ELECTROCHEMICAL DEVICES BASED IN MIXING ENTROPIC BATTERY FOR BLUE ENERGY RECOVERY. A REVIEW

DISPOSITIVOS ELECTROQUÍMICOS BASADOS EN LA MEZCLA DE PILAS ENTRÓPICAS PARA LA RECUPERACIÓN DE ENERGÍA AZUL. UNA REVISIÓN

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ABSTRACT

Blue energy, an intriguing alternative, takes advantage of the chemical energy that is spontaneously released when two water solutions with different salt concentrations coincide, such as at the mouths of rivers that flow into ocean basins. This article aggregates the latest research on this form of energy, emphasizing the mixing entropic battery (MEB) as a fundamental electrochemical device for recovering entropic energy. SEM technology takes advantage of the redox reactions between cathodic and anodic materials to optimize energy recovery from salinity gradients. We review best practices in device optimization, highlighting the most effective redox reactions and materials employed. By assessing the volumetric availability and theoretical potential of blue energy, our findings underscore the viability of this renewable energy source and justify continued research efforts. This comprehensive synthesis aims to inform and guide future blue energy extraction and recovery innovations.

RESUMEN

La energía azul, una intrigante alternativa, aprovecha la energía química que se libera espontáneamente cuando coinciden dos soluciones de agua con distintas concentraciones de sal, como ocurre en la desembocadura de los ríos que desembocan en las cuencas oceánicas. Este artículo reúne las últimas investigaciones sobre esta forma de energía, haciendo hincapié en la pila entrópica de mezcla (MEB) como dispositivo electroquímico fundamental para recuperar la energía entrópica. La tecnología MEB aprovecha las reacciones redox entre materiales catódicos y anódicos para optimizar la recuperación de energía a partir de gradientes de salinidad. Revisamos las mejores prácticas en la optimización de dispositivos, destacando las reacciones redox más eficaces y los materiales empleados. Al evaluar la disponibilidad volumétrica y el potencial teórico de la energía azul, nuestros resultados subrayan la viabilidad de esta fuente de energía renovable y justifican la continuación de los esfuerzos de investigación. Esta exhaustiva síntesis pretende informar y orientar futuras innovaciones en materia de extracción y recuperación de energía azul.

Keywords: blue energy, Mixing Entropic Battery (MEB), Salinity gradient energy, chemistry energy
Palabras clave: energía azul, Batería de Mezcla Entrópica (MEB), Energía de gradiente de salinidad, energía química

INTRODUCTION

The exponential escalating which has had global demand for energy and the detrimental environmental impact of fossil fuel usage have necessitated the exploration of sustainable alternatives derived from abundant natural resources. This shift has shifted the focus from petroleum-based fuels to cleaner, renewable energy sources. Among the successful alternatives are solar, wind, geothermal, and biomass energies. However, the vast expanses of the ocean remain an untapped, inexhaustible reservoir of renewable energy. Marine sources such as waves, tides, ocean currents, offshore winds, ocean thermal gradients, and salinity concentration differences have emerged promising avenues for sustainable energy generation (Marino *et al*., 2015). Notably, the chemical energy released during the natural mixing at the mouth of river water with seawater, commonly referred to as Blue Energy or the Energy due to Salinity Gradient Difference (Marino *et al*., 2014; Lee *et al*., 2017), presents a unique opportunity. Entropic energy is released at a point between the river water and the sea flow, estimated at 2.2 kJ of free energy per liter of fresh water (Marino *et al.,* 2015; Brogioli, 2009; La Mantia *et al*., 2011; Brogioli *et al*., 2012; Kim *et al*., 2016a; Kim *et al*., 2016b; Morais *et al*., 2016; Md Hasan *et al*., 2017; Jia *et al*., 2013; Ye *et al*., 2014; Marino *et al*., 2016; Rica *et al*., 2013).

This manuscript compiles relevant information on several electrochemical devices that utilize the technology and concept of electrochemical ion pumping in blue energy recovery.

THEORETICAL BACKGROUND

The battery proposed by Brogioli on the entropic mixture concept works through a process in stages, where the electrodes, both anionic and cationic, interact selectively with Cl^- and Na^+ ions. In the first step, the battery is charged by removing M+ and A- ions from the cathode and anode electrodes in a low ionic strength solution. The second step consists of the solution change, where the recovery solution is replaced by a solution with high concentration, causing the voltage in the cell or the open circuit potential to increase, causing the phenomenon known as "voltage rise" (Marino *et al*., 2015; Marino *et al*., 2014; Brogioli, 2009; La Mantia *et al*., 2011; Kim *et al*., 2016a; Jia *et al*., 2013; Ye *et al*., 2014; Marino *et al*., 2016; Rica *et al*., 2013). In the next step, the battery is discharged due to a high potential, resulting in the capture of the M^+ and A^- ions by the electrode material, intercalating these ions from the concentrated solution into the crystalline structure, both for the year as in the cathode, through a constant current in the closed circuit, thus generating an increase in energy. In the last step, the concentrated solution in the battery is replaced by another recovery solution of low ionic strength, closing the circuit to begin a new cycle of the energy device. It is worth mentioning that in intermediate steps 2 and 4, electrolyte exchange, there is no consumption or generation of energy. The energy extraction, W, is given by the following equation presented below:

$$W = \oint \Delta E dq = \int_1^2 \Delta E \cdot I \cdot dt + \int_3^4 \Delta E \cdot I \cdot dt \quad (1)$$

The terms of the equation are, where E is the voltage corresponding to the electrochemical system, and I is the applied current. E and I change as the concentration changes over time. Also, During the ion capture and release stages, the energy output (W) of the system is given by the sum of each thermodynamic and kinetic contribution, and W is expressed as follows:

$$W = \oint_1^2 \Delta E_{eq} \cdot I \cdot dt + \int_3^4 \Delta E_{eq} \cdot I \cdot dt + \int_1^2 \eta \cdot I \cdot dt + \int_3^4 \eta \cdot I \cdot dt = W_{th} + W_k = \oint \Delta E \cdot I \cdot dt \quad (2)$$

Where ΔE_{eq} is the equilibrium potential corresponding to the electrochemical system, η is the generated overpotential of the system and W_{th} and W_k respectively are the energy consumption due to each thermodynamic and kinetic contribution.

