

# Comparison of Reverse Electrodialysis Stack Performance Under a Variety of Experimental Conditions Using Various Electrode Rinse Solutions

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**Abstract**— The impact of electrode rinse solution on the reverse electro dialysis (RED) stack remains a scarcely explored area. Despite the significant advancements in reverse electro dialysis technology, there is a notable gap in understanding the effect of electrode rinse solutions on stack performance. The study examined the effect of several flow rates and compositions of electrode rinse solutions on voltage and power density, varying from 9.15 to 18.3 L/h and 5 to 30 g/L. The high and low-concentration solutions were prepared by mimicking local seawater (38 g/L NaCl) and Umgeni River water (0.4 g/L NaCl). The highest open circuit voltage (4.354 V) and power density (6.68 W/m<sup>2</sup>) were obtained when using the mixture of K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>, NaCl. The findings indicated that the makeup of the electrode rinse matters the most. Moreover, the results didn't clearly establish a connection between the flow rate of the electrode rinse solution and the open circuit voltage or power density. However, lower concentrations of the electrode rinse solution had a more significant impact on the open circuit voltage than higher concentrations for all electrode rinse solutions.

**Keywords**—Reverse Electro dialysis, Electrode rinse solution, Open Circuit Voltage, Power Density

## I. INTRODUCTION

Throughout history, energy has been a fundamental driver of human progress and prosperity. Initially, our primary energy source was the sun, providing heat and light. As societies evolved, we transitioned from burning wood and coal to harnessing nuclear power, all of which played pivotal roles in advancing our way of life. However, this energy evolution has taken a toll on the environment. Access to energy is a cornerstone of any society's development. Early humans relied on their own physical energy, using muscles for basic sustenance and improving their living conditions. Gradually, we shifted away from human and biomass power, embarking on the monumental transition to fossil fuels.

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Today, the potential of renewable energy sources is vast, with the capacity to exceed the world's energy demands several times over. Resources like wind, solar, biomass-to-energy, hydropower, and geothermal energy offer sustainable alternatives, relying on domestic, daily available sources. This transition to renewable energy systems gains momentum, driven by fluctuating oil and gas prices and falling renewable energy costs. Governments worldwide are actively adopting renewable energy technologies through supportive policies and investments. This concerted effort reflects the global commitment to a more sustainable and environmentally friendly energy future.

Marine renewable energy development aims to harness the vast resources of the coastal environment to meet the growing energy demand. Among various coastal energy sources, Salinity Gradient Energy (SGE) technology is the energy created from the difference in salt concentration between two fluids, commonly fresh water and seawater, e.g., when a river flows into the sea [1]. It is estimated that the available Salinity gradient energy in the world is about 2,6 TW, and the technical exploitable energy amount is about 9.8 gigawatts [1], [2]. The most abundant natural salinity gradient sources are seawater and river water.

Reverse Electro dialysis (RED) is a sustainable and innovative technology that harnesses the energy potential of salinity gradients between solutions with different salt concentrations. This process involves passing these solutions through a series of alternating ion-exchange membranes and selective ion-conductive channels to create an electric potential. This potential can then be converted into electrical power, making RED a promising method for generating clean and renewable energy from mixing freshwater and saltwater sources. RED has the potential to play a crucial role in addressing the world's growing energy demands while minimizing its environmental impact.

Reverse Electro dialysis (RED), introduced by Pattle in 1954 [3], exploits the chemical potential disparity between concentrated and diluted solutions for renewable energy. Wick [4], in 1978, highlighted the global potential of Salinity Gradient Power (SGP) but flagged membrane costs as a hurdle. Lacey (1980) identified U.S. brine salt sources and

proposed geothermal brines for to be the feed for the REED stack [5]. Audinos (1990), demonstrated RED's power generation from different salinity solutions, achieving 400 mW/m<sup>2</sup> [6]. While RED's concept originated in 1954, substantial advancements occurred after 2007 [7]–[10]. Tailor-made Ion Exchange Membranes (IEMs) in 2012 yielded 1.27 W/m, and subsequent IEM enhancements continued [11]. Pilot RED plants in the Netherlands and Italy, from 2010 to 2019, marked progress towards commercialization, accompanied by fouling studies [12]. Despite strides, current RED electricity costs exceed traditional sources, but ongoing innovations in materials, membranes, and system design are anticipated to enhance RED's cost-effectiveness and efficiency, potentially positioning it as a more economically viable and appealing renewable energy alternative [13].

