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Grand Challenge

Grand Challenges in Salinity Gradient Energy Generation

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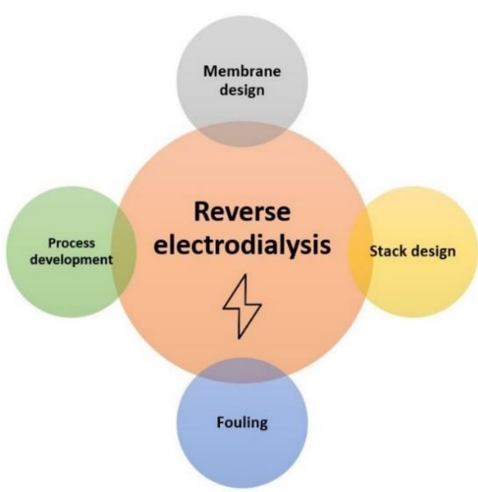
ABSTRACT

Reverse electrodialysis (RED) generates energy from salinity gradients, such as the one between seawater and river water, by selectively transporting ions through ion-exchange membranes. This paper discusses the challenges facing RED in four areas: ion exchange membranes, stacks, fouling, and processes, although it may not cover all issues as new advancements arise. Although bench-scale RED has impressive power generation, pilot-scale RED operations present challenges for widespread adoption. However, the main advantage of RED lies in its potential for synergetic applications with other processes like energy conversion/storage, wastewater treatment, and desalination. The development of low-cost, innovative membranes and integration processes with high energy efficiency and power generation capabilities for both scaled-up and-down approaches is essential for RED's continued advancement. Dedicated research will contribute to its potential for integration with other processes and viability as a renewable energy source. RED has the potential to be a significant player in the renewable energy market, but new advancements also present new challenges.

KEYWORDS: Blue energy; Reverse electrodialysis; Ion exchange membrane; Renewable energy.

GRAPHICAL ABSTRACT



HIGHLIGHTS

- The main challenges of reverse electrodialysis discussed.
- New advancements rise to new challenges.
- Membrane fabrication at low cost is crucial.
- Hybrid process integration is to continue.

1. Introduction

The high consumption of fossil fuels and related issues concerning climate change have encouraged the development of renewable energy technologies. While none of these technologies have fully achieved sustainability, energy harvesting from salinity gradients is a promising approach, utilizing the natural salinity differences between seawater and river water to generate power year-round. Across the world, it has been estimated that the salinity gradient power (SGP) in estuaries can reach up to 30 TW, with 2.6 TW of that amount being available for extraction (Wick 1978). Therefore, this clean, zero-emission renewable energy has huge global potential considering the fact that the scale of water use for energy production is growing significantly (Shahzad et al. 2017).

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Reverse electrodialysis (RED) is an effective method for generating energy from the salinity gradients, especially the one between seawater and river water (Post et al. 2007, 2010). Unlike other techniques such as pressure-retarded osmosis (PRO) (Yip et al. 2011) and capacitive mixing (CapMix) (Brogioli et al. 2013) processes, RED relies on the selective transport of ions through ion-exchange membranes with opposite charges. This transport occurs from high-concentration to low-concentration streams, resulting in an ionic current that is then converted into electrical current via redox reactions at the electrodes (Moreno et al. 2018). The ion exchange membranes are arranged alternatingly between the anode and cathode forming a *stack*.

Since its initial introduction by Pattle in the 1950s (R. Pattle 1954), RED has undergone significant evolution in terms of process components and design, while preserving its basic working principle. New membranes, electrodes, and spacers, along with novel concepts of hybrid processes, have been explored, all contributing to the development of RED technology (Lee, Wang, and Wang 2023; Mehdizadeh et al. 2019; Simões et al. 2020; Tian et al. 2020). Moreover, beyond pilot studies, micro/nano-level RED investigations have been conducted (Khatibi, Sadeghi, and Ashrafizadeh 2021; D. Kim et al. 2019), although to some extent they are limited. As this technology advances, new challenges emerge daily. Therefore, it is crucial to comprehend these challenges, identify feasible solutions, and surmount technological obstacles.