It is worth mentioning that the kinetic effects related to reaction overpotentials determine the amount of energy extracted, which is crucial for obtaining and comparing results. Conversely, kinetic limitations are closely associated with mass diffusion processes. Rafael Tricoli et al. present various equations that model thermodynamic and kinetic energy consumption, including expressions for electrolyte potential, concentration overpotential, and diffusion overpotential (Trocoli *et al*., 2016). The Nernst equation (Ye *et al*., 2014) is used to determine the theoretical potential of the system, following the expression below:

$$\Delta E = \frac{RT}{zF}\left[\frac{C_{M^+,Concentrated\ solution} \cdot C_{A^-,Concentrated\ solution}}{C_{M^+,Recovery\ solution} \cdot C_{A^-,Recovery\ solution}}\right] \quad (3)$$

The mixing entropy battery works under the concept of the Nernst equation on the dependence of the potential against a salt concentration gradient (Marino *et al*., 2014; La Mantia *et al*., 2011; Brogioli *et al*., 2012; Marino *et al*., 2016). Therefore, this salinity difference or gradient generates a significant increase in entropic energy, which can be recovered and converted into electrical energy. The Gibbs free energy and the difference between stages 2 and 4, due to the concentrated and low-concentration solutions, can be calculated by the volume fraction of the solution with a high ionic strength. This is due to the reaction of the mixture of different salt solutions with different concentrations. The theoretical energy that can be recovered from the system can be calculated using equation 4.

$$\frac{\Delta G}{RT} = C_T ln(C_T) - \chi C_1 ln(C_1) - (1-\chi) C_2 ln(C_2) \quad (4)$$

Where R is the universal gas constant, T is the absolute temperature; C_T is the salt concentration resulting from the final product of the mixture, C_1 is the salt concentration corresponding to the solution with the lowest ionic strength and C2 is the salt concentration corresponding to the solution with the highest ionic strength (La Mantia *et al*., 2011).

ELECTROCHEMICAL DEVICE FOR BLUE ENERGY RECOVERY

Nowadays, there are different techniques to recover chemical energy resulting from the salinity difference between two solutions, such as reverse electrodialysis (RED) (Marino *et al*., 2014; Lee *et al*., 2017; Brogioli, 2009; La Mantia *et al*., 2011; Kim *et al*., 2016b; Md Hasan *et al*., 2017; Jia *et al*., 2013; Logan & Elimelech, 2012; Ahualli *et al*., 2014), pressure reverse osmosis (PRO) (Ye *et al*., 2014; Ahualli *et al*., 2014; Jia *et al*., 2014; Tehrani *et al*., 2015; Bag, 2017), semipermeable membranes (Brogioli, 2009; La Mantia *et al*., 2011; Brogioli *et al*., 2012), selective ion membranas (Brogioli, 2009; La Mantia *et al*., 2011; Bag, 2017) and concentration cells (Brogioli, 2009; La Mantia *et al*., 2011; Jia *et al*., 2013; Bag, 2017), all of which have seen significant technological advancements in recent years. Pattle in 1954, based on his experience, he was the first to proposed obtaining renewable energy through mixing at the mouth of the river in the sea, where fresh water meets water with a higher ionic concentration, as an alternative to generate clean energy (Pattle, 1954; Fernandez *et al*., 2015). Later Bert H. Clampitt et al. in 1976, he proposed an electrochemical device that wcould recoverenergy from the concept of mixing different concentrations of salt between river water and seawater (Kiviat, 1976). In 2009, Doriano Brogioli (Brogioli, 2009) explained a new and interesting technique of obtaining blue energy under the concept of electrochemistry called CAPMIX (Figure 1a and 1b) (Marino *et al*., 2014; Lee *et al*., 2017; Brogioli *et al*., 2012; Ye *et al*., 2014; Marino *et al*., 2016; Jia *et al*., 2014; Tehrani *et al*., 2015; Fernandez *et al*., 2015; Iglesias *et al*., 2014; Gomes *et al*., 2015), based on the storage of Na^+ and Cl^- ion capacitive electrodes inside activated carbon electrodes (Marino *et al*., 2015; Brogioli, 2009; Marino *et al*., 2016; Jia *et al*., 2014; Fernández *et al*., 2015; Iglesias *et al*., 2014; Lima *et al*., 2017). This technology has technical disadvantages due to the high sensitivity of activated carbon electrodes to impurities in the mixing solutions, such as dissolved oxygen (La Mantia *et al*., 2011; Rica *et al*., 2013). These impurities generate uncontrolled discharges (Brogioli, 2009; La Mantia *et al*., 2011; Marino *et al*., 2016) which makes entropic energy storage inefficient. In 2011, Fabio La Mantia et al. (La Mantia *et al*., 2011) A revolutionary system was introduced, obtaining energy from the salinity gradient, which was called Mixed Entropic Battery (MEB). This technology generated expectations and advanced the technology by working similarly to Brogioli's device, utilizing the mixture of two solutions with varying salinity concentrations. However, the MEB distinguishes itself by storing energy as entropic or

chemical energy within the crystalline structure of the electrode, effectively addressing technical drawbacks found in Brogioli's design. The MEB functions as a reversible electrochemical system, causing electroactive ions in the solution with high ionic strength to be stored pseudo-capacitively at the cathode and anode of the system, respectively. These specialized electrodes are capable of selectively capturing dissolved ions of interest, on the one hand, cationic ions (M^+), such as Li^+, Na^+, Mg^{2+} among others, interact with the cathodic electrode, while on the other hand, anionic ions (A^-) such as Cl^-, interact with the anodic electrode. Commonly referred to as "Mix Accumulators" or "AccMix" (Jia *et al.*, 2014). The CAPMIX and MEB signify significant strides in energy storage technology. Furthermore, it's important to highlight that the text now comprehensively addresses Figure 1.

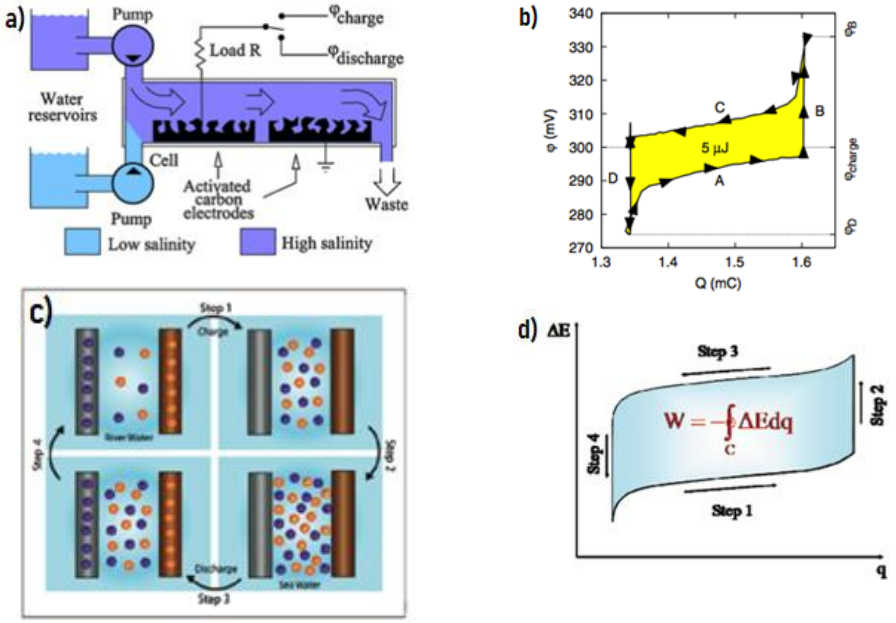

Fig. 1: Electrochemical Devices for Energy Recovery (Brogioli, 2009). (a) Brogioli's Device: Schematic of an electrochemical device proposed by D. Brogioli, featuring two porous and conductive activated carbon electrodes functioning as capacitors for charge and discharge. Containers with solutions of varying salt concentrations enable controlled mixing. (b) Brogioli Cycle: Illustration of the Brogioli Cycle depicting potential (mV) vs load (mC) during the energy recovery process. (c) La Mantia's Mixing Entropic Battery: Schematic representation of F. La Mantia et al.'s systematic work in the mixing entropic battery. (d) Typical Brogioli Cycle: Representation of a typical Brogioli cycle displaying battery cell voltage (ΔE) vs charge (q). The closed integral symbolizes the energy that can be extractable (W) of the cycle (La Mantia *et al.*, 2014).

