

Study on capacitive flow electrodes used as energy conversion systems for scaled-up reverse electro dialysis devices

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I. INTRODUCTION

SEAWATER presents itself as a potential resource that can contribute to the advancement of sustainable development goals in the context of an energy transition. Salinity gradient power (SGP) is a promising source of marine energy with the potential to meet the power demand of specific communities, especially those living near river mouths, where the salinity difference is naturally available. In the Colombian context, SGP availability has been studied for several rivers, with the highest potential found at the mouth of the Magdalena River in Barranquilla, accounting for 97% of the total potential in the country. According to estimations of average specific site potential calculated by [1], it is possible to obtain 1.3 MJ/m³ of treated seawater by installing an SGP facility in that location.

Several technologies for harnessing SGP are being developed, including Reverse Electro dialysis (RED), which converts the chemical energy from mixing different salinity streams into usable electrical current. For that purpose, RED devices require an energy conversion system (ECS) comprising a set of electrodes that allow electron transfer, along with outermost membranes that connect the ECS to the RED membrane stack and prevent the passage of redox species into the feed streams.

Most of the experimental studies regarding RED technology have employed redox couples (that involve faradaic phenomena) as ECS. Hexacyanoferrate-based systems are particularly popular, along with Ti/Ir-Ru oxide or Ti/Pt mesh as current collectors.

Other articles have reported the utilization of reactions where gaseous species such as hydrogen, oxygen and chlorine evolve from seawater as electron transfer proceeds [2].

In earlier works, metal participant electrodes such as copper, zinc and silver were also used, offering the

advantage of opposing reactions that avoid the generation of any chemical species during energy conversion [3].

Some authors have also proposed ECS based on non-faradaic processes: capacitive electrodes that store charge by the expansion of the electrical double layer [4]. Such electrodes have been widely researched in other technologies such as capacitive deionization or capacitive mixing [5].

While the most critical development for the commercial availability of RED technology is focused on improving the performance of stacked ion exchange membranes in natural water operation [2], research on new ECS contributes to solving some important problems that hinder the scale-up process of the technology, namely:

- Instability of redox couples: hexacyanoferrate can easily decompose if exposed to sunlight or oxygen, leading to cyanide formation that represents an environmental risk [3], and forms deposits that cover the current collectors, negatively affecting the long-term performance of the RED device [6].
- Gas management challenges: although Hydrogen and Chlorine can be products of interest, their production expends a fraction of the produced energy, creates additional resistance that compromises the stability of the current and represents operational risks due to its flammability or corrosive character [3].
- Current stability during operation: Both participant and static capacitive electrodes are unable to sustain continuous operation without the inversion of the feed stream channels, which requires a special design of the stack and additional equipment costs.

An alternative to the previously mentioned ECS is the use of Capacitive flow electrodes (CFE). These are suspensions of conductive material particles in an electrolyte that can continuously convert chemical energy

from dissolved ionic species to electrical energy. This distinction sets CFE apart from other capacitive systems and makes them ideal for use in energy devices. Activated carbon is the most common material used in these suspensions because of its large surface area and its ability to conduct electricity.

A schematic depiction of a simplified RED device is presented in Fig. 1. The activated carbon particles collide and transfer the electrons, while simultaneously adsorbing electrolyte ions into the surface which constitute the electrical double-layer capacitor. After the CFE slurry passes through the cathode compartment (charge) it is conducted to the anode compartment for the opposite process, ceding electrons through collision with the current collector. In this way, a continuous electrical current can be achieved.

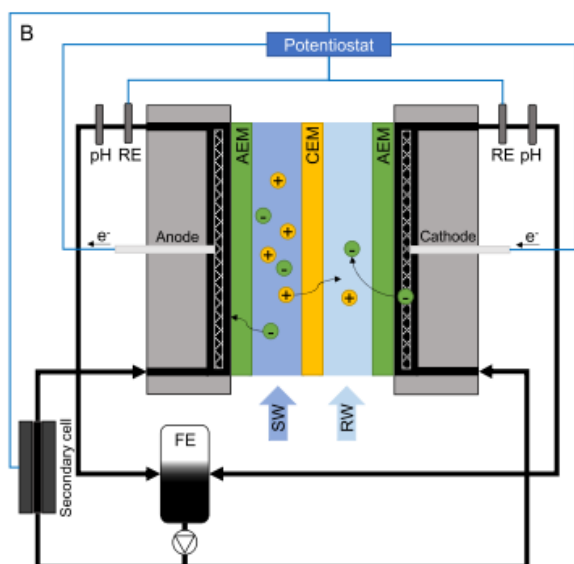


Fig 1. Schematic diagram of a RED device with CFE as the energy conversion system. The RED membrane stack is simplified, showing only one cell pair. Adapted from [7].