However, with these advancements come new challenges that must be addressed to overcome technological difficulties. This paper addresses the challenges of RED technology in four clusters: ion exchange membranes (IEMs), stacks, fouling, and processes, as shown in Figure 1. It is important to note that while this paper covers significant challenges, it may not encompass all issues, as new advancements in RED may give rise to new challenges.

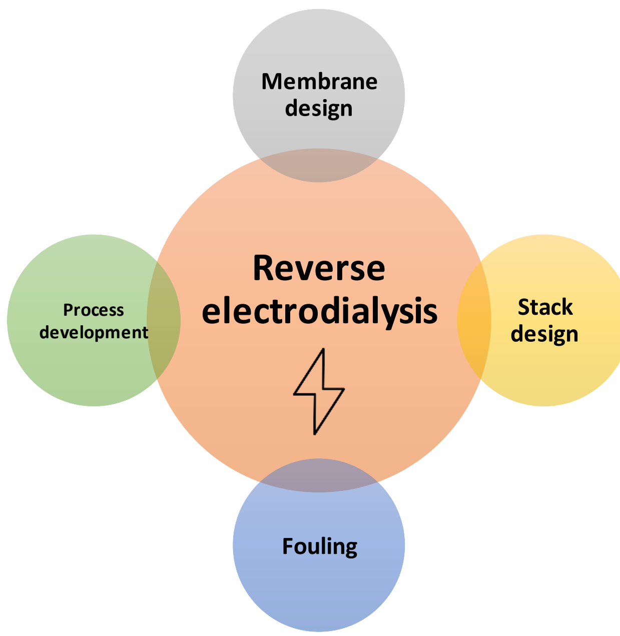

Figure 1. Topics of challenges in salinity gradient energy generation by reverse electrodialysis.

2. Challenges in membrane fabrication

Ion exchange membranes are critical components of reverse electrodialysis (RED) systems that generate salinity gradient power. According to the types of fixed charges, IEMs are classified as cation exchange membrane (CEM) and anion exchange membrane (AEM). Unlike CEM, AEM materials are still in the stage of being developed, followed by further progress in the development of large-scale processing and low-cost manufacturing in order to fulfil their role in global energy production (Yang and Cunman 2023).

High conductivity and permselectivity are the essential properties for a viable and efficient RED process, and they are the dominant performance determinants (Güler et al. 2013; Susanto et al. 2023). It is easy to understand the concept of low electrical resistance (or high conductivity) as membrane property. However, it is still difficult to conceptualize the (perm)selectivity as there are several types, such as co-ion counter ion selectivity, valence selectivity, and ion-solvent selectivity (Fan, Huang, and Yip 2023), which must be well-understood.

Initially, only co-ion or counter ion selectivity was considered sufficient, but later, monovalent ion selectivity became crucial as it was discovered that multivalent ions had detrimental effects on RED performance when especially natural waters are used as feed. Monovalent ion selectivity is a type of charge selectivity that defines the allowance of transport of monovalent ions only while retaining the multivalent ions. Multivalent ions are undesired in RED processes because they tend to migrate towards salinity gradient (i.e., uphill transport (J. Moreno et al. 2018)), increase the resistance and reduce permselectivity especially in heterogenous membranes where ion exchange resins are hot-pressed in a polymer matrix (Rahman 2023). To achieve high conductivity and low resistance, fast ion mobility is necessary. To accomplish this, membrane structure or physicochemical properties can be modified to facilitate ion transfer, or ions can be selectively transported, and multivalent ions can be retained (Besha et al. 2020; Güler, E, et al. 2014; Kotoka, Merino-Garcia, and Velizarov 2020). However, one must remember that there is always a trade-off between ion permeability and selectivity in IEMs, which is usually challenging to optimize these properties (Fan et al. 2023). In addition, permselectivity is rather difficult to control at high concentrations.

