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Harnessing 'Blue energy': A Review on Techniques and Preliminary Analysis

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Abstract. Energy harvesting from the ocean called 'blue energy' began in the 1970's and should have reached its peak by today, but due to varying interests in the field and the growing potentials of other sources, its development was delayed. Recently, it receives more interest and a number of institutes has deployed their pilot plant. Blue energy is a type of renewable energy based on salinity gradient where power is generated from different salt concentration in saltwater (the ocean) and freshwater (river). When the mixing of seawater and freshwater occurs, an increase in the entropy of this system is observed and free energy is dissipated. This research aims to identify and compare existing techniques or methods of blue energy harvesting developed over time. Five different techniques were reviewed, looking at their principle of operation, configuration and performance. Based on the review, capacitive mixing method was selected for further analysis. Experiment was conducted to evaluate different factor including the concentration of sea water, volumes and type of electrodes. The highest output power obtained is 89.7 mW, while the average is about 30 mW.

1 Introduction

The world's increasing demand for energy encourages the use of renewable energy as an alternative to fossil fuels that are getting scarce. Renewable energy is also important to reduce pollution and carbon emission caused by the usage of fossil fuels as energy sources. There is another source of renewable energy called "Blue Energy" [1] or better known as salinity gradient power that has yet to be fully utilized. Salinity gradient power relies on the different salt concentration in saltwater and freshwater to generate energy. When the mixing of seawater and freshwater occurs, an increase in the entropy of this system is observed and free energy is dissipated. This renewable energy is clean and green as it does not produce any wastes. Globally, with an estimated 2.6 TW [2] of energy output from blue energy, this renewable energy will be able to provide a significant amount of the global energy needs.

In order to harness blue energy, many techniques with different power generation mechanism were developed. Five different techniques in extracting blue energy will be discussed, which are: Pressure Retarded Osmosis (PRO), Electrodialysis (RED), Capacitive Double Layer Expansion (CDLE), Capacitive Donnan Potential (CDP) and Mixing Entropy Battery (MEB). Three of the techniques, which are CDLE, CDP and MEB are under

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capacitive mixing (CAPMIX) category. The main problem faced by blue energy technology is the non-economical energy production based on current methods of harvesting blue energy. These methods such as PRO and RED, requires expensive materials especially the membrane. The relatively new methods, CAPMIX, was introduced aimed to eliminate the use of membrane. Besides the cost effectiveness, blue energy is still a developing technology that yet to acquire more attention along with other alternatives.

1.1 Review of Blue Energy Technology

1.1.1 Pressure-Retarded Osmosis (PRO)

PRO is a method that extracts osmosis pressure difference between seawater and freshwater. By utilizing a semi-permeable membrane, this pressure difference can be used in power generation. The amount of energy produced depends on both concentration of the solutions as well as the membranes used. In [6], power density between 0.11 – 1.22 W/m^2 was obtained. By using different type of membranes, which is cellulose acetate, [8] reported that it yields favourable results, with power density up to 2-5 W/m2 being obtained. This relationship can be explained by the osmotic potential difference equation developed by Van't Hoff, that is expressed by the activity of the salt in the two varying solutions:

$$\Delta\pi = RT(a_c - a_d) \tag{1}$$

Where $\Delta\pi$ is Osmotic Potential Difference, R is Molar Gas Constant (8.314 m^2 kg s-2 K-1 mol-1), T is temperature (°c), a_c and a_d is activity of the salt in concentrated and diluted solution, respectively. A pilot plant for power generation through PRO was commissioned at Tofte, Norway on 24th November 2009 with capacity of 4 kW. The membrane used by the pilot plant can only generate roughly 1 W/m² which is an improved performance from the previous membrane type [4], but it is still far lower than the targeted power density of 5 W/m². This means that that membrane was unable to reach an economical break-even for the power generated per square meter and cost of the membrane. As a result, an economical barrier prevents the PRO from being a cost-effective method of generating power. It is also reported that the PRO plant is facing fouling problem, which is very detrimental causing the performance to deteriorate over time [5]. The fouling problem is classified into pore narrowing, pore plugging and gel/cake formation. Review papers on PRO were reported in [5-8] which provides thorough review in PRO process, membrane technology development, current development up to 2015, the fouling and cleaning process and the viability of the technology itself. Improvement area for PRO focuses on to reduce cost of osmotic power to increase membrane power output to at least 5 W/m^2, improved membrane design to get higher membrane area, improve efficiency of the PRO process, scale-up the system to commercial production and handling the fouling and cleaning issue [7].