The primary focus of research is on blue energy extraction centers on seawater-freshwater mixtures, with few considering alternative solutions such as altiplano brine, discarded freshwater, or synthetic saline solutions. Research conducted by Fabio La Mantia has contributed significantly to this field [5,27]. The redox reactions that govern the blue energy extraction by the following expressions.

$$5MnO_2 + 2Ag + 2NaCl \leftrightarrow Na_2Mn_5O_{10} + 2AgCl \quad (5)$$

$$FePO_4 + Ag + LiCl \leftrightarrow LiFePO_4 + AgCl \quad (6)$$

Reaction (5) corresponds to a seawater-river water mixture when employing $Na_2Mn_5O_{10}$ (NMO) as a cathode material, while reaction (6) pertains to freshwater-synthetic brines containing Li^+ ions, utilizing $LiFePO_4$ as a cathode material. Both cathode materials operate by integrating the respective ions (Na^+ or Li^+) into the crystalline structure between the bulk and the electrode surface. However, the interaction between the Ag surface layer and the Cl- ion in both reactions follows the same mechanism. Nonetheless, Ag metal as an anodic material is not the most practical option

due to its high cost and substantial energy consumption when reacting with Cl^-, resulting in the formation of a thin film of AgCl over the Ag electrode (La Mantia *et al*., 2011; Ye *et al*., 2014; Pasta *et al*., 2012). The interaction between Ag and Cl^- in the presence of seawater can be through many reaction alternatives that originate a variety of silver complexes (Ye *et al*., 2014). The solutions used to simulate the extraction of energy from seawater were synthesized by NaCl with a concentration of 0.6 M for the solution with high ionic strength and 0.024 M for the solution with low ionic strength, for fresh water. By applying a current density of 0.25 mA cm^{-2} in the loading and unloading process, an energy recovery of 29 mJ cm^{-2} (10.5 μWcm^{-2}) was obtained, corresponding to 75% efficiency concerning the total free energy. In addition, the solutions that are used to generate electrical energy from LiCl solutions were 1.5 M (LiCl) for the concentrated solution and 0.03 M (LiCl) for the diluted solution. Accordingly, a stable energy recovery of 38.2 mJ cm^{-2} (13.8 μW cm^{-2}) was obtained in a 100-cycle procedure.

In 2012, Mauro Pasta et al. introduced a groundbreaking concept known as the Desalination Battery (Pasta *et al*., 2012), inspired by the principles of the MEB process. This innovative device, depicted in Figure 2, operates akin to capacitive desalination techniques, storing the load pseudocapacitively, where the ions can integrate within the crystalline structure of each respective electrode or electroactive material. The desalination process entails a reversible reaction akin to Eq. (5). Like the MEB, the Desalination Battery operates within the Brogioli cycle, consisting of four charge and discharge steps. In step 1, the desalination process sequesters Na^+ and Cl^- ions from seawater at a constant current. Step 2 involves replacing desalinated water with fresh seawater. Step 3 releases the captured Cl^- and Na^+ ions into the freshwater introduced in step 2, while step 4 replenishes the device with seawater, preparing it for a new desalination cycle. Utilizing $Na_{2-x}Mn_5O_{10}$ (NMO) electrodes with a capacity of 35 mAh g^{-1} and Ag, like MEB, the Desalination Battery exhibits a high surface area and efficient ion exchange between liquid and solid phases (Marino *et al*., 2015; Logan & Elimelech, 2012; Salazar-Avalos *et al*., 2023; Galleguillos *et al*., 2020). Furthermore, in 2013, Zhijun Jia *et al*. (Jia *et al*., 2013) introduced a device capable of harnessing energy from salt concentration differences. This device features CuHCF as the anodic material selective to Na^+ ions and metallic Ag as a cathode material selective to Cl^- ions, using river water (0.024M NaCl) and seawater (0.6M NaCl) as electrolytes. Examining the specific current profile (A g^{-1}) vs potential applied (V), two peaks corresponding to the oxidation (0.8V) and reduction (0.5V) processes are observed. These peak values occur and align exactly with the insertion and extraction process of Na+ ions within the CuHCF crystal structure (Salazar-Avalos *et al*., 2023). The reduction reaction corresponds to the process in which the ion intercalates within the crystalline structure, while the oxidation reaction represents the inverse process, the deintercalation of the Na^+ ions. CuHCF exhibits remarkable reversibility as an anodic material, highlighting its potential to harness energy from the salt concentration difference (Galleguillos *et al*., 2020). Furthermore, Na^+ intercalation/deintercalation process elucidates critical aspects, offering insights into their electrochemical behaviors and performance metrics.

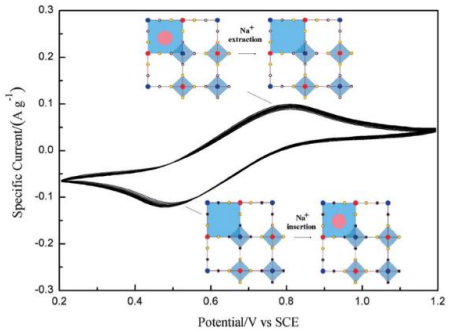

Fig. 2: CuHCF Anodic Material (Proposed by Zhijun Jia et al.): Schematic representation of the collation and deintercalation process of Na^+ ions in the crystalline structure of the anodic copper hexacyanoferrate material (CuHCF) (Jia *et al*., 2013)

In 2014, Meng Ye et al. (Ye *et al*., 2014) explored the potential application of an MEB utilizing water from a coastal wastewater treatment plant flowing into the sea. Despite its innovative approach, a significant limitation arises from freshwater availability. The reversible redox reactions involved in harnessing blue energy are depicted as follows:

$$10Na_4Mn_9O_{18} \leftrightarrow 18Na_2Mn_5O_{10} + 4Na^+ + 4e^- \quad (7)$$

$$4Ag + 4Cl^- \leftrightarrow 4AgCl + 4e^- \quad (8)$$

Utilizing parallel plate-shaped electrodes on a 3x3 cm carbon fabric energy collector with a 1.7 mm separation, the design achieved a recovery of 68% of theoretical energy, yielding 0.11 kWh per 3 m^3 of wastewater. However, the study lacks crucial information on wastewater quality parameters and the origin stage of the water treatment process. The concentration of dissolved Ag^+ in wastewater after 12 cycles was 0.02 ppm, exceeding the EPA's maximum allowable limit (0.1 ppm) when seawater concentration reached 0.9 ppm. Notably, no details on wastewater quality indicators were provided. The manuscript's key finding underscores that the longer the battery charge time, the greater the recovery of blue energy. In the same year, Massimo Marino et al. (Marino *et al.*, 2014) introduced an alternative technology for extracting energy from salt concentration differences. This approach employed a solid zinc electrode to be used as the cathode, and for the anode, a silver electrode in a zinc chloride solution was used, resulting in the generation of up to 2 Wm^{-2} per electrode surface. While emphasizing the electrochemical process, this method also integrates thermal processes for solution regeneration. This discussion aligns with the content of Figure 3, which shows a general flowsheet of the Zn – Ag/AgCl electrochemical system, and power generation cycles of the AccMix device.