Recently, a discussion is interesting about making a “super” ion exchange membrane with superior selectivity properties (i.e., 100% selective membrane at highest degree of conductivity) (Kozmai et al. 2023). Some desired properties and the need for stabilization of membrane polymers were presented since membrane degradation over time is usually the case limiting the membrane lifetime. There are also other techniques to make the IEMs more conductive and selective such as decreasing the membrane thickness (i.e., shortening the path of ion transport) (Liu et al. 2020), aligning the path of ion transport in a specific direction (i.e., creating molecularly ordered ion conductive channels) (Zhang, Wen, and Jiang 2021), and even design of porous structure in membranes (Rahman 2023).

Swelling and osmotic water permeation are two other parameters that need to be discussed when RED membrane fabrication is considered. Increasing the density of fixed charges increases hydrophilicity of the polymer matrix and consequently increases the membrane swelling (Heintz, Wiedemann, and Ziegler 1997). Thus, that should be controlled to guarantee mechanical stability. So again, there is another trade-off between mechanical strength and ion exchange capacity of IEMs. Thus, some techniques have been applied so far in literature such as crosslinking, addition of inert polymer to cast solution, reinforcing, (Y. Kim et al. 2019). Water permeation, on the other hand, should be avoided too in RED because water decreases the salinity gradient in the stack when permeated through the membrane resulting in decreased potential and power. For that reason, in general, non-porous IEMs are designed for RED via solvent-evaporation. However, there are few studies discussing porous IEMs which enable nanofluidic ion transport at high level of permeability which are summarized in (Rahman 2023).

When fabrication of IEMs at large scale is considered, some methods should be searched for cost effectiveness and ease of continuous production. Because it is very likely to meet different experiences and challenges in mass production of lab-designed membranes. Recently, photopolymerization (Deboli, Van der Bruggen, and Donten 2022; Yang et al. 2019), extrusion of membrane materials (Altıok et al. 2023; Smolinska-Kempisty, Siekierka, and Bryjak 2020), radiation-grafting (Bance-Soualhi et al. 2021) seem to have promising potential in membrane production at industrial scale.

Therefore, in summary, for an efficient RED process, it is critical to ensure high conductivity and permselectivity, understand different types of selectivity for appropriate ions to be transported while retaining multivalent ions.

3. Challenges in stack design

A stack in RED system consists of alternating membranes mounted between an anode and a cathode. Spacers separate the membranes and create channels for fluid flow, while gaskets seal the stack. Stack design directly impacts performance as it relates to hydrodynamics. The goal of stack design may be ultimately minimizing hydrodynamic losses to maximize net power density and efficiency. Some key factors determining stack design include intermembrane distance, number and size of cells (AEM, CEM, and channels for fresh and concentrated water comprise a "cell"), inlet/outlet manifold design, selection and design of electrodes, electrolyte (e.g., redox solutions), and spacers. These parameters were all investigated in several related works (Jang et al. 2020; Moreno et al. 2018; Pawlowski, Crespo, and Velizarov 2014; David A Vermaas, Saakes, and Nijmeijer 2014).

Recently, Simões et al. proposed carbon slurry electrodes enabling redox-free reverse electrodialysis (Simões, Saakes, and Brilman 2022). Another study showed capacitive solutions as electrode solutions in RED provide good electrochemistry at low cost, scalability, and safety compared to hexacyanoferrate (Gueorguiev Velizarov, Cristina Maria Grade Couto da Silva Cordas, and Auxiliar 2020). In another study, electrode segmentation is investigated where current density can be adjusted at each segment (Simões et al. 2020). By doing so, a 39% of increase in net power density with 40% of net energy efficiency was achieved. Thus, we must recognize that the redox solution and the electrode design still remain in development and one can expect more studies on this issue in future.