1.1.2 Reverse Electrodialysis (RED)

Reverse electrodialysis (RED) utilizes two different types of membranes: anion exchange membrane (AEM) and cation exchange membrane (CEM) are stacked alternatingly between each other and placed in between an anode and a cathode. By flushing salt water and fresh water thorough the space in between these membranes, electrochemical potential is produced due to concentration difference between the solutions and ion-selectivity of the membranes. Positive ions, Na+ will diffuse thorough the CEM while the Cl- will diffuse thorough the AEM producing ionic current, thus generating power. Available research in the area covers many factors including the RED simulation model, membranes, configuration, other factors

affecting performance and even implementation of RED in micro and nano sizes. In a research by Z. Jia et al. [4], experimental results showed a power density of 0.93 W/m² based on artificial seawater and river water. It is not up to the targeted power density needed in order for RED to be economical in commercial uses. Currently, a pilot plant located at Afsluitdijk, the Netherlands is expected to produce 50 kW per hour, aiming to raise the output to 200 kW per plant. The progress of RED technology also evolved around the membrane technology. In [10], electro dialyzer equipped with a 0.19-mm spacer was tested with different concentration of dilute and power peak of 460 mW/m^2 was found at 0.54 cm/s linear flow velocity that gives an estimation of $6.79/kWh for the investment cost. J.Vermaan in 2009 has evaluated 6 commercial membrane to compare their performance and found out the best membrane could produce up to 1.2 W/m^2 with thermodynamic efficiency is around 14% - 35% [13]. In [14], besides evaluating performance of commercially available membrane, they had tested a tailor made membrane with significant reduction in resistance and achieved 1.3 W/m^2. More recent type of membrane was reported such as pore-filling ion exchange membranes with open area spacer that achieved 2.4 w/m^2 [15], asymmetric heterogeneous membrane [16] which can be applied in nanofluidic application and membrane with chevron corrugation that reduce the pressure drop is able to produce up to 0.89w/m^2. Works on modelling and simulation of RED process including the cell pair model based on thermodynamic and transport equation was proposed by Veerman [17]. An enhanced model is proposed by Tedesco to improve it to a wider range of concentration [18] but lacking few non-ideal effects. The work by [19] proposed to improve this model by including non-ideal effect such as water transport through membranes, concentration polarisation and parasitic currents.

1.1.3 Capacitive Double Layer Expansion (CDLE)

CDLE is a method where two electrodes are immersed into an ionic solution to form a super capacitor. When the electrodes are connected to power supply and charged, electrical charge is stored in the electric double layers (EDL) between the carbon and solution. When the salinity of the solution decreases, the potential difference across EDLs increases with constant charge. This occurs due to counter-ions in the EDL moving away from the electrode using free energy of the solutions, hence the name of this technique.

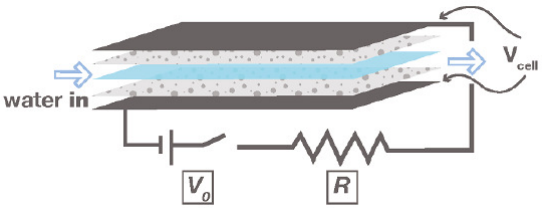

Fig. 1. Cell design of CDLE [4]

Fig. 1 shows the cell design of CDLE where the black layer indicates the electrodes, the grey layer is carbon and the middle layer is the solution. An experiment was done by D. Brogioli, et al. [20], in which the highest power density of 50 mW/m² was produced using A-PC-2 and NS30 as activated carbon materials. He stated that in order to improve the energy extraction thorough CDLE, different materials should be used for positive electrodes and negative electrodes. When two electrodes with different potential rises were used, the cell will experience a voltage rise, or called “zero charging” in which no external supply was needed for charging and discharging phase. This finding is supported by work by C.Hatzell which analyse the effect of strong acid functional group on electrode potential [21]. It was also reported that porous electrode produced more power as the total surface area are huge [22].

