

Cite this: *Catal. Sci. Technol.*, 2022, 12, 3412Received 6th March 2022,
Accepted 1st May 2022

DOI: 10.1039/d2cy00443g

rsc.li/catalysis

Oxygen depolarised cathode as a learning platform for CO₂ gas diffusion electrodes

Sandra Hernandez-Aldave^a and Enrico Andreoli *^{bc}

Scientists and engineers worldwide are developing carbon dioxide utilisation technologies to defossilise the bulk chemical industry and support global efforts toward net-zero targets. Electrolysis can make oxygenate and hydrocarbon products from CO₂, water, and renewable electricity. Opposed to such striking simplicity, CO₂ electrocatalysis and electrolyzers are fraught with challenges hampering the deployment of CO₂ electrolysis on a large scale. The chlor-alkali electrochemical industry has already tackled various issues encountered today in the development of stable CO₂ reduction gas diffusion electrodes (GDEs). The oxygen depolarised cathode (ODC) is a very stable GDE currently used to make multiple kilotonnes of NaOH and Cl₂. In this review, we present the principle of operation of the ODC including bespoke cell designs implemented to deliver year-long process stability. We do this in parallel to discussing the needs of CO₂ electrolysis and close with a proposed CO₂ electrolyser design integrating the learning from the development of the chlor-alkali ODC. The rationale is to help advance robust CO₂ electrolysis with industrially relevant performance.

Introduction

Commonly associated with fossil fuel combustion for power, transport, and heating generation, CO₂ emissions in a not-too-distant future should be linked largely to industrial processes powered with renewable carbon-free energy. Predominantly, foundation industries (metals, ceramics, glass, chemicals, paper, and cement manufacturing) will be

^a School of Applied Sciences, University of Huddersfield, Huddersfield, HD1 3DH, UK

^b Energy Safety Research Institute, Swansea University, Swansea SA1 8EN, UK.
E-mail: e.andreoli@swansea.ac.uk

^c Department of Chemical Engineering, School of Engineering and Applied Sciences, Faculty of Science and Engineering, Swansea University, Swansea SA1 8EN, UK

**Sandra Hernandez-Aldave**

Dr. Sandra Hernandez Aldave obtained her PhD in Nanotechnology from Swansea University in 2019. After involvement in academic and industrial research, investigating novel nanomaterials and developing new biosensors, she started as a postdoctoral researcher at the Energy Safety Research Institute of Swansea University, where she worked in the carbon capture and utilisation field investigating the

development of new gas diffusion electrodes for the electrochemical conversion of CO₂. Currently, she is a Lecturer in the School of Applied Sciences at the University of Huddersfield.

**Enrico Andreoli**

Dr. Enrico Andreoli is an Associate Professor and the current Head of Department of Chemical Engineering at the Faculty of Science and Engineering of Swansea University. His broad industrial and academic experience spans materials and technology development and innovation, also applied to carbon capture and utilisation (CCU). He started working on CCU as a postdoctoral researcher at Rice

University, where he drew on expertise gained at the Giulio Natta Research Center of LyondellBasell. He holds a PhD in Chemistry from Maynooth University, a Master's degree in Industrial Chemistry from the University of Padua, and a Master of Science, Technology and Management from the University of Ferrara.



responsible for the majority of CO₂ emissions. Foundation industries will not only need to be decarbonised (*i.e.* stop releasing carbon dioxide generated from the manufacturing processes), but also defossilised (*i.e.* stop using carbon feedstocks of fossil origin as raw materials for their processes). Within this context, the role of carbon dioxide utilisation in industry defossilisation is crucial. Indeed, already emitted CO₂ is recognised as a primary alternative carbon feedstock^{1–4} from which defossilised bulk chemicals could be manufactured without the use of fossil carbon.^{5–7} Virtuous circularity can be realised by placing CO₂ at the centre of the manufacturing industry when carbon dioxide generated from any of the foundation industries is recycled into new products by the bulk chemicals industry.^{8,9} For this reason, next-generation CO₂ conversion processes have to be devised, developed, scaled, and deployed whilst fossil carbon must stay underground to achieve a net-zero carbon future. The pervasive impact of such an approach is as essential as the research to deliver the carbon utilisation technologies sought to transform the foundation industries.

Electrochemical CO₂ reduction (CO₂R) brings the opportunity of converting CO₂ into value-added carbon-based products, such as formic acid, methane, ethanol, ethylene, propanol to name a few.^{4,10–12} Moreover, the conversion is viable using electricity obtained from low-carbon or carbon-free renewable sources.^{10,13} Although significant progress has been made in the last decade in this field, there are still challenges to overcome to deliver industrial outcomes.

For industrial applications, CO₂ conversion cells, also named electrolyzers, are required to have long-term stability of several thousands of hours,¹⁴ and high selectivity with current densities greater than 250 mA cm⁻².¹⁵ Aqueous-fed electrolyzers, where the CO₂ gas is dissolved into aqueous electrolytes, cannot fulfil the industrial requirements due to low CO₂ solubility in water and limited CO₂ mass transport.¹⁶ The low solubility of CO₂ (0.0006 mole fraction in water at 298 K and 1 atm,¹⁷ corresponding to about 33 mM) hinders mass transfer and consequently the current density. Thus, the current density of an aqueous-fed electrolyser configuration, like the H-cell, only reaches values up to 35 mA cm⁻², for a two-electron reduction process;¹⁸ a number way below the requirement for commercial application. On the other hand, gas-fed electrolyzers overcome mass transfer limitations. These types of electrolyzers often show current densities greater than 250 mA cm⁻².¹⁴ In these cells, the CO₂ gas is directly introduced using a gas diffusion electrode (GDE), which facilitates the transport of CO₂ to the catalyst.^{16,19–21} Although gas-fed electrolyzers have shown remarkable selectivities in the conversion of CO₂ to CO, formic acid, and ethylene;²⁰ the use of gas diffusion electrodes arouses new challenges.^{16,22}

A GDE is a gas diffusion layer (GDL) bearing a catalyst layer (CL) on its surface (Fig. 1). The gas diffusion layer typically consists of a macroporous layer or substrate (MPS), usually carbon-fibre paper or cloth) and a microporous layer

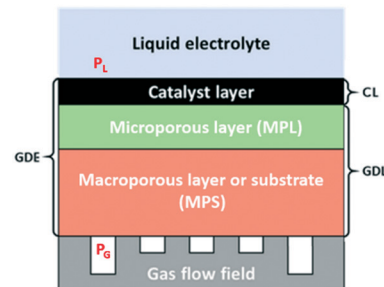


Fig. 1 Schematic of a gas diffusion electrode (GDE) installed between gas flow field and liquid electrolyte, as commonly found in the cathodic compartment of a gas-fed CO₂ electrolyser. The GDE includes a gas diffusion layer (GDL) with on top a catalyst layer (CL) in contact with the electrolyte. The GDL is made of a macroporous substrate (MPS) and a microporous layer (MPL). During operation, liquid electrolyte and CO₂ gas feeds are at pressure P_L and P_G , respectively. Adapted from ref. 16.