Scialdone et al. [14], delved into the application of different iron-based redox couples on graphite and DSA electrodes for Reverse Electrodialysis (RED). Their findings emphasized the feasibility of utilizing these couples in the absence of light and oxygen, particularly with elevated redox couple concentrations. Meanwhile, Severin and Hayes [15], undertook investigations into the optimal composition of electrode rinse solutions for effectively treating high salt concentrations in pilot electrodialysis stacks. Their study pinpointed the significance of minimizing resistance at the electrode cells to enhance the overall rate of ion transport from dilute to concentrated. The identified challenge was substantial, given that electrode cells could contribute up to 30% of the total resistance in the entire process. Additionally, Wu et al. [16] conducted experimental analyses exploring the impacts of electrode rinse solution, flow rate, and electrolyte composition on RED stack performance, encompassing output voltage, power density, and hydrogen production. Notably, their results indicated that increasing the flow rate of the Electrode Rinse Solution (ERS) correlated with an augmentation in output voltage, albeit with a simultaneous decline in hydrogen production.

However, it is noteworthy that despite these valuable insights, a critical gap persists in the existing literature. Most studies on RED have not extensively examined the influence of the electrode rinse solution on power production in RED stacks. Furthermore, the limited studies addressing the composition of the electrode rinse solution predominantly focus on iron-based redox couples. This underscores the need for a more comprehensive exploration of the effects of different electrode rinse solutions on the overall power production efficiency of RED stacks, a gap that the present study aims to address.

The impact of electrode rinse solution on the reverse electrodialysis stack remains a scarcely explored area. Despite the significant advancements in reverse electrodialysis technology, there is a notable gap in understanding the effect of electrode rinse solutions on stack performance. Despite the growing interest in RED as a sustainable energy source,

limited research has been dedicated to investigating the effects of different rinse solution parameters on RED stack operation. In this study, we utilized electrode rinse solutions previously explored in existing literature. Our investigation was centered on the impact of different flow rates and compositions of electrode rinse solutions on voltage and power density. We varied the flow rates within the study and explored a range of concentrations. Additionally, we selected a mixture comprising four widely documented compositions from the literature for further examination [17]–[20].

## II. EXPERIMENTAL SECTION

### A. Chemicals and materials

All chemicals used in this research were of analytical grade and used directly as received. Both high and low-concentration solutions were prepared by dissolving NaCl in deionized (DI) water. All the chemicals that formed ERS were mixed and appropriately dissolved in DI water. In the solution preparation, deionized water (ELGA PURELAB Option-Q water deionizer, UK) was utilized. Chem Lab Supplies supplied Sodium Chloride (99.5%), Potassium Ferricyanide anhydride [K<sub>3</sub>Fe(CN)<sub>6</sub>], Potassium Ferrocyanide trihydrate [K<sub>4</sub>Fe(CN)<sub>6</sub>], Potassium Chloride (KCl) as well as the other chemicals used to prepare electrode rinse solutions.

### B. Reverse electrodialysis stack

RED stacks, with 30-cell pairs were used (supplied by Beijing Jingo Desalination, China). The stack had titanium mesh electrodes coated with platinum and iridium (Ti/Pt-Ir) to ensure efficient electron transfer. Cation Exchange Membranes (CEMs) and Anion Exchange Membranes (AEMs) were combined in the stack, each offering an active membrane area of 0.0297 m<sup>2</sup> (0.11×0.27). A CEM was used as a shielding membrane on the stack's outer sides to prevent the transfer of negatively charged iron complexes. The total membrane area of the cell was 0.0594 m<sup>2</sup>. A woven spacer of 0.5 mm thickness improved solution flow and mixing and maintained stability. To prevent leaks and maintain a sealed environment, rubber seals were installed.

### C. Experimental procedure

Literature suggestions were used to select electrode solutions [19], [21]–[24]". Salts (NaCl, KCl, and Na<sub>2</sub>SO<sub>4</sub>) were dissolved in deionized water to prepare electrode rinse solutions. Precise amount of Potassium Ferricyanide, Potassium Ferrocyanide, and NaCl were prepared to create solutions with specific molar concentration. Impurities were removed from the solutions by filtering. Furthermore, artificial aqueous solutions were prepared to recreate river water and seawater's ionic composition without altering their strength. Finally, high (38 g/L) and low (0.4 g/L) salinity concentrations mimicking river water and seawater were prepared. Before the experiments, the solutions were filtered and stabilized for 24 hours.

