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Direct Electrosynthesis of Sodium Hydroxide and Hydrochloric Acid from Brine Streams

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Abstract

Water is an abundant resource across the world, and its purification and byproduct recovery methods are crucial for economical, environmentally safe, and sustainable utilization. Desalinating seawater generally produces brine as a byproduct that cannot be purified economically with current technologies and which is instead released to the environment. In this perspective, we discuss direct electrosynthesis of sodium hydroxide (NaOH) and hydrochloric acid (HCl) from seawater-desalination brine as an emerging alternative solution. In this direct electrosynthesis (DE) process, the water splitting reaction is used to produce H^+ and OH^- , which combine with the brine stream to produce NaOH and HCl. After introducing the scope of the process, we describe developments in earth-abundant catalysts for water splitting and the competing chlorine evolution reaction (CER), as well as challenges in inefficiency and productivity. Finally, we discuss the economic impact and feasibility of direct electrosynthesis.

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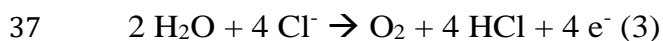
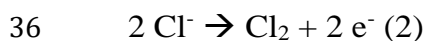
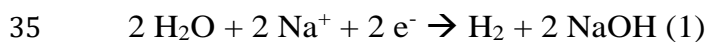
4 **Introduction**

5 Desalination of seawater provides an abundant source of fresh water, a critical resource for human
6 health and agriculture. As the use of desalination continues to grow, the discharge of high-salinity
7 brine is an environmental concern, owing to potential negative impact on the receiving ecosystems.¹
8 While the marine impact can be limited through proper discharge systems design, the associated
9 construction costs can be prohibitive.² Instead of dumping it into the ocean as a waste product, brine
10 can be used as a resource instead.

11 To reduce costs associated with brine management, it has been proposed that brine treatment could
12 be coupled with the production of sodium hydroxide (NaOH).³ NaOH is an important chemical
13 serving multiple purposes in desalination, mostly related to raising pH. By raising the pH during
14 reverse osmosis (RO) — a major technique for water desalination — mineral salts such as CaCO₃
15 can become supersaturated in the effluent causing them to precipitate onto the membrane. This
16 phenomenon, known as scaling, can significantly reduce performance.⁴ Pretreating the effluent with
17 NaOH to raise pH has been shown to cause Ca(OH)₂ and other ions to precipitate, which in turn
18 prevents scaling later in the process.⁵ Additionally, certain harmful elements such as boron in the
19 form of boric acid are able to pass through RO membranes due to their neutral charge. Adding NaOH
20 causes boric acid to dissociate and eventually become borate, which is charged and can no longer
21 pass through the RO membrane.⁶ Silicon and carbon dioxide behave in a similar manner to boron and
22 are also better rejected at a higher pH induced by NaOH addition.^{7,8} NaOH has also been shown to
23 hinder the growth of microorganisms that can cause the fouling of reverse osmosis membranes.⁹
24 NaOH is also used as part of a cleaning solution for the removal of multiple compounds and possible
25 foulants.¹⁰

26 NaOH production from brine has proved to be difficult because salt water contains many
27 impurities beside NaCl and after RO these impurities are even more concentrated in the brine, despite
28 the removal of some impurities in RO pretreatment. In particular, typical brine from seawater usually
29 contains on the order of 100–300 mg/l of Mg^{2+} and Ca^{2+} , which are detrimental to all NaOH
30 production methods.

31 Currently, the chlor-alkali process is the most widely used electrochemical reaction to produce
32 NaOH; it produces NaOH and Cl_2 and H_2 gas through the electrolysis of aqueous sodium chloride
33 (NaCl), as shown in equations 1 and 2.¹¹ Alternatively, the use of NaCl can be coupled with water
34 splitting to produce NaOH and HCl, as well as O_2 and H_2 gas, as seen in equations 1 and 3:



38 Developing technologies that can simultaneously produce HCl and NaOH with low energy
39 consumption has both economic and environmental benefits. By generating the chemicals on-site
40 from brine, the need to buy and transport the chemicals from elsewhere can be eliminated.
41 Additionally, by recovering these valuable resources from the brine, the brine may be partially
42 recycled back into fresh water, minimizing the impact of brine discharge to the environment.
43 However, the simultaneous production of HCl and NaOH has yet to gain prominence because the
44 technology is still being developed and optimized.

45 Here we discuss a promising approach for conversion of brine to NaOH and HCl: direct
46 electrosynthesis (DE). DE is attractive due to fewer membranes and a lower energy requirement than
47 other methods such as bipolar membrane electrodialysis (BMED). First, we compare DE to BMED.

48 Then, we describe recent advances in earth-abundant catalysts for the reactions relevant to DE,
49 namely hydrogen evolution reaction (HER), the oxygen evolution reaction (OER), and the chlorine
50 evolution reaction (CER). Finally, the feasibility and economics of brine management potential using
51 DE or similar approaches for other industries is discussed.