(MPL, carbon black powder mixed with a hydrophobic agent, often PTFE). Commercial GDEs are available and have been applied to CO₂R.^{19,22} However, CO₂R GDE-based electrolyzers suffer from short-term stability.^{13,20}

There are some difficulties linked with the operation of GDE-based electrolyzers, such as electrode degradation affecting electrolyser stability in different flow configurations. Under CO₂ conversion conditions, *e.g.* in alkaline media at high current densities, the carbon support of GDEs loses hydrophobicity, leading to the flooding of the electrode after a few hours of operation.^{23–26} Despite the efforts of researchers to develop more stable gas diffusion electrodes and layers, for example by increasing the number of hydrophobic agents, the stability of CO₂ electrolyzers has not been better than 500 h,²⁰ which is far from the 20 000 h target. Even new approaches like polymer-based non-commercial GDEs are stable for 150 h.²⁷ At the same time, the flow configuration plays a central role in the long-term stability of CO₂ electrolyzers. The differential pressure across the GDE ($P_L - P_G$, Fig. 1) determines the flow configuration governing the electrolyser.^{16,28} When the pressure of the gas is higher than that of the electrolyte ($P_G > P_L$, flow-through configuration), CO₂ gas is pushed through the GDE pores to eventually dissolve in the electrolyte, however, this can result in CO₂ bubbling in the electrolyte. The presence of bubbles will disturb the electrolytic processes, lowering the efficiency of the system. Moreover, the gas flow can dry the electrolyte forming crystal salts on the GDE, causing physical blockages to gas flow, reducing mass transport, and decreasing productivity. Conversely, when the gas is at lower pressure than the electrolyte ($P_G < P_L$, flow-by configuration), the electrolyte enters the GDE and CO₂ goes into pores by diffusion, in this case a common issue is perspiration leading to the flooding of the gas chamber.^{23,28} Therefore, it is critical to develop GDEs with stable wet configurations where gas and electrolyte coexist inside the catalyst layer without hampering the transport of reactants and products across the electrode.²⁹ This should allow to overcome



Mini review

pressure differential instability and deliver robust CO₂R electrolyzers.

Helpfully, the working principles of gas diffusion electrodes are not just applied to CO₂ conversion systems. They are also employed in other technologies, notably in hydrogen fuel cells^{30–32} and zinc–air batteries,^{33–35} and above all in the chlor-alkali industry for the large scale production of Cl₂ and NaOH.³⁶ The specific type of GDE used in the chlor-alkali process is the oxygen depolarised cathode (ODC) capable of achieving stable operation for more than 26 400 h (over 1100 days).³⁷

In this minireview, we aim to identify and discuss similarities between chlor-alkali ODC electrodes and CO₂R GDEs in the attempt to show a way forward for large scale CO₂ electrolyzers.

Chlor-alkali electrolysis

Chlorine is one of the most valuable products of the chemical industry.^{38–40} A country's chlorine production is an indicator of its chemical industry scale of activity.⁴¹ In recent years, Cl₂ production has grown drastically due to the demand for polymers, such as polyvinyl chloride, polyurethanes, and polycarbonate, as well as chloroaromatics. The worldwide demand for chlorine has increased by more than 20% from 2000 to 2010. In fact, in 2020, 9221 kilotonnes of chlorine were produced.⁴² It is estimated that about 10% of world electricity is used by the chlor-alkali industry.⁴³

There are three different electrolytic processes currently in use for the production of chlorine and caustic soda: (a) diaphragm cell (b) mercury cell and (c) membrane cell.³⁶ In all the processes chloride ions are oxidised at the anode leading to the production of gaseous chlorine. The membrane cell process is by far the most used (83.3% of European production⁴²) due to the environmental and health impact of the other two. In the diaphragm process, water is converted to hydrogen gas and hydroxyl ions using asbestos for the diaphragm.⁴¹ Instead in the mercury cell, sodium amalgam is formed and reacted with water to produce hydrogen gas and sodium hydroxide solution that must be freed from mercury.^{41,44} Given the environmental concerns, mercury technology is being retired in Europe by the end of 2022.⁴² Therefore, the membrane-based chlor-alkali industry has led to new and more efficient cells.

Initially, the membrane chlor-alkali cell was an aqueous-based cell, where anode and cathode were submerged in electrolyte and each chamber divided by a membrane. At the cathode, sodium hydroxide and hydrogen gas were formed (Fig. 2a). Later, a different approach was developed using an oxygen depolarised cathode, where O₂ is reduced in place of H₂O allowing to “depolarise” the chlor-alkali process by 1.23 V (Fig. 2b). The ODC is a porous gas-diffusion electrode similar to those used on CO₂R. In this case, a gas chamber is added to the system where oxygen gas is introduced and reduced to hydroxyl ions, avoiding the formation of undesired hydrogen.³⁶ The result is a more efficient process

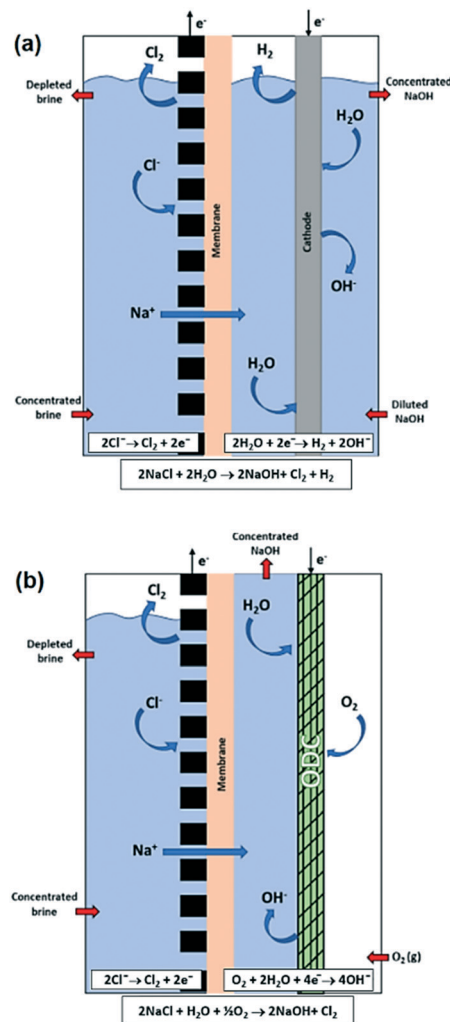


Fig. 2 Schematics of two membrane chlor-alkali electrolyzers using different cathodic processes. (a) Cell with hydrogen evolving cathode: the redox processes are (i) reduction of water to hydrogen gas and hydroxide ($E_c = -0.83$ V vs. SHE) and (ii) oxidation of chloride ions to chlorine gas ($E_a = 1.36$ V vs. SHE) resulting in a theoretical cell voltage of 2.19 V. (b) Cell with oxygen depolarised cathode (ODC): the redox processes are (i) reduction of oxygen gas to hydroxide ($E_c = 0.40$ V vs. SHE) and (ii) oxidation of chloride to chlorine ($E_a = 1.36$ V vs. SHE) resulting in a theoretical cell voltage of 0.96 V vs. SHE. The ODC electrolyser requires 1.23 V less than the hydrogen evolving electrolyser to generate Cl₂ and NaOH.