The ion-conductive electrolyte solution is usually prepared with NaCl before the activated carbon suspension. The absence of any additional species susceptible to side reactions is an advantage over previously described ECS.

In addition to ohmic charge transfer mechanisms, there is another phenomenon that plays an important role in the way CFE work, denominated charge percolation. It consists of the conduction of electrons through dynamic particle networks formed while the suspension flows. Such formation of networks is limited by a minimum carbon charge named the percolation threshold, below which the resistance drastically increases.

Like static capacitive electrodes, CFE have been used for capacitive deionization. Their application in RED was first reported by [8] who in 2017 proposed titanium core carbon brushes as current collectors. They reported a

power density slightly inferior to static capacitive carbon electrodes tested in the same device, reaching up to 260 mW/m², suggesting further research about the system resistances to improve obtained power density.

Recently, [7] presented an experimental study evaluating the electrochemical and rheological behaviour of activated carbon suspensions with various carbon loadings and additives during external powered galvanostatic experiments analogous to RED operation, as well as real RED prolonged operation with a crossflow ten-cell-pairs stack. The current collector employed was a Ti-mesh electrode with 2.5 μm Pt coating.

The authors reported stable behaviour during 7 days of real RED operation, and a maximum current density of 150 A/m² during externally powered operation, demonstrating the suitability of CFE for higher voltage scaled-up operation with such configuration. However, the maximum voltage reached in the experiments was below 1,23 V, deliberately chosen to prevent gas evolution.

Their attempt for using a cheaper material such as graphite flat plate as the current collector was not successful due to a lack of adequate support of the membrane pile in the proposed assembly. Thus, further work on the matter was encouraged.

They also suggest the characterization of the potential effects of multivalent ions present in natural feedwaters on the stability or electrical performance of CFE.

The scaled-up operation involves a higher number of cell pairs and thus a higher voltage. Therefore, the stability window of aqueous suspensions would be surpassed and the evolution of gas in this configuration would not be avoidable. Ti/Pt and other metal dimensionally stable current collectors widely used in the literature present low overpotentials to hydrogen and other gas evolution, so a considerable amount of redox gaseous products is expected due to the presence of these materials.

Graphite current collectors and activated carbon are expected to present higher overpotentials for these reactions [3].

High-voltage capacitive deionization studies with static carbon electrodes have reported the presence of faradaic reactions that cause the change in pH (which can compromise electrode and device integrity while changing the pH of the feed streams) and the production of hydrogen peroxide [9].

Other possible reactions involve the chlorine species evolution (if anion exchange membranes are used to connect the stack with the ECS), and the oxidation of the carbon electrode itself, which again can change the structure of current collectors and particles and affect the performance. A comprehensive review of anodic and cathodic reactions is presented by [10], who also report CFE deionization as a strategy to control pH changes by mixing charge and discharge slurries.

The same pH changes occur under static capacitive RED operation, although the discontinuous nature of this process led [11] to develop a strategy for controlling such reactions by changing the cutoff voltage where flow channels of feedwaters are inverted, leading to a negligible change in pH during prolonged operation. Such a strategy is not available in continuous CFE operations.

The composition of the electrode suspension also plays a role in the control of faradaic reactions. The authors in [12] operate a high voltage desalination (up to 4.8V) with CFE, achieving a higher charge efficiency when including 1% of carbon black, a common additive included in CFE formulations. This improvement is attributed to the higher electron conductivity of the carbon black, which makes the capacitive phenomena dominant over the faradaic ones.