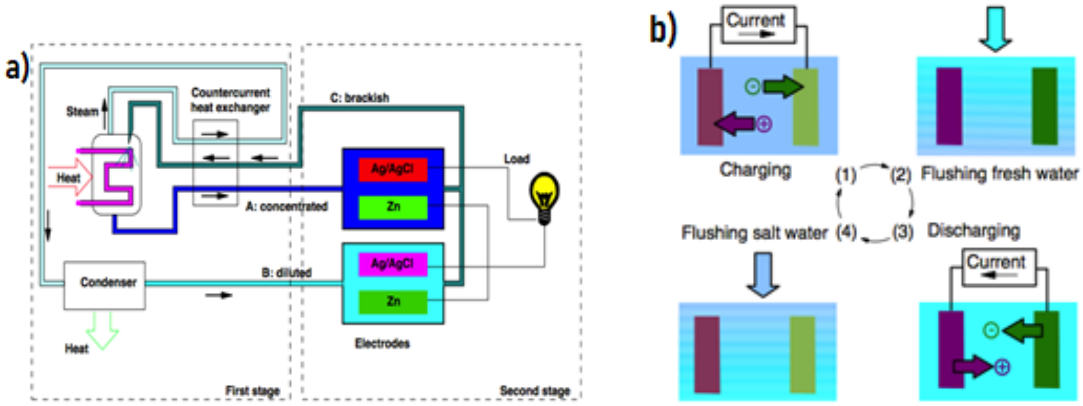

Fig. 3: Zn – Ag/AgCl electrochemical device. (3a) Offers a comprehensive overview of Massimo Marino et al.'s general flowsheet for a Zn – Ag/AgCl electrochemical system, outlining salt concentration restoration through distillation and potential applications of thermoelectric conversion for electrical energy production. Finally, (3d) details the power generation cycles of the AccMix device, encompassing charging, flushing fresh water, discharge, and flushing salt water after feeding a concentrated solution, encapsulating key stages of the AccMix device's power generation process.

Zinc, commonly used as a cathode, has demonstrated success in secondary batteries, such as Silver/Zinc Oxide cells and Zinc-Bromide flow batteries. The first stage of the thermoelectric process, illustrated in Figure 3a, aims to maintain a constant salinity difference between flows A and B. The second stage takes advantage of the difference in salt concentration between the two flows to generate an increase in electrical energy following the principle of the entropic mixing battery. In this device, during the charging process in step 1, $Cl^-$and Na^+ ions are absorbed by the electrodes and later released into the solution during discharge in step 3. This approach differs markedly from the entropic mixing battery described by Fabio La Mantia, as it is charged during step 1 by releasing Cl^- and Na^+ ions from the cathode material into the electrolyte and discharged in step 3 by replenishing Cl^- and Na^+ ions inside the cathode and anode electrode. To enhance energy extraction efficiency from the salt concentration difference, minimizing energy losses is paramount. To achieve this, electrodes must adhere to criteria including low self-discharge or electrical charge leaks, good energy efficiency or low overpotential, and high cycling loading and unloading capabilities.

In 2015, another promising device was proposed by Samira Haj Mohammad Hosein Tehrani et al. (Teharni *et al*., 2015). This device uses Cobalt Hexacyanoferrate (CoHCF) sheets as a cathode material and metallic Ag as an anodic material. Like the previous cases, water with a concentration of 0.024M NaCl was used for the diluted solution, which represents river water, and another of 0.6M NaCl for the concentrated solution, which simulates seawater (Salazar-Avalos *et al*., 2023). This proposed electrochemical system presents two peaks, which are attributed to the two possible forms of CoHCF material ($NaCo^{II}{}_{1.5}Fe^{II}(CN)_6$ and $Na_2Co^{II}Fe^{II}(CN)_6$), and are also attributed to the oxidation process [8,16] of Fe^{+2} to Fe^{+3} according to the following redox reactions.

$$Co^{II}_{1.5}[Fe^{III}(CN)_6] + e^- + Na^+ \leftrightarrow NaCo^{II}_{1.5}[Fe^{II}(CN)_6] \quad (10)$$

$$NaCo^{II}[Fe^{III}(CN)_6] + e^- + Na^+ \leftrightarrow Na_2Co^{II}[Fe^{II}(CN)_6] \quad (11)$$

$$NaCo^{II}[Fe^{III}(CN)_6] + e^- + Na^+ \leftrightarrow Na_2Co^{II}[Fe^{II}(CN)_6] \quad (12)$$

These redox reactions represent the process of intercalation and deintercalation of the Na^+ ion into the crystalline structure of CoHCF. System stability was maintained for 100 cycles at a sweep speed of 100 mVs^{-1}. The energy recovered by this device was close to 24,000 μWg^{-1}. In 2016, Taeyoung Kim *et al*. (Kim *et al*., 2016) advised how to generate electricity using a system with saline solutions in a thermolytic process, using Ammonium Bicarbonate salts (NH_4HCO_3 - AmB) taking advantage of residual heat. Salinity differences can be obtained by using AmB in the solution through unitary distillation and condensation operations at temperatures close to 40.8 °C. The operating temperatures of these cells do not exceed 130°C, which becomes a viable alternative, considering the varied ways to obtain or recover low-quality heat using thermo solar systems or recovering heat in industrial chemical processes in general. Moreover, this cell operates similarly to an entropic mixing battery proposed by Fabio La Mantia and the electrochemical system designed by Massimo Marino and Doriano Brogioli in 2014, which uses an external heat generation system for the process of Distillation. In this publication, the researchers worked on the evaluation of materials that have been used in conventional batteries capable of interacting with NH_4^+ ions and CO_3^{-2} ions generated in the dissociation of NH_4HCO_3 (see Figure 5). The materials used were Copper Hexacyanoferrate (CuHCF), Manganese Oxide (MnO_2), Lead Dioxide (PbO_2), Iron Phosphate ($FePO_4$), Metal Lead (PbO), and Metallic Silver (AgO). The testing was carried out using MnO_2, CuHCF, and $FePO_4$ as cathode materials interacting with the NH_4^+ and PbO_2, PbO, and AgO as anodic materials interacting with CO_3^{-2} ions. The solutions used were 1 M of NH_4HCO_3 for the concentrated solution and 0.02 M of NH_4HCO_3 for the diluted solution.

