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# Chlor-alkali electrolysis with oxygen depolarized cathodes: history, present status and future prospects

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**Abstract** The historical development, current status and future prospects of chlor-alkali electrolysis with oxygen depolarized cathodes (ODCs) are summarized. Over the last decades, membrane chlor-alkali technology has been optimized to such an extent that no substantial reduction of the energy demand can be expected from further process modifications. However, replacement of the hydrogen evolving cathodes in the classical membrane cells by ODCs allows for reduction of the cell voltage and correspondingly the energy consumption of up to 30%. This replacement requires the development of appropriate cathode materials and novel electrolysis cell designs. Due to their superior long-term stability, ODCs based on silver catalysts are very promising for oxygen reduction in concentrated NaOH solutions. Finite-gap falling film cells appear to be the technically most mature design among the several ODC electrolysis cells that have been investigated.

**Keywords** Chlor-alkali electrolysis · Oxygen depolarized cathode · Oxygen reduction · Catalyst · Gas diffusion electrode

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## 1 Introduction and scope

This review article describes the present status and future prospects for chlor-alkali electrolysis with oxygen depolarized cathodes (ODCs). After a brief introduction to the relevance of chlorine production and the existing manufacturing processes, the principle of oxygen depolarized cathodes is described. In conventional chlor-alkali electrolysis, hydrogen is always formed as an additional product on the cathode. Only a part of this hydrogen is presently used for chemical transformations such as hydrogenation reactions, while a considerable fraction is used thermally through combustion. By use of oxygen depolarized electrodes on the cathode side the formation of hydrogen can be prevented while the cell voltage and consequently the energy demand of the process are significantly reduced. Reaction paths and catalysts for oxygen reduction in alkaline media are briefly reviewed. Furthermore, the article describes in detail how different types of oxygen depolarized cathodes are manufactured and assembled in the electrolysis cell. Solutions to overcome difficulties arising from a possible pressure difference between liquid electrolyte and gas are highlighted. Finally, remaining open questions are summarized and the chances for future industrial application of chlor-alkali electrolysis with oxygen depolarized cathodes are discussed.

## 2 Chlorine production

Chlorine is one of the most important products of the chemical industry. Chlorine production has risen enormously in the last decades, because the demand for polymers, notably polyvinyl chloride, polyurethanes and polycarbonate as well as chloroaromatics and many other components is strongly increasing. The production of chlorine can therefore be regarded as an indicator of the state of development of the chemical industry in a country. The worldwide chlorine annual capacity reached about 52 million tons in 2003 [1]. On the global market, Western Europe ranks number 3 behind Asia and North America. World demand for chlorine is forecast by industry watchers to rise by more than 20% between 2000 and 2010 [1]. By far most of the chlorine production is based on the so-called chlor-alkali electrolysis, where solutions of sodium chloride are electrolyzed to convert chloride ions to elemental chlorine on the anode. At the same time, sodium hydroxide solution and hydrogen are formed on the cathode, resulting in the following overall stoichiometry.

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2 \qquad (1)$$

Only a minor part of worldwide chlorine production is based on other processes, the most important of which is the recycling of chlorine by electrolysis of hydrogen chloride solutions with a share of about 1% [2].

## 3 Industrial chlor-alkali processes

Three different electrolytic processes are currently used for the production of chlorine and caustic soda: (a) the diaphragm cell process (Griesheim cell) introduced in 1885, (b) the mercury cell process (Castner-Kellner cell) used industrially since 1892 and (c) the membrane cell process developed in the early seventies of the last century [2]. The processes mainly differ in the method by which the anode products are kept separate from the cathode products. In all processes, chloride ions are oxidized at the anode forming gaseous chlorine:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (2)$$

At the cathode of the diaphragm and membrane process, water is converted to gaseous hydrogen and hydroxyl ions:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3)$$

In these processes, the migration or diffusion of hydroxyl ions to the anode is prevented by the separator and thus the undesirable side reaction between chlorine and hydroxyl ions to hypochlorite ions can be prevented. In the mercury process, the cathodic formation of hydroxyl ions is avoided by forming a sodium/mercury amalgam ($NaHg_x$) in the first reaction step. This amalgam is transported to a separate reactor (decomposer) where hydrogen and sodium hydroxide are formed by the reaction of the sodium in the amalgam with water.

$$2NaHg_x + 2H_2O \rightarrow 2Hg_x + H_2 + 2Na^+ + 2OH^- \qquad (4)$$

The world-wide geographic distribution of chlor-alkali processes differs appreciably. The mercury cell process is still the predominant process in Western Europe with 55% of the chlorine production capacity. In the United States the diaphragm cell process has a share of almost 70%, while in Japan more than 95% of the production is based on the modern membrane cell process [1]. In Table 1 a few characteristics of the industrial processes are summarized.

