Caustic Production, Energy Efficiency, and Electrolyzers

AUTHOR INFORMATION

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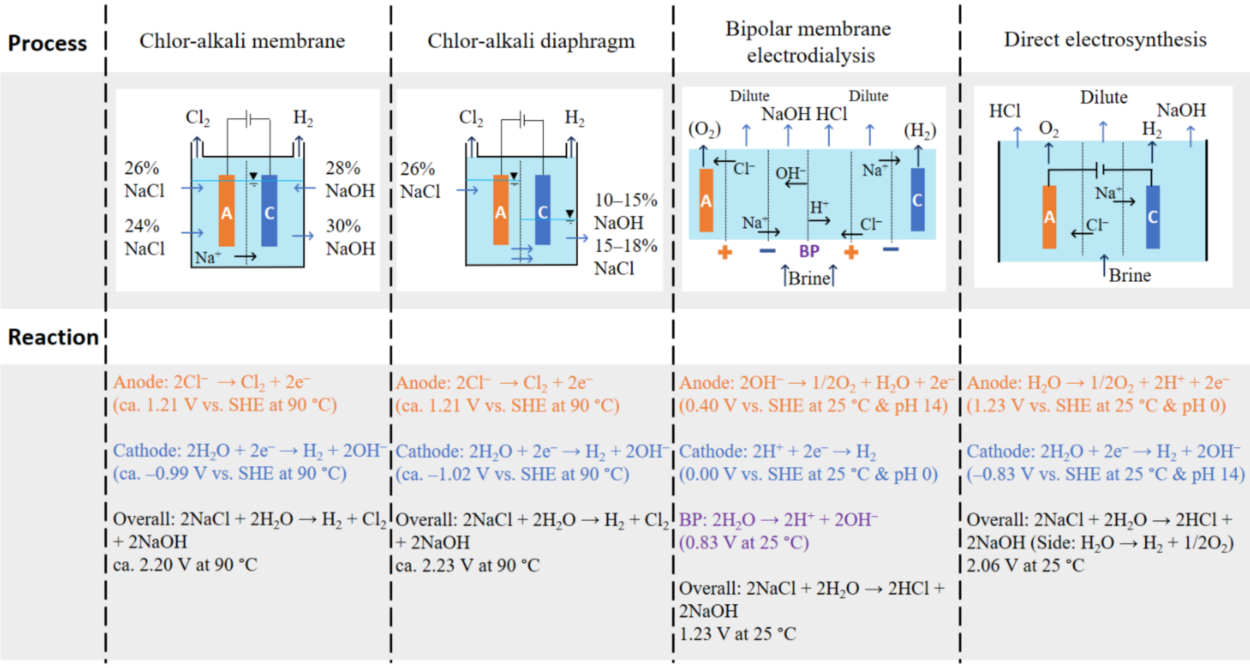
Approximately 99.5% of caustic soda worldwide is produced through the traditional chlor-alkali process which simultaneously generates chlorine and hydrogen gas. The wider spectrum of caustic production technologies (Figure 1) are: the chlor-alkali membrane process, the chlor-alkali diaphragm process, bipolar membrane electrodialysis (EDBM), and direct electrosynthesis (DE). Both of the chlor-alkali processes produce H_2 and Cl_2 in addition to NaOH, while EDBM and DE produce HCl in addition to NaOH. Based on these underlying reactions, all of the methods can produce the same maximum amount of NaOH per kg of 7% w/w NaCl brine.