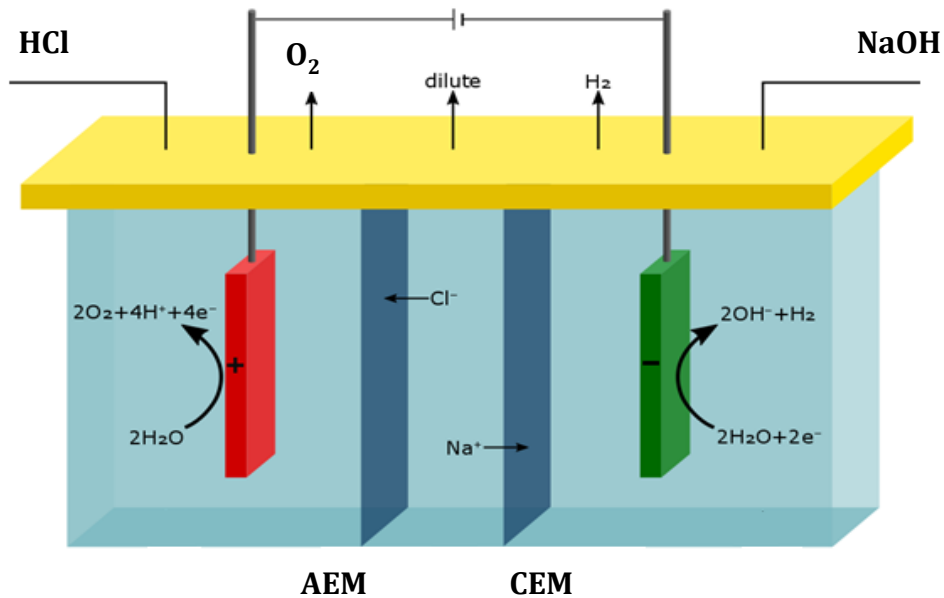
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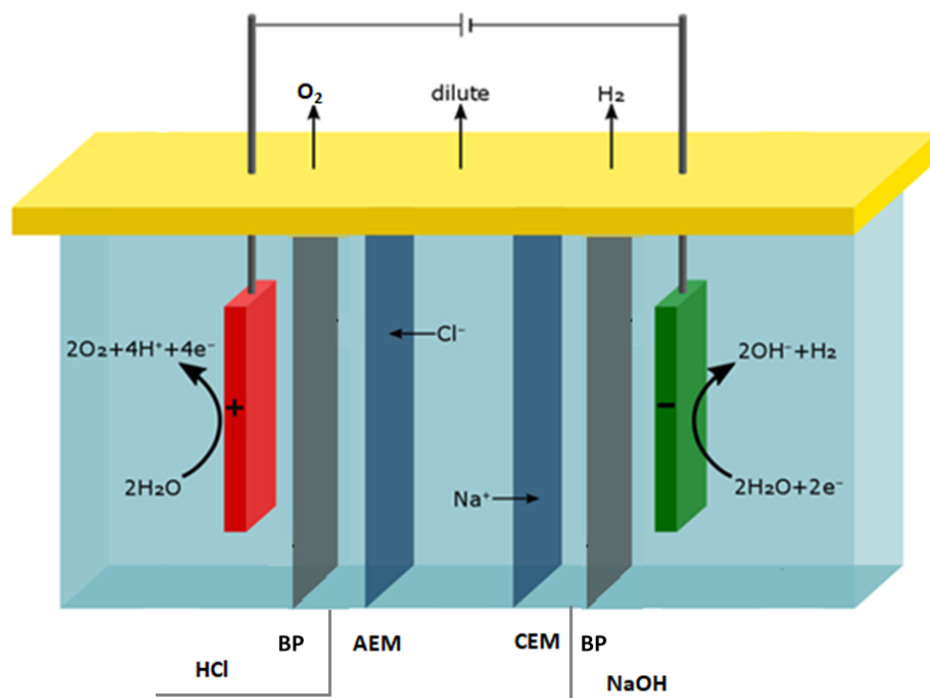
54 **Comparison of BMED and DE**

55 HCl and NaOH can be produced using bipolar-membrane electro dialysis (BMED)¹² (Figure 1(b)),
56 in which membranes isolate the cathode and anode from the NaOH and HCl that is produced.
57 However, the material and operation costs and complex designs of BMED processes make them
58 unfavorable for industrial-scale use at present.¹³

59 (a)



69 (b)



70

71 **Figure 1.** Schematic drawings of electrodialysis systems. (a) Direct electrosynthesis and (b) bipolar-
 72 membrane electrodialysis. AEM: Anion exchange membrane; CEM: Cation exchange membrane; BP:
 73 Bipolar membrane; NaOH: Sodium hydroxide; HCl: Hydrochloric acid.

74 Another method for the concurrent production of HCl and NaOH is direct electrosynthesis (DE)
 75 (Figure 1(a)), in which O₂ and H₂ are produced at the anode and cathode, respectively, producing
 76 HCl and NaOH upon reaction with the brine. Compared to BMED, DE can require less energy
 77 consumption since it avoids the operation of multiple bipolar membranes. DE would only require
 78 cation and anion exchange membranes separating three compartments: one for HCl production;
 79 another for NaOH production; and, between these, one for the circulation of a NaCl solution.
 80 However, with existing anode materials, chlorine evolution dominates over O₂ and HCl
 81 production.^{14,15} A handful of studies that have attempted NaOH production are shown in Table 1.
 82 Most of the studies used BMED as the method of NaOH production due to its simplicity and novelty
 83 compared to the chlor-alkali process.

Table 1. Production of NaOH and HCl from brine using BMED and DE.