Further work by [23] reported that the porous electrode possesses an optimal charging potential and the pore size is an important parameter to optimize the power generated. This is also reflected in the study by [24] where the porous electrode is used and configuration of stacking them was evaluated. This technique has an advantage because it does not utilize membrane which has been a determinant factor for the technology to mature. It is expected that this technique or technology will be evolved faster.

1.1.4 Capacitive Donnan Potential (CDP)

In CDP, membranes are used to extract the salinity gradient energy. It is proposed by B.B Sales after the CDLE where an external supply is replaced by 'Donnan Potential' produced by adding ion-exchange membrane [25-26]. There are layers of AEM and CEM in between the layer of carbon and water flow. As a result, when water seawater flows through, ions from the concentrated seawater diffuse thorough the AEM and CEM into the electrodes. This movement of ions will produce current to an external load. After reaching equilibrium, freshwater will flow into the system and the ions inside the electrodes and membranes will diffuse out to form current in the opposite direction. The advantage of this technique is it does not require external power supply as the power is 'internally' generated [27]. Based on a research done by B.B. Sales et al. [28], maximum power density of 131.7 mW/m² was reached and an average power of 8.36 mW/m² was produced for one cycle of CDP technique. Optimization of distance between the electrodes in respect to the hydrodynamics of the flow of solution is recommended by them in order to improve this technique. Some works on CDP explaining the physics of the reaction, impact of electrode parameters, membrane and configuration are presented in [29].

1.1.5 Mixing entropy battery (MEB)

In MEB or sometimes known as faradaic pseudo capacitor [4], the energy is extracted from salinity difference between two solutions and stored inside the electrode. Through the use of battery-like electrodes, the ions are captured in the solution through redox reactions. The voltage of the electrodes used changes with respect to the solution and this will reflect chemical potential ions in the solution. The working principle of MEB can be divided into 4 steps. First, the electrodes are immersed into a low concentration solution such as river water, in which the battery is charged and the ions are removed from the electrodes. Step 2, the river water is exchanged with sea water which has higher concentration of ions and thus higher potential difference between the electrodes. The battery is discharged in step 3 and the ions are restored into the electrodes. Finally, the seawater is flushed out and replaced with river water which results in decrement of potential difference between the electrodes. In an experiment done by F. L. Mantia et al., they managed to produce power density of 138 mW/cm² [30]. The process was repeated for over 100 cycles (times) and the power density produced was stable. As mentioned, MEB might be a potential technique to harness blue energy due to the renewable nature of this technique; no loss of reagent even with repeated usage of the materials in MEB. Research conducted in [31-32] in evaluating different materials of electrodes and the chemical reaction formed that results in power generated. The electrolyte or the solution is also determinant factor in this technique. It has simple design but more studies are required in determining its reliability and the cost per power generated. Table 1 shows comparison among 5 techniques on their working principle (type), membrane characteristic, maximum power density reported to date and important remark.

Table 1. Review of five salinity gradient techniques

Technique	Type	Membrane Characteristics	Max. Power density produced	Remarks
PRO	Osmotic pressure difference	Water selective	1 W/m²	Pilot plant
RED	Electrochemical reactions	Ionic selective	0.93 W/m²	Pilot plant
CDLE	Ultra Capacitor	None	50 mW/m²	Experimental scale
CDP	Ultra Capacitor	Ionic selective	131.7mW/m²	Experimental scale
MEB	Electrochemical reactions	None	138mW/m²	Experimental scale

2 Experimental Procedure

Analysis was carried out on the mixing entropy battery technique. It can produce more power for the same dimension of setup and did not require any membrane which reduced the cost and complexity. However, the technique requires nano-electrodes. The solution used in this work is the salty water. Experiment was carried out to analyse several factors including the concentration of sea water, volumes and type of electrodes on the power density produced.