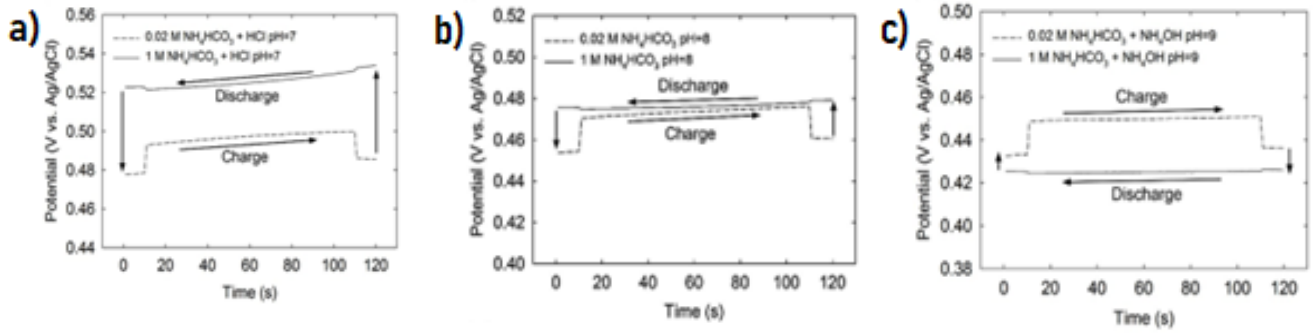

Fig. 5: Electrochemical system evaluation using NH_4HCO_3 and HCl. (a) illustrates NH_4HCO_3 + HCl; (b) displays NH_4HCO_3; (c) represents NH_4OH. The electrochemical system employs three electrodes: a MnO_2 electrode as the working electrode, a platinum mesh as the counter electrode, and an Ag/AgCl electrode (3M NaCl) as the reference electrode. The cell is loaded with a solution of NH_4HCO_3 at concentrations of 0.02M (dotted line) and 1M (continuous line) at ± 0.2 mA for 120 seconds.

From the evaluation of cathode materials, it was observed that CuHCF in contact with NH_4HCO_3 solutions at pH 8 exhibited a high propensity to dissolve during the loading and unloading process. Conversely, $FePO_4$ demonstrated better stability but exhibited a significantly lower loading capacity, attributed to intercalation issues with NH_4^+ ions within the crystalline structure of $FePO_4$. However, MnO_2 remained stable throughout the experimentation, with

NH_4^+ ions intercalating into its crystalline structure. The result of this reversible reaction resulted in the reduction of Mn^{4+} to Mn^{3+} according to the equation below:

$$MnO_2 + {NH_4}^+ + e^- \leftrightarrow MnOONH_4 \quad (13)$$

Figures 5a to 5c illustrate the impact of pH variation on energy extraction. In this instance, the pH was adjusted from 7 to 9 to assess the performance of energy extraction. It will be observed that the potential difference and the recovered energy had a decrease, even reversing in response to the modification of the pH, which indicates a direct variation between the low energy extraction and the pH of the electrolyte. In alkaline conditions, the redox reaction of water with MnO_2 can be seen in equation 14 below:

$$MnO_2 + H_2O + e^- \leftrightarrow MnOOH + OH^- \quad (14)$$

Using the Nernst equation, the potential was determined by the OH^- and NH_4^+ activity when the hydroxide activity is quite high. Both OH^- and NH_4^+ can react with the MnO_2 electrode, however, the one that would react in greater numbers would be the NH_4^+ ion, considering that OH^- activity is relatively low (10^{-6} M at pH 8). On the other hand, the behavior of the anodic electrode was evaluated using AgO, PbO, and PbO_2, because they encountered faradic reversible reactions in the presence of carbonate (CO_3^{-2}). Metallic silver would react according to the following redox reaction:

$$Ag_2CO_{3(s)} + 2e^- \leftrightarrow 2Ag + CO_3^{-2} \quad (15)$$

Using the same working concentrations in the concentrated (1M) and diluted (0.02M) solutions, there were no observable energy gains from the energy consumption generated by reacting AgO with CO_3^{-2} to form Ag_2CO_3. The same situation was visualized when capturing Cl^- ions to form AgCl on the device presented by Fabio La Mantia. These ohmic losses are increased by the formation of complexes when reacting to the metallic Ag with ammonia ions (NH_3) according to the following reaction:

$$Ag + 2NH_3 \leftrightarrow Ag(NH_3)_2^+ + e^- \ (E_0 = 0.37V_{vs}SHE) \quad (16)$$

When using PbO as an anodic material, it reacts with CO_3^{2-} to form $PbCO_3$ generating a potential dependent on CO_3^{2-} concentration in both NH_4HCO_3 solutions, indicating that PbO can be a promising material to be used as an anodic material. However, throughout the loading and unloading cycles the potential changes due to the irreversible formation of $PbCO_3$ in the potential range utilized. This slowed down energy recovery. PbO_2 in the presence of CO_3^{2-}, reacts according to the following equation.

$$PbO_2 + CO_3^{-2} + 2H_2O + 2e^- \leftrightarrow PbCO_3 + 4OH^- \quad (17)$$

The PbO_2 in contact with a concentrated solution of NH_4HCO_3 generates a positive potential between 10 to 20 mV which is why this material could work perfectly as a positive electrode. However, the energy generated was consumed as ohmic losses, making it clear that lead oxide is not a good material to be used as an anodic electrode. The energy recovered from the electrochemical system, using MnO_2 as cathodic material together with a cation exchange membrane and PbO as anodic material was 6.3 mW m^{-2}.

In contrast, Taeyoung Kim et al. (Kim *et al.*, 2016) in the same year (2016), introduced a technological breakthrough in blue energy recovery. They developed a MEB utilizing Copper Hexacyanoferrate (CuHCF) as both anode and cathode electrodes, along with a Titanium energy collector, separated by a cost-effective, non-selective filtration membrane. The power generation from various solutions was conducted in parallel as depicted in Figure 6. This study comprehensively evaluated energy recovery behavior, considering factors such as hydraulic retention times, operational conditions, cell design, generated power, energy losses in the system, and the impact of the filtration membrane on energy recovery.

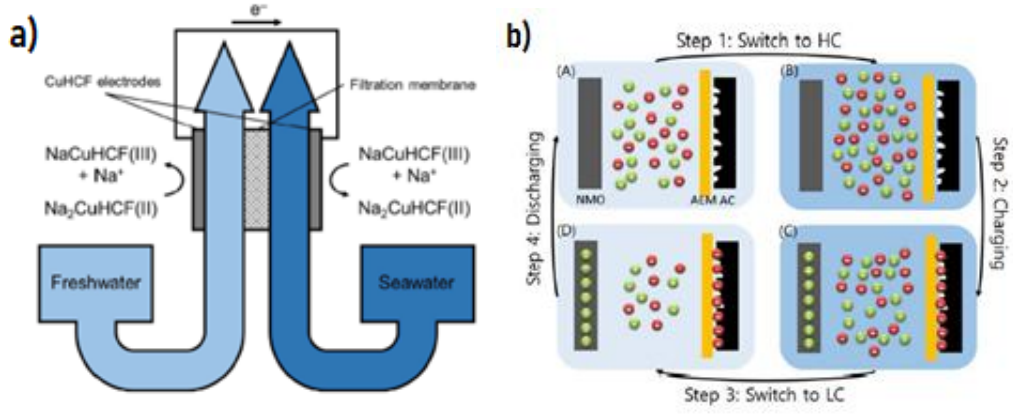

Fig: 6: a) Proposed by Taeyoung Kim et al. (Kim *et al*., 2016), the concentration cell's operation is depicted, employing CuHCF electrodes and a filtration membrane. b), proposed by Jiho Lee et al. (Lee *et al*., 2017), illustrates the four steps of the Brogioli cycle governing energy extraction from salt concentration differences. This system integrates a battery and a capacitive electrode with an ion exchange membrane.