The mercury process has the advantage of producing high-quality caustic soda at simple brine purification. However, it is the most energy intensive process and consumes up to 3600 kWh of electric energy per ton of chlorine. The diaphragm process produces a lower-quality caustic soda at higher energy demand than required for the membrane process. Consequently, both mercury and diaphragm process capacity shares have been declining. All new plants are based on the favourable membrane cell process because of low capital investment and operating costs relative to diaphragm and mercury processes [2]. This latest technology already completely dominates the chlor-alkali industry in Japan, where the energy prices are high and the environmental regulations are very strict. In Western Europe, the chlorine and caustic soda producers have

**Table 1** Comparison between chlor-alkali electrolysis processes [2, 3]

| | Amalgam process | Diaphragm process | Membrane process |
|---|---|---|---|
| Electrical energy demand (kWh/t $Cl_2$) | 3100–3400 | 2300–2900 | 2100–2600 |
| Total energy demand (kWh/t $Cl_2$) for 50 % NaOH, $O_2$-free $Cl_2$ | 3100–3400 | 3200–3800 | 2400–2900 |
| NaCl purification | Simple | Simple | Expensive ($Ca^{2+} + Mg^{2+} < 20$ ppb) |
| NaOH quality | 50 wt% from cell, low chloride content | ca. 12 wt% from cell, up to 1% chloride in 50 wt% NaOH | ca. 32 wt% from cell, low chloride content |
| Chlorine quality | <1% $O_2$ in $Cl_2$, no further cleaning | 2–3% $O_2$, further cleaning required | 1–3% $O_2$, further cleaning required[a] |
| Environmental issues | Hg used as cathode material | Asbestos used for diaphragms | None |

[a] 0.5% $O_2$ with HCl addition to analyte

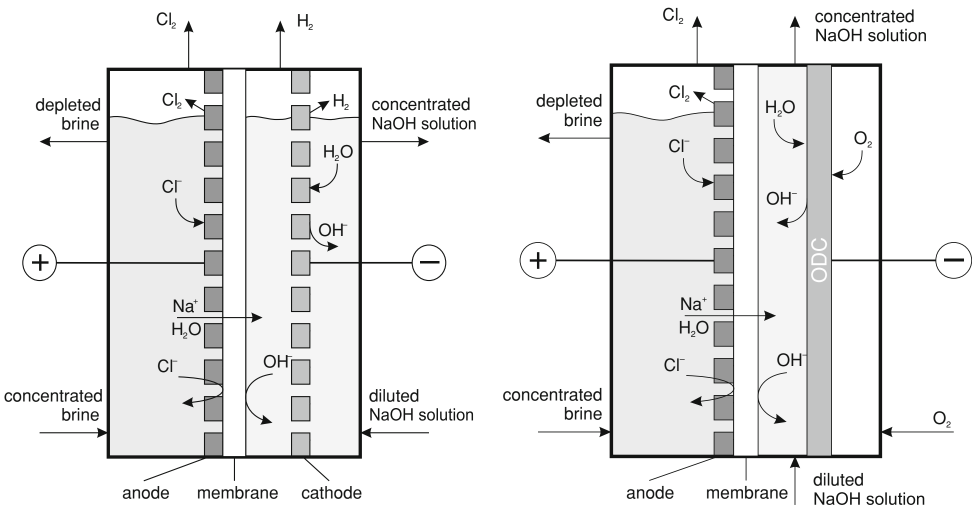

**Fig. 1** Comparison of chlor-alkali electrolysis with hydrogen evolving (left) and oxygen depolarized cathodes (right)

voluntarily committed to a conversion of all existing mercury processes by 2020 (http://www.eurochlor.org).

Chlorine production is one of the most energy intensive industrial processes in the world. It has been estimated that chlorine production requires about 2% of the total electric energy generated in the USA [4]. If one assumes a mean energy demand of 3000 kWh/t $Cl_2$, the present overall energy consumption amounts to more than $1.5 \times 10^{11}$ kWh/a. It is obvious from these data, that a significant reduction of energy demand in the chlor-alkali industry is highly desirable.

## 4 Principle of chlor-alkali electrolysis with oxygen depolarized cathodes

A possibility for an alternative chlor-alkali electrolysis process with considerably lower energy demand is the use of so-called oxygen depolarized cathodes. Using such a porous gas-diffusion cathode of the fuel cell type, the formation of undesired hydrogen is prevented by electrochemical reduction of oxygen to hydroxyl ions.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (5)$$

Given that the formation of chlorine on the anode remains unchanged the following overall stoichiometric equation for the simultaneous formation of chlorine and sodium hydroxide results.

$$2NaCl + H_2O + {}^1/_2O_2 \rightarrow 2NaOH + Cl_2 \quad (6)$$

A comparison of classical electrolysis with hydrogen evolving electrode and the new process with oxygen depolarized cathode is shown in Fig. 1.

Although a change of cathodes in existing cells appears to be relatively simple on first sight, the replacement of the hydrogen evolving electrode in membrane cells requires significant changes in cell design as will be shown later.

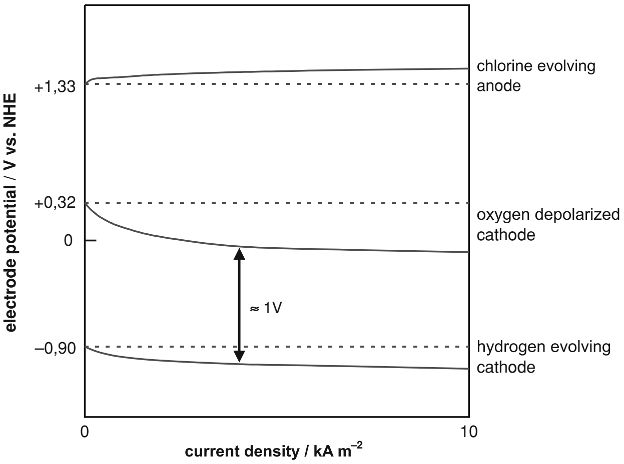

**Fig. 2** Electrode potentials in chlor-alkali electrolysis as a function of current density

The main thermodynamic advantage of the novel electrolysis with ODC is explained in Fig. 2, where the electrode potentials as a function of current density are depicted. It can be seen that the thermodynamic potential difference for the classical electrolysis with hydrogen evolving cathode is about 2.2 V. In practice the overall total cell voltage at typical current densities of 4–6 kA/m$^2$ (related to the geometric electrode surface area) including the anode and cathode electrode over-potentials as well as the ohmic resistances in membrane, electrodes and electrolyte is approximately 3.0 V.[1] The open cell voltage of chlor-alkali electrolysis with ODC is reduced by 1.23 V compared to the classical process. However, due to higher over-potentials during oxygen reduction, it can be expected that one might gain approximately 1.0 V at current densities of industrial relevance.