with energy consumption reduced by 30%, striving for zero waste and lower carbon footprint.⁴⁵

Oxygen depolarised cathode (ODC)

The oxygen depolarised cathode is a porous structure that facilitates a three-phase interface process, where oxygen gas is reduced in the presence of liquid water on the surface of a solid electrocatalyst.⁴⁶ This process is comparable to the one found in CO₂ conversion, where CO₂ gas interacts with the electrolyte as it is electrochemically converted at the catalyst surface.



Considering that the electrochemical reaction of the chlor-alkali process takes place where the three reactants merge, the ODC need to meet very stringent requirements for the process to be successful:³⁶

- High chemical stability in concentrated sodium hydroxide at 80–90 °C;
- High mechanical stability in electrolyzers with electrodes having multiple m² area;
- High electronic conductivity and low thickness;
- High surface area active electrocatalysts;
- Appropriate hydrophobic/hydrophilic pore structure for straightforward access of gases and liquids without breakthrough of either gas or liquid at various pressure differences across the electrode;
- High long-term stability;
- Affordable costs.

Remarkably, the above requirements are very closely related to those of CO₂R GDEs. Considering that the chlor-alkali industry has been developing the ODC since 1973 to achieve today's industrial long-term stability, it surely is an opportunity to study the ODC technology, learn from it and possibly adopt demonstrated approaches to CO₂ electrolysis.

Learning from ODC technology

The idea of using an oxygen depolarised cathode in the chlor-alkali electrolysis was proposed in early 1950 by Butler.^{36,47} Afterwards Juda suggested a chlor-alkali process with cation exchange membrane and oxygen-consuming cathode.⁴⁸ However, they could not demonstrate its industrial application because of the lack of stability of the membranes available at that time. It was in the 1970s when ODC applied research boomed. By the 1980s multiple commercial size cells were operational for extended periods. Several companies, especially in the USA and Germany, started developing and improving the ODC technology:³⁶ Hooker,⁴⁹ Dow Chemicals,^{50–52} Hoechst,^{53–55} Olin,^{56,57} PPG Industries,^{58,59} Engelhard,⁶⁰ General Electric,⁶¹ United Technologies,⁶² and DeNora.⁶³ Likewise, Japanese companies were active, including Asahi Glass,⁶⁴ Tokuyama Soda,⁶⁵ Toyo Soda,⁶⁶ and Kureha Chemical.⁶⁷

In the 1990s, new research and development in ODC chlor-alkali electrolysis were promoted by the Japanese Ministry of Trade and Industry in cooperation with the Japan Soda Industry Association,⁶⁸ with partners like Asahi Glass,⁶⁹ Permelec Electrode,⁷⁰ Tanaka Precious Metals, and DuPont Japan.³⁶ The effort attracted the attention of universities too, with the Furuya group at Yamanashi University focused mainly on the development of the ODC,^{71,72} a large program was also led by Bayer in cooperation with Uhde and DeNora in Germany.⁷³ In 1998, large-scale chlor-alkali electrolysis cells (2.7 m²) were operating with ODC electrodes successfully.³⁶

From the challenges and solutions devised by the chlor-alkali industry, we aim to find valuable learnings to help stir research and innovation efforts for CO₂R GDEs.

Challenges arising from the materials

Several materials were investigated as catalysts for oxygen reduction in alkaline conditions, but most of them showed poor long-term stabilities under hot concentrated alkaline conditions. Useful results were achieved using carbon-supported platinum or silver, or silver as a pure metal.^{36,43}

Researchers, however, soon found out that carbon-based electrodes suffered major deactivation resulting in short-term stability.^{71,74} Carbon-based ODCs deteriorated after some days or even hours.⁷⁵ Instead, metal ODCs were stable even after several months. It was clear that carbon degraded in concentrated alkaline electrolyte, damaging the ODC, increasing its hydrophilicity and altering the contact between catalyst particles and carbon support.³⁶ These conclusions were backed by several research groups such as Furuya and coworkers,^{37,76,77} Morimoto *et al.*,⁶⁹ and Chatenet *et al.*⁷⁸ In addition, Staab and coworkers also reported that carbon-based electrodes exhibit much greater deactivation, especially after shut-down of the electrolyser.^{36,94}

Accordingly, the chlor-alkali industry started developing novel carbon-free electrodes capable of longer-term operation. Metal wire gauze or mesh (typically nickel or silver) was used to stabilise the electrode mechanically while providing electric conductivity.⁷³ The electrocatalyst was often made using silver or silver oxide, mixed with PTFE, made into a “wet filter cake” that was then pressed onto the metal wire gauze.⁷⁹ Often this process was performed by a cold rolling process. Finally, the fabricated ODC was sintered at high temperatures (~250 °C) to improve the mechanical stability and to remove the pore builder.

Using this type of carbon-free ODC, Wagner *et al.* reported promising results using silver ODCs stable for 1400 h at 100 mA cm⁻².⁷⁹ Staab *et al.* achieved a current density of 2 kA m⁻² with 450 cm² electrodes stable over a period of 7.5 months; the cell voltage only rose from 2.15 V to 2.20 V.^{80,81} The average energy consumption was about 1600 kW h t⁻¹ of NaOH with a current yield of about 92%.⁸⁰ Possibly the best reported long-term stability was that obtained by Sugiyama *et al.*,⁷² where a stable operation for more than 3 years (1200 days) was achieved with similar fabrication procedures. The effective working area of the chlor-alkali cell was 33.4 cm², using a current density of 3 kA m⁻²; a temperature of 88 °C; catholyte concentration of 32 wt% NaOH; and oxygen concentration of 93%.