Process	Chlor-alkali membrane	Chlor-alkali diaphragm	Bipolar membrane electrodialysis	Direct electrosynthesis
Reaction	Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ (ca. 1.21 V vs. SHE at 90 °C)	Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ (ca. 1.21 V vs. SHE at 90 °C)	Anode: $2OH^- \rightarrow 1/2O_2 + H_2O + 2e^-$ (0.40 V vs. SHE at 25 °C & pH 14)	Anode: $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ (1.23 V vs. SHE at 25 °C & pH 0)
	Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (ca. –0.99 V vs. SHE at 90 °C)	Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (ca. –1.02 V vs. SHE at 90 °C)	Cathode: $2H^+ + 2e^- \rightarrow H_2$ (0.00 V vs. SHE at 25 °C & pH 0)	Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (–0.83 V vs. SHE at 25 °C & pH 14)
	Overall: $2NaCl + 2H_2O \rightarrow H_2 + Cl_2 + 2NaOH$ ca. 2.20 V at 90 °C	Overall: $2NaCl + 2H_2O \rightarrow H_2 + Cl_2 + 2NaOH$ ca. 2.23 V at 90 °C	BP: $2H_2O \rightarrow 2H^+ + 2OH^-$ (0.83 V at 25 °C)	Overall: $2NaCl + 2H_2O \rightarrow 2HCl + 2NaOH$ (Side: $H_2O \rightarrow H_2 + 1/2O_2$) 2.06 V at 25 °C
			Overall: $2NaCl + 2H_2O \rightarrow 2HCl + 2NaOH$ 1.23 V at 25 °C	

Figure 1. *Schematic diagram of a chlor-alkali membrane, a chlor-alkali diaphragm, a bipolar-membrane electrodialysis, and a direct electrosynthesis process. The half reactions and energy requirements are given (sources: chlor-alkali processes*[1]*, bipolar membrane electrodialysis*[2]*, direct electrosynthesis*[3]*). A, Anode; C, Cathode; BP, Bipolar membrane; NaOH, Sodium hydroxide; HCl, Hydrochloric acid.*

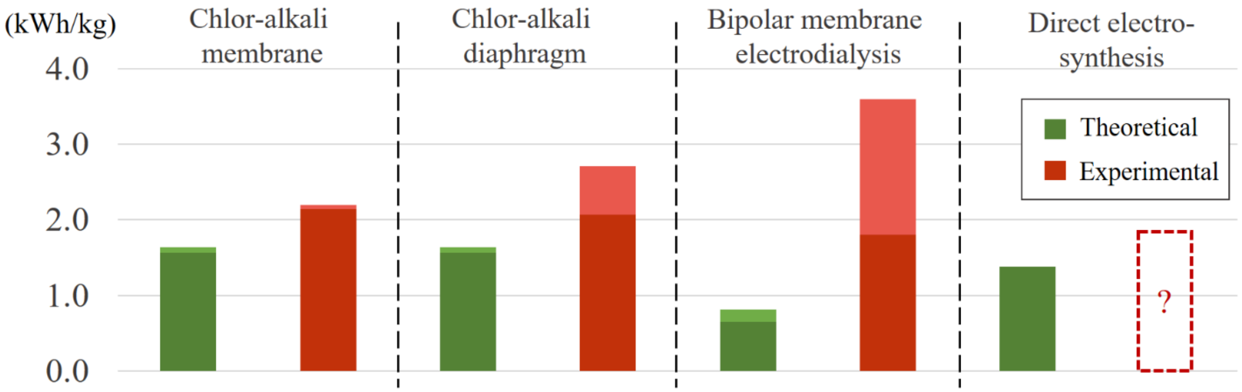


Figure 2. Theoretical and practical energy requirements *of a chlor-alkali membrane, a chlor-alkali diaphragm, a bipolar-membrane electrodialysis, and a direct electrosynthesis process. Theoretical numbers are taken from Thiel et al.*[4] *or estimated based on the theoretical voltage (for direct electro-synthesis). Practical numbers are taken from Thiel et al.*[4] *and Reig et al.*[5] *No study has yet reported on the practical energy requirements of direct electrosynthesis.*

Energy usage is one for the most important factors for caustic production and makes up a significant portion of the variable cost (Figure 2). The minimum energy required for each method can also be determined from the underlying chemical reaction.[4] EDBM and DE have a lower minimum energy requirement (0.65-0.81 kWh/kg NaOH for the former[4]; and around 1.38 kWh/kg NaOH for the latter, estimated using the cell voltages in Figure 1) than that of the chlor-alkali processes (1.56-1.64 kWh/kg NaOH [4]). This indicates that if all methods had similar efficiencies, EDBM and DE would use less energy to produce NaOH than the chlor-alkali processes. In practice, the chlor-alkali membrane process consumes 2.10–2.15 kWh_e/kg NaOH of electrical energy and 0.128–0.196 kWh_t/kg NaOH of thermal energy.[4] The chlor-alkali diaphragm process tends to use less thermal energy (0.038–0.047 kWh_t/kg) on the cost of slightly higher electrical energy usage (1.94–2.51 kWh_e/kg NaOH). Considering only the electrical part (note that the thermal energy is of less thermodynamic quality and also cheaper), the energy efficiency of conventional chlor-alkali processes therefore amounts to around 75%.