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[1] http://www.uhde.biz/cgi-bin/byteserver.pl/archive/upload/uhde_brochures_pdf_en_10.00.pdf

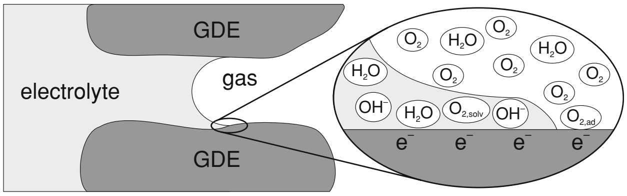

**Fig. 3** Oxygen reduction at three-phase boundary in oxygen depolarized cathodes

Therefore oxygen depolarized cathodes have the potential to reduce the electric energy demand of membrane cells by up to 30%. On the other hand, overall comparison of the two processes must take into account that electrolysis with ODC no longer produces hydrogen usually employed by combustion and that oxygen depolarized cathodes may require pure oxygen for satisfactory performance instead of air.

Usually, the oxygen depolarized cathode is a porous structure that allows for an intimate contact at the so-called three-phase boundary, where gaseous oxygen reacts with liquid water according to Eq. 5 at the solid electrocatalyst (Fig. 3).

The electrochemical reaction takes place where the three reactants (oxygen from the gas phase, water from the liquid phase and electrons from the solid phase) meet. Direct contact of all reactants is only possible at the three-phase boundary that has a very limited extension. However, indirect contact of the reactants is enabled by dissolution of oxygen in the liquid electrolyte and transport to the active sites of the catalyst by diffusion. Overall, it is evident that a gas diffusion electrode used as oxygen depolarized cathode has to meet extremely high requirements for successful operation:

- Chemical stability in concentrated sodium hydroxide solution at temperatures between 80 and 90 °C
- High mechanical stability in technical electrolyzers with several $m^2$ area
- High electronic conductivity and low thickness
- High surface area and activity of electrocatalyst
- Suitable hydrophobic/hydrophilic pore structure for easy access of gases and liquids without breakthrough of gas and flooding by liquid electrolyte even at different pressure differences between gas and liquid
- High long-term stability
- Affordable costs

## 5 History and present status of chlor-alkali electrolysis with ODC

The idea of operating the chlor-alkali electrolysis with oxygen depolarized cathodes is by no means new. As early as 1950, Butler suggested the application of this principle for the diaphragm process [5]. Juda described in 1959 a chlor-alkali process with cation exchange membrane and oxygen consuming cathode [6]. While he could successfully demonstrate that cell voltages are significantly reduced by use of an ODC, sufficiently stable membranes for industrial chlor-alkali electrolysis were not available at that time. Vielstich also described how ODCs in principle allow for substantial reduction of cell voltage [7]. In 1963 Yeager presented a fuel cell operated with a sodium amalgam as liquid anode and an oxygen depolarized cathode [8]. This concept was aimed at replacement of the traditional amalgam decomposers in amalgam electrolysis where no usable electric energy can be obtained.

After the membrane process became technically available in the 1970s research and development of oxygen depolarized cathodes in chlor-alkali electrolysis was renewed. Starting with 1977 the first real attempts for the development of ODCs for use in diaphragm and membrane cells were made by Diamond Shamrock, which later was taken over by Eltech Systems [9–17]. Here, both laboratory and commercial size cells were operated for extended periods of time [18, 19]. These experiments have clearly shown that significant energy savings can be achieved by replacing the hydrogen evolving electrodes with oxygen depolarized cathodes. From that time on intensive work has been conducted by several other companies especially in the USA and Germany including Hooker [20], Dow Chemicals [21–31], Hoechst [32–40], VEB Bitterfeld [41], Olin [42, 43], PPG Industries [44–46], Engelhard [47], General Electric [48], United Technologies [49], and DeNora [50]. Japanese companies were equally active with Asahi Glass [51, 52], Tokuyama Soda [53], Toyo Soda [54, 55], and Kureha Chemical [56]. In addition, scientific studies were carried out at the University of Dortmund in Germany [57, 58], the University of British Columbia in Canada [59] and the Case Western Reserve University in the USA [60]. This "first generation" work, as it was called by Foller [61], is summarized in Table 2.