Electrode Material	Feed and experimental conditions				Product recovery			Energy consumption HCl (kWh. Kg ⁻¹)	Reference
	Concentration of NaCl (M)	Primary other constituents	Current density (A m ⁻²)	Current efficiency (%)	NaOH Maximum concentration (M)	HCl Maximum concentration (M)	NaOH (kWh. Kg ⁻¹)		
-	0.002 Cl ⁻ , 0.005 Na ⁺	3.0 mg l ⁻¹ (TOC), 230 mg l ⁻¹ (TDS)	1000	53.9–65.7	1.5	1.5	3.7-5.1	4.6-5.5	Mavrov et al. (1999) ⁶⁹
Anode: Pt/Ir-coated titanium Cathode: V4A steel	0.079 Cl ⁻ , 0.040 Na ⁺	24.9 mg.l ⁻¹ (TOC), metals	100–900	40–90	0.2	0.2	-	-	Badruzzaman et al. (2009) ⁸⁷
Titanium coated with ruthenium oxide	0.09 Cl ⁻ , 1.00 Na ⁺	0.0549 M SO ₄ ²⁻	250–1000	50–80	1	0.8	-	-	Ibáñez et al. (2013) ⁸⁸
Titanium coated with ruthenium oxide	0.45 Cl ⁻ , 0.32 Na ⁺	Conductivity 40 mS.cm ⁻¹ Mg ²⁺ , Ca ²⁺ <1 mg.l ⁻¹		35–60	-	0.5-1.3	-	4.7-8	Wang et al. (2014) ⁸⁹
Anode: Pt/Ir-coated titanium Cathode: V4A steel	0.048 –0.39	-	2.6–260	10–100	0.3	0.3	0.2 -2	0.6-3	Davis et al. (2015) ⁹⁰
Titanium coated with ruthenium	0.653 Cl ⁻ , 0.655 Na ⁺	0.039 M SO ₄ ²⁻	340-570	52-74	1	1.2	-	7.2-9.0	Yang et al. (2014) ¹²
Anode: Pt/Ir- coated titanium Cathode: V4A steel	0.86	3 < pH < 4 Mg ²⁺ 9.3 mg l ⁻¹ Ca ²⁺ 16.6 mg l ⁻¹	200-500	20-77	1.1	1.2	2.6	-	Reig et al. (2016) ⁹¹
Anode: Pt/Ir- coated titanium Cathode: V4A steel	1.7-3.4	-	300-400	55-88	2	2	1.7-3.6	1.9-3.8	Reig et al. (2016) ¹⁶
Anode: Titanium coated with Mn _{0.84} Mo _{0.16} O _{2.23} Cathode: Stainless steel	0.6	-	250	65-88	0.29	0.22	-	-	Lin et al. (2016) ¹⁷

85

86

87 n.a.: either not available/ or not enough.

88

89

90 These studies tried a range of input parameters, varying initial concentrations of NaCl, NaOH, and HCl, as
91 well as current density and electrode type. The first five studies in Table 1 used synthetic brine, while the
92 next three studies used real brine from seawater RO. Of these studies, the one done by Reig et al. (2016)¹⁶
93 shows the most promise. This study used electrodialysis (ED) to concentrate the brine, leading to the highest
94 initial NaCl of any of the studies. This study also produced NaOH at the highest final concentration, 2 M, and
95 had the lowest energy required, 1.8 kWh/kg NaOH, although this was achieved at a lower final NaOH
96 concentration.

97 While DE is not a new technology, it had previously been ruled out due to chlorine gas formation on
98 the anode. The study done by Lin et al. (2016)¹⁷ attempted to solve this problem using a novel electrode
99 coating, $Mn_{0.84}Mo_{0.16}O_{2.23}$. While initial results were promising, as shown in the final entry in Table 1, the
100 concentration of NaOH produced in the process was quite low, and the study did not report energy usage in
101 the process.

102 **Electrode materials**

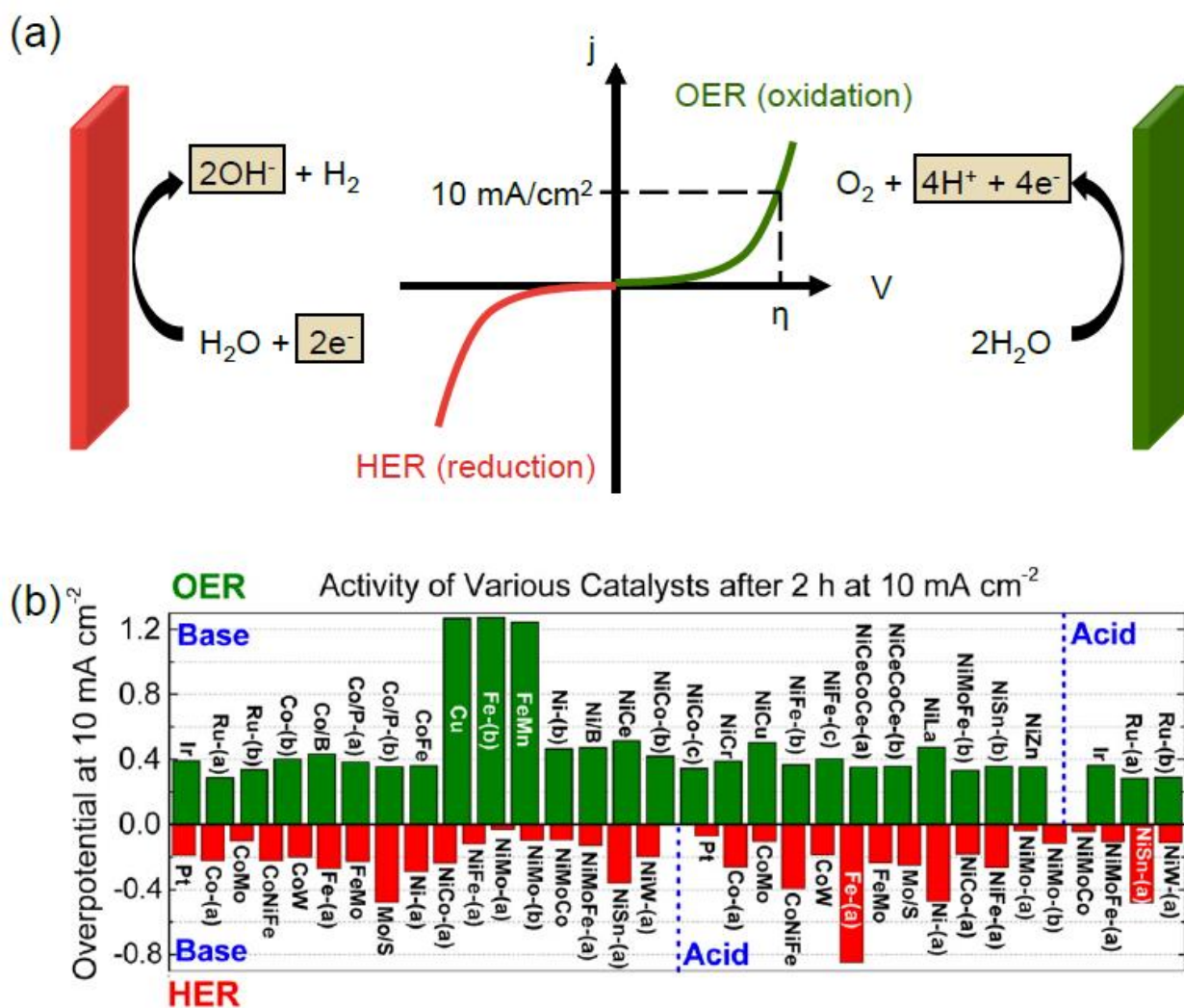
103 In order to further advance DE, better catalysts are needed that selectively produce oxygen while
104 suppressing chlorine production under acidic conditions. Catalysts for splitting water have been
105 extensively studied, including both water oxidation, also referred to as the oxygen evolution reaction
106 (OER), and water reduction, or the hydrogen evolution reaction (HER). In particular, much work has
107 focused on HER and OER in the context of forming hydrogen as a solar fuel; in that case, solar
108 energy is used to drive the water splitting reaction, storing the solar energy in the H–H chemical
109 bond, either directly in a photoelectrochemical system or by coupling an electrocatalyst with a
110 photovoltaic cell.¹⁸⁻²⁰ The energy can later be released by burning the hydrogen or using it in a fuel

