Catalysis
Science &
Technology

ROYAL SOCIETY
OF CHEMISTRY

MINI REVIEW

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Cite this: *Catal. Sci. Technol.*, 2022, **12**, 3412

Received 6th March 2022,
Accepted 1st May 2022

DOI: 10.1039/d2cy00443g

rsc.li/catalysis

Oxygen depolarised cathode as a learning platform for CO_2 gas diffusion electrodes

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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 CO_2, water, and renewable electricity. Opposed to such striking simplicity, CO_2 electrocatalysis and electrolysers are fraught with challenges hampering the deployment of CO_2 electrolysis on a large scale. The chlor-alkali electrochemical industry has already tackled various issues encountered today in the development of stable CO_2 reduction gas diffusion electrodes (GDEs). The oxygen depolarised cathode (ODC) is a very stable GDE currently used to make multiple kilotonnes of NaOH and Cl_2. 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 CO_2 electrolysis and close with a proposed CO_2 electrolyser design integrating the learning from the development of the chlor-alkali ODC. The rationale is to help advance robust CO_2 electrolysis with industrially relevant performance.

Introduction

Commonly associated with fossil fuel combustion for power, transport, and heating generation, CO_2 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

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responsible for the majority of CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 reduction (CO_2R) brings the opportunity of converting CO_2 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, CO_2 conversion cells, also named electrolysers, 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 electrolysers, where the CO_2 gas is dissolved into aqueous electrolytes, cannot fulfil the industrial requirements due to low CO_2 solubility in water and limited CO_2 mass transport.[16] The low solubility of CO_2 (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 electrolysers overcome mass transfer limitations. These types of electrolysers often show current densities greater than 250 mA cm^{-2}.[14] In these cells, the CO_2 gas is directly introduced using a gas diffusion electrode (GDE), which facilities the transport of CO_2 to the catalyst.[16,19–21] Although gas-fed electrolysers have shown remarkable selectivities in the conversion of CO_2 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 (MPL, carbon black powder mixed with a hydrophobic agent, often PTFE). Commercial GDEs are available and have been applied to CO_2R.[19,22] However, CO_2R GDE-based electrolysers suffer from short-term stability.[13,20]

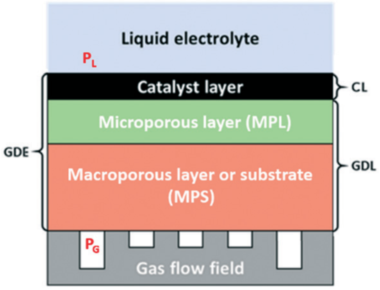

Fig. 1 Schematic of a gas diffusion electrode (GDE) installed between gas flow field and liquid electrolyte, as commonly found in the cathodic compartment of a gas-fed CO_2 electrolyser. The GDE includes a gas diffusion layer (GDL) with on top a catalyst layer (CL) in contact with the electrolyte. The GDL is made of a macroporous substrate (MPS) and a microporous layer (MPL). During operation, liquid electrolyte and CO_2 gas feeds are at pressure P_L and P_G, respectively. Adapted from ref. 16.

There are some difficulties linked with the operation of GDE-based electrolysers, such as electrode degradation affecting electrolyser stability in different flow configurations. Under CO_2 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 CO_2 electrolysers 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 CO_2 electrolysers. 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), CO_2 gas is pushed through the GDE pores to eventually dissolve in the electrolyte, however, this can result in CO_2 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 CO_2 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 pressure differential instability and deliver robust CO_2R electrolysers.

Helpfully, the working principles of gas diffusion electrodes are not just applied to CO_2 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 Cl_2 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 CO_2R GDEs in the attempt to show a way forward for large scale CO_2 electrolysers.

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, Cl_2 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 production[42]) 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 O_2 is reduced in place of H_2O 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 CO_2R. 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 with energy consumption reduced by 30%, striving for zero waste and lower carbon footprint.[45]