#### D. Experimental measurements

RED stacks were cleaned with DI water before each experimental measurement and then left to soak for 2 hours in DI water. When the RED stack dried, it was reassembled, and the electrode rinse solution and feed solution lines were connected back. In the next step, the system was flushed continuously with DI water for 10 minutes to stabilize it. To introduce a load into the system, a 4.7  $\Omega$  resistor was connected to the ERS anode and cathode chambers. Electrical measurements were recorded as soon as the system reached a steady state using a multimeter (Fluke 177 TRUE-RMS). Real-time voltage outputs were continuously monitored. 20 runs were carried out at ambient conditions with flow rates and concentrations ranging from 5 to 30 g/L and 9.15 to 18.3 L/h.

### III. RESULTS AND DISCUSSION

#### A. The Effect of Flowrate

In this study, flow rates were varied for each salt used (NaCl, KCl, and Na<sub>2</sub>SO<sub>4</sub>) to examine its effect on system performance at 153, 244 and 305 ml/min and the results are illustrated in Fig. 1.

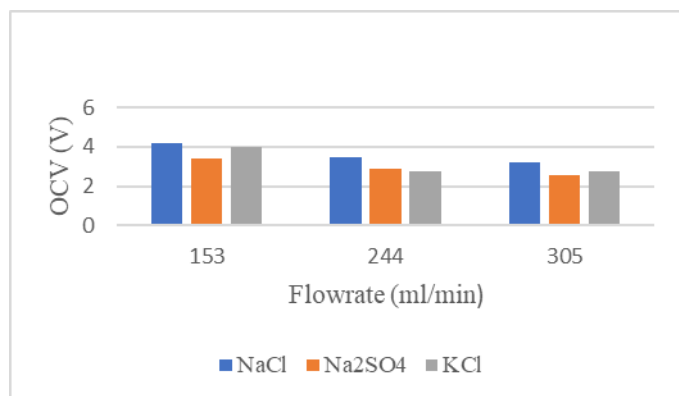


Fig. 1: The relationship between flowrate and OCV

As depicted in Fig.1, an increase in the rinse solution flow rate results in a decrease in OCV. This occurs because the residence time is reduced as the flow rate increases. This decreased residence time results in a lower Open Circuit Voltage (OCV) because efficient electrochemical reactions generating OCV depend on ions staying close to the electrode. Faster flow carries ions away from the electrode vicinity. Higher flow rates cause the electrode rinse solution to pass over the electrode more rapidly, diluting the ion concentration near the electrode surface. This rapid flow effectively mixes the ions initially present near the electrode with the incoming rinse solution, leading to a more even distribution of ions within the electrode rinse solution. NaCl consistently produces the highest OCV among the three electrode rinse solutions, with Na<sub>2</sub>SO<sub>4</sub> showing the highest OCV at 20g and a trend of decreasing OCV with increasing flow rate. The highest OCV for each individual electrode rinse solution is observed at the lowest flow rate. However, there is a

significant drop in OCV as the flow rate increases from 153 mL/min to 244 mL/min, with a more pronounced decrease compared to the shift from 244 ml/min to 305 mL/min. Specifically, the OCV increases by 37% from 153 mL/min to 244 mL/min and by 20% from 244 mL/min to 305 mL/min. The mixture demonstrates the highest OCV due to the presence of a redox couple. Redox-active species engage in reversible oxidation-reduction reactions at the electrodes, generating or consuming electrons and leading to an elevated OCV. Redox couples possess a higher electrochemical potential compared to simpler ions like Cl<sup>-</sup> or K<sup>+</sup>, resulting in a greater voltage disparity and higher OCV. Additionally, redox reactions exhibit enhanced kinetics at the electrode surface, promoting more efficient charge transfer and further elevating the OCV.

#### B. Effect of Concentration

Concentration of the electrode rinse solutions were varied from 10 to 30 g/L to examine the effect on the system's performance. The results are illustrated in Fig. 2 to 4.

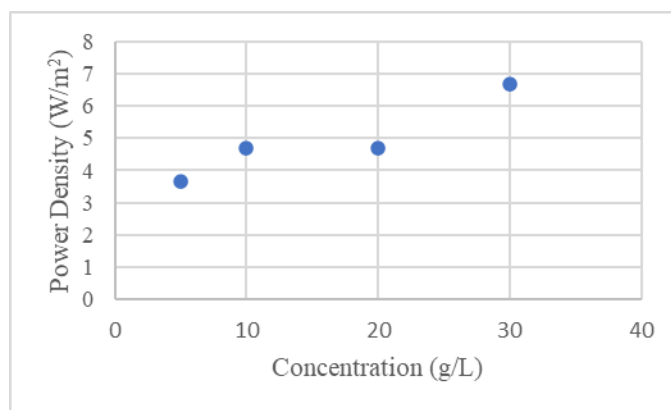


Fig. 2: the relationship between the concentration of the mixture and power density. The concentrations are at a flow of 153 ml/min.