Challenges arising from the pressure differential

A vertical electrode layout enables the collection of gas products from the electrolyser efficiently. The importance of flow configuration in CO₂ electrolyzers has been mentioned in the previous sections. The differential pressure across the GDE is a paramount factor for the performance of the electrolyser. The challenges arising from the differential pressure were also investigated in chlor-alkali cells. At the early stages of chlor-alkali cell design, researchers discovered that even though large pressure differences between the



catholyte and the gas compartment were theoretically possible, the reality was very different.³⁶ Even the hydrostatic pressure column in cell heights as low as 30 cm was too high for optimal ODC operation,^{36,73} hampering the development of commercial cells taller than 1 m. The height-dependent differential pressure between electrolyte and gas across the ODC was resolved using pressure compensation systems. The first approach was adding modular gas pockets in the cell.⁸² The cell had gas pockets on the oxygen side leading to the independent adjustment of the pressure. The height of these compartments was small enough to avoid electrode flooding or gas breakthrough. The first successful piloting of this cell was performed by Bayer engineers in 1995. A four-gas-pocket element was employed, each segment of $180 \times 180 \text{ mm}^2$, leading to a pressure compensation of a cell of overall 90 cm height (Fig. 3). The collaboration between Bayer and DeNora resulted in an improved system utilising vented gas pockets in a cascade-type oxygen supply.⁸³ By December 1998, they were able to test the first industrial-scale ODC electrolyser,

presenting 16 bipolar elements of area 2.5 m^2 each in a filter press arrangement.⁷³ The ODC electrolyser was commissioned up to 3 kA m^{-2} with an energy consumption of less than 1400 kW h per tonne of NaOH and continued operation without any issues for a long period of time (more than 180 days).

Cell design versus electrode structure

It is essential to point out that even though the cell design of the electrolyser is of utmost importance for a successful electrochemical process, the electrode structure is also a key factor. Even using the pressure-compensation system above, the electrode does not have to exceed a certain critical height because of the pressure differential between the gas and liquid sides. When the critical height is exceeded, the gas eventually breaks across the GDE into the electrolyte where the hydrostatic pressure is lower at the top of the electrode. A shallower column of catholyte is unable to compensate for the uniform pressure of the gas. In such a situation, the electrode structure can be tuned to avoid gas breakthrough by:⁷³

- Increasing the thickness of the electrode;
- Changing the volume occupied by the pores, the average pore diameter, and pore tortuosity;
- Applying a hydrophilic layer on the liquid side of the electrode to retain electrolyte and build up a capillary pressure within the pores preventing significant gas leakages.

Thicker electrodes can hinder gas leaks but are expensive and hard to manufacture. Tuning the microstructure is a good option but it is somewhat challenging to make uniform large-scale electrodes. Therefore, adding a hydrophilic layer seems the most convenient approach to prevent gas leaks.

ODC technology today

In 1998, Krupp Uhde patented a new design of the falling film electrolyser (FFE).⁸⁴ In the FFE,⁸⁵ the electrolyte flows from the top of the cell downward by gravity. The hydrostatic pressure of the electrolyte column is compensated by a counteracting hydrodynamic pressure drop as a result of fluid friction. Accordingly, the pressure exerted by the electrolyte on the GDE and the pressure difference between electrolyte and gas are constant over the entire electrode. Moreover, the falling film can be as thin as 1 mm, or thinner, depending on the gap between membrane and GDE. The advantages of the FFE are multiple: (i) improved mass and heat transfer; (ii) low gas content in the electrolyte; (iii) low concentration difference; (iv) constant differential pressure; (v) lower cell voltage of 2.70 V at 3 kA m^{-2} leading to energy consumption reduction of 70 kW h per tonne of NaOH at 4 kA m^{-2} .⁷³ Moreover, the introduction of the ODC electrode in the FFE led to the further decrease of cell voltage to 1.9–2.0 V, therefore, lowering specific power consumption. With the cooperation of Covestro, ThyssenKrupp Uhde Chlorine Engineers, became leaders in the field, employing an FFE three-compartment cell and a silver-based oxygen depolarised

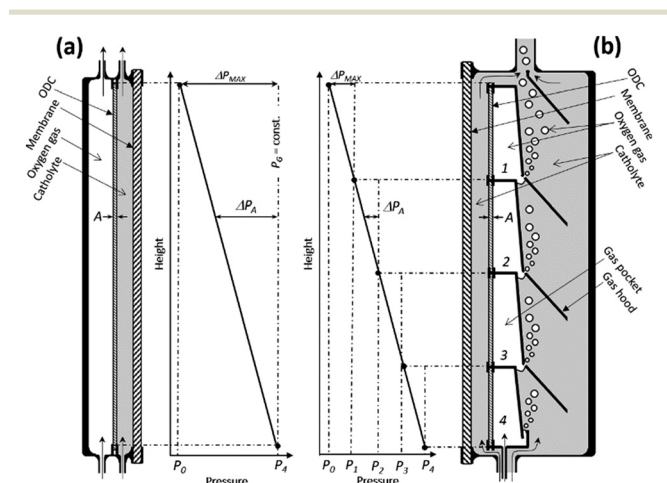


Fig. 3 Schematics of the cathodic compartments of two ODC chlor-alkali electrolyzers using different oxygen intake systems. (a) Standard system with the ODC sandwiched between oxygen gas and catholyte, both entering from the bottom of the compartment. The solid line in the plot shows the hydrostatic pressure created by the column of catholyte on the ODC at different heights: the pressure is lowest at the top, P_0 , and increases linearly moving towards the bottom where it is the largest, P_4 . P_4 is also the operating pressure of oxygen gas within the entirety of the compartment ($P_G = \text{const.}$), in mechanical equilibrium with the catholyte only at the bottom of the compartment. ΔP_{MAX} is the pressure differential at the top of the compartment where the gas is at a higher pressure than the liquid eventually causing oxygen breakthrough in the catholyte. (b) Pressure compensation system with the ODC receiving oxygen via four gas pockets each fitted with a gas hood. Again, gas and electrolyte enter from the bottom of the compartment. Oxygen fills the gas pockets bubbling up from one to the next via openings in the gas hoods. In the plot, the pressures of oxygen and catholyte (P_1, P_2, P_3, P_4) are the same at the bottom of each gas pocket, accordingly the ΔP_{MAX} of each pocket is much smaller than that of the standard system, avoiding gas breaking through the ODC. ΔP_A is the pressure differential across the ODC at a generic point A of the ODC, once more it is evident how the gas pocket reduces the pressure difference between gas and electrolyte compared to the standard system.