As a more novel process, EDBM has been reported to consume in the range of 1.8-3.6 kWh_e/kg NaOH of electrical energy (setups used in research)[5], thus having an energy efficiency of around 40%. Despite having the thermodynamic potential to require significantly less energy than the chlor-alkali process, at present, EDBM at best consumes only slightly less electrical energy than the chlor-alkali process and on average requires slightly more, although no heat energy is required. It becomes evident that more research is necessary to increase its efficiency and lower the realized energy consumption.

No study has yet reported on the practical energy requirements of DE, necessitating further research in this area. Lower theoretical energy consumption is expected for DE than the conventional chlor-alkali process, yet the theoretical energy use is not as low as the EDBM process as a result of the relatively higher amount of water splitting taking place. A practically attractive feature of DE could be its fewer number of electrolyte chambers and membranes (in addition, the absence of BP), which potentially reduces energy consumption by lowering ohmic resistances compared to EDBM processes. At the same time, the attractiveness of DE process will also increase if H_2 is additionally a desired side product.

We now direct our discussions toward the energy efficiencies of the above-mentioned caustic production processes. Table 1 compares the specific energy consumption based on theoretical and practical performance.

Table 1. *Comparison of theoretical and practical energy consumption of electrolysis processes. U is the cell voltage (in V), Q the provided charge (in C), M the molar mass (40 kg/kmol for NaOH), and n the produced molar amount (in mol).*

$$E_{\mathrm{spec}}[\mathrm{J/kg}] = U \cdot \frac{Q}{n \cdot M} \tag{1}$$

	Voltage U	Charge Q
Theoretical	$U_{\min}$ as shown in Figure 1	$Q = n \cdot F$ by Faraday's law
Practical	$U_{\min} + \Sigma\, \eta_{\mathrm{kin}} + \Sigma\, \eta_{\mathrm{ohm}} + \ldots$ due to loss terms, e.g. overpotentials of OER or ohmic resistances in the system	$Q > n \cdot F$ due to side reactions, e.g. competing reactions of ClER and OER

Generally, causes of energy inefficiency (additional energy consumption relative to the thermodynamic limit) can roughly be subdivided into the following two categories:

- Voltage efficiency: additional voltage needed beyond the thermodynamic driving force $U_{\min}$ (which is the difference of the thermodynamic equilibrium potentials on both half-cell reactions). Additional voltage results from various sources of overpotential ($\Sigma\, \eta_{\mathrm{kin}}$) as well as ohmic losses in the electrolysis cell ($\Sigma\, \eta_{\mathrm{ohm}}$). Further losses may also be incurred, e.g., by limitations on reactant mass transport. In the case of EDBM process, one of the major voltage losses stems from the activation barrier of water splitting (to proton and hydroxyl ions) within the bipolar membrane (Oener et al., 2020). For DE processes, it may be expected that the major inefficiency will result from the oxygen evolution reaction (OER) on the anode, which is well-known to be a kinetically strongly-hindered reaction in acid media.
- Current efficiency: additional current/charge required beyond the stoichiometry dictated by Faraday's law, e.g. due to side reactions, shunt currents, or membrane crossover. For

typical chlor-alkali process, current inefficiencies are mainly caused by OER as a side reaction, chlorine dissolution in the anode solution (both of which reduce chlorine yield), as well as crossover of OH^- ions (reduces caustic yield).[6] In case of DE, OER is the desired reaction on the anode, and chlorine evolution reaction (ClER) is the main competing reaction and contributes to current inefficiency.[3]

Therefore, the potential directions for improving energy efficiency in the caustic production processes include optimizing the electrodes (reduce overpotentials, increase selectivity) and reducing membrane/electrolyte resistances, among other areas. These aspects are elaborated in the following paragraphs.