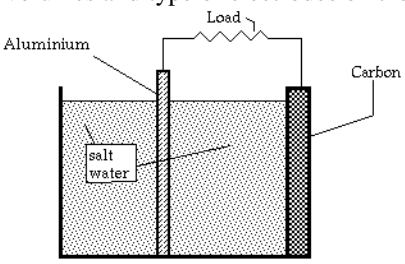

Fig. 2. Mixing entropy battery experimental setup

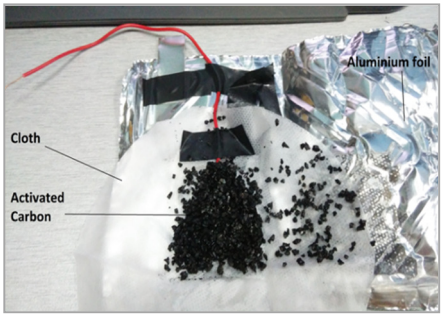

Fig. 3. Activated carbon in aluminium sheet

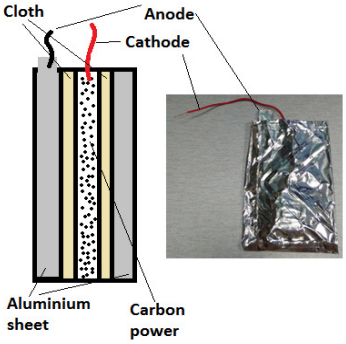

Fig. 4. Side view of the interiors

Figure 2 is a representative of how a mixing entropy experimental cell look like. Two electrodes, an aluminium electrode and a carbon electrode is prepared. A solution of salt water is also prepared by dissolving salt into water. When the aluminium electrode and carbon electrode are immersed into the salt water, a redox reaction occurs. The open circuit voltage Voc or the potential difference between the two electrodes is measured using multimeter. The current is measured by applying load or resistance in between the two terminals (both aluminium and carbon electrodes). In order to increase the voltage or current,

multiple cells can be connected in series to increase the voltage or connected in parallel to increase the current. Activated carbon powder were filled into layers of cloth (as a hydrophobic membrane between carbon and aluminium) connected with a multi-cores wire and an aluminium foil was wrapped around the cloth as shown in Figure 3 and Figure 4. The aluminium foil acted as anode while the activated carbon acted as air cathode. No continuity was allowed between the anode and cathode to prevent the anode and cathode from short-circuiting. Readings are measured and recorded accordingly.

3 Result and Discussion

Multimeter was used to measure the voltage and current of the cell. Different parameters such as concentration of solute, volume of water and type of electrolytes were used as variables in the experiment. The readings for both voltage and current were tabulated in detail, but is not included due to space. For all experiment, reading was taken over 30 min at 5 min interval. In the first experiment, three different concentrations are tested for the same type of electrodes and volume. The electrode used is carbon-aluminium, volume of water is 1000 ml and type of electrolyte is NaCl. For the second experiment, volume is varying from 500 ml, 750 ml and 1000 ml. In the third experiment, different type of electrolytes tested are water, salty solution and water with vinegar. Overall, the power density obtained reduced over time with the highest reading was obtained for carbon-aluminium electrodes. Graphs of output power was plotted for the three different variables.