111 cell. Additionally, HER can be used in chlorine production,²¹ and OER can be used for metal-air
112 batteries.^{22,23} Electrocatalytic OER and HER have been widely studied in these contexts, with several
113 exhaustive review articles describing the variety of different catalyst materials that have been studied
114 for both HER²⁴⁻²⁸ and OER^{25,26,29,30}, as well as for selectivity of OER over the chlorine evolution
115 reaction (CER); here, we provide a brief overview with a focus on how to apply these catalysts to DE
116 systems.

117 Two of the key parameters for electrocatalysts are the overpotential (energy required) and the price
118 (material costs and stability). A given reaction has a certain thermodynamic potential, but it requires a
119 driving force beyond this thermodynamic requirement; the overpotential (η) provides a measure of this
120 required driving force on a given catalyst. The overpotential is defined as the difference between the
121 applied potential and the thermodynamic potential ($\eta = E - E_0$); increasing the overpotential will then
122 increase the current, as described by the Butler–Volmer equation, resulting in polarization curves such
123 as those shown in Figure 2a. Catalysts lower the activation energy by adjusting the binding energy of
124 intermediates, so that the reaction can occur at lower overpotentials. The term overpotential is often
125 used to describe the overpotential at a specific current density (typically 10 mA/cm², and labelled j_{10}
126 in Figure 2a), which allows the facile comparison of catalysts when conditions such as the catalyst’s
127 loading are kept constant. The lower the overpotential required to reach a certain current density, the
128 less energy required for the reaction to take place, providing efficiency and thus cost improvements.^{31,32}
129 As for economic considerations, the standard OER and HER catalysts are based on Ru, Ir, and Pt; thus,
130 much recent work across laboratories has moved to developing active, stable catalysts made from
131 earth-abundant, cheaper elements such as carbon, cobalt, iron, molybdenum, nickel, and sulfur.^{29,30,33}
132 The stability of catalysts also affects the economic feasibility of different electrolysis reactions.
133 Catalyst stability is particularly important for scaling up, and academic stability studies have generally
134 been limited to a few days³⁴ when performed at all (despite activity and stability often being inversely
135 related³⁵).

136 A comparison of several HER and OER catalysts are provided in Figure 2b. Because pH plays a
 137 large role in a catalyst's activity towards HER and OER (as discussed in more detail below), the
 138 overpotential is provided for catalysts in both acidic and basic conditions.

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143 **Figure 2.** Scheme and activity of water splitting catalysts. (a) Schematic and polarization curves for hydrogen
 144 evolution (red) and oxygen evolution (green), where j_{10} is the current at a current density of 10 mA/cm². (b)
 145 Comparison of hydrogen evolution reaction (HER, shown in red) and oxygen evolution reaction (OER, shown in
 146 green) catalysts tested in acidic and basic media in the same conditions.³⁴

147 Note that the exact overpotential can be hard to compare across labs due to slight variations in the
148 electrolyte, catalyst loading, support electrode, etc.; however, the benchmarking study by McCrory et
149 al. provides a consistent comparison across several materials for both HER and OER in both acidic
150 and alkaline conditions.³⁴

151 The key challenge for implementing DE from the catalysis perspective is finding a stable OER
152 catalyst with high activity for oxygen production as well as high selectivity over chlorine evolution.
153 Catalysts that break scaling relations with defects such as dopants are a promising research direction
154 for this area.

155
156 **HER electrocatalysts.** Focusing first on catalysts for HER, noble metal catalysts for hydrogen
157 evolution can achieve high current densities (and thus high hydrogen evolution rates) at low
158 overpotentials, with Pt achieving 10 mA/cm² at <20 mV overpotential.³⁶ Thus, recent work has
159 focused on developing less expensive catalysts with the same high activity level.^{25,36} These studies
160 have spanned metals, alloys, dichalcogenides, phosphides, and carbides, and have been summarized
161 in detail elsewhere.^{20,24,25,28,33,36-38} However, many studies have focused on HER in acidic media
162 because the adsorption of hydrogen at low pH has a lower barrier, since adsorbed hydrogen can form
163 by dissociating hydronium rather than water,²⁸ and the mechanisms in acid are well-studied.^{20,27}
164 However, for direct electrosynthesis, as in standard chlor-alkali electrolysis, alkaline conditions are
165 required (equation 1).