To reduce membrane and electrolyte resistance, we believe research should be directed towards advanced system design. For the purpose of reducing ohmic losses in the electrolyte, for instance, a well-known design feature is the so-called zero-gap configuration by positioning the electrodes very close to the membrane.[7] Reducing membrane-related losses can be achieved, e.g., by reducing the number of compartments in EDBM processes. DE is also predicted to consume less energy than EDBM in practice as a result of lower membrane areas.[3] Recently, Hashemi et al. introduced a membrane-less 3D-printed microfluidic electrolyzer for water splitting and chlor-alkali processes.[8] Although energy consumption is not elaborated in the publication, ohmic losses are minimized in this type of design. The microfluidic approach is just one demonstration of potential energy efficiency improvements in future electrolyzer designs.

Aiming to reduce electrode overpotentials, research has been focused on developing new materials for hydrogen evolution (e.g., Ru/WNO@C introduced by Zhang et al.[9]; metal-organic frameworks (MOFs) by Sun et al.[10]; and intermetallic Co_3Mo by Shi et al.[11]) and, more critically, oxygen evolution. For instance, Ni/Co-doped defect-rich Cu-based sulfide nanorods modulate the *OH adsorption state while effectively adsorbing and isolating *H to improve OER kinetics.[12] Kumar et al.[3] pointed out the necessity of long-term stability of the OER catalyst alongside with its initial high activity for successful DE processes. NiFe oxyhydroxide, MnO_x, or NiO_x based materials have been demonstrated as suitable catalysts for OER in alkaline media.[13,14] Additionally, some research has been directed towards activity-improving defects, e.g. dopants and grain boundaries that can selectively stabilize OER intermediates.[13]

In order to increase the current efficiency of DE or EDBM processes, the anode material must be designed to favor OER instead of ClER. OER is thermodynamically favored over ClER under standard conditions (1.23 V vs. 1.36 V), yet the potentially high chloride concentration in feed brine shifts the ClER equilibrium potential downwards and weakens this difference (for instance, the equilibrium potential of ClER under chlor-alikali conditions is around 1.21 V vs. SHE, see Figure 1). At the same time, OER is well-known to be kinetically hindered as a four-electron process, necessitating special attention in increasing its selectivity. Ab initio kinetics and thermodynamics of ClER/OER is studied, e.g., by Exner et al.[15] The concept of suppressing ClER has been explored by Traini et al.[16] To this day, it is well-known that the selectivity towards OER is intrinsically higher at high pH,[13] yet a strongly alkaline condition may not be practically feasible on the anode due to the direct local proton production (or OH^- consumption, see also the reactions in Figure 1).[14] On the other hand, extremely low or high current densities favor OER;[14] however, these conditions have limited practical relevance. The most promising solution for these selectivity issues, therefore, still lies in the development of a suitable catalyst. The development of selective OER sites or chloride-blocking overlayers (e.g., via a protective MnO_x layer) has been introduced and may present a viable solution towards high OER selectivity.[13] Abe et al. introduced an oxygen-deficient thin film with disordered manganese oxide nanolayers on a fluorine-doped tin oxide (FTO) electrode.[17] They measured high selectivity for OER over ClER in 0.5M NaCl solution, obtaining a Faradaic efficiency of 87% in galvanostatic electrolysis at 10 mA cm^{-2}. Recently, Mu et al. developed a graphite carbon anode with significantly higher OER selectivity in a DE design operating with brine compared to other anodes (e.g. Ti-Pt, Ti-Ir) operating under similar conditions.[18]

For traditional chlor-alkali processes, the focus leans instead towards ClER activity and selectivity instead. For instance, kinetics of the ClER in saline solution (5M NaCl) was studied using ultrathin single-crystalline $RuO_2(110)$ films as model electrodes at various temperatures[19]. New materials (e.g., transitional metal antimonates[20]) have been proposed as viable anodes, which may (over the lifetime of the electrolyzer) have similar or improved selectivity compared with the typical dimensional-stable anodes (DSAs) based on $RuTiO_x$.