The average power obtained, as maximum recovery by the device, was 411 mWm-2 without showing fluctuation in 20 continuous cycles, improving the results of the devices that only recover energy intermittently. Hydraulic retention time is a delicate operational parameter since the difference in salinity within the cell is generated because of continuous feed with a flow rate of 7.5 mLmin-1 for the solutions inside the electrochemical device. In 2017, Jiho Lee et al (Lee *et al*., 2017) proposed a MEB using NMO as cathode material and activated carbon as anode material together with an anion exchange membrane, calling this device Hybrid Capmix (Figure 6b). The concept of Hybrid Capmix refers to the mixture of the concept of MEB by Fabio La Mantia et al., a product of which the utilization of a pseudo-capacitive cathodic electrode like NMO captures Na^+ ions based on faradaic reactions and an anionic capacitive electrode such as activated carbon with an anionic exchange membrane which captures Cl^- inside its pores. This device can recover up to 97 mW m^{-2}, which was demonstrated in 3 continuous cycles. Meng Ye et al. show the potential of harnessing salinity gradient energy, referred to as blue energy, particularly at mouths where freshwater from rivers meets seawater on the coast. Wastewater treatment plants, discharging into saline environments, offer an untapped source of this energy. The study introduces chargeless MEB using low-cost materials for electrode fabrication, including Prussian blue (PB) specifically as a cathodic material and polypyrrole (PPy) as the anodic part. It is estimated that the global potential of the system to obtain blue energy from the concentration gradient of seawater with river water is 2 TW, in addition, there is an important source with great potential not yet investigated, such as wastewater treatment plants. Previous attempts at systems to recover energy from the salt gradient, such as the most powerful system known to date, pressure retarded osmosis (PRO), and on the other hand, reverse electrodialysis (RED), have faced commercial viability challenges. The MEB operates through a four-step cycle involving the exchange of seawater and wastewater effluent, enabling energy recovery. Previous challenges included the cost and solubility of electrodes. PB and PPy are introduced as low-cost electrode materials for the MEB. By matching the potentials of the PB and PPy electrodes, the study achieves a charge-free MEB, eliminating the need for upfront energy investment [31]. Both PB and PPy exhibit excellent electrochemical properties, with PB demonstrating stability over 150 cycles and PPy showing close to 100% coulombic efficiency through 50 cycles. A full-cell MEB, constructed with Prussian blue and Polypyrrole electrodes, demonstrates energy recovery through alternating exchanges of wastewater effluent and seawater. The chargeless MEB with PB and PPy electrodes proves stable over 50 cycles, with a decrease of less than 7% in energy recovery. The use of a PVA/SSA coating enhances capacity retention over 180 cycles. The study concludes that a charge-free MEB is feasible, simplifying the energy recovery process and improving scalability. PB and PPy are deemed ideal candidates for electrode materials due to their low cost, overlapping potential range, and stability. The findings present a promising approach to efficiently harnessing blue energy, addressing cost considerations and operational complexities associated with traditional methods (Ye *et al*., 2019).

In 2019, Guangcai Tan et al. study a new method to obtain energy under the concept of salinity gradient, this work introduces bismuth oxychloride (BiOCl) as a cost-effective alternative for harvesting blue energy. The MEB is composed of electrodes, BiOCl as anode and CuHCF as cathode, both without coating, which exhibited an energy density of 59 mW m^{-2} when tested with 30 and 1 g L^{-1} NaCl solutions. To enhance power output, polyelectrolyte coatings were applied to the BiOCl and CuHCF electrodes. The coated SEM demonstrated substantial improvement, achieving energy and power densities of 12 J m−2 and 87 mW m^{-2} respectively. This represents an increase of almost 50% compared to the uncoated MEB, and notably, the performance rivaled or exceeded that of MEBs utilizing Ag as an anionic electrode. These findings suggest that BiOCl can serve as a cost-effective alternative to Ag, and the polyelectrolyte coatings are a more economical option than ion exchange membranes in SEM for more effective recovery of blue energy (Tan & Zhu, 2020).

The study further investigates the MEB's capability to recover SG energy from hypersaline water (up to 300 g L^{-1} NaCl). Energy recovery, together with energy production, increases considerably with a higher concentration of salinity, which demonstrates the potential for blue energy recovery from brines. Stability tests after 50 cycles indicated that the coated MEB had acceptable stability, with the power density stabilizing at approximately 12 J m^{-2} and the average power density remaining close to 87 mW m^{-2}. Comparative analysis showed that the coated MEB's average power density surpassed that of capacitive double-layer expansions (CDLEs) and being competitive with capacitive energy extraction, based on the Donnan potential theory (CDP). Moreover, the coated MEB's power density was comparable to or higher than MEBs with AgCl anionic electrodes and certain hybrid MEB configurations. The results highlight the potential of BiOCl as an economical alternative for MEB anionic electrodes and demonstrate the viability of polyelectrolyte coatings as cost-effective substitutes for ion-exchange membranes, making the MEB a promising avenue for efficient blue energy recovery, particularly from brines (Tan & Zhu, 2020). The Galleguillos *et al*. (2020) is a groundbreaking approach to harnessing blue energy, offering a cost-effective and environmentally friendly alternative to traditional marine energy harvesting methods. In this study, we delve into the intricate details of the MEB, focusing on the exploration of various cathode and anode materials to optimize energy recovery efficiency. Cathode materials, including Sodium Manganese Oxide (NMO) and Lithium Iron Phosphate (LFP), have been meticulously examined for their ability to store energy efficiently. The investigation extends to the anode materials—Silver (Ag), Bismuth Oxychloride (BiOCl), and Polypyrrole (PPy)—each evaluated for their distinct capacity to capture chloride ions during cycling. Among the cathode materials, NMO and LFP stand out for their potential to facilitate high-capacity and reversible electrochemical processes. The study highlights the importance of the quality of the interface corresponding to the material-collector in the supercapacitor equipment, emphasizing its influence on the overall charge storage. In the realm of anode materials, Ag electrodes emerge as popular choices due to their reversibility and adaptability in the presence of chloride ions. However, the study reveals challenges related to Ag cost and partial solubility in seawater or hypersaline solutions. On the other hand, Bismuth Oxychloride (BiOCl) and Polypyrrole (PPy) are introduced as compelling alternatives, each with its unique advantages. BiOCl demonstrates a tetragonal structure and exhibits reversible reactions during cycling, presenting major conversion reactions and minor intercalation processes. Meanwhile, PPy, as an organic conducting polymer, boasts a wide potential window, high electron conductivity, and excellent mechanical properties, making it an appealing candidate for anionic electrode material. The research highlights PPy as a standout material, showcasing its superior performance in capturing chloride ions with lower energy consumption. This organic polymer not only proves to be cost-effective but also demonstrates impressive cycling stability and efficiency.