166 While the mechanistic understanding is lacking, many catalysts are promising for hydrogen
167 evolution in alkaline media (Figure 2b). Alkaline media can lead to oxide formation on metal
168 surfaces, but Ni, the most active non-precious metal, is stable and active at high pH.^{20,25,27} Ni alloys

169 have also been reported, particularly Ni-Mo catalysts with <100 mV overpotential,^{26,39-42} that are
170 highly promising for DE conditions. More recently, ruthenium-based catalysts on carbon-nitrogen
171 supports have been reported with even higher activity in basic media.^{31,43} For all catalysts, long-term
172 stability (in terms of maintaining activity over many months) must be shown before they can be used
173 in an industrial process.^{25,28,36}

174
175 **OER electrocatalysts.** In a DE process, the oxidation side is less straightforward. OER is widely
176 studied because it is applicable in a number of areas in addition to DE, including metal–oxygen
177 batteries^{22,23} and solar fuels (including both water splitting to produce H₂ and CO₂ reduction to
178 produce hydrocarbons and alcohols).^{19,36} However, OER is more kinetically hindered than HER
179 because it is a four-electron process with chemically similar intermediates.^{19,26,29} The binding
180 strength of hydroxide, oxide, and peroxide intermediates scale with each other on planar metal oxide
181 surfaces,⁴⁴ so OER catalysts generally have much higher overpotential requirements than HER
182 catalysts³⁶; indeed, the theoretical overpotential for OER is 300 mV unless the catalyst can be
183 engineered to selectively stabilize only some of the intermediates.^{26,36} Additionally, the chlorine
184 evolution reaction (CER) is a competing oxidation reaction that must be prevented in a DE system,
185 making the oxidation reaction even more challenging.

186 In terms of the OER catalysts themselves, RuO₂ and IrO₂ are the standard benchmark catalysts,
187 but they contain relatively rare Pt-group metals (note that, typically, oxides rather than metals are
188 used as OER catalysts due to the oxidizing aqueous conditions). Thus, many studies have moved
189 towards earth-abundant catalysts.^{26,34,45-47} In order to design new (earth-abundant) catalysts, much
190 work has focused on identifying the key descriptors of activity trends by looking at the electronic

191 structure of the catalyst as well as the binding energies of different intermediates.^{44,46,48,49} They found
192 that the optimally binding surface will still have a relatively large OER overpotential due to scaling
193 relations, since the OER intermediates are all chemically similar and their binding energies are
194 correlated.^{26,44,48} Based on this theoretical understanding of the binding energies, planar metal oxides
195 are not expected to overcome these limitations. Recent work has instead moved to developing
196 different ways of introducing activity-improving defects such as grain boundaries and dopants that
197 could selectively stabilize some of the intermediates, for example by introducing nanostructuring,
198 using alloys, or altering the catalyst support.^{26,50} More specifically, these methods include sol-gel
199 synthesis,⁵¹ leaching a binary oxide,⁵² sulfurizing/reoxidizing,⁵³ and lithiation/delithiation cycles.⁵⁴
200 These studies included long-term activity measurements of the catalysts, which in some cases
201 confirmed stable activity over several hundred hours.^{51,54} This research direction is also promising in
202 the context of DE. Even more than for HER, the vast majority of electrocatalyst studies for OER
203 investigate a pH window not applicable for use in DE.^{25,34} Instead of the basic conditions typically
204 investigated, acidic conditions are required as direct electrosynthesis will produce HCl in addition to
205 O₂ (equation 3). While many OER catalysts are either not active³⁴ or not stable^{26,30,55} in acidic
206 conditions, IrO₂ and RuO₂ catalysts can be used in acidic conditions^{30,34} (Figure 2b). More recent
207 work has improved their activity and decreased their mass loading, including an IrO_x/SrIrO₃
208 catalyst⁵² as well as a thin ruthenia coating,⁵⁶ both of which achieved relatively low overpotential
209 (~280 mV for 10 mA/cm²) in acid. More work is needed in this area to further improve their activity.

210
211 **Competition between oxygen and chlorine evolution.** In addition to having a high activity towards
212 OER, a catalyst for the DE process should limit Cl₂ evolution at the anode. The relative selectivity of