Although the physical phenomena involved in static and flow capacitive deionization are common to CFE-RED operation, the objective of both devices is different. Suspensions suitable for the latter do not require a high capacitance value but a high conductivity and intraparticle ion mobility which reflects directly on the ability to hold high current densities that guarantee the ECS not to play a limiting role in RED devices.

There is a lack of understanding of the interaction between chemical species produced under high voltage operation and the electrochemical and rheological performance and stability of CFE, where other phenomena such as adsorption and precipitation could play a significant role, as shown in previous works in electrodialysis [13].

Pressure drops are also important in a scenario of commercial-scale devices using this ECS. A higher expected power requires more collector areas, which implies an increase in pumping power required. The shape of the ECS compartments and collectors also plays a role in the amount of power obtained, the stability of the suspension and the pressure drops. The viscosity of carbon suspensions depends on their composition, carbon loadings and the additives or particle modifications used. Various formulations, as well as surface modifications of activated carbon, have been proposed and tested to tweak the mentioned properties and increase net power production, such as the formation of a polyaniline layer on the surface of carbon particles [14].

Both electrochemical and rheological data are necessary to assess the suitability of CFE for scaled-up RED devices and to develop design proposals that ensure reliable and efficient operation. In addition, CFE scale-up developments are applicable to other technologies like flow capacitors for energy storage and devices for mineral recovery, which are of interest in the scenario of the development of a marine economy.

II. EXPERIMENTAL PROPOSAL

OUR work proposes the evaluation of CFE at voltages expected for a commercial-scale RED device, implementing an adequate graphite current collector with semi-circular carved channels as shown in Fig. 2, that provide adequate support to the stack while allowing the flow of carbon suspensions.

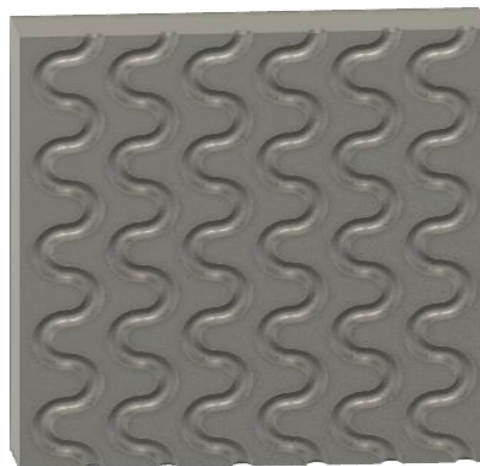


Fig 2. Graphite current collector with carved flow channels.

The specific objectives are:

- Assess electrochemical behaviour under *scaled-up expected voltage* conditions with *natural waters* or laboratory-prepared waters simulating natural composition. Using electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy, along with prolonged operation in our own designed prototype and stack, we intend to evaluate: gas evolution behaviour, presence of other chlorine soluble species, adsorption of generated gases and other species and its consequences for double layer charge and discharge, stability of surface functional groups and its influence on capacitive currents, and the influence of multivalent ions on capacitive currents.
- Characterize rheological behaviour: Activated carbon surface modification for pressure drop reduction. Stability of electrode suspensions during operation. Pressure-drop measurements and correlation with viscosity or other rheological parameter that characterizes the thixotropic nature of the fluid and the pumping energy consumption.
- Propose ECS design: determine required membranes, optimization of suspension composition, design of conduits and reservoirs for the avoidance of precipitation, operational variables optimization and/or novel operational proposals to guarantee a stable and sustainable RED operation.

III. RESULTS

Although the experimental assembly is yet being consolidated, preliminary tests of electric performance at low voltage have been performed to characterize capacitive behaviour separately.

Experimental cells for electrochemical measurements were built with the help of resin 3D printing technology that allows for fast prototyping.

Results of the preliminary tests still present some flaws because of the usage of stainless-steel current collectors that participate in corrosion reactions thus interfering with the measured current, so we do not present them in this abstract.

Also, we have made attempts to characterize the rheological expected performance of fresh and surface-modified activated carbon suspensions using a rotating viscometer. The results of these tests have confirmed the thixotropic behaviour of such suspensions but are yet to be measured with a more repeatable protocol to obtain useful comparative data.

The experimental design will proceed when the RED prototype is finished, and leakages of feed current are corrected.

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