In 2020, Smolinska-Kempisty et al. explored the interpolymeric Ion exchange membranes for the Capacitive Mixing (CapMix) process to improve energy generation during the mixing of waters with different salinities (Smolinska-Kempisty *et al*., 2020). The study was conducted to inform and describe renewable energy sources, with a primary focus on blue energy.

To improve the efficiency of ion accumulation, the study employs solid ion exchange membranes (IEM) synthesized with polyethylene and styrene-co-divinylbenzene (PE//St-co-DVB) interpolymer. To obtain these membranes, they must undergo an extrusion process of the interpolymeric matrix followed by a chemical modification reaction. The article provides detailed procedures for membrane preparation, including chlorosulfonation and amination. The results indicate that the membranes with the best results for the energy harvesting process were obtained by synthesizing the

interpolymer with 2% by weight of divinylbenzene. The study considers several factors that affect the CapMix process, including the ion exchange capacity ratio, the percentage of water absorption, the dimensions of the membrane, along the concentration of saline solutions with high and low content of dissolved ions. The selection of optimal membrane pairs is based on energy production, with emphasis on voltage rise as a critical parameter.

In the same year (2020), Muhammad Nasir et al. investigated certain parameters considered essential for the capacitive energy extraction and harvesting process based on a double layer expansion (CDLE) system. Muhammad Nasir et al. studied the most relevant parameters that affect the reaction occurrence such as the pore size of the materials, the dimensions of the porous electrodes and other operational parameters. Thus, studying the variability and responses of these parameters is essential to improve the performance of CDLE devices to be alternatives for practical applications. The different CDLE cycles were carried out with variation of the flow rate and using a set of different activated carbon samples, varying the average pore size. The analysis of the results was based on the Gouy-Chapman-Stern (GCS) theory. The study determined that smaller average pore sizes in the electrodes led to higher energy extraction. This was attributed to the higher number of transferred charges, facilitated by the lower separation of the ion diffusion layer. The rearrangement of ions was verified by accelerating the rate of potential increase. Furthermore, the research shows that the energies extracted in the different experiments were identical, even with the variation of the flow rates, since there were no significant changes in the formation of the electric double layer (EDL). In any case, as the flow rate is modified, a response is obtained by increasing the flow, accelerating the diffusion of ions, which produces better energy production (Nasir *et al*., 2020). Brogioli proposed the CDLE method, which involves connecting an external power source that supplies electrical energy to electrodes immersed in saline water. The solution is then replaced by draining and adding a new fresh flow, causing the EDL to expand, which generates a voltage rise within the CDLE cell. Porous materials such as activated carbon, with different pore sizes, are commonly used as materials for CDLE electrodes. The study focused on understanding the effects of pore size, especially on the diffusion process and how the pore size of the activated carbon influences and optimizes the performance of the CDLE cycle. The experimental equipment included three activated carbon samples where different average pore sizes were used, and different flow rates were tested. The study presented detailed methods, including the materials used, the experimental setup, and the analysis of parameters such as effective surface dimensions and Stern layer capacitance. The results highlighted the importance of pore size in activated carbon electrodes, as smaller average pore dimensions contribute to higher energy extraction. The study also compiled the effects on performance of the responses of external voltage and flow rate for CDLE cycles. It was concluded that an increase in power output could be achieved by carefully adjusting the flow rate to reduce potential current leakage (Nasir *et al*., 2020).

Mingzhe Chen in his groundbreaking paper contributes significantly to improving the understanding and capabilities of electrochemical energy storage systems (ESSs) operating under extreme conditions. The authors investigate the fundamental scientific aspects, covering the thermodynamics of electrochemical reactions, as well as the reaction rate described by kinetics and mechanical design, which are crucial for improving the system and implementing, under increasing performance and applicability of ESSs in environments characterized by high and low temperatures, as well as environmental conditions. stretching and compression. An important contribution lies in the urgent call to explore new approaches, with the mission of addressing the critical challenges posed by extreme conditions. It is important to emphasize the need to understand the mechanisms related to electrochemical reactions and the different possible phenomena in various scenarios, the authors pave the way for innovative solutions that transcend the limitations of ESSs under normal conditions. This fundamental idea constitutes the cornerstone for future research in this field. The article systematically summarizes the scientific points that are fundamental and key to the operation of ESSs systems under demanding conditions, offering a comprehensive overview of thermodynamics, in conjunction with reaction rate or electrochemical kinetics of materials, as well as consideration of the mechanical design of the system. This structured approach provides a valuable resource for researchers seeking to navigate the complex landscape of energy storage in extreme environments (Chen *et al*., 2021).

In addition, this review meticulously describes the drawbacks or challenges that influence the use of existing ESS systems under various extreme conditions and proposes effective strategies to overcome these challenges. By

shedding light on issues such as high overpotential, voltage hysteresis, and unexplored phenomena, the article serves as a guide for researchers and engineers actively working on improving the electrochemical performance of energy storage systems. In the broader context, the article underscores its contribution to bridging the gap between research reports that predominantly focus on mild conditions and the practical application of ESSs in extreme cases. The authors highlight the importance of studying key limiting parameters and potential design concepts to achieve high performance in extreme environments, providing a roadmap for future investigations in the realm of materials chemistry and electrochemistry. The perspectives and outlooks presented in the article significantly contribute to shaping the future trajectory of research in energy storage systems. By emphasizing the importance of a full understanding of materials, coupled with rational engineering and innovative concepts, the authors offer a visionary outlook on the potential advancements required to meet the demands of extreme conditions (Chen *et al*., 2021).

In 2022, Zhou et al. used CuHCF as a promising candidate for anode electrodes. This complex exhibits a three-dimensional network structure that forms the framework with six base atoms of the nitrogen element, creating a large interconnection known as the "A site." This site or space can host the aquatic alkaline cations, particularly K^+, facilitating their transfer through channels in the ⟨100⟩ direction. The unique structure allows rapid ion transfer without altering the overall structure (Zhou *et al*., 2022). CuHCF has found possible applications as an anode electrode in batteries, showing its potential in energy conversion and being an alternative for energy storage. Furthermore, in sodium ion battery systems, the reduction reaction of the system corresponds to the coordination sequence, while the complementary oxidation reaction involves the deintercalation of the sodium battery ions. CuHCF has been used in supercapacitors resulting in high cyclic stability and specific capacitance. It has been employed in a membrane-less sodium-ion battery to extract energy from salinity gradients, exhibiting significant energy and power densities. Researchers have explored reactions where ion insertion and extraction of polyvalent ions occur as a possible alternative for energy storage. Recent advances include the preparation of monoclinic CuHCF nanosheets (CuHCF-P), which exhibit improved sodium storage properties and outperform traditionally synthesized CuHCF-C nanoparticles. The resulting batteries, which use CuHCF-P cathodes and commercial high-hardness carbon anodes, demonstrate superior performance, including high energy density and cycle stability (Zhou *et al*., 2022).