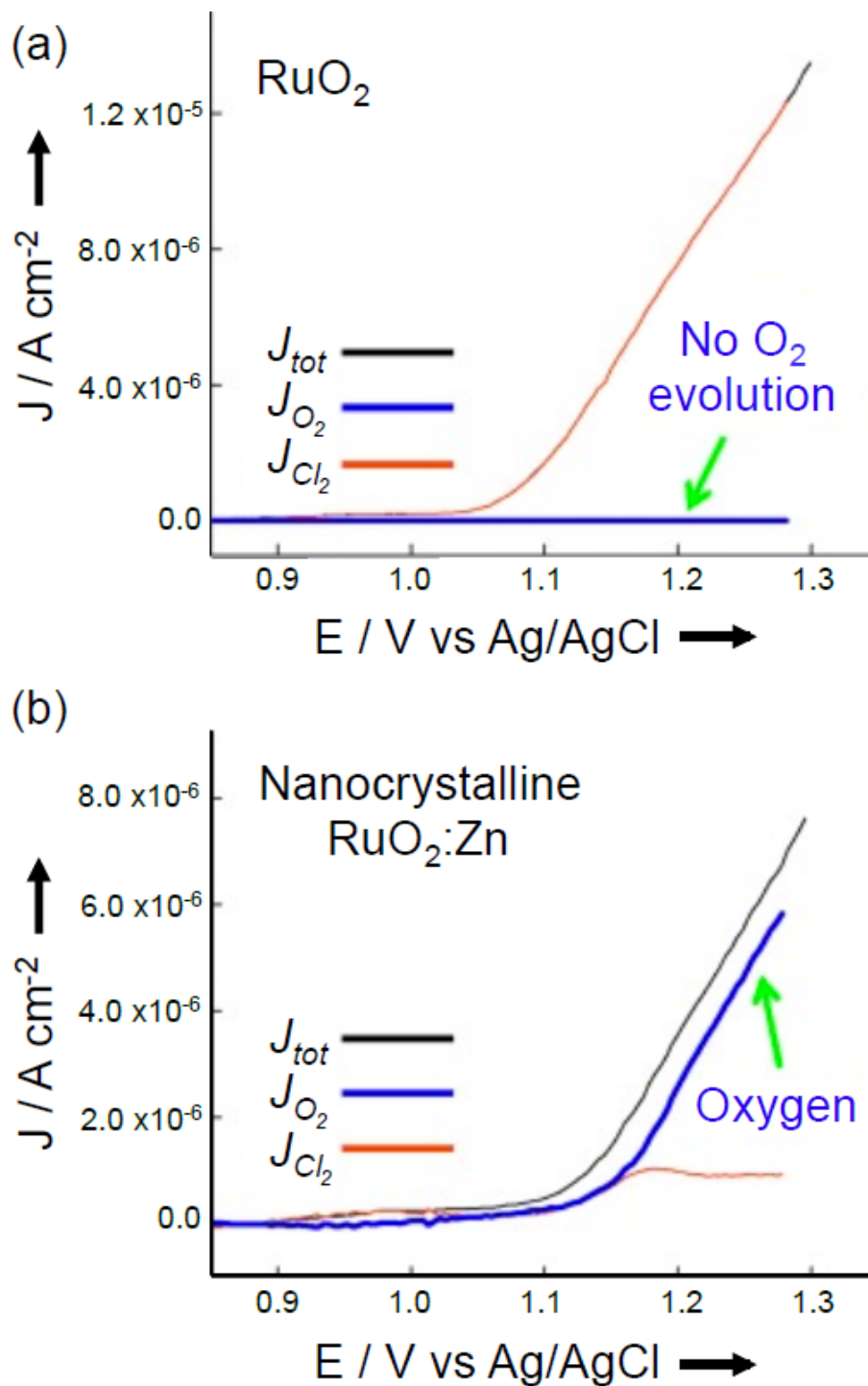
213 Cl_2 vs. O_2 production, primarily in the context of limiting parasitic oxygen production during a chlor-
214 alkali process (i.e., to selectively produce Cl_2 in aqueous conditions), has been studied for over one
215 hundred years and was recently reviewed in detail.²¹ Additionally, reactive chlorine species have
216 been generated for wastewater treatment.⁵⁷⁻⁵⁹ The reverse selectivity is of interest here (i.e., selective
217 O_2 production in the presence of Cl^-), and it has been investigated for seawater splitting (i.e., water
218 splitting of brine solutions, where CER would compete with OER).^{14,60-63} A further description is
219 provided by Nikolic and Panic (2014)⁶⁴. Although OER is thermodynamically more favorable than
220 CER overall, it is more kinetically hindered, in part because OER requires four electron transfers
221 instead of the two needed for CER, leading to a higher theoretical overpotential requirement as
222 discussed above.⁶⁵

223 Instead, process conditions have typically been used to control selectivity,²¹ for example the
224 electrolyte pH. Indeed, CER is generally preferred at low pH,⁶⁵ and Cl_2 can be produced from neutral
225 brine⁵⁸ or high concentrations of HCl (e.g., 17%)⁶⁶; conversely, studies of oxygen production from
226 seawater have primarily been performed at neutral or basic pH.^{60,61} In the acidic conditions required
227 for DE, OER selectivity can be aided by a low concentration of chloride ions at the electrode
228 surface^{21,64} or by increasing the overpotential.^{67,68} However, these conditions are not realistic for
229 scale-up of DE, and instead improved catalysts are needed. Additionally, the other ions present in
230 seawater could make selectivity even more challenging.

231 Recently it was found that the catalyst surface can be modified to control the CER vs OER selectivity.
232 Initial studies suggested that OER and CER activities followed the same trend,⁶³ attributed to the scaling
233 relation between the O and Cl binding energies⁶⁵; indeed, the OER catalyst RuO_2 is used as the catalyst in the
234 widely used dimensionally stable anode (DSA) for chlorine production.^{32,64} However, despite these scaling
235 relations, there are several recent reports of adjusting the selectivity of OER over CER using dopants to

236 modulate the catalyst electronic structure and thus the active site.^{65,67-70} Indeed, Zn-doped RuO₂ catalysts have
237 selectivity for OER over CER (shown in Figure 3), with their activity attributed to additional oxygen vacancies
238 forming over Zn sites.⁷⁰ Conversely, studies on IrO₂ suggest that enhanced activity with Co and Zn doping
239 stems from the dopant activating bridging binding sites that stabilize the peroxo OER intermediate.⁶⁷

240



241

242 **Figure 3. Comparison of oxygen and chlorine selectivities for different ruthenia-based catalysts.**
 243 Measured current density (black) and its components corresponding to chlorine (red) and oxygen (blue)
 244 evolution during anodic polarization of a) RuO₂ and b) Ru_{0.8}Zn_{0.2}O₂ electrodes in 0.1M HClO₄ / 0.15M NaCl
 245 solution.⁷⁰

246 Additionally, several MnO_2 -based materials have been found to be selective, although this was
247 primarily studied in alkaline conditions and without probing the origin of the selectivity. A more recent study
248 by Lin et al. (2016)¹⁷, described in the previous sections, produced HCl and O_2 from aqueous NaCl using a
249 titanium anode coated with $\text{Mn}_{0.84}\text{Mo}_{0.16}\text{O}_{2.23}$, with an overall coulombic efficiency in the same range as
250 BMED, 65–88%. These doped oxide catalysts represent the most promising anode materials for DE at this
251 time, although the origin of the selectivity was not discussed and therefore is challenging to apply to the
252 development of novel catalysts. Additionally, novel catalysts for DE will need to be robust towards the variety
253 of ions found in industrial brine. The conditions for DE have more contaminants than typical water oxidation
254 and warrant additional research into catalysts that can achieve high activities despite these constraints.

