and Figure 4 show the result for the first set up.
Based on the results, the most effective energy generation is obtained for copper/aluminium, since the generated current is higher than the rest and its voltage is comparable to the carbon/aluminium. Though carbon/aluminium shows the highest voltage output out of the three sets (between 1.7-1.8 V), the current output is much less (1 mA) which makes it an unreasonable pick. Carbon and copper showcases by far the worst power generations in terms of both voltage and current. What is interesting to note, is that a concentration of 1.150 M of solution was utilized in order to determine the power outputs for a solution that is neither saturated nor completely distilled.

The second set of experiments was using a saturated solution to identify the effect on energy generation. The concentration was calculated at 2.875 M. This specific concentration was obtained and tested as it is saturated and increasing the concentration further will not have much impact on the results obtained. Figure 5 and Figure 6 shows the result for the second experiment.

![Figure 3. Voltage Comparison at Concentration 1.150 M](image)

![Figure 4. Current Comparison at Concentration 1.150 M](image)

![Figure 5. Voltage Comparison at 2.875M](image)
Figure 6. Current Comparison at 2.875M

The experimental results for the saturated solution of 2.875 M further proves that the most effective electrode combination is copper/aluminium with higher current outputs being produced at more concentrated solutions.

We can see that in general, the more concentrated solution provides a better power output, and maximum of 15.65 mA was achieved initially. Carbon and aluminium continued to provide the highest voltage from the sets (1.92 V), but still did not provide sufficient current as compared to copper and aluminium. One major observation is that over time, the electrodes went through a slow disintegration process, though copper reacted the most and there were significant amounts of copper in the solution. This can cause the water to be contaminated, though if the set up was placed in a flowing mechanism or even the sea, the solution will be continually renewed thus avoiding this issue.

4.1. Boost Converter Circuit

The techniques mentioned above produces low voltage and current. With low supply of energy, they are unsuitable to be used for electronic devices and many other applications. So, in order to utilize the blue energy, an electronic circuit is required. According to [16], most of the energy harvesting circuit involves power levels that are low, in which a low power consumption circuit must be designed and used to avoid the loss of already low level power harvested by these methods. DC-DC step down converters were mentioned to be a low performance circuit that can be used in energy harvesting circuit. Besides that, [17] uses different topology for their low energy harvesting circuit. In their paper, a step-up voltage regulator was used instead of a step-down converter. The step-up voltage regulator was also efficient due to the implementation of a system in which it will not be turned on if the starting voltage is below the specified voltage. This is done to avoid consummation of power even if the circuit is not boosting the output voltage.

The average output voltage obtained is around 0.5 – 0.7 V for each cell. Since the voltage obtained per cell is only ~0.5 V, we need to boost the voltage to a higher voltage. By combining two of these cells, up to 1 V can be achieved. This 1 V can be boosted to 3.3 V or 5 V using a DC-DC boost converter circuit for powering sensor nodes that requires higher voltage but lower current. So, a boost converter will be chosen instead of a buck converter due to the already low voltage produced by the cell. Table 1 shows the parameter of the circuit.

| Parameters                              | Boost Converter |
|-----------------------------------------|-----------------|
| Inductance value (H)                    | 625 µH          |
| Switching frequency for the transistors (Hz) | 100 kHz         |
| Load resistance value (Ω)               | 1 kΩ            |
| Duty cycle of the transistors           | 0.5             |
| Capacitance value (F)                   | 0.5 µF          |
Table 2 Voltage, current and power for boost converter

| No. | $V_{in}$ (V) | $I_{in}$ (mA) | $P_{in}$ (mW) | $V_{out}$ (V) | $I_{out}$ (mA) | $P_{out}$ (mW) | Eff. (%) |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|----------|
| 1   | 1.02         | 0.26         | 0.27         | 1.25         | 0.13         | 0.17         | 38.2     |
| 2   | 1.02         | 0.25         | 0.26         | 1.25         | 0.12         | 0.16         |          |
| 3   | 1.01         | 0.24         | 0.25         | 1.25         | 0.12         | 0.15         |          |
| Ave | 1.02         | 0.25         | 0.26         | 1.25         | 0.12         | 0.16         |          |

In the circuit simulation results, the boost converter is able to boost the 1 V supplied to 1.61 V. The theoretical voltage calculated is 2V with duty ratio, $D = 0.5$. The output voltage obtained was not exactly 2 V due to switching losses and other external factors. For the buck converter, an input voltage of 1 V was also used and an output voltage of 0.347 V was obtained. Table 2 shows the output of the converter. Due to switching losses, the output voltage dropped to 0.347 V from 0.5 V. For the physical implementation of the boost converter circuit, an average of 1.255 V output voltage was obtained from an input voltage of 1.022. Based on the equation above, with a duty ratio of 50 %, the theoretical output voltage obtained should be 2.51 V. This means that the boost converter tested has an efficiency of 50 % for stepping up voltage. In terms of efficiency for power, the output power obtained was 0.162 W from an input power of 0.262 W. This means that 0.1 W was lost due to switching losses and other factors.

5. Summary
The development of a system for energy harvesting from salt water with the ability to extract as much electricity from the concentration gradients between fresh and salty water is required, as it would help industries in developing more efficient power plants. Study, experimentation and circuit simulation was carried out to determine the viability of the capacitive deionization technique and determine the amount of electricity that can be produced as well as devices that can be powered. From the experiment, copper and aluminium electrodes were found to be the most effective among the rest. It was able to produce about 1.4 V and 20 mA, approximately 28 mW for the test electrode. A DC-DC boost converter was used to step-up the voltage. Based on the simulation done, the boost converter was able to boost supply voltage of 1 V to 1.61 V. Physical implementation of the circuit was done and the circuit was tested in which an input voltage of 1.022 V was boosted to 1.255 V. The efficiency of the boost converter was 38.17 % based on input power and output power obtained. The output power per square centimetre was also calculated to be 0.664 mW / cm², which is economically viable.

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