Apart from consideration of energy consumption within the electrolyzer itself, additional energy inputs are likely required for feed stream pretreatment in any industrial process. Typically, pretreatments involve purification and/or pre-concentration of the feed. For example, in the case of membrane chlor-alkali cells, the feed flow must consist of a near-saturated NaCl solution with less than 20 ppb of Ca/Mg in addition to other stringent requirements (e.g., no heavy-metal ions).[2] The coupling of, say, desalination processes as a pre-concentration step, would both reduce pre-treatment effort considerably and move toward the “circular water economy” described by Bears et al.[21]

To conclude, we re-emphasize the potential of EDBM and DE technologies for caustic production, primarily in consideration of their significantly improved thermodynamic limits relative to conventional chlor-alkali technology. In addition, the possibility that less pretreatment will be required for EDBM/DE processes further reduces the potential energy consumption for the complete process train in comparison to other methods. We believe that further research on this topic should first be directed to quantitative understanding of voltage losses, including the fraction of single terms (i.e., anode/cathode kinetics, ohmic losses in the membrane/electrolyte) and current inefficiencies within EDBM/DE systems (e.g., Du et al.[22]). At the same time, since design and development of novel OER catalysts with better activity, selectivity, and durability are expected to remain a high priority in the near future (for water electrolyzer applications), adoption and testing of these novel catalysts under EDBM/DE conditions will be highly beneficial for optimizing the performance and energy requirements of these processes. With these improvements, the low thermodynamic limits of EDBM/DE energy consumption will become significantly more attainable. Finally, advanced designs targeting increased system efficiency and scale-up of existing lab systems will pave the way for successful commercialization of these two exciting technologies.

Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interest.

REFERENCES

(1) O'Brien, T.F.; Bommaraju, T.V.; Hine, F. (2005) Chemistry and Electrochemistry of the Chlor-Alkali Process. In: Handbook of Chlor-Alkali Technology. Springer, Boston, MA. https://doi.org/10.1007/0-306-48624-5_4

(2) Oener, S.Z.; Marc, J.F.; Shannon W.B. Accelerating water dissociation in bipolar membranes and for electrocatalysis. *Science* **2020**, *369*, 1099-1103.

(3) Kumar, A.; Phillips, K. R.; Thiel, G. P.; Schroder, U.; Lienhard, J. H. Direct Electrosynthesis of Sodium Hydroxide and Hydrochloric Acid from Brine Streams. *Nature Catalysis* **2019**, *2*, 106-113.

(4) Thiel, G. P.; Kumar, A.; Gómez-González, A.; Lienhard, J. H. Utilization of Seawater Desalination Brine for Sodium Hydroxide Production: Technologies, Engineering Principles, Recovery Limits and Future Directions. *ACS Sustainable Chemistry & Engineering* **2017**, *5*, 11147–11162.

(5) Reig, M.; Casas, S.; Valderrama, C.; Gibert, O.; Cortina, J. L. Integration of Monopolar and Bipolar Electrodialysis for Valorization of Seawater Reverse Osmosis Desalination Brines: Production of Strong Acid and Base. *Desalination* **2016**, *398*, 87–97.

(6) Du, F.; Warsinger, D.M.; Urmi, T.I.; Thiel, G.P.; Kumar, A.; Lienhard, J. H. Sodium Hydroxide Production from Seawater Desalination Brine: Process Design and Energy Efficiency. *Environmental Science & Technology* **2018**, *52*, 5949–5958.

(7) Haverkort, J.W.; Rajaei J.W. Voltage Losses in Zero-gap Alkaline Water Electrolysis. *Journal of Power Sources* **2021**, 497, 15.

(8) Hashemi, S. M. H.; Karnakov, P.; Hadikhani, P.; Chinello, E.; Litvinov, S.; Moser, C.; Koumoutsakos, P.; Psaltis, D. A Versatile and Membrane-less Electrochemical Reactor for the Electrolysis of Water and Brine. *Energy & Environmental Science*, **2019**, *12*, 1592-1604.

