Review Article

Electrochemical synthesis of chemicals and treatment of wastewater promoted by salinity gradients using reverse electrodialysis and assisted reverse electrodialysis
Onofrio Scialdone

Abstract

In the last years, an increasing attention has been devoted to the utilization of waters with different salt content to drive valuable redox processes at the electrodes by reverse electrodialysis processes (RED) or assisted RED (A-RED), thus allowing to significantly reduce the energetic costs associated to conventional electrolyses. In this review, the most relevant findings were presented and were critically discussed. The use of RED and A-RED for the synthesis of chemicals, the conversion of CO_2, and the treatment of wastewater contaminated by organic and inorganic pollutants resistant to traditional biological processes was analyzed. The main advantages and disadvantages of these routes were commented, as well as the key points that should be addressed to favor the utilization on an applicative scale.

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Introduction

Electrolyses are largely used for the synthesis of bulk and fine chemicals and fuels [1–3]. In many cases, they are a more environmentally benign and cost-effective technique than competitive chemical routes. Moreover, the use of various electrochemical methods for the treatment of wastewater contaminated by many kinds of pollutants was extensively studied [4a,b,5]. However, the cost of electric energy limited the economic appealing of many of these processes. To reduce the energetic costs of some electrolyses, the utilization of microorganisms was proposed [6]; however, these processes are characterized by very low productivities imposed by small current densities given by microorganisms. In the last years, it was shown that some valuable electrochemical processes can be promoted by salinity gradients energy (SGE) using reverse electrodialysis (RED) or assisted reverse electrodialysis (A-RED) processes [4]. Indeed, the supply of solutions with different salt concentrations to a RED stack allows to obtain an electromotive force E, which can be used to drive the target redox processes at suitable electrodes. If the potential difference generated by salinity gradient is sufficient to sustain the process, we have a RED process, whereas when we have to couple it with an external supply of electric energy, an A-RED is involved. Salinity gradients can be obtained from the combination of many sources largely available in nature (such as seawater, brackish water, and freshwater), in industrial plants (as wastewaters with different salinities) or in salt ponds or from synthetic saline solutions that can be regenerated with waste heat (>40 °C) in closed-loop routes [7–9]. As an example, the world theoretical potential energy resulting from rivers discharging into seas and oceans was estimated to be 1.4–2.7 TW, while waste heat potentially available in the US in 2011 was reported to correspond to 833,3 GWh [7]. In the last few decades, it has been proposed to use SGE in RED processes to generate electric energy [7–9] and various prototype plants, operating under real conditions, were developed [10,11]. Very large stacks equipped with hundreds or thousands of membrane pairs are necessary to produce electricity, resulting in high investment costs for RED systems [7,8]. In most of these investigations, redox processes were selected with the aim of reducing the energetic loses at the electrodes and to provide stable operating conditions [12,13]. However, in the last years, various authors proposed to select the redox processes to add an economic value to the overall system [4,8]. Hence, three potential applications of salinity gradients in RED stacks can be considered: (i) the conventional technology aimed to generate electric energy which requires a large

number of membrane pairs; (ii) a more recent route focused on the use of SGE to sustain useful electrolyses processes using small RED stacks, which requires a relatively small number of membrane pairs; and (iii) a coupled approach aimed to both generate electric energy and provide useful chemical reactions. In this manuscript, the literature pertaining the use of SGE to sustain redox processes by RED and A-RED for both the synthesis of chemicals and fuels and the treatment of wastewater contaminated by organic and inorganic pollutants will be critically reviewed.