It appears that the most extensive programs were carried out at Diamond Shamrock/Eltech Systems, Dow, and Hoechst [61]. Relatively detailed information is only available about the results obtained at Diamond Shamrock/Eltech Systems and especially for the Hoechst development program. Diamond Shamrock/Eltech Systems used carbon-based electrodes known from polymer electrolyte fuel cells. Laboratory scale cells were successfully operated for 350 days with air at a current density of 3 $kA/m^2$. The air was scrubbed for removal of carbon dioxide to prevent sodium carbonate formation in the electrolyte. Tests with commercial sized cells were carried out for 2500 h and had to be terminated because of insufficient durability of the ODC [61]. Hoechst developed a different type of electrode consisting of a silver/PTFE mixture that was processed together with a metallic net to a porous

**Table 2** First generation work between 1973 and 1988 on chlor-alkali electrolysis with ODC

| Priority[a]/publication year | Patent/paper/author[b] | Comments | References |
|---|---|---|---|
| 1973 | US 4035254, Gritzner G, Dow Chemical | Membrane electrolysis cell with carbon-based ODC and regulated moisture content of oxygen | [29] |
| 1973 | US 4035255, Gritzner G, Dow Chemical | Diaphragm electrolysis cell with ODC | [30] |
| 1977 | JP 54084893, Matsuura S et al., Tokuyama Soda | ODC with precious metal catalyst in electrolysis cell operated with 30–60 vol% oxygen | [53] |
| 1978 | JP 55089486, Ookai O et al., Toyo Soda | Electrolysis cell operated with oxygen permeating through porous ODC | [54] |
| 1978 | US 4135995, Welch CN, PPG Industries | Carbon-PTFE electrode for ODC electrolysis | [44] |
| 1978 | US 4224129, McIntyre JA et al., Dow Chemical | Electrolysis cell with trickling flow of electrolyte and oxygen between membrane and ODC | [24] |
| 1978 | US 4187350, McIntyre JA et al., Dow Chemical | Porous electrode with specified pore structure for use in ODC electrolysis | [22] |
| 1978 | US 4213833, Lefevre JD, Dow Chemical | Metallic support for separator in ODC electrolysis | [21] |
| 1978 | US 4191618, Coker TG et al., General Electric | Membrane electrode assembly for ODC electrolysis | [48] |
| 1978 | US 4278525, Gestaut LJ, Diamond Shamrock | Carbon-based ODC, optionally with metallic mesh core and hydrophobic PTFE backing | [12] |
| 1978 | US 4260469, McIntyre JA et al., Dow Chemical | Dual porosity ODC with finer pores for electrolyte contact and larger pores for access of oxygen | [25] |
| 1979 | JP 56047578, Ookai O et al., Toyo Soda | See [54] | [55] |
| 1979 | US 4221644, LaBarre RL, Diamond Shamrock | Carbon-based electrode for ODC electrolysis with $CO_2$ scrubbed and moisturized air | [13] |
| 1979 | US 4292197, Chamberlin RD, PPG Industries | Carbon-silver catalyst with activity for $HO_2^-$ disproportionation for use in ODC | [46] |
| 1979 | US 4244793, Johnson HB et al., PPG Industries | ODC consisting of a fixed bed of porous particles containing carbon-silver catalyst | [45] |
| 1979 | US 4340459, McIntyre JA et al., Dow Chemical | Dual porosity ODC in pocket shaped arrangement | [26] |
| 1980 | US 4332662, Pouli D et al., Hooker | Silver-copper ODC with dual porosity structure | [20] |
| 1980 | Yeager E et al., Case Western Reserve University | Review on catalysts for oxygen reduction and development status of ODC electrolysis | [60] |
| 1980 | US 4337140, Solomon F, Diamond Shamrock | Fibrillating of carbon-PTFE mixtures during preparation of ODC | [10] |
| 1981 | US 4341606, McIntyre JA et al., Dow Chemical | See [25] | [28] |
| 1981 | JP 57194283, Oda Y et al., Asahi Glass | Electrolysis cell with porous ODC made from PTFE and catalysts (Fe, Ni) coated on carbon paper | [51] |
| 1981 | US 4379034, Rogers DK, Diamond Shamrock | Start-up procedure for ODC at reduced pressure | [14] |
| 1981 | US 4486276, Cohn JGE et al., Engelhard | ODC electrolysis process with additional oxygen permeable membrane | [47] |
| 1981 | US 4377496, Solomon F, Diamond Shamrock | Preparation method for silver-PTFE ODC | [10] |
| 1982 | JP 59133386, Morimoto T et al., Asahi Glass | Preparation method for carbon-PTFE ODC with dual pore structure | [52] |
| 1982 | US 4436608, Bennett WR et al., Diamond Shamrock | Electrolytic cell with reduced space between separator and ODC | [15] |
| 1982 | Schmid D et al., Hoechst | Development status of carbon- and silver-based ODCs at Hoechst | [35] |