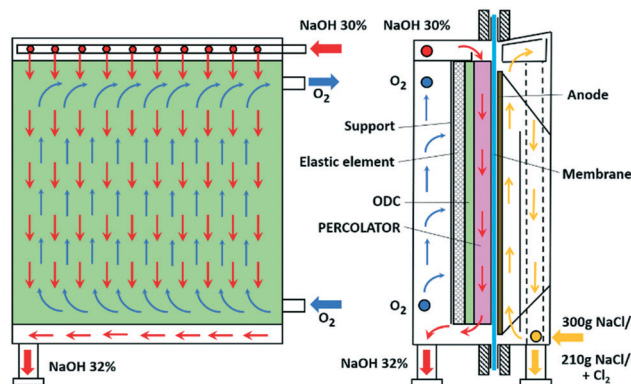


Fig. 4 Schematics of NaCl-ODC cell technology from ThyssenKrupp Uhde Chlorine Engineers. In contact with the oxygen depolarised cathode (in green), a percolator (in pink) is used to feed a thin film of caustic soda from the top of the electrolyser. Support and elastic element allow compressing membrane, percolator, and ODC together. The result is a more concentrated NaOH solution at the output of the cathodic compartment, whilst chlorine is produced at the anode. Reproduced and adapted with permission from ref. 46.

cathode. In the cell caustic soda flows from the top of the electrolyser through a percolator, resulting in a homogenous distribution of catholyte in the cathodic chamber (Fig. 4). The homogenous distribution is key in (i) obtaining a long membrane lifetime; (ii) improving the performance of the GDE; (iii) maintaining a constant caustic pressure over the full cell height; and (iv) avoiding flooding of the GDE or gas chamber.⁴⁶ The FFE technology is currently used in chlor-alkali cells, as a way to mitigate the pressure issue and avoid flooding.

Nowadays, chlor-alkali electrolyzers follow the principles of those invented in 1998, using optimised ODC cathodes and improved cell designs. ThyssenKrupp Uhde Chlorine Engineers continue to be a leader in the field with NaCl-ODC electrolysis technology developed in collaboration with Covestro (formerly Bayer Material Science). The NaCl-ODC technology is based on an ODC integrated into a single cell element with similar characteristics to the FFE.

A single cell element is made of different layers assembled as shown in Fig. 5. First, a current and oxygen distributor is laid horizontally (Fig. 5a), and an elastic element is placed on top of it (Fig. 5b). ODC sheets are put on the elastic element (Fig. 5c), the sheets are positioned next to each other, covering the whole area of the cell. Afterwards, a percolator layer is placed on the ODC (Fig. 5d).

The percolator is a textile continuously moist with falling caustic soda enabling the formation of a thin film of catholyte between the ODC and a membrane during operation. The membrane is placed and pressed on the percolator to yield a cathodic single cell element. An exploded diagram of the different layers is shown in Fig. 5e. Cathodic and anodic elements are combined to form a single cell; a modular stack of single cells (Fig. 5f) is then connected to other stacks in the final chlor-alkali plant (Fig. 5g and h). The modularity of the stacks translates into ease of

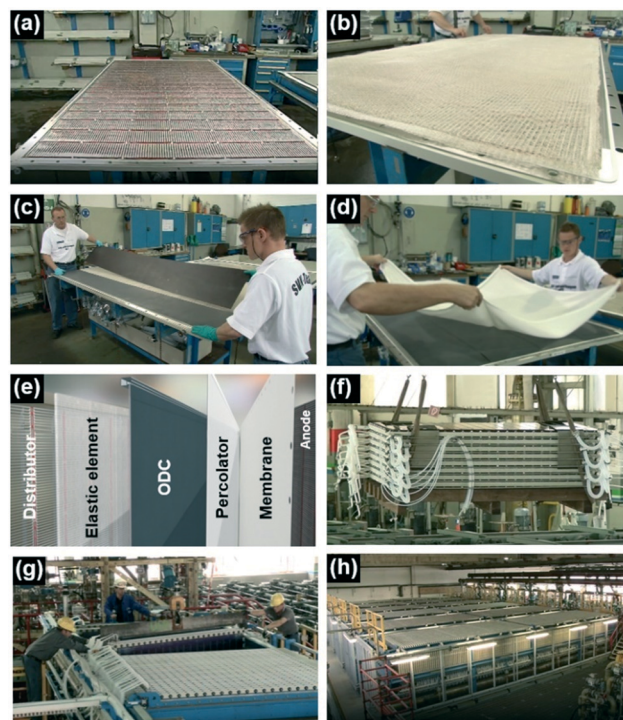


Fig. 5 Assembly and installation of ThyssenKrupp Uhde chlor-alkali cells. (a) A metallic slatted current and gas distributor is covered with (b) a reticulated elastic element, on top of which (c) Covestro's ODC sheets are placed and topped with (d) percolator textiles. (e) A diagram showing the parts of the cathodic single cell element: distributor, elastic element, ODC, percolator, and membrane. The membrane separates the cathodic element from the anodic one to form a complete single cell. (f) A stack of single cells is lifted and (g) installed in line with other modular stacks. (h) A chlor-alkali plant based on ThyssenKrupp Uhde ODC single cell technology. All images reproduced with permission from ref. 88; copyright© thyssenkrupp nucera.

installation and maintenance, and space-saving chlorine production.

ODC technology and CO₂ electrolysis

The chlor-alkali electrochemical industry has faced technical and engineering challenges currently seen in the development of CO₂ electrolyzers. The ODC was first proposed in the 1950s,³⁶ leading to its large scale demonstration with the silver-based ODC in 2011, and a 40 000 tonnes Cl₂ per year plant operational in 2015.⁴⁶ The same technology is currently being deployed to cut energy cost and carbon emissions of chlor-alkali manufacturing, one of the most energy-demanding industrial processes. Silver-based ODC electrodes have been applied to CO₂ electrolysis^{86,87} and learning more broadly from the ODC technology could improve CO₂ electrolyzers since both chlor-alkali and CO₂R share a common goal: deliver suitable electrode and cell design for stable long-term electrolysis operation.

The key process steps in the cathodic compartment of an ODC-based electrolyser are:



Mini review

- Oxygen transport in the porous structure of the ODC;
- Oxygen dissolution in alkaline electrolyte and diffusion to the catalyst surface;
- Electrochemical reduction of oxygen gas to hydroxide in the presence of water to form NaOH;
- Removal of the products by convective transport.

Almost the same steps are found in the cathodic compartment of a CO₂ electrolyser:

- CO₂ transport in the pore structure of a GDE;
- CO₂ “dissolution” in alkali electrolyte and diffusion to the catalyst surface.
- Selective electrochemical reduction of CO₂ to a specific product in the presence of water;
- Removal of the products by convective transport, liquid products are found in the electrolyte, gaseous products in the gas outlet.

Despite the similarities, there are some major added challenges in CO₂ reduction compared to O₂ reduction:

- CO₂ is carbonated in alkaline media preventing the formation of the desired product, this is not the case with O₂;
- CO₂ reduction in water results in a variety of different products, whereas O₂ converts to hydroxide only;
- CO₂ conversion products are formed and diluted in the reaction media, instead hydroxide ions are added directly to the product stream in the case of O₂ reduction;
- CO₂ is diluted in the gas products as it runs through the cathodic compartment creating ununiform reaction conditions in the electrode, this is not the case with O₂.