Reverse electrodialysis and assisted reverse electrodialysis

As described more in detail in [13,27,28], RED and A-RED stacks are composed by N couples of cationic exchange membranes (CEMs) and anionic exchange membranes (AEMs), two electrode compartments, and two outer membranes selected in order to avoid the passage of components of electrode solutions to the side compartments and vice versa (Figure 1). CEMs and AEMs are alternately aligned to create low and high-concentration compartments, fed, respectively, with low-concentration (LC) and high-concentration (HC) saline solutions. When the two solutions (with solute activities in concentrate and dilute solutions a_c and a_d, respectively) are fed to the stack at an absolute temperature T, an electromotive force E given by eq. (1) is generated [9,10]:

$$E = 2 N \alpha R T \ln(a_c/a_d)/F \qquad (1)$$

where α is the average permselectivity of the membrane pair, R the gas constant, and F the Faraday constant. For pure NaCl solutions of 1 and 30 g/L and for ideal membranes with $\alpha = 1$, this equation gives 0.175 V for each membrane pair at 298 K. The real potential generated by each membrane pair is significantly lower due to the resistance of the stack and due to the real permselectivity of membranes, and it was estimated to be close to 50−70 mV. Hence, for these salt solutions, a stack with $N = 40$ is expected to deliver a potential of about 2.0−2.8 V that can be used to drive target cathodic and anodic processes. The potential generated by the salinity gradient can be increased using larger a_c/a_d or N or using an A-RED process by connecting the stack with a power supply instead of the external load involved in RED (see Figure 1), thus enhancing the spontaneous ion fluxes. The target redox processes can be performed directly in the electrode compartments of the stack, or alternatively, they can be carried out in a different electrolysis cell alimented by the energy generated in the RED stack.

Synthesis of chemicals and fuels

RED systems were proposed in the last years for the synthesis of few chemicals and, in particular, to produce hydrogen [14−27] and chlorine [28] and to convert CO_2 to formic acid (FA) [29] (Figure 1). Most of researchers

Figure 1
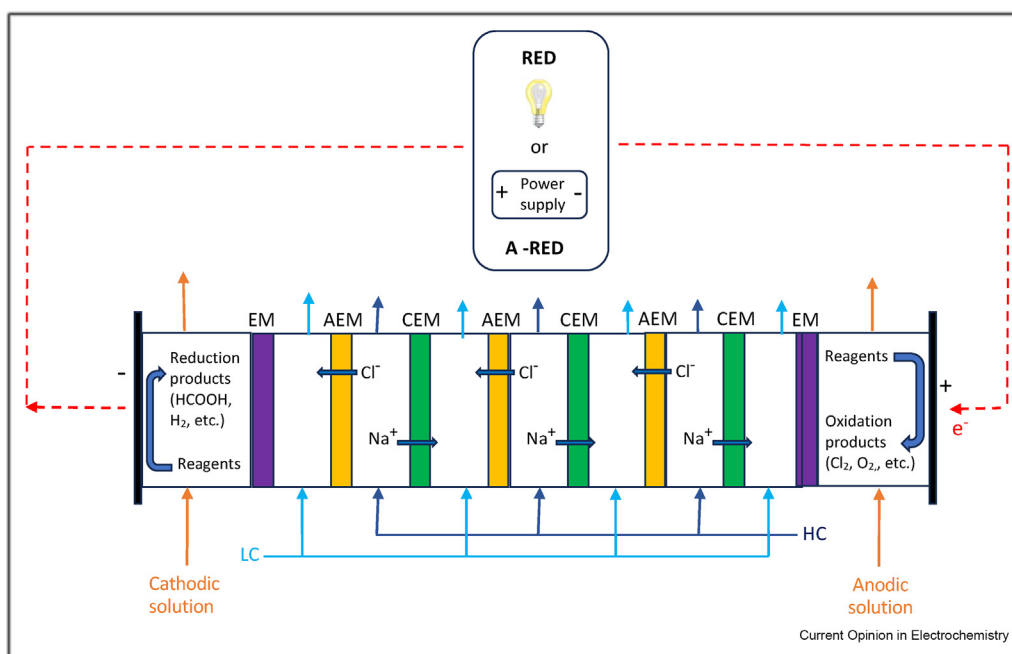
Scheme of reverse electrodialysis (RED) and assisted reverse electrodialysis (A-RED) stack for the synthesis of chemicals. The stack is equipped with alternate cationic membranes (CEMs) and anionic membranes (AEMs) used to selectively drive the flow of positive ions to the right and the negatively charged ions to the other side, two external membranes (EMs) and electrodes and it is fed with high concentrated (HC) and low concentrated (LC) saline solutions and with electrolyte solutions.