**Table 2** continued

| Priority[a]/publication year | Patent/paper/author[b] | Comments | References |
|---|---|---|---|
| 1982 | US 4431567, Gestaut LJ et al., Diamond Shamrock | Carbon-PTFE ODC with silver or platinum catalyst of specified surface area | [9] |
| 1982 | US 4430177, McIntyre JA et al., Dow Chemical | See [26] | [27] |
| 1983 | US 4603118, Staab, R, Hoechst | Silver-PTFE electrode for use in ODC electrolysis | [34] |
| 1983 | US 4459197, Solomon F, Diamond Shamrock | Carbon-based ODC laminated on both sides with porous hydrophobic layers | [16] |
| 1983 | US 4496437, McIntyre JA et al., Dow Chemical | Dual porosity ODC with controlled pore structure | [23] |
| 1983 | US 4563261, Staab R, Hoechst | ODC with hydrophobic electrocatalyst layer and hydrophilic layer with transition metal or oxide | [36] |
| 1983 | WO 85/01072, Sutter RC, Eltech Systems | ODC with compartments to overcome hydrostatic pressure differences | [17] |
| 1984 | US 4584080, Staab R et al., Hoechst | Bipolar electrolysis cell for ODCs | [33] |
| 1984 | US 4564427, Gruver GA et al., United Technologies | ODC with barrier layer | [49] |
| 1984 | US 4615783, Staab R, Hoechst | Horizontal cell design for ODC electrolysis | [37] |
| 1984 | US 5104497, Tetzlaff KH, Hoechst | Details of falling film electrolysis cell | [38] |
| 1984 | US 4744879, Kaminaga T et al., Kureha Chemical | Preparation of carbon-based ODC for chlor-alkali electrolysis with compact carbonaceous carrier | [56] |
| 1985 | Staab R et al., Hoechst | Development status of carbon- and silver-based ODCs at Hoechst | [32] |
| 1985 | US 4578159, Miles RC et al., Olin | Electrolysis process using carbon-based ODC in direct contact with membrane | [42] |
| 1985 | US 4919791, Miles RC et al., Olin | See [42] | [43] |
| 1986 | US 4657651, Wainerdi TJ, Dow Chemical | Vertical electrolysis cell with gas compartments | [31] |
| 1986 | Poblotzki J, University of Dortmund | Use of ODCs in electrolysis cells with oxygen and pressurized air | [57] |
| 1986 | Oloman C et al., University of British Columbia | Electrolysis cell with trickle-bed electrode as ODC | [59] |
| 1987 | Staab R, Hoechst | Development status of ODC electrolysis at Hoechst | [39] |
| 1988 | Wendel W et al., Hoechst | Falling film electrolysis cell for ODCs | [40] |
| 1988 | US 5015344, Nidola A et al., DeNora | Membrane-electrode assembly for electrolysis with ODC | [50] |
| 1988 | Simmrock KH et al., University of Dortmund | See [57] | [58] |

[a] Earliest date of filing

[b] Only affiliation of first author is given for joint publications

structure of 300–500 μm thickness. These electrodes were subjected to a durability test in a 40 $cm^2$ laboratory cell at 2 $kA/m^2$ and 85 °C and found to be stable for at least 13000 h. The measured cell voltage after long-term treatment using air amounted to ca. 2.1 V. A pilot cell with 0.16 $m^2$ worked at 2.17 V under a current density of 3 $kA/m^2$ [32]. Hoechst also studied several possibilities to overcome problems that may arise from height dependent pressure differences between catholyte and oxygen such as falling film cells or horizontal cells.

The extensive effort of the 1970s and 1980s clearly demonstrated technical feasibility of membrane-type chlor-alkali electrolysis with oxygen depolarized cathodes even at pilot scale. However, no further development and commercial demonstration programs followed. According to the analysis of Foller [61], economic reasons were responsible for this result. At the then relatively low electric energy costs the achieved savings in cell voltage of 0.8–0.9 V was judged insufficient for an economic change to the new ODC technology.

In the 1990s a second era of research and development in chlor-alkali electrolysis with ODC was started by the Japanese Ministry of Trade and Industry (MITI) in cooperation with the Japan Soda Industry Association (JSIA) [61]. Further partners of this program were Asahi Glass [62], Permelec Electrode [63–67], Tanaka Precious Metals, DuPont Japan, and Yamanashi University. Electrolyzer tests were conducted [61] at Toagosei in Aichi [68–71], Mitsui Chemical in Osaka [72, 73], and Kaneka in Hyogo [74, 75]. The Furuya group at Yamanashi University was mainly focused on development of the ODC [76–84]. A second large program was started by Bayer [85] in cooperation with Uhde and DeNora in Germany. In 1998, large-scale industrial electrolysis cells with elements of 2.7 $m^2$ were equipped with ODCs and successfully operated [86, 87]. Further scientific studies were carried out at the Academy of Sciences of the Czech Republic [88], the University of Tokyo in Japan [89, 90] and at LEPMI in France [91, 92]. The “second generation” work is summarized in Table 3.

Impressive progress has been made during this second generation work. In several cases it was demonstrated that a gain in cell voltage of ca. 1.0 V can be achieved when ODCs are used in replacement of hydrogen evolving cathodes. This was not only accomplished on laboratory scale but also in pilot cells of varying size and even in large-scale technical electrolyzers. Both the Japanese and the German program have provided several options for electrolysis cell designs that are capable of dealing with a possible pressure difference between catholyte and gas chamber. In addition to traditional finite-gap cell designs, zero-gap arrangements of ODCs have also been successfully tested with little difference in cell voltage. Details of cathode arrangements and cell designs will be discussed in the following sections. Much effort was devoted to durability tests of ODCs under the severe conditions of chlor-alkali electrolysis. It could be clearly shown that hot concentrated sodium hydroxide solution is capable of oxidizing carbon until the required intimate contact between the finely dispersed catalyst particles and the carbon carrier is eventually lost. In contrast, studies revealed an apparently higher long-term stability of carbon-free electrodes with silver as electrocatalysts. Details of these findings will be discussed in the section dealing with catalysts for oxygen reduction.