Nonetheless, CO₂ electrolysis would benefit from the integration of solutions analogous to the falling film electrolyser to control the pressure differential across the GDE. Also, gas diffusion electrodes based on metal supports should prevent issues of instability due to loss of hydrophobicity during operation, as seen with carbon-based GDEs. Carbonate and bicarbonate formation is a fundamental issue of alkaline CO₂ electrolysers where hydroxide reacts with CO₂ to give HCO₃⁻ and CO₃²⁻ anions. Once formed at the cathode, both HCO₃⁻ and CO₃²⁻ can cross the anion exchange membrane (AEM) to be then protonated and converted back to CO₂ at the anode.⁸⁹ This translates into a major loss of efficiency given that energy is used purposelessly to “pump” CO₂ from the cathode to the anode.

The use of a cation exchange membrane (CEM) to avoid HCO₃⁻ and CO₃²⁻ crossing through the AEM, is not a viable option in alkaline CO₂ electrolysis since caustic electrolytes are largely deficient in protons. Protons must be replenished at the cathode as they are used in the conversion of CO₂ to products. We note that a CEM can instead be utilised in the ODC chlor-alkali process since the Na⁺ cations are required to pair with hydroxide ions and form the product NaOH. Sodium cations are present in high concentrations in the caustic electrolyte, contrary to protons. A better option could be using a bipolar membrane (BPM) which allows the delivery of protons to the cathode, and hydroxide ions to the anode, *via* a water dissociation

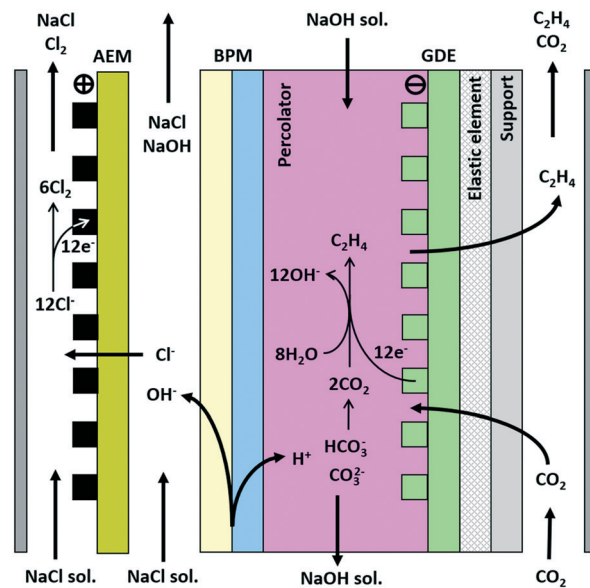


Fig. 6 Proposed design of a CO₂ electrolyser integrating technology solutions from chlor-alkali ODC electrolysis. At the cathode, a GDE (in green) converts CO₂ to C₂H₄, e.g. Chen *et al.*,^{92,93} with the help of a percolator (in pink) to generate a uniform pressure differential over the electrode. At the anode (in black), Cl⁻ anions are converted to Cl₂ gas. A bipolar membrane (BPM) is used to dispatch protons at the cathode and help CO₂ reduction, whilst hydroxide ions displace Cl⁻ transported to the anode for oxidation. The overall process is 2CO₂ + 8H₂O + 12NaCl → C₂H₄ + 6Cl₂ + 12NaOH.

mechanism (under reverse bias).^{90,91} In Fig. 6, we propose a cell design resulting from the integration of (i) a metal-supported CO₂R GDE cathode, (ii) a percolator, as used in ODC electrolysers to achieve uniform pressure differential across the GDE, (iii) a BPM to feed protons and decarbonate the catholyte, (iv) and an AEM to deliver chlorine ions to the anode (since OH⁻ facilitates H₂O oxidation at the expense of Cl₂ evolution). The overall process generates Cl₂ and ethylene (C₂H₄) at the anode and cathode, respectively. This is one example of other possible combinations in which ODC technology solutions could be integrated within CO₂ electrolysers.

Conclusions

The use of a falling film electrolyser configuration along with a selective metal-supported CO₂R GDE appears to be a promising option to attain long-term stability in CO₂ electrolytic processes. Furthermore, the integration of a bipolar membrane could in principle curtail the impact of CO₂ carbonation in alkaline electrolytes by feeding protons into the cathodic compartment freeing CO₂ in favour of the conversion process. These findings were determined from a valuation of the key progress made in CO₂ electrolysis in parallel to a study of established electrolyser ODC chlor-alkali technology. Learning from the achievements of the large-scale electrochemical industry is surely a plausible and valuable opportunity for the CO₂ electrolysis community.



Author contributions

S. H.-A.: conceptualization, writing – original draft, writing – review & editing. E. A.: conceptualization, writing – original draft, writing – review & editing, visualization, supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Support was provided by the UK Engineering and Physical Sciences Research Council through the project EP/N009525/1 and the SUSTAIN Manufacturing Hub EP/S018107/1.