Another notable material in MEBs is lithium iron phosphate ($LiFePO_4$), favored for its thermal stability, low cost, non-toxicity, and high theoretical capacity. The $LiFePO_4$ polyanion frame structure, comprising LiO_6 (octahedra), FeO_6 (octahedra), and PO_4 tetrahedra, contribute to its safety and excellent cycling performance. While $LiFePO_4$ has been used as a material for lithium-ion batteries, being the cathode element. its performance rate has been a focus of research. Strategies such as incorporating graphene into $LiFePO_4$ have been explored to improve ion lithium diffusion capacity, resulting in enhanced rate performance and cycle stability (Zhou *et al*., 2022).

In a recent study (2023), A device was built that uses the concept of capacitive mixing as a new technology, its anode electrodes being molybdenum disulfide (MoS_2) and using activated carbon (AC) as cathode electrodes. This device exhibited a notable energy density of 6.12 Jg^{-1}, showcasing its potential for applications in renewable energy development [36]. The choice of MoS_2 as the anode material is significant due to its layered structure, widely known for applications in the automotive and machinery industries. The MoS2 electrode demonstrated pseudocapacitor behavior during electrochemical tests, obtaining results on the specific capacity close to 131 Fg^{-1} in a 0.6 M sodium chloride solution. Electrochemical performance, including cyclic voltammetry (CV), electrochemical impedance spectroscopy and galvanostatic charge-discharge, indicates its suitability for extracting salinity gradient energy. The study provides valuable insights into the feasibility of using MoS_2 in CapMix technology for extracting salinity gradient energy. However, challenges such as the low cycle life of the MoS_2 electrode need further attention to enhance its capabilities for prolonged and sustainable energy extraction (Li *et al*., 2023).

DISCUSSION AND OUTLOOKS

The energy that develops the concept of salt concentration difference harvesting systems has made significant progress through methodologies such as reverse electrodialysis (RED) and efficient pressure retarded osmosis (PRO), capacitive reverse electrodialysis (CRED) and innovative capacitive mixing (CapMix). While PRO and RED

have been established as reliable methods, the relatively nascent CapMix, although still in the research phase, promises further advances in this field.

CapMix, as highlighted in the article, hinges on the controlled mixing of solutions, allowing for the periodic alteration between high and low-saline solutions. An essential aspect emphasized in the study is the importance of ion accumulation at the electrical double-layer reaction site (EDL) of activated carbon. Additionally, the augmentation of ion transport, facilitated by ion exchange membranes, is crucial for optimizing the energy-harvesting process.

A notable development in membrane technology involves the utilization of solid ion exchange membranes (IEM) composed of polyethylene and styrene-co-divinylbenzene (PE//St-co-DVB) interpolymer. On the other hand, the preparation of these membranes, detailed in the article, involves a meticulous process encompassing extrusion of the interpolymer matrix, chlorosulfonation, and amination. This methodology contributes to enhanced ion accumulation and transport efficiency, providing a foundation for more effective energy harvesting. The experimental phase of the study involved testing four pairs of membranes with varying thicknesses in the CapMix process. The results, illuminating the influence of membrane thickness on energy harvesting, revealed that the most efficient membranes were derived from the interpolymer with 2 wt% of divinylbenzene. This finding not only underscores the importance of membrane composition but also opens avenues for fine-tuning the CapMix process for optimal performance.

Looking forward, the integration of advanced materials and membrane technologies, as demonstrated in this study, propels salinity gradient energy harvesting into a realm of greater efficiency and reliability. Further research and development can delve into refining CapMix, potentially unlocking its full potential as a viable method for harnessing the untapped energy within salinity gradients. Furthermore, various efforts to generate collaboration and participation between the scientific academic world, energy industry companies and state policy legislators are imperative to expand these technologies and integrate them into mainstream energy solutions, contributing significantly to the global transition towards the use of clean, sustainable and climate change conscious energy. For instance, materials like Na2Mn5O10, CuHCF, and NiHCF demonstrate promising results in terms of energy recovery potential and efficiency, (ii) The electrode area, thickness, spacing, and volume play crucial roles in determining the behavior of electrochemical systems. Larger electrode areas and smaller electrode spacings generally lead to higher energy recovery potentials, as they facilitate better ion transfer and reaction kinetics, (iii) The ranges provide insights into the operating conditions of the electrochemical systems and offer more flexibility and versatility in energy extraction, allowing for better optimization based on specific environmental conditions, (iv) The concentration of the electrolyte, both high and low, affects the ion flux and driving force for ion migration, thereby influencing the energy recovery efficiency. Optimal concentration levels need to be determined to maximize energy extraction while minimizing energy losses, (v) The number of cycles performed in the experiment reflects the system's stability and durability over multiple charge-discharge cycles. Systems capable of sustaining high energy recovery potential and efficiency over numerous cycles are deemed more reliable for practical applications, and (vi) the recovered energy and their efficiency parameters can directly quantify the behavior of the electrochemical systems in terms of energy recovery. Higher recovered energy values and efficiency percentages indicate superior performance and viability for real-world applications.

CONCLUSIONS

The exploration of blue energy as a viable alternative to conventional renewable sources signifies a critical milestone in the pursuit of environmentally sustainable technologies. Recent advancements, particularly in electrochemical devices designed to harness entropic energy, present a promising roadmap for future technological development that not only mitigates environmental impact but also capitalizes on naturally occurring energy dissipation. The significance of blue energy lies in its ability to extract chemical energy from the interplay between river water and sea water converging into the ocean. The latest research, as described in this study, demonstrates the effectiveness of different electrochemical methods such as pressure retarded osmosis (PRO), being the most powerful system to date, reverse electrodialysis (RED) with the growing technology, together with capacitive reverse electrodialysis (CRED) and capacitive mixing (CapMix) to take advantage of this valuable energy resource. Furthermore, the

potential of blue energy becomes even more apparent when considering that the energy extracted can offset or even exceed natural dissipation. Beyond traditional seawater and river water mixtures, exploring synthetic or natural saline solutions such as electrolytes for energy extraction opens new possibilities. This diversification not only broadens the a/0pplications of blue energy but also enhances its adaptability to various environmental contexts, expanding its potential implementation. In conclusion, blue energy emerges as a forefront solution for sustainable energy production. The electrochemical methodologies, particularly the promising CapMix process detailed in this research, provide a solid foundation for further optimization and scaling. In the future, collaborations between researchers from different scientific centers, industry players, energy-related companies and state policymakers are crucial for the transition to blue energy from a theoretical concept to a practical and impactful reality, driving the global shift towards a greener and more sustainable energy landscape.

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