Although no information on the present status and possible plans for commercialization of this new technology is available, one can assume that development in Japan and Germany continues. This is especially highlighted by the fact that Bayer has recently commercialized a novel hydrogen chloride electrolysis process with ODC in cooperation with Uhde and DeNora. After commissioning in 2004 of a smaller installation with 20 kt/a $Cl_2$ in Brunsbüttel, Germany, Bayer has announced an intention to build a much larger HCl electrolysis plant with a chlorine capacity of 215 kt/a in Caojing, China by 2008 (Bayer press release 17.04.2007). In 2006, Bayer also started a joint project with several partners from industry and universities targeted at the industrial implementation of chlor-alkali electrolysis with ODC. This project is funded by the German Ministry of Education and Research (BMBF) under the klimazwei research programme (http://www.klimazwei.de). In the light of ongoing industrial effort to develop a commercial chlor-alkali process with ODC, further research groups have also started to investigate electrodes and processes. The US Department of Energy funded a research project at Los Alamos National Laboratory where carbon-based electrodes were developed and tested in a fuel cell type zero-gap cell for chlor-alkali electrolysis [95]. Recently, SINTEF in Norway [96] and the Royal Institute of Technology in Sweden [97] started research targeted at the development and investigation of carbon-based electrodes.

## 6 Oxygen reduction in alkaline media

### 6.1 Reaction paths

According to Yeager [60] the oxygen reduction reaction in alkaline solutions takes place via two different paths. In the main route (7) oxygen is reduced directly to $OH^-$ by a four-electron transfer reaction, while in the second path (8) $HO_2^-$ is produced firstly in a two-electron transfer process.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{7}$$

$$H_2O + O_2 + 2e^- \rightarrow HO_2^- + OH^- \tag{8}$$

In the four-electron path oxygen is directly reduced to $OH^-$ in a number of steps without the formation of hydrogen peroxide in the solution. This does not exclude that the overall reduction requires an adsorbed peroxide-intermediate. The two-electron path produces peroxide as a product detectable in the electrolyte solution. The peroxide which is formed will be either reduced to $OH^-$ or end up as a by-product in the solution. The reduction of peroxide to $OH^-$ occurs either electrochemically (9) or catalytically (10).

$$H_2O + HO_2^- + 2e^- \rightarrow 3OH^- \tag{9}$$

$$2HO_2^- \rightarrow 2OH^- + O_2 \tag{10}$$

A parallel mechanism where both paths take place on an electrode surface is also possible [98]. If peroxide reduction occurs with high rate, it is possible to prevent the formation of the intermediate peroxides to a large extent. Since peroxide reduction (9) produces an equivalent

**Table 3** Second generation work between 1994 and 2003 on chlor-alkali electrolysis with ODC

| Priority[a]/publication year | Patent/paper/author[b] | Comments | References |
|---|---|---|---|
| 1994 | Spalek O, Czech Academy of Sciences | Trickle-bed electrode consisting of fixed-bed of carbon particles as ODC | [88] |
| 1996 | US 5676808, Nishiki Y et al., Permelec Electrode | Zero-gap type electrolysis cell, ODC with grooves allowing for controlled removal of liquid | [65] |
| 1996 | US 6251239, Gestermann F et al., Bayer | Electrochemical cell with ODC and pressure compensation | [85] |
| 1996 | US 5733430, Ashida T et al., Permelec Electrode | ODCs made from PTFE, silver and/or gold | [66] |
| 1996 | US 5827412, Shimamune T et al., Permelec Electrode | ODCs with direct contact with membrane with electrolyte guide plates | [93] |
| 1996 | US 5938901, Shimamune T et al., Permelec Electrode | ODCs with direct contact with membrane with electrolyte guide plates | [94] |
| 1997 | Ashida T et al., Permelec Electrode | Porous silver-PTFE on nickel as ODC for zero-gap type electrolysis cell | [64] |
| 1997 | Uchimura A et al., Yamanashi University | Electrolysis cell with flow of sodium hydroxide solution and oxygen in contact with ODC | [78] |
| 1997 | Furuya N et al., Yamanashi University | Silver-carbon catalyst for ODC electrolysis with 3 mg/cm$^2$ as active as Pt-carbon with 0.56 mg/cm$^2$ | [79] |
| 1997 | Wang XL et al., University of Tokyo | Analysis of hydrostatic force balance and influence of ODC performance | [89] |
| 1997 | Wang XL et al., University of Tokyo | Model of ODC in alkaline media using the thin-film flooded-agglomerate model | [90] |
| 1998 | Furuya N et al., Yamanashi University | Influence of silver particle size in silver-PTFE electrodes used as ODC electrolysis | [81] |
| 1998 | Sakata A et al., Toagosei | Long term tests with ODCs containing Ag and Pt catalysts | [70] |
| 1998 | Saiki K et al., Kaneka | Tests in ODC electrolyzers with 10 and 60 cm height, influence of current density, oxygen concentration, and time on stream | [74] |
| 1998 | Uchimura A et al., Mitsui Chemicals | ODC made from carbon and nickel | [72] |
| 1998 | US 6117286, Shimamune T et al., Permelec Electrode | Zero-gap type electrolysis cell for ODC | [67] |
| 1998 | US 6368473, Furuya N et al., Yamanashi University | Trickle flow electrolyzer for ODC without pressure difference between catholyte and oxygen | [80] |
| 1998 | US 6428722, Furuya N et al., Yamanashi University | Method for preparation of carbon-PTFE ODC by spraying | [77] |
| 1999 | Furuya N et al., Yamanashi University | Preparation method for a Pt-carbon-PTFE ODC with separate reaction and diffusion layers | [82] |
| 1999 | Saiki K et al., Kaneka | See [74] | [75] |
| 1999 | Nakamatsu S et al., Permelec Electrode | Silver-PTFE on nickel foam as ODC, both in finite- and zero-gap arrangement | [63] |
| 1999 | Hayashi K et al., Toagosei | Use of multilayered ODC in pilot electrolyzer, measurement of current density distribution | [71] |
| 1999 | Ichinose O et al., Mitsui Chemicals | Scale-up of ODC manufacture from laboratory to pilot scale (0.72 m$^2$) | [73] |
| 1999 | Sakata A et al., Toagosei | Comparison of Pt and Ag based ODCs in long-term laboratory cell measurements | [68] |
| 1999 | US 6488833, Sakata A et al., Toagosei | Chlor-alkali electrolysis process with ODC and recycle of oxygen | [69] |
| 2000 | Furuya N et al., Yamanashi University | Pt catalysts showed higher oxygen reduction activity but lower long term stability than Ag catalyst | [76] |