Notes and references

- M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709–1742.
- M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975–2992.
- M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz and T. E. Müller, *ChemSusChem*, 2011, **4**, 1216–1240.
- G. Wang, J. Chen, Y. Ding, P. Cai, L. Yi, Y. Li, C. Tu, Y. Hou, Z. Wen and L. Dai, *Chem. Soc. Rev.*, 2021, **50**, 4993–5061.
- P. Gabrielli, M. Gazzani and M. Mazzotti, *Ind. Eng. Chem. Res.*, 2020, **59**, 7033–7045.
- J. P. Lange, *Energy Environ. Sci.*, 2021, **14**, 4358–4376.
- C. Ampelli, S. Perathoner and G. Centi, *Philos. Trans. R. Soc., A*, 2015, **373**, 20140177.
- P. Tsvetkov, A. Cherepovitsyn and S. Fedoseev, *Sustainability*, 2019, **11**, 5834.
- M. Lieder and A. Rashid, *J. Cleaner Prod.*, 2016, **115**, 36–51.
- P. D. Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo and E. H. Sargent, *Science*, 2019, **364**, eaav3506.
- J. Wyndorps, H. Ostovari and N. von der Assen, *Sustainable Energy Fuels*, 2021, **5**, 5748–5761.
- M. G. Kibria, J. P. Edwards, C. M. Gabardo, C.-T. Dinh, A. Seifitokaldani, D. Sinton and E. H. Sargent, *Adv. Mater.*, 2019, **31**, 1807166.
- R. A. Tufa, D. Chanda, M. Ma, D. Aili, T. B. Demissie, J. Vaes, Q. Li, S. Liu and D. Pant, *Appl. Energy*, 2020, **277**, 115557.
- S. Verma, B. Kim, H.-R. M. Jhong, S. Ma and P. J. A. Kenis, *ChemSusChem*, 2016, **9**, 1972–1979.
- J. M. Spurgeon and B. Kumar, *Energy Environ. Sci.*, 2018, **11**, 1536–1551.
- S. Hernandez-Aldave and E. Andreoli, *Catalysts*, 2020, **10**, 713.
- J. J. Carroll, J. D. Slupsky and A. E. Mather, *J. Phys. Chem. Ref. Data*, 1991, **20**, 1201–1209.
- M. Li, S. Garg, X. Chang, L. Ge, L. Li, M. Konarova, T. E. Rufford, V. Rudolph and G. Wang, *Small Methods*, 2020, 2000033.
- D. Higgins, C. Hahn, C. Xiang, T. F. Jaramillo and A. Z. Weber, *ACS Energy Lett.*, 2019, **4**, 317–324.
- H. Rabiee, L. Ge, X. Zhang, S. Hu, M. Li and Z. Yuan, *Energy Environ. Sci.*, 2021, **14**, 1959–2008.
- T. N. Nguyen and C.-T. Dinh, *Chem. Soc. Rev.*, 2020, **49**, 7488–7504.
- Y. Cheng, P. Hou, X. Wang and P. Kang, *Acc. Chem. Res.*, 2022, **55**, 231–240.
- G. L. De Gregorio, T. Burdyny, A. Lojudice, P. Iyengar, W. A. Smith and R. Buonsanti, *ACS Catal.*, 2020, **10**, 4854–4862.
- B. Kim, F. Hillman, M. Ariyoshi, S. Fujikawa and P. J. A. Kenis, *J. Power Sources*, 2016, **312**, 192–198.
- A. Reyes, R. P. Jansonius, B. A. W. Mowbray, Y. Cao, D. G. Wheeler, J. Chau, D. J. Dvorak and C. P. Berlinguette, *ACS Energy Lett.*, 2020, **5**, 1612–1618.
- Z. Xing, L. Hu, D. S. Ripatti, X. Hu and X. Feng, *Nat. Commun.*, 2021, **12**, 136.
- C.-T. Dinh, T. Burdyny, M. G. Kibria, A. Seifitokaldani, C. M. Gabardo, F. P. Garcia de Arquer, A. Kiani, J. P. Edwards, P. De Luna, O. S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton and E. H. Sargent, *Science*, 2018, **360**, 783.
- B. De Mot, J. Hereijgers, M. Duarte and T. Breugelmans, *Chem. Eng. J.*, 2019, **378**, 122224.
- L.-C. Weng, A. T. Bell and A. Z. Weber, *Phys. Chem. Chem. Phys.*, 2018, **20**, 16973–16984.
- V. Mehta and J. S. Cooper, *J. Power Sources*, 2003, **114**, 32–53.
- S. Litster and G. McLean, *J. Power Sources*, 2004, **130**, 61–76.
- Q. Liu, F. Lan, J. Chen, C. Zeng and J. Wang, *J. Power Sources*, 2022, **517**, 230723.
- D. Fenske, I. Bardenhagen and J. Schwenzel, *Chem. Ing. Tech.*, 2019, **91**, 707–719.
- M. Wu, G. Zhang, M. Wu, J. Prakash and S. Sun, *Energy Storage Mater.*, 2019, **21**, 253–286.
- W.-W. Tian, J.-T. Ren, X.-W. Lv and Z.-Y. Yuan, *Chem. Eng. J.*, 2022, **431**, 133210.
- I. Moussallem, J. Jörissen, U. Kunz, S. Pinnow and T. Turek, *J. Appl. Electrochem.*, 2008, **38**, 1177–1194.
- A. Sakata, M. Kato, K. Hayashi, N. Furuya, H. Aikawa and K. Saiki, ECS Proceedings, 1999, 21, 223.
- J. Jörissen, in *Encyclopedia of Applied Electrochemistry*, ed. G. Kreysa, K.-I. Ota and R. F. Savinell, Springer New York, New York, NY, 2014, pp. 194–200, DOI: [10.1007/978-1-4419-6996-5_297](https://doi.org/10.1007/978-1-4419-6996-5_297).
- F. Klauke, C. Hoffmann, M. Hofmann and G. Tsatsaronis, *Appl. Energy*, 2020, **276**, 115366.
- T. F. O'Brien, T. V. Bommaraju and F. Hine, in *Handbook of Chlor-Alkali Technology: Volume I: Fundamentals, Volume II: Brine Treatment and Cell Operation, Volume III: Facility Design and Product Handling, Volume IV: Plant Commissioning and Support Systems, Volume V: Corrosion, Environmental Issues, and Future Development*, Springer US, Boston, MA, 2005, pp. 1463–1489, DOI: [10.1007/0-306-48624-5_17](https://doi.org/10.1007/0-306-48624-5_17).
- J. Crook and A. Mousavi, *Environ. Forensics*, 2016, **17**, 211–217.
- EuroChlor, *Chlor-alkali industry Review 2020–2021*, <https://www.eurochlor.org/wp-content/uploads/2021/11/Euro-Chlor-Industry-Review-2020-2021.pdf>, (accessed March 2022).