(9) Zhang, L.; Lang, Z.; Wang, Y.; Tan, H.; Zang, H.; Kang, Z., Li, Y. Cable-like Ru/WNO@C Nanowires for Simultaneous High-efficiency Hydrogen Evolution and Low-energy Consumption Chlor-alkali Electrolysis. *Energy & Environmental Science*, **2019**, *12*, 2569-2580.

(10) Sun, Y.; Xue, Z.; Liu, Q.; Jia, Y.; Li, Y.; Liu, K.; Lin, Y.; Liu, M.; Li, G.; Su, C. Modulating Electronic Structure of Metal-organic Frameworks by Introducing Atomically Dispersed Ru for Efficient Hydrogen Evolution. *Nature Communications* **2021**, *12*, 1369.

(11) Shi, H.; Zhou, Y.; Yao, R.; Wan, W.; Ge, X.; Zhang, W.; Wen, Z; Lang, X.; Zheng, W; Jiang, Q. Spontaneously Separated Intermetallic Co_3Mo from Nanoporous Copper as Versatile Electrocatalysts for Highly Efficient Water Splitting. *Nature Communications* **2020**, *11*, 2940.

(12) Wang, X. H.; Ling, Y.; Wu, B.; Li, B. L.; Li, X. L.; Lei, J. L.; Li, N. B.; Luo, H. Q. Doping Modification, Defects Construction, and Surface Engineering: Design of Cost-effective High-performance Electrocatalysts and their Application in Alkaline Seawater Splitting. *Nano Energy* **2021**, *87*, 106160.

(13) Tong, W.; Forster, M.; Dionigi, F.; Dresp, S.; Erami, R. S.; Strasser, P.; Cowan, A. J.; Farras, P. Electrolysis of Low-grade and Saline Surface Water. *Nature Energy* **2020**, *5*, 367-377.

(14) Dresp, S.; Dionigi, F.; Klingenhof, M.; Strasser, P. Direct Electrolytic Splitting of Seawater: Opportunities and Challenges. *ACS Energy Letters*, **2019**, *4*, 933-942.

(15) Exner, K. S.; Over, H. Kinetics of Electrocatalytic Reactions from First-Principles: A Critical Comparison with the Ab Initio Thermodynamics Approach. *Accounts of Chemical Research*. **2017**, *50*, 1240-1247.

(16) Traini, C.; Faita, G. Apparatus and Process for Electrochemically Decomposing Salt Solutions to Form the Relevant Base and Acid. **1997**. US Patent 5595641.

(17) Abe, H.; Murakami, S. T.; Okada, T.; Wakabayashi, T.; Yoshida, M.; Nakayama, M. Selective Catalyst for Oxygen Evolution in Neutral Brine Electrolysis: An Oxygen-Deficient Manganese Oxide Film. *ACS Catalysis* **2021**, *11*, 6390-6397.

(18) Mu, L.; Wang, Y.; Willian, A. A. Validation and Mechanism of a Low-Cost Graphite Carbon Electrode for Electrochemical Brine Valorization. *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 8648-8654.

(19) Sohrabnejad-Eskan, I.; Goryachev, A.; Exner, K. S.; Kibler, L. A.; Hensen, E. J. M.; Hofmann, J. P.; Over, H. Temperature-Dependent Kinetic Studies of the Chlorine Evolution Reaction over RuO_2 (110) Model Electrodes. *ACS Catalysis* **2017**, *7*, 2403-2411.

(20) Moreno-Hernandez, I. A.; Brunschwig, B. S.; Lewis, N. S. Crystalline Nickel, Cobalt, and Manganese Antimonates as Electrocatalysts for the Chlorine Evolution Reaction. *Energy & Environmental Science* **2019**, *12*, 1241-1248.

(21) Bears, R. C. Developing the Circular Water Economy. **2020**. ISBN: 978-3-030-32574-9, https://doi.org/10.1007/978-3-030-32575-6.

(22) Du, C.; Du, J. R.; Zhao, X.; Cheng, F.; Ali, M. E.; Feng, X. C. Treatment of Brackish Water RO Brine via Bipolar Membrane Electrodialysis," *Industrial & Engineering Chemistry Research* **2021**, *60*, 3115–3129.