focused on hydrogen, which is considered the most promising energy carrier and a relevant alternative to fossil fuels. In most of cases, H_2 was produced at the cathode by reduction of protons in acidic media (eq. (2)), while the anodic process was the oxygen evolution in basic solutions (eq. (3)) (Table 1).

$$2H^+ + 2e- \rightarrow H_2 \qquad (2)$$

$$2OH^- \rightarrow 0.5\ O_2 + H_2O + 2e^- \qquad (3)$$
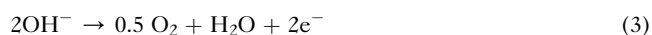
The potential required to drive such reactions is relatively low. As an example, it was about 1.5−1.6 V for a current density j of 10 mA cm^{-2} considering both the equilibrium potentials and the overpotentials under the conditions mentioned in [14,15]. Hence, a small N is necessary to generate the potential necessary to drive the redox reactions and to compensate the internal resistance of the stack at least for low j. Different HC and LC solutions were used: (i) synthetic solutions with NaCl concentrations similar to that of natural sources, (ii) solutions regenerable by waste heat, and (iii) waters coming from real plants (see Table 1). Hatzell et al. [16] propose to use a RED stack to produce H_2 and to reduce the acid content of the catholyte (Table 1). Ammonium bicarbonate (AmB) was used since it is relatively easy to be distilled at low temperatures (40−60 °C), allowing the potential use of waste heat for the regeneration of HC and LC solutions. Raka et al. [15] found that the cost of membranes dramatically affects the economics

of the system and that AmB RED for hydrogen production is expected to have economic potential for membrane costs lower than 2.9 €/m^2 and/or a membrane life of 7 years or more. Chen et al. [20] used a bipolar membrane, as an external membrane (EM) close to the catholyte compartment, to generate the acid and the base necessaries for cathodic and anodic reactions, respectively, while Higa et al. [18] used a commercial ED pilot plant fed with brine from a salt water desalination plant as HC and sewage-treated water from a water treatment center (treated by fiber filtration) as LC solution to produce hydrogen. It is worth to mention that stable operations for 1.100 h were reported even if with relatively low js [17]. A pilot-plant application (N 200) was also used to supply energy to a separated alkaline polymer electrolyte water electrolysis cell for the hydrogen production [18]. A-RED was recently used to enhance j maintaining a small N [21]. Indeed, an enhancement of j and H_2 productivity (up to 250 %) was obtained using an external cell potential (in the range 0.65−3.1 V) [21].

Recently, Ranade et al. proposed the utilization of the anodic compartment of a RED stack for the production of chlorine coupled with the cathodic production of H_2 even if this interesting route was investigated only by a simplified one-dimensional model [28], while Ma et al. [29] investigated the use of RED and A-RED to drive the cathodic reduction of CO_2 to FA (eq. (4)) at tin cathodes.

Table 1

Examples of publications devoted to the use of reverse electrodialysis systems for the production of H_2.