Spacerless RED stack design is entirely a new field of focus that has significantly improved power generation. Many authors showed profiled membranes' advantages, but the challenge is finding the most effective membrane geometry, including for instance, lines, chevrons, pillars, waves, etc. at low cost (Güler, Elizen, et al. 2014; Pawlowski, Crespo, and Velizarov 2019).

Scalability must be considered as well when designing a RED stack. Moreno et al. evaluated scalability by studying how stack size changes with membranes (Moreno et al. 2018). However, specific considerations for upscaling electrode design remain. Upscaling the profiled membranes is likely upcoming research, though quite challenging.

4. Challenges in process protection from fouling

One of the most important parameters that affects the performance and efficiency of the RED process is membrane fouling. Among different types of fouling, biological fouling is particularly problematic in real pilot applications of RED, especially when using natural water streams as feed solutions. Biological fouling occurs when microorganisms attach to the membrane or spacer surface and form biofilms that obstruct the flow of ions or solutions through the membrane channels. This results in a significant decrease in the net power density generated by RED, ranging from 28% to 60%, depending on the water quality and operating conditions (Santoro et al. 2021; Vermaas et al. 2014; Vital et al. 2021). Moreover, biological fouling causes a substantial increase in the pressure drop along the membrane channels, which in turn increases the pumping power required to maintain a constant flow rate (Cosenza et al. 2022).

Membrane fouling also leads to changes in the intrinsic properties of the ion-exchange membranes (IEMs) used in RED, such as electrical resistance, permselectivity, ion exchange capacity, and water uptake. These changes affect the transport phenomena and thermodynamics of RED and reduce its overall performance. Although there are existing studies on membrane modification for RED focusing on enhancing these properties for prevention or control of fouling (Choi et al. 2022), there is a need for more research on developing anti-fouling membranes for RED applications.

In addition to membrane modification, several other strategies have been proposed and tested to mitigate or eliminate fouling in RED processes. These include feed pretreatment methods such as filtration or disinfection (Susanto et al. 2023); spacer design optimization (He et al. 2016); cleaning/washing protocols to remove foulants from membrane surface (Cosenza et al. 2022); and process design modifications such as changing flow directions or configurations to minimize concentration polarization and biofilm formation (Choi et al. 2022; Mei and Tang 2018).

To some extent, these strategies do not apply or work for all forms of organic foulants found in natural waterways. Each type of organic foulant has a different chemical composition, molecular size, charge distribution, and adsorption behaviour on IEMs (Song and Choi 2022). Therefore, different fouling reduction scenarios must be investigated and tailored to the specific characteristics of each foulant. In addition, IEM modification, specifically for RED, is still limited in the literature, indicating that there is still room for further improvements and innovations. Thus, anti-fouling strategies for RED still need to be carefully integrated and tuned to achieve optimal performance and efficiency.

5. Challenges in RED process development

RED technology has been used in many fields. Therefore, the discussion of the replacement or comparison of RED with other renewable energy technologies, such as wind and solar energy, has become less significant as this is not the main advantage of RED. More importantly, the integration of RED with other technologies in the fields of energy conversion, desalination, and wastewater remediation is feasible and useful (Tian et al. 2020). By doing this, the synergistic effects of different processes have been utilized, which is more important rather than to solely aim for the RED performance in terms of power generation.