- 43 K. Li, Q. Fan, H. Chuai, H. Liu, S. Zhang and X. Ma, *Trans. Tianjin Univ.*, 2021, **27**, 202–216.
- 44 P. Schmittinger, T. Florkiewicz, L. C. Curlin, B. Lüke, R. Scannell, T. Navin, E. Zelfel and R. Bartsch, in *Ullmann's Encyclopedia of Industrial Chemistry*, 2011, DOI: [10.1002/14356007.a06_399.pub3](https://doi.org/10.1002/14356007.a06_399.pub3).
- 45 Covestro, *Oxygen Depolarized Cathode (ODC) Technology*, https://www.covestro.com/-/media/covestro/corporate/sustainability/flagship-solutions/oxygen-depolarized-cathode/documents/3_6_covestro_produktblatt_oxygendepolarized_cathode_en_2017_te_v02.pdf?la=en&hash=6099CDF7D4CD229E68CF03BBE4E5D36AE73E2C5C, (accessed March 2022).
- 46 J. Kintrup, M. Millaruelo, V. Trieu, A. Bulan and E. S. Mojica, *Electrochem. Soc. Interface*, 2017, **26**, 73–76.
- 47 C. A. Butler Jr, *US Pat.*, 2681884, 1950.
- 48 W. Juda, *US Pat.*, 3262868, 1966.
- 49 D. Pouli, L. S. Melnicki and E. J. Rudd, *US Pat.*, 4332662, 1982.
- 50 J. D. Lefevre, *US Pat.*, 4213833, 1978.
- 51 J. A. McIntyre, R. F. Phillips and J. D. Lefevre, *US Pat.*, 4430177, 1982.
- 52 T. J. Wainerdi, *US Pat.*, 4657651, 1986.
- 53 R. Staab, *US Pat.*, 4603118, 1983.
- 54 R. Staab and K. Hannesen, *US Pat.*, 4584080, 1984.
- 55 R. Staab, *US Pat.*, 4615783, 1984.
- 56 R. C. Miles, R. D. Justice and R. L. Dotson, *US Pat.*, 4578159, 1985.
- 57 R. C. Miles, R. D. Justice and K. E. Woodard Jr, *US Pat.*, 4919791, 1985.
- 58 H. B. Johnson and R. D. Chamberlin, *US Pat.*, 4244793, 1979.
- 59 R. D. Chamberlin, *US Pat.*, 4292197, 1979.
- 60 J. G. E. Cohn and O. J. Adlhart, *US Pat.*, 4486276, 1981.
- 61 J. Coker, R. M. Dempsey and A. B. LaConti, *US Pat.*, 4191618, 1978.
- 62 G. A. Gruver and H. R. Kunz, *US Pat.*, 4564427, 1984.
- 63 A. Nidola and G. N. Martelli, *US Pat.*, 5015344, 1988.
- 64 Y. Oda, T. Morimoto and K. Suzuki, *Jp. Pat.*, 59133386, 1981.
- 65 S. Matsuura, H. Matsui and Y. Mizutani, *Jp. Pat.*, 54084893, 1977.
- 66 O. Ookai, K. Igawa and Y. Hiraga, *Jp. Pat.*, 56047578, 1979.
- 67 T. Kaminaga, M. Shigeta and H. Fukuda, *US Pat.*, 4744879, 1984.
- 68 P. C. Foller, in *Advances in Mathematical Modeling and Simulation of Electrochemical Processes and Oxygen Depolarized Cathodes Activated Cathodes for Chlor-alkali Chlorate Processes*, ed. J. W. Van Zee, P. C. Foller, T. F. Fuller and F. Hine, The Electrochemical Society, Pennington, USA, 1998, pp. 213–219.
- 69 T. Morimoto, K. Suzuki, T. Matsubara and N. Yoshida, *Electrochim. Acta*, 2000, **45**, 4257–4262.
- 70 T. Shimamune, K. Aoki, M. Tanaka, K. Hamaguchi and Y. Nishiki, *US Pat.*, 6117286, 1998.
- 71 N. Furuya and H. Aikawa, *Electrochim. Acta*, 2000, **45**, 4251–4256.
- 72 M. Sugiyama, K. Saiki, A. Sakata, H. Aikawa and N. Furuya, *J. Appl. Electrochem.*, 2003, **33**, 929–932.
- 73 F. Gestermann and A. Ottaviani, in *Modern Chlor-Alkali Technology*, ed. J. Moorhouse, Society of Chemical Industry, 2001, vol. 8, pp. 49–56.
- 74 M. Chatenet, L. Genies-Bultel, M. Arousseau, R. Durand and F. Andolfatto, *J. Appl. Electrochem.*, 2002, **32**, 1131–1140.
- 75 G. N. Martelli, E. Reduzzi, A. Calderara and C. Urgeghe, Performance of the Falling Film Chlor-Alkali Cell equipped with Carbon-free Oxygen Depolarized Cathode, *Joint International Meeting*, The Electrochemical Society, Honolulu, USA, 2004, <https://www.electrochem.org/dl/ma/206/pdfs/1836.pdf> (accessed March 2022).
- 76 K. Hayashi, A. Sakata, N. Furuya, H. Aikawa and K. Saiki, in *Chlor-Alkali and Chlorate Technology: R. B. MacMullin Memorial Symposium*, ed. H. S. Burney, N. Furuya, F. Hinea and K.-I. Ota, ECS Proceedings, 1999, vol. 21, pp. 209–215.
- 77 N. Furuya and H. Aikawa, in *Chlor-Alkali and Chlorate Technology: R. B. MacMullin Memorial Symposium*, ed. H. S. Burney, N. Furuya, F. Hinea and K.-I. Ota, ECS Proceedings, 1999, vol. 21, pp. 180–187.
- 78 M. Chatenet, M. Arousseau, R. Durand and F. O. Andolfatto, *J. Electrochem. Soc.*, 2003, **150**, D47.
- 79 N. Wagner, M. Schulze and E. Gülzow, *J. Power Sources*, 2004, **127**, 264–272.
- 80 R. Staab, *US Pat.*, 4603118, 1986.
- 81 R. Staab and J. Russow, *US Pat.*, 4563261, 1986.
- 82 F. Gestermann and H.-D. Pinter, *US Pat.*, 5693202, 1997.
- 83 F. Gestermann and H.-D. Pinter, *Ger. Pat.*, 19622744C1, 1996.
- 84 T. Borucinski, J. Gegner, K.-H. Dulle and M. Wollny, *Ger. Pat.*, 19816334A1, 1996.
- 85 K. H. Tetzlaff, D. Schmid and J. Russow, *US Pat.*, 5104497, 1992.
- 86 T. Haas, R. Krause, R. Weber, M. Demler and G. Schmid, *Nat. Catal.*, 2018, **1**, 32–39.
- 87 P. Jeanty, C. Scherer, E. Magori, K. Wiesner-Fleischer, O. Hinrichsen and M. Fleischer, *J. CO2 Util.*, 2018, **24**, 454–462.
- 88 T. U. C. Engineers, <https://www.thyssenkrupp-uhde-chlorine-engineers.com/en/products/chlor-alkali-electrolysis/odc-technology> (accessed April 2022).
- 89 M. Ma, E. L. Clark, K. T. Therkildsen, S. Dalsgaard, I. Chorkendorff and B. Seger, *Energy Environ. Sci.*, 2020, **13**, 977–985.
- 90 R. Pärnamäe, S. Mareev, V. Nikonenko, S. Melnikov, N. Sheldeshov, V. Zabolotskii, H. V. M. Hamelers and M. Tedesco, *J. Membr. Sci.*, 2021, **617**, 118538.
- 91 J. A. Rabinowitz and M. W. Kanan, *Nat. Commun.*, 2020, **11**, 5231.
- 92 X. Chen, J. Chen, N. M. Alghoraibi, D. A. Henckel, R. Zhang, U. O. Nwabara, K. E. Madsen, P. J. A. Kenis, S. C. Zimmerman and A. A. Gewirth, *Nat. Catal.*, 2021, **4**, 20–27.
- 93 E. Andreoli, *Nat. Catal.*, 2021, **4**, 8–9.
- 94 R. Staab and D. Schmid, Entwicklungsstand der Membranelektrolyse mit Sauerstoffverzehrkathode, *Dechema-Monographien* 98, 1985, 83–91.