Cathode and catholyte	Anode and anolyte	HC and LC	N	Products	Reference and notes[a]
Ti-Ru/Ir HCl (0.2−2 M)	Ti-Ru/Ir NaOH (0.5 M)	1.5−5. 0 M NaCl 0.008−0.5 M NaCl	20	H_2 and O_2	[14] i_{max} ~ 20 A/m^2
Nickel/nickel mesh 1 M KOH	Nickel/nickel mesh 1 M KOH	2 and 0.06 M ammonium bicarbonate	10	H_2 and O_2	[15] Theoretical study
Ti-Pt/Ir Waste acid (0.01 M HCl)	Ti-Pt/Ir NaOH (0.5 M)	1.4 M and 5 mM ammonium bicarbonate	20	H_2 and O_2	[16] FE_{max} ~ 70 %; i_{max} ~ 20 A/m^2
Ti-Pt 5 wt.% Na_2SO_4	Ti-Pt 5 wt.% Na_2SO_4	simulated seawater sewage treated water	200	H_2 and O_2	[17] stable operation for 1100 h; FE_{max} ~ 100 %; i ~ 15 A/m^2
Ti/Pt 0.5 M Na_2SO_4	Ti/Pt 00.5 M Na_2SO_4	0.3/0.01 M Na_2SO_4	200	H_2 and O_2	[18] The power generated in the RED stack is used to drive an alkaline water electrolysis cell
Ti-Ru/Ir HCl (0.1−1 M)	Ti-Ru/Ir 0.5 M NaOH	4 and 0.017 M NaCl	8−24	H_2 and O_2	[20] The system involves the presence of a bipolar membrane to self-maintain the strongly acidic/basic electrode reaction conditions; FE ~ 91
Ti−Pt/Ir 0.5 M HCl	Ti - Pt/Ir 0.5 M NaOH	0.6−6 and 0.017 M NaCl	20	H_2 and O_2	[21] Use of both RED and A-RED FE ~ 100 %; i ~ 50−100 A/m^2
n.a. 0.05 M NaOH	n.a. 0.05 M NaOH	3 and 0.017 M NaCl	40	H_2 and O_2	[27] The study shows that the existence of multivalent ions in brine significantly degrade the hydrogen production

Abbreviations: A-RED = assisted reverse electrodialysis; HC = high concentration; LC = low concentration; RED = reverse electrodialysis; FE = faradic efficiency for the production of hydrogen.
[a] Values are in most of cases estimated using data present in the references.

$$CO_2 + 2e- + 2H^+ = HCOOH \qquad (4)$$

The anodic process was the conversion of chlorides to active chlorine. The reduction of CO_2 at tin cathodes to FA is a quite promising process, even if further improvements are necessary to improve the economic data [30]. The process takes place at a potential close to $-1.8 - -2.0$ V vs. saturated calomel electrode (SCE). Hence, if the anodic process is the oxygen evolution reaction or the chlorides oxidation, a ΔV often higher than $3.3-3.5$ V is necessary. Hence, the use of SGE and RED or A-RED technologies could be particularly useful to reduce the energetic consumptions. It was shown, using a stack with $N = 60$, that SGE can drive the redox processes with an initial j close to 20 mA cm^{-2} that strongly decreased with time [29]. Also A-RED was used, with an external cell potential of 0.5, 0.65, and 0.8 V [29]; using the smaller external cell potential of 0.5 V, the production of FA after 4 h was doubled with respect to RED; moreover, the initial j was about 80 mA cm^{-2}, and it was more stable with the time. Even higher js and [FA] were achieved using higher external cell potentials.
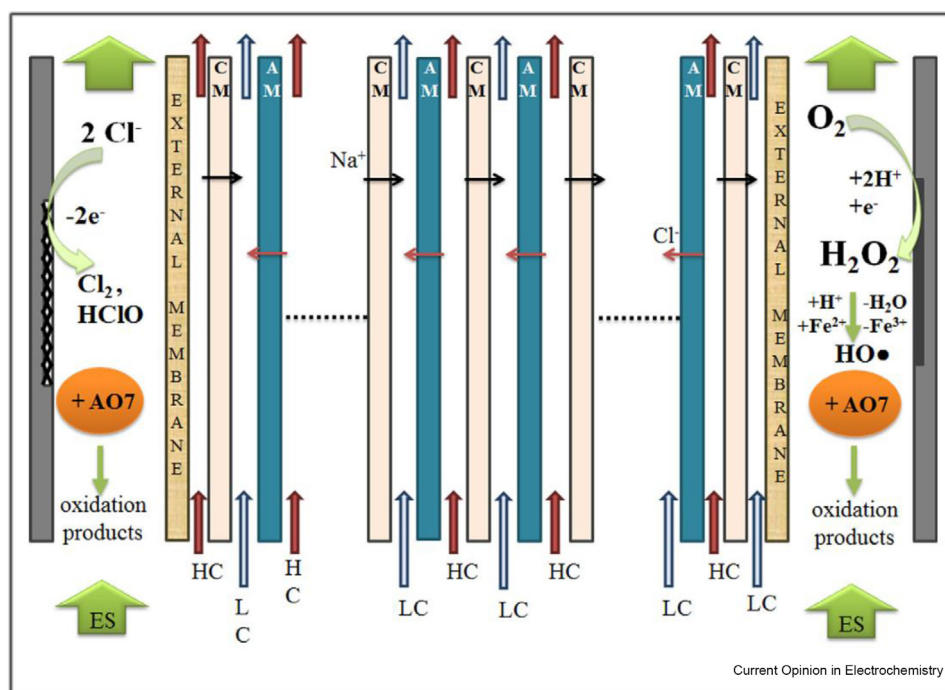
Treatment of wastewater contaminated by pollutants resistant to conventional biological processes