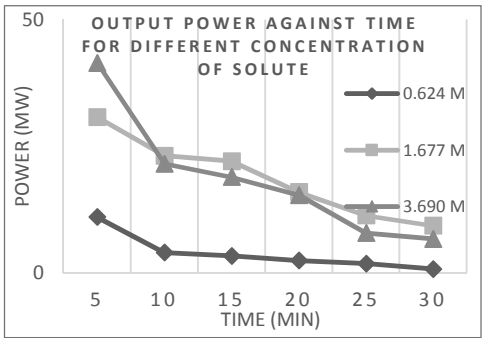

Fig. 5. Graph of output power against time for different solute concentration

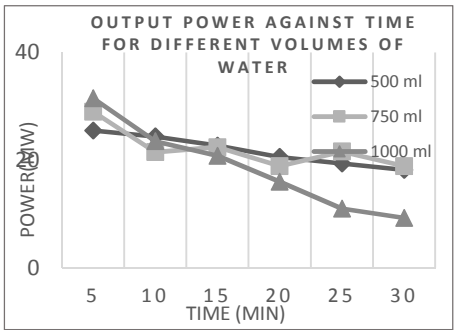

Fig. 6. Graph of output power against time for different volume of water

For experiment 1, it is worth to mention that more concentrations of solutes were tested before the three concentration is chosen to show the obvious finding. Voltage and current produced is measured accordingly. It is observed that the output voltage depreciated at higher rate in the solution with lower concentration. In Figure 5, it can be observed that higher concentration of solute provides higher output power. However, this is true only for the initial 5 minutes of operation. After 5 minutes, the output power for both 1.677 M and 3.69 M was almost equal. On the other hand, solute with lower concentration (0.624 M), consistently producing lower output. It can be concluded that concentration of solute has an optimal value which will produced maximum output power and increasing the concentration beyond this will not increase the output power. For this, the optimal concentration of solute for the cell would be 1.677 M. In experiment 2, three different volumes which having same solute concentration of 1.677 M were tested. The output power produced were consistent with the first experiment as plotted in Figure 6. It is observed that the volume of the water did not affect much on the output power. The purpose of third experiment is to analyse the output power produced by different type of electrolyte. Acetic acid+water is chosen to compare whether it can achieve more output power. Volume of the solution is 500 ml and concentration of NaCl solute is 1.677 M.

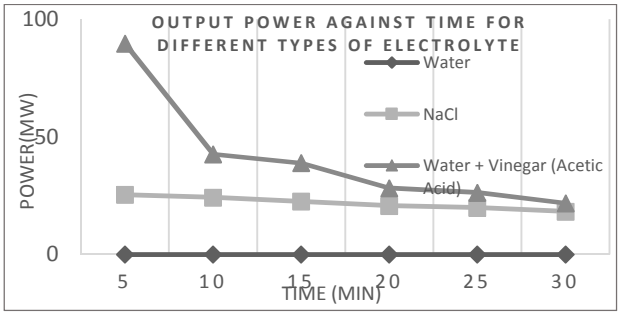

Fig. 7. Graph of output power against time for different types of electrolyte

Figure 7 represents the graph of output power against time for three different solutes, which were water, salt solution and water mixed with vinegar. The highest output power achievable was the mixture of water and vinegar. The salt solution provided the most stable output power among all three electrolytes. Water did not provide any output power due to the inability of water as an electrolyte.

3 Conclusion

Based on the comparison of techniques, mixing entropy battery was chosen for the experimental part of this research paper. Using dissimilar materials with different electrical potential for the anode and cathode electrodes such as aluminium and carbon, an experiment was conducted. Different variables such as volume of water, concentration of solute and type of electrolyte were tested in order to study their effects on the efficiency of the cell. It was found that volume of water does not affect the cell but the concentration of the solute is crucial for the cell. Besides that, the mixture of water and vinegar (acetic acid) was found to be the best electrolyte among all three different electrolytes used. The highest achievable output power was 89.7mW which is high enough to power low-power sensors. The output voltage and output current can be further increased or optimized. By using different configurations of placement for the electrodes, the surface area of the carbon can be increased which will increase the current obtained. Besides that, several cells can also be produced and connected in series to obtain higher voltage from the setup for higher voltage uses.

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