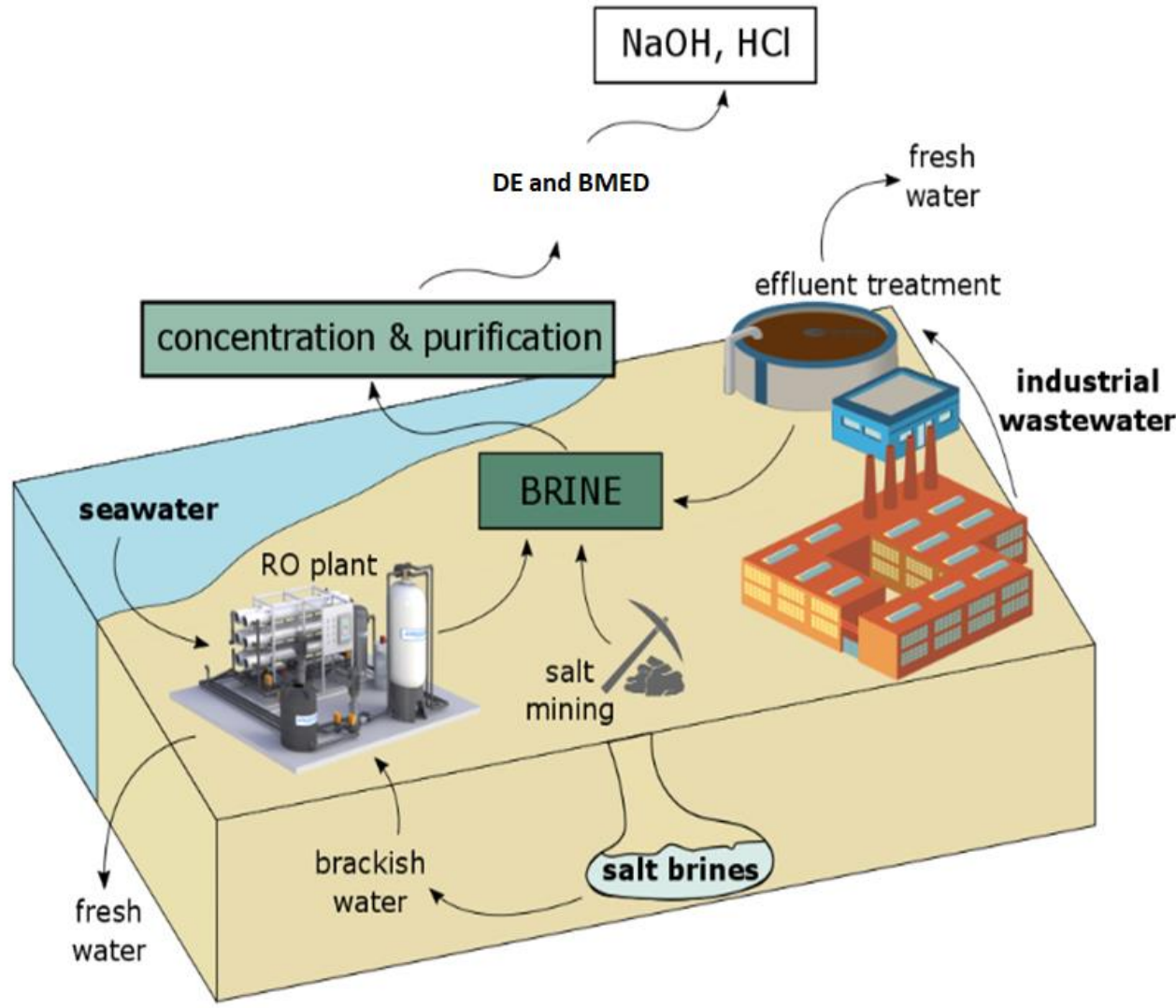
255 Catalysts that break scaling relations using dopants and other defects to lower the overpotential for
256 OER are particularly promising in the context of DE due to the competing CER. One key challenge with defect-
257 driven activity is finding defects that provide high activity while remaining stable long-term.

259 **Implications/outlook for the future Practical and economic implications**

260 Implementation of NaOH production from brine steam via DE and BMED can offer sustainable desalination,
261 economic benefits as well as environmentally sound strategies.

262 **Sustainable desalination.** Urbanization and rising population drive a growing need for sustainable
263 water production and management, compounded by changing patterns of freshwater availability.⁷¹
264 With this growing demand for clean water, the environmental impact of water production has drawn
265 attention. Globally, an estimated 76 M m^3 /day of seawater desalination brine,^{72,73} containing 4.5 M
266 tonnes/day of sodium chloride, is discharged back into the sea. As an alternative, these brines can be
267 concentrated, treated, and fed into a DE or BMED system to recover NaOH and HCl. Thus, DE and
268 BMED have the potential to limit environmental impact through resource recovery, reduced brine
269 discharge, and possible lower overall energy consumption. DE and BMED have potential economic
270 and environmental benefits for other industries beyond desalination, including salt mining and even
271 agriculture. Additionally, DE and BMED may reduce the energy needs for NaOH production and

272 enable the de-centralized production of related chemicals. Figure 4 conceptually outlines these feed
273 streams and applications, illustrating the potential route to sustainable desalination provided by DE
274 and BMED.



275
276
277 **Figure 4. Schematic illustration of different sources of brine for the DE-BMED process.** In the top right,
278 brine is produced through desalinated seawater. In the bottom, the salt brines are created by the desalination
279 of brackish ground water as well as through salt mining. Finally, on the left-hand side, industrial wastewater
280 that goes through effluent treatment also produces brine as a by-product.

281

282 **Economic potential.** Globally, the production of NaOH and HCl from the chlor-alkali process is a
283 large-scale industrial activity generating around \$80 billion in revenue⁷⁴ while using nearly 50% of the
284 world's annual salt production.⁷⁵ The production methods require the use of pure NaCl salts to create
285 saturated solutions which are electrolyzed to generate NaOH and HCl.¹¹ However, DE and BMED can
286 be implemented directly on seawater desalination brine without a pure NaCl salt stream. By using the
287 waste stream from water desalination to produce high-value, marketable chemicals, DE and BMED
288 may provide a new and sustainable avenue for chemical production in both seawater desalination and
289 the chlor-alkali industry. Depending on the local market demand for water and chemicals (NaOH and
290 HCl), desalination plants and DE and BMED can be coupled appropriately to target the production of
291 either chemical.