Scialdone et al. showed for the first time that SGE can be effectively used to treat various kinds of wastewater contaminated by organic or inorganic compounds by properly redox processes in RED stacks [31–33]. In the successive years, other groups decided to use salinity gradients and RED stacks to treat wastewater contaminated by organics [34–43], Cr(VI) [32,44,45], ammonia [46], perchlorate [47], and microorganisms [48,49]. It was shown that organics pollutants can be removed in cathodic compartment by electro-Fenton and/or in the anodic one by direct anodic oxidation or oxidation by electrogenerated active chlorine [33–43]. As an example, water solutions of Acid Orange 7 (AO7), a model organic compound very resistant to conventional biological processes, were treated in both electrode compartments (Figure 2). Both the color of the solution and the organic were completely removed at both electrodes, and the total organic content (TOC) of the solution was reduced of more than 60% [33].

Moreover, Jia et al. [42] proposed to use a RED stack to treat waters containing dye methyl orange in the electrode compartments using coagulants produced at the electrodes and to produce H_2 in the anodic compartment. In 2021, Shiming et al. [36] proposed the utilization of five RED stacks ($N = 40$) in series with respect to NaCl HC and LC solutions (salinity ratio: 100) and in parallel for what concern the synthetic solution of AO7, thus allowing to treat a larger volume of the synthetic wastewater with respect to single stacks, even if a quite

Figure 2

Scheme of a reverse electrodialysis (RED) stack for the treatment of wastewater contaminated by an organic model pollutant in both cathodic and anodic compartments. Electrode processes: electro-Fenton at the cathode and indirect oxidation with electrogenerated active chorine at the anode. The system is fed with high-concentration (HC) and low-concentration (LC) saline solutions and with electrode rinse solutions (ES). From O. Scialdone, A. D'Angelo, A. Galia, energy generation, and abatement of Acid Orange 7 in RED cells using salinity gradients. Copyright 2015 Elsevier [33].

large overall N (200) was used. Even if most of the works cited earlier used synthetic solutions of NaCl for HC and LC solutions, the treatment of solutions of AO7 was effectively performed also by reactions reported in Figure 2 in a pilot plant (N 500, 44×44 cm^2) located in the south of Sicily (Italy) using real solutions (brackish water and brine) [50].

SGE was used to remove Cr(VI) in RED stacks by (i) direct cathodic reduction to Cr(III) [32], (ii) Fe-anode dissolution to generate Fe^{2+} for reducing Cr(VI) and subsequent Fe^{3+} coagulation for removing total Cr [44], and (iii) microbial RED, that combined in the same stack a microbial fuel cell and a RED, allowing to reduce the number of membranes necessary to drive the process [45].

The production of electrogenerated active chlorine in the anodic compartment of the RED stack was effectively used also for the removal of ammonia [46] and disinfection purposes [48,49]. In particular, it was shown that domestic aquaculture wastewater can be disinfected in RED stacks either by anodically electrogenerated NaClO or by H$_2$O$_2$ generated at the cathode [48].

Recently, Ma et al. investigated the use of A-RED for the treatment of synthetic wastewaters contaminated by organics [29]. Indeed, A-RED required lower applied cell potentials than electrolysis and gave higher abatement of TOC with respect to RED. In particular, A-RED allowed to significantly reduce the TOC of the solution also using quite-low-salinity gradients ther were not sufficient for RED [29].