**Table 3** continued

| Priority[a]/publication year | Patent/paper/author[b] | Comments | References |
|---|---|---|---|
| 2000 | Morimoto T et al., Asahi Glass | Investigation of deterioration mechanism of carbon-based ODCs | [62] |
| 2001 | Gestermann F et al., Bayer | State of the joint development program of Bayer and DeNora for NaCl and HCl ODC electrolysis | [86] |
| 2001 | Federico F et al., DeNora | State of the joint development program of Bayer and DeNora for NaCl and HCl ODC electrolysis | [87] |
| 2002 | Chatenet M et al., LEPMI | Electrokinetic study of platinum and silver catalysts for oxygen reduction in alkaline solutions | [91] |
| 2003 | Chatenet M et al., LEPMI | Development of bimetallic silver-platinum catalysts for oxygen reduction in alkaline media | [92] |
| 2003 | Sugiyama M et al., Yamanashi University | Degradation tests of carbon-based ODCs under chlor-alkali electrolysis conditions | [84] |
| 2003 | Furuya N, Yamanashi University | Preparation method of carbon-based ODC by electrophoresis of carbon-PTFE suspensions | [83] |

[a] Earliest date of filing

[b] Only affiliation of first author is given for joint publications

amount of hydroxide ions, the overall caustic current efficiency remains unchanged.

It is well known that the oxygen reduction to peroxide is strongly favoured by carbon surfaces in alkaline solutions [60, 91, 99, 100]. Peroxide is a rather troublesome by-product, because it might produce gaseous oxygen upon decomposition and may also precipitate in the highly concentrated NaOH solution according to (11).

$$2\mathrm{Na}^{+} + \mathrm{OH}^{-} + \mathrm{HO}_2^{-} \rightarrow \mathrm{Na_2O_2} \downarrow + \mathrm{H_2O} \qquad (11)$$

Precipitation of sodium peroxide can cause liquid and gas flow problems, block the active surface area of the electrode and may even destroy the microporous structure of the gas diffusion electrode [95, 101]. Los Alamos National Laboratory has studied the effects of various factors on the undesired generation of hydrogen peroxide during chlor-alkali electrolysis with oxygen depolarized cathodes employing carbon-supported platinum catalysts. The rate of peroxide generation was found to decrease with platinum loading and increases with current density. The quantity of peroxide generated also increased with electrolysis time, and reached a steady state value after a few 100 h of cell operation at 10 kA/m$^2$. The steady-state peroxide to hydroxide molar ratio was found to increase with brine concentration. This phenomenon is believed to originate from a decrease of water activity at the reaction site that accompanies the brine concentration increase [95].

## 6.2 Activity and durability of catalysts and electrodes

Many different materials such as palladium [102–104], ruthenium [105], gold [106–108], nickel [72], transition metal oxides [109] and sulfides [110], metal porphyrins and phthalocyanins [60, 97, 99, 111, 112], and perovskites [97] were studied as catalysts for the oxygen reduction in alkaline solutions. Although interesting results were obtained, the activity and/or stability of these materials can be regarded as insufficient for long-term operation under the severe conditions in hot concentrated alkaline solution. The frequently used catalysts for oxygen reduction in sodium hydroxide solution are carbon-supported platinum [35, 68, 76, 82, 91, 113, 114] and silver either supported on carbon [68, 76, 79, 91, 101, 115–117] or as pure metal [35, 63, 81, 118, 119]. Examples of these studies, if not already listed in Tables 2 or 3, are summarized in Table 4.

The high catalytic activity of platinum for oxygen reduction is well known. In alkaline solutions, however, it is possible to obtain similar activities with silver catalysts. Staab and Schmid reported similar initial activities of Pt and Ag based ODCs [32]. Furuya and Aikawa have shown that the activity of oxygen cathodes loaded with 3 mg/cm$^2$ of Ag was very similar to electrodes loaded with 0.56 mg/m$^2$ Pt. In both cases, chlor-alkali electrolysis with ODC could be carried out at a cell voltage of 2.0 V at 3 kA/m$^2$ and 90 °C [76]. Chatenet et al. could also clearly show that silver as electrocatalyst becomes competitive to platinum in hot and highly concentrated sodium hydroxide solutions [91].