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295 **Practical feasibility and product usage.** The product quality depends upon the purity of the brine,
296 similar to chlor-alkali, where higher purity brines translate to higher purity acids and bases. The
297 difference here is that seawater brine is likely to contain more non-NaCl species than most chlor-alkali
298 brines made from rock salt. While we use NaOH and HCl in this text, most brine is not purely NaCl
299 and therefore will not produce pure NaOH and HCl. The maximum amount of NaOH producible on a
300 single site is limited by the available Na⁺ ions in the seawater. Standard seawater has a sodium molality
301 of about 0.47 mol/kg and total salinity of 3.5% by mass. Thus, the maximum producible NaOH is
302 approximately (0.47 mol Na/kg-water) (1-0.035 kg-water / kg-seawater) (39.997 g/mol NaOH) = 18.1
303 g/kg-seawater. However, typical plants use orders of magnitude less. Three typical plants use NaOH
304 in amounts producible from 0.002 – 0.01% of total concentrate flow (Table 2).

305 Numerous chlorine-based byproducts are used within a typical desalination plant. For example, HCl is used
306 for cleaning and CaOCl, Cl₂, and NaOCl are used for chlorination.¹³ NaOH is used to precipitate several ions;
307 for example, El-Manharawy and Hafez (2003)⁷⁶ conducted detailed experiments on removing divalent cations
308 from Red Sea seawater.⁷⁶ They found about 1.3 g NaOH/kg seawater removed between 50 and 100% of Ca²⁺,
309 Mg²⁺, Ba²⁺, Sr²⁺, SiO₃²⁻, Fe²⁺, CO₃²⁻, HCO₃⁻, SO₄²⁻, and PO₄³⁻. Only 0.5% of the dose was used to precipitate
310 minor species and neutralize the seawater's acidity; 99.5% was consumed in precipitating Ca and Mg

311 compounds. Of course, the exact amount of NaOH required to remove divalent cations will depend on local
312 seawater chemistry.

313 **Table 2.** Summary of NaOH usage and available brine supply at three typical, large-scale seawater reverse
314 osmosis (SWRO) plants*.

Plant	1	2	3
NaOH Conc. Req'd. [%]	–	26.3	3.1
NaOH Use [t/yr, dry]	38	60	324
Brine Flow [$\times 10^6$ m ³ /yr]	39.81	10.38	31.76
Req'd Brine [t/yr]	792	1250	6750
% of Brine Flow	0.002%	0.01	0.02

315 *NaOH usage is quoted on a dry basis. Brine density taken as 1.04 kg/L.

316 **Other industrial and environmental considerations.** The production of NaOH and HCl are
317 particularly beneficial for agricultural water purification. To meet food security challenges, seawater
318 desalination is increasingly being deployed globally to provide water for agricultural purposes.⁷⁷⁻⁸⁰
319 However, desalinating seawater for agriculture requires the removal of boron ions,⁷⁸ which are toxic
320 to most crops at a concentration of 2 mg/L.⁸¹ Boron may be removed from seawater feed by
321 pretreatment with NaOH and HCl to adjust the pH. With the DE and BMED process, NaOH and HCl
322 can be recovered from the seawater desalination brine for pH control, creating closed-loop chemical
323 production.

324

325 Apart from desalination brine, brines from salt mines and solution mining⁸² can also be utilized for
326 NaOH and HCl production. For efficient production of NaOH and HCl through the DE and BMED
327 process, feed streams that have sodium chloride as the dominant constituent salt are preferable. A major
328 method of mining for sodium chloride is the use of solution mining where water is pumped into mines,
329 dissolves crystalline sodium chloride, and then is pumped back to the surface. The NaCl-concentrated
330 brine can be fed into a DE or BMED system for direct, on-site production of NaOH and HCl,⁸³ products
331 that have higher value than the NaCl salt itself. Furthermore, similar applications of DE and BMED
332 might include high-salinity wastewaters from other industries including oil and gas production⁸⁴ and
333 power plant operation.^{3,13,85}

334 To further evaluate the potential of DE and BMED treatment of brine streams, a life cycle assessment of the
335 environmental benefits is needed. Furthermore, the potential for DE and BMED to treat waters beyond
336 desalination brine should be explored in terms of their economic and technical feasibility.

338 **Summary and Future Outlook**

339 DE can be implemented directly on seawater desalination brine without the need for a pure NaCl salt
340 stream. This capability makes the technology environmentally and economically interesting. Despite
341 early promise, selective catalysts for OER over CER are still needed to improve the energetics of the
342 DE process, particularly for reactions in such mixed brine solutions. OER catalysis in basic conditions
343 is now well established despite relatively high overpotentials, and research is ongoing into catalysts
344 that are active in acidic media for water splitting. However, the relative activity of electro-oxidation
345 catalysts for OER over CER is comparatively less well studied. Fundamental studies are needed that
346 take advantage of the current mechanistic understanding of OER to improve the activity of these
347 catalysts in the presence of chloride (and other) ions, for example, to probe the role of dopants, grain
348 boundaries, and/or alloying on improving OER selectivity. Much work is needed for a better
349 fundamental understanding of these competing processes, as selective OER catalysts have the potential
350 to make an impact in the DE process as well as in other areas such as seawater splitting or even some
351 carbon capture processes.⁸⁶

353 Direct electrosynthesis of NaOH and HCl from brine streams can help enable global water and food
354 security through the sustainable deployment of seawater desalination for various applications,
355 including agricultural use among others.⁸⁷⁻⁸⁹ With the DE process, NaOH and HCl can be recovered
356 from the seawater desalination brine for pH control, creating closed-loop chemical production. DE is
357 also expected to substantially reduce the energy needs and environmental impact of brine producing
358 industries, including desalination, salt and solution mining.

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