Advantages and disadvantages and key aspects to be addressed

Overall, the use of SGE in RED stacks can be considered a very promising tool both to reduce the operative costs of electrolyses and to exploit available SGE. As an example, the use of RED can allow to save about $42-66$ KWh Kg$_{H2}^{-1}$ with respect to state-of-art electrolyzers used for H$_2$ production [21]. Moreover, the use of SGE to drive valuable redox processes allows a drastic reduction of N with respect to that necessary for the production of electric energy. However, the use of the RED stacks presents some disadvantages with respect to electrolysis cells: (i) the utilization of a more complex device and the related increase of the capital costs caused by the use of tens of membrane pairs; (ii) the necessity to achieve HC and LC solutions with a suitable salinity gradient at a low cost in loco; (iii) stability problems due to potential channels' clogging and membrane fouling for real HC and LC solutions; and (iv) for some tested processes (as an example, for H$_2$ and CO$_2$ production), the results (in terms of FE or productivity or stability) were not comparable to that achieved in electrolyses.

The use of both microbial RED [45,51,52] and A-RED was proposed to decrease N and the capital costs of the system. The coupled use of microbial cathodes and SGE allows to use a very low number of membrane pairs, but it requires to deal with the intrinsic limitations due to microorganisms (such as temperature and compositions constraints). For A-RED, Ma et al. [29] have conducted an economic analysis for the anodic treatment of wastewater showing that (i) electrolyses gave the highest operative and the lowest capital costs; (ii) RED presented the lowest operative and the highest capital costs; and (iii) A-RED presented intermediate values of both operative and capital costs and, in most of adopted conditions, the best overall economic data [29]. In particular, it was shown, in the case of the treatment of wastewater contaminated by AO7, that RED and A-RED allowed to save, respectively, about 30 kWh and $20-27$ kWh m^{-3} with respect to conventional electrolysis, depending on the salinity gradient and on the value of the external cell applied, under the operative conditions reported in [29]. In the case of H$_2$ production, the use of A-RED was reported to save about $16-43\%$ of the energy consumptions of electrolyzers under the operative conditions used in [21]. Moreover, A-RED can also exploit the SGE present in solutions with relatively small salinity gradients not sufficient for RED processes and can increase the productivity of the cell.

The problem of the availability of water with different levels of salt content *in situ* is also a key issue. As an example, the use of SGE and RED for the treatment of wastewater was investigated mainly using artificial solutions of NaCl, seawater and freshwater, and brine and seawater/freshwater, but industrial sites that generate/treat the wastewater are in most of cases not located in river estuaries or in salt ponds, where these salinity gradients are easily available. However, the sites that generate/treat wastewaters in most of cases are centralized plants that deal with many different kinds of liquid effluents usually characterized by different salinities [53]. As an example, it was proposed to use a RED stack to treat one synthetic wastewater with high salinity by active chlorine electrogenerated at the anode using as HC solution the same wastewater [53]. However, it was shown that the use of real wastewater can cause channels' clogging and membrane fouling, dramatically affecting the system stability [54] even if these problems were minimized by *in situ* backwashing.

Overall, in spite of the very promising results achieved, the use of SGE to sustain redox processes will require deep investigations in the next years, aimed mainly to (i) decrease the capital costs by proper use of A-RED or selection/development of cheap membranes; (ii) evaluate for long times the proposed processes using various kinds of real HC and LC solutions coming both from natural and industrial sites; (iii) investigate the

performances of the proposed process for real liquid effluents for the treatment of wastewater; (iv) define a set of operative conditions that can guarantee performances similar to those given by conventional electrolyzers for the synthesis of chemicals; (v) evaluate more in deep the utilization of both anode and cathode to produce valuable chemicals; and (vi) analyze more in detail the potential use of SGE produced by waste heat by focusing both on RED stack and regeneration section.

Declaration of competing interest

There are no competing interests to disclose.

Data availability

No data was used for the research described in the article.

Acknowledgment

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