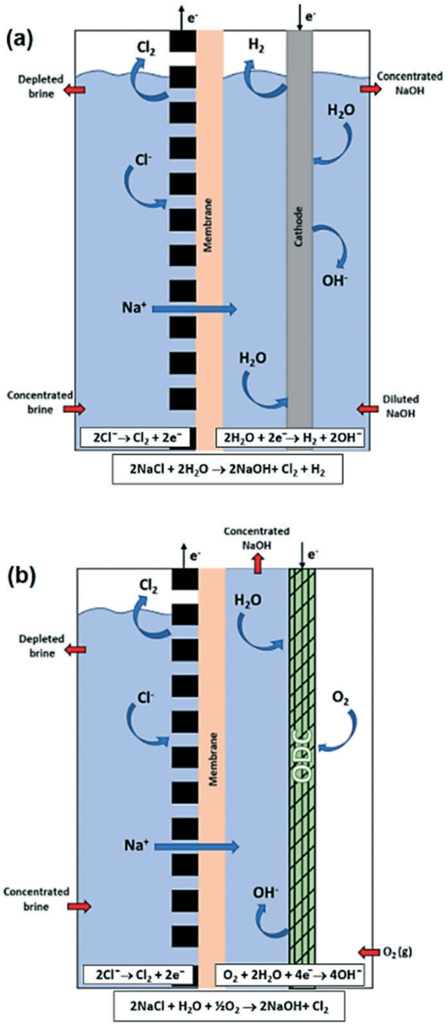

Fig. 2 Schematics of two membrane chlor-alkali electrolysers using different cathodic processes. (a) Cell with hydrogen evolving cathode: the redox processes are (i) reduction of water to hydrogen gas and hydroxide (Ec = −0.83 V *vs.* SHE) and (ii) oxidation of chloride ions to chlorine gas (Ea = 1.36 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 (Ec = 0.40 V *vs.* SHE) and (ii) oxidation of chloride to chlorine (Ea = 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 Cl_2 and NaOH.

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 CO_2 conversion, where CO_2 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 electrolysers with electrodes having multiple m^2 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 CO_2R 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 CO_2 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 m^2) 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 CO_2R 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 cm^2 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 cm^2, 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 CO_2 electrolysers 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 × 180 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).

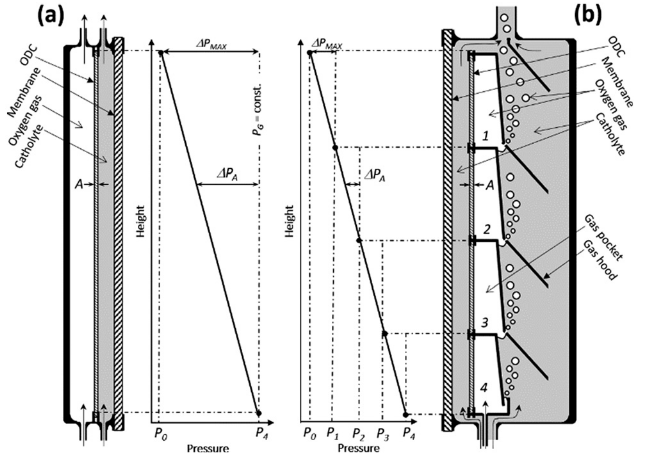

Fig. 3 Schematics of the cathodic compartments of two ODC chlor-alkali electrolysers using different oxygen intake systems. (a) Standard system with the ODC sandwiched between oxygen gas and catholyte, both entering from the bottom of the compartment. The solid line in the plot shows the hydrostatic 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 = 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.

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

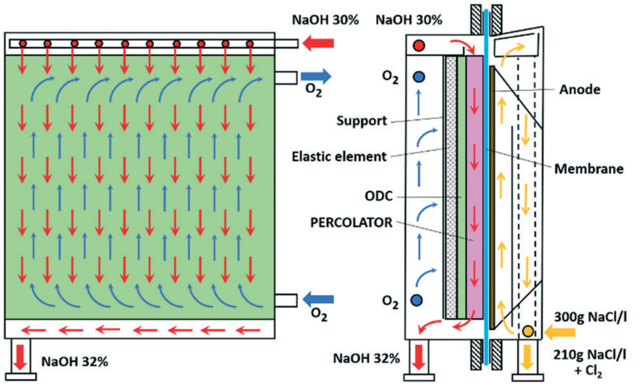

Fig. 4 Schematics of NaCl-ODC cell technology from ThyssenKrupp Uhde Chlorine Engineers. In contact with the oxygen depolarised cathode (in green), a percolator (in pink) is used to feed a thin film of caustic soda from the top of the electrolyser. Support and elastic element allow compressing membrane, 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.

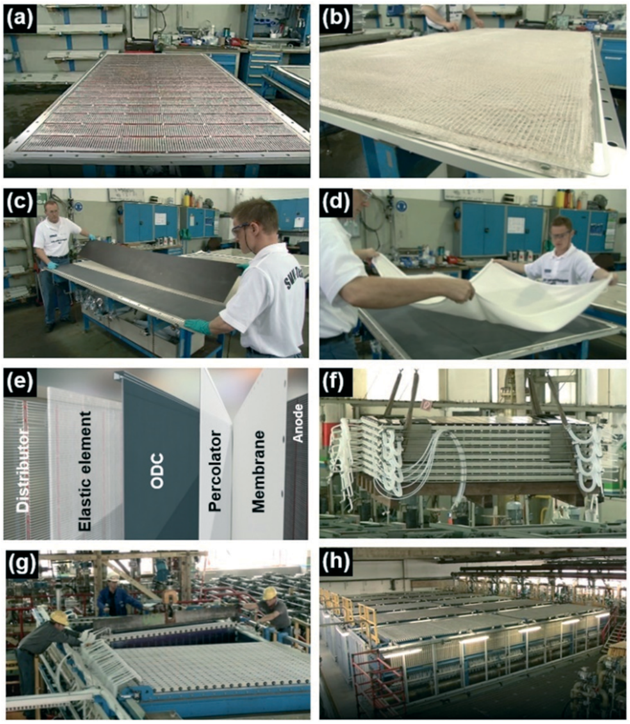

Fig. 5 Assembly and installation of Thyssenkrupp Uhde chlor-alkali cells. (a) A metallic slatted current and gas distributor is covered with (b) a reticulated elastic element, on top of which (c) Covestro's ODC sheets are placed and topped with (d) percolator textiles. (e) A diagram showing the parts 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.