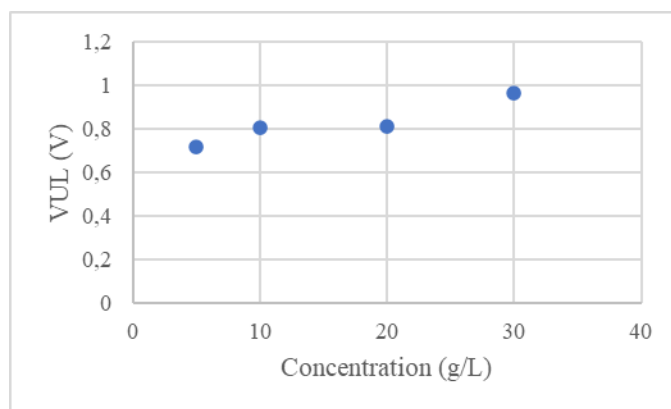


Fig. 3: The effect of the concentration of the mixture on voltage under load. The concentrations are at a flow of 153 ml/min.

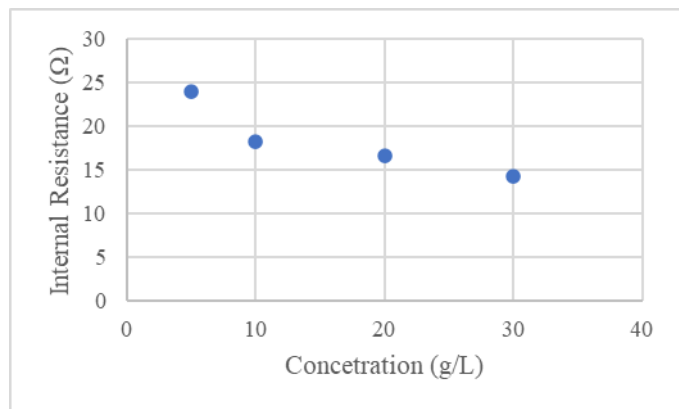


Fig. 4: Effect of the concentration of the mixture on internal resistance. The concentrations are at a flow of 153 mL/min.

The NaCl, KCl, and Na<sub>2</sub>SO<sub>4</sub> concentrations did not appear to have a discernible effect on power density, open circuit voltage (OCV), or internal resistance. This may be attributed to the possibility that the concentrations chosen for these electrode rinse solutions were not optimal for the functioning of the RED stack.

However, a noteworthy contrast was observed when considering mixture of K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>, and NaCl solution. Increasing the concentration of the mixture had a more pronounced and favourable impact. Power density (Fig. 2) and VUL (Fig. 3) demonstrated noticeable increases with rising concentration, suggesting that the mixture's performance was enhanced with higher concentrations.

Concurrently, there was a reduction in internal resistance as the concentration of the mixture increased as shown in fig.4. This effect is crucial as it indicates that the internal resistance, a factor that can limit the efficiency of the RED system, was alleviated with higher concentrations of the mixture. In essence, increasing the concentration of the mixture led to improved electrical performance in terms of power generation (power density), maximum voltage output (OCV and VUL), and reduced hindrance from internal resistance.

#### IV. CONCLUSION

The study revealed a significant influence of electrode rinse flow rate on the operating parameters. As flow rates increased, OCV decreased due to reduced residence time, impacting the efficiency of electrochemical reactions near the electrode surface. As the flow rate increased, the ion concentration near the electrode diluted, allowing for an even distribution of ions within the electrode rinse solution due to a higher flow rate. Among the tested electrode rinse solutions, NaCl consistently produced the highest OCV amongst the electrode rinse solutions that did not contain a redox reaction, while a mixture of K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>, and NaCl outperformed the others due to the presence of redox-active species, promoting efficient charge transfer and resulting in an elevated OCV.

Regarding the effect of concentration, it was observed that NaCl, KCl, and Na<sub>2</sub>SO<sub>4</sub> did not significantly impact power

density, OCV, or internal resistance. This lack of discernible effects may be attributed to suboptimal concentrations for RED stack functionality. In contrast, the concentration of the mixture had a pronounced and favorable impact. Increasing the concentration improved power density, maximum voltage output (OCV and VUL), and reduced internal resistance, signifying enhanced electrical performance for power generation. This insight suggests the potential for optimizing the concentration of specific electrode rinse solutions to maximize the efficiency of RED systems, ultimately contributing to improved power generation capabilities.

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