Another discussion or debate that has been active from time to time is whether this technology should evolve towards scaling up or down. It has been proven that when the RED system is smaller, which is defined by the smaller dimensions of the stack, it is possible to obtain more power per unit membrane area (or fluid flow path), that is, power density. This is due to less hydraulic friction and lower pumping power (Pawlowski et al. 2014; Tsai, Liu, and Yang 2016). Thus, microfluidic or nanofluidic RED studies have recently emerged in the literature (Hsu et al. 2017; Lee, Kim, and Kim 2016; Tsai et al. 2016). On the other hand, successful pilot studies, such as the one first conducted in Afsluitdijk (The Netherlands), have shown that this technology is quite suitable for scaling up. Upscaling can be performed by increasing the active membrane area and implementing multistages (Hu et al. 2019; Simões, Vital, et al. 2022; Veerman 2020). When a multistage RED is used, the process can be significantly improved in terms of energy efficiency and generated power. Several studies have investigated this multi-staging – performance relationship (Hu et al. 2019; Simões, Vital, et al. 2022; Veerman 2020). Hydrogen production was investigated in a study of a serial system of RED technology (Zhang et al. 2022). Similarly, wastewater treatment with multistage RED was also used (Xu et al. 2021). So, it can be realized from these studies that upscaling can be used in variety of application fields of RED.

Nevertheless, the challenges in different scaled up processes of RED may also be different. Thus, it may be difficult to deal with them all at times. It is a completely different field and beyond academia, as it often requires extensive studies in different disciplines, such as hydraulic engineering, water management, and infrastructural works (Post et al. 2010).

Some factors directly affect the cost of scaled up RED processes. For example, the cost of the membranes still dominates the overall cost of the pilot plant. In addition, pretreatment, which relies on modifying the content of the feed streams, is another field that needs to be thoroughly investigated because there are numerous options for pretreatment (Ju et al. 2022). Apart from these parameters, it is also a big challenge to consider RED process for energy storage (Kingsbury, Chu, and Coronell 2015). RED is so versatile that it can also be used for energy storage, which has been less considered up to now than just harnessing salinity gradient energy. Thus, a battery structure could be formed using a typical RED system for energy storage.

In summary, the integration of RED with other technologies and the consideration of scaling up or down depend on the application and pose their own challenges that require extensive study and consideration of various factors. An overview of the significant challenges faced by RED technology can be found in Table 1, which summarizes these challenges in a concise manner.

6. Future Prospects

RED is a widely studied technique for salinity gradient energy generation and has been recognized as a form of ocean energy. Although bench-scale RED has shown impressive power generation performance, pilot-scale RED operations have posed a challenge to widespread adoption. However, the main advantage of RED is not in generating large amounts of energy, but in its potential for synergetic applications with other processes such as energy conversion/storage, wastewater treatment, and desalination. This potential for integration with other processes will likely continue to be the focus of research in the upcoming years.

RED technology has the potential to become an important player in the renewable energy market in the future. However, achieving new advancements in RED technology also presents new challenges, including specific needs in terms of membranes, stack and process designs, and fouling issues. Membrane design and development at low cost are critical for viable and economical RED operations. Continued research into the development of novel membranes specifically designed for RED, innovative integration processes with high energy efficiency, and power generation capabilities for both scaled-up and-down approaches will be essential for the continued advancement of RED technology. Dedicated pilot projects and more intensive research across different regions of the world will contribute to a technological leap forward in potential of RED for integration with other processes and its viability as a renewable energy source.

Table 1
Overview of significant challenges in reverse electrodialysis.

Challenge category	Specific challenge
Membrane fabrication	• Selectivity control at high concentrations • Management of multivalent ion transport • Elimination of water permeation • Cost-effective and continuous production methods for large-scale fabrication
Stack design	• Scalability considerations • Upscaling electrode design • Upscaling profiled membranes • Reduction of stack resistance
Fouling mitigation	• Need for foulant-specific anti-fouling membranes • Investigation of tailored fouling reduction scenarios • Integration and tuning of membrane properties for optimal performance and efficiency
Process development	• Understanding the multi-staging-performance relationship • Upscaling hybrid processes • Consideration of scaling up or down

Author contributions

EG contributed to outline and wrote the first draft of the manuscript. Both EG and NK contributed to manuscript revision, read and approved the submitted version.

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