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 electrolysers 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 installation and maintenance, and space-saving chlorine production.

ODC technology and CO_2 electrolysis

The chlor-alkali electrochemical industry has faced technical and engineering challenges currently seen in the development of CO_2 electrolysers. 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 Cl_2 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 CO_2 electrolysis[86,87] and learning more broadly from the ODC technology could improve CO_2 electrolysers since both chlor-alkali and CO_2R 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:

- 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 CO_2 electrolyser:

- CO_2 transport in the pore structure of a GDE;
- CO_2 "dissolution" in alkali electrolyte and diffusion to the catalyst surface.
- Selective electrochemical reduction of CO_2 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 CO_2 reduction compared to O_2 reduction:

- CO_2 is carbonated in alkaline media preventing the formation of the desired product, this is not the case with O_2;
- CO_2 reduction in water results in a variety of different products, whereas O_2 converts to hydroxide only;
- CO_2 conversion products are formed and diluted in the reaction media, instead hydroxide ions are added directly to the product stream in the case of O_2 reduction;
- CO_2 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 O_2.

Nonetheless, CO_2 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 CO_2 electrolysers where hydroxide reacts with CO_2 to give HCO_3^- and CO_3^{2-} anions. Once formed at the cathode, both HCO_3^- and CO_3^{2-} can cross the anion exchange membrane (AEM) to be then protonated and converted back to CO_2 at the anode.[89] This translates into a major loss of efficiency given that energy is used purposelessly to "pump" CO_2 from the cathode to the anode.

The use of a cation exchange membrane (CEM) to avoid HCO_3^- and CO_3^{2-} crossing through the AEM, is not a viable option in alkaline CO_2 electrolysis since caustic electrolytes are largely deficient in protons. Protons must be replenished at the cathode as they are used in the conversion of CO_2 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 mechanism (under reverse bias).[90,91] In Fig. 6, we propose a cell design resulting from the integration of (i) a metal-supported CO_2R 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 H_2O oxidation at the expense of Cl_2 evolution). The overall process generates Cl_2 and ethylene (C_2H_4) at the anode and cathode, respectively. This is one example of other possible combinations in which ODC technology solutions could be integrated within CO_2 electrolysers.

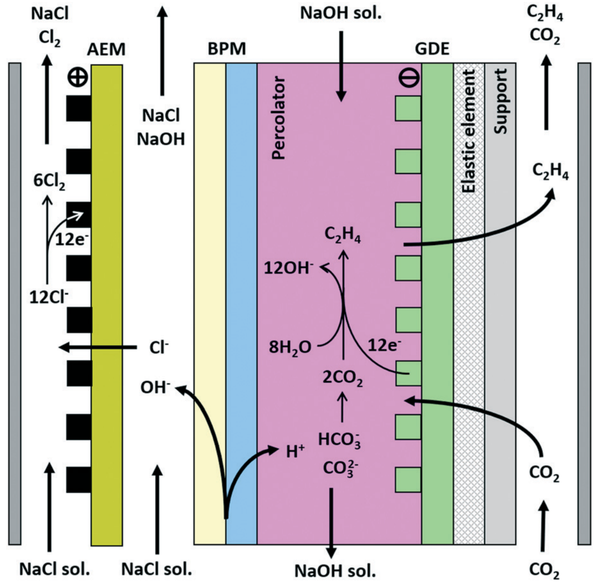

Fig. 6 Proposed design of a CO_2 electrolyser integrating technology solutions from chlor-alkali ODC electrolysis. At the cathode, a GDE (in green) converts CO_2 to C_2H_4, *e.g.* Chen *et al.*,[92,93] with the help of a percolator (in pink) to generate a uniform pressure differential over the electrode. At the anode (in black), Cl^- anions are converted to Cl_2 gas. A bipolar membrane (BPM) is used to dispatch protons at the cathode and help CO_2 reduction, whilst hydroxide ions displace Cl^- transported to the anode for oxidation. The overall process is $2CO_2 + 12NaCl + 8H_2O \rightarrow C_2H_4 + 6Cl_2 + 12NaOH$.

Conclusions

The use of a falling film electrolyser configuration along with a selective metal-supported CO_2R GDE appears to be a promising option to attain long-term stability in CO_2 electrolytic processes. Furthermore, the integration of a bipolar membrane could in principle curtail the impact of CO_2 carbonation in alkaline electrolytes by feeding protons into the cathodic compartment freeing CO_2 in favour of the conversion process. These findings were determined from a valuation of the key progress made in CO_2 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 CO_2 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.

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