Given the drastic price difference of both materials it appears that silver has a higher potential for technical application in ODCs. Moreover, it has also been demonstrated in several studies that silver based catalysts have a higher long-term stability under the conditions of chlor-alkali electrolysis. Staab and coworkers have reported that

**Table 4** Examples for papers describing catalysts for oxygen reduction in alkaline solutions

| Publication year | Paper/author[a] | Comments | References |
|---|---|---|---|
| 1974 | King WJ et al., City University London | Oxygen reduction over spinel type catalysts in KOH solution | [109] |
| 1981 | Miura N et al., Kyushu University | Particle size effect of silver supported on carbon for oxygen reduction in NaOH solution | [117] |
| 1985 | Holze R et al., Case Western Reserve University | Carbon-based ODCs with thermally treated porphyrines as catalysts | [112] |
| 1990 | Kivisaari J et al., Helsinki University of Technology | Carbon-based ODCs with Co-tetramethoxyphenyl porphyrine as catalyst | [111] |
| 1990 | Anderson E et al., PSI Technology | Gold-carbon catalysts for oxygen reduction in alkaline media and hydrogen-chlorine fuel cells | [108] |
| 1994 | Brito PSD, Instituto Superior Technico Lisboa | Review on cathodic oxygen reduction on noble metal and carbon electrodes | [99] |
| 1995 | Kim J et al., Korea Advanced Institute of Science and Technology | Mechanism of oxygen reduction on Pd surfaces in alkaline media | [102] |
| 1995 | Yang Y et al., Wuhan University | Electrocatalytic activity of Pd dispersed on carbon during oxygen reduction in alkaline solution | [103] |
| 1996 | Strbac S et al., University of Belgrade | Reaction pathways of oxygen reduction on gold surfaces in NaOH solution | [106] |
| 1996 | Strbac S et al., University of Belgrade | See [106] | [107] |
| 1996 | Chang CC et al., National Cheng Kung University | Oxygen reduction in KOH solution over Pd derived catalysts from PdO | [104] |
| 1998 | Gautier JL et al., University Santiago de Chile | Oxygen reduction in alkaline medium using copper and iron sulfides | [110] |
| 1998 | Genies L et al., LEPMI | Study of oxygen reduction in NaOH solution using Pt nanoparticles on different carbon carriers | [114] |
| 1998 | Perez J et al., Institute of Chemisty Sao Carlos | Mechanistic studies of oxygen reduction on Pt-carbon catalysts in acidic and NaOH solutions | [113] |
| 2001 | WO 03/042430, Faita G, Uhdenora | Falling film electrolysis cell with porous polymeric element in catholyte compartment | [120] |
| 2002 | Gamburzev S et al., Texas A&M University | Silver supported on different carbon carriers for oxygen reduction in KOH solution | [115] |
| 2003 | Yu EH et al., University of Newcastle upon Tyne | Oxygen reduction over carbon supported Pt and Pt/Ru catalysts | [105] |
| 2004 | Ichinose O et al., Yamanshi University | Electrocatalytic and mechanistic studies of silver catalysts for oxygen reduction | [101] |
| 2004 | Burchardt T, SINTEF | Electrocatalytic activity and stability of Pt-carbon ODCs | [96] |
| 2004 | Gülzow E et al., DLR | Long term study of silver-PTFE cathodes and various anodes for alkaline fuel cells | [119] |
| 2004 | Wagner N et al., DLR | Long term study of silver-PTFE ODCs for alkaline fuel cells | [118] |
| 2004 | Kiros Y et al., Royal Institute of Technology Stockholm | Investigation of ODCs with different thickness using silver and pyrolyzed macrocycles | [116] |
| 2005 | Lipp L et al., Los Alamos National Laboratory | Peroxide formation during chlor-alkali electrolysis with carbon-based ODC | [95] |
| 2006 | Kiros Y et al., Royal Institute of Technology Stockholm | Use of cobalt porphyrin and LaCaMn perovskites as novel oxygen reduction catalysts | [97] |

[a] Only affiliation of first author is given for joint publications

carbon based electrodes exhibit much stronger deactivation, especially after shut-down of the electrolyzer, than silver-PTFE ODCs [32, 35]. Similar observations have been made by Furuya and coworkers [68, 70, 76, 79, 84], Morimoto et al. [62], and Chatenet et al. [92]. Sakata et al. reported that ODCs with Pt as catalyst strongly deteriorated after 350 days on stream, resulting in increasing cell voltage and leakage of catholyte through the electrode. On the other hand, the electrode with Ag as catalyst had been stable for 1100 days [68, 70]. It is assumed that the reason for the faster deterioration of Pt based ODCs is oxidation of the carbon carrier catalyzed by platinum. This leads to loss of intimate contact between the two components and to dissolution of platinum [62]. Corrosion resistance of carbon carriers may be improved to some extent by graphitization through heat treatment [62, 121]. Recently a silver-platinum bimetallic catalyst has been studied and was found to be as active as pure platinum while this catalyst did not deteriorate when the cell was shunted and the cathode compartment was not flushed with an inert gas [92].

Although silver based ODCs are more stable than platinum-carbon electrodes, long-term investigation of silver cathodes also revealed a decrease of the electrochemical performance of these materials. Wagner et al. have reported an approximately linear voltage increase of about 20 µV/h resulting in a total cell voltage increase of 100 mV after 5000 h during oxygen reduction at 70 °C in 30 wt% KOH [118]. This degradation was mainly attributed to a loss of hydrophobicity through alteration of the PTFE in the electrode.

## 7 Types of oxygen depolarized cathodes and their assemblies

Oxygen depolarized cathodes are gas diffusion electrodes that can be prepared in many different ways. Basically, one can distinguish between dry and wet preparation processes. In the dry preparation process a mixture of the catalyst and a polymeric component (usually PTFE) is ground to form particles that will be distributed on a current collector. Typical current collectors consist of Ni mesh [32, 70], Ni foam [72] or Ag mesh [81]. In some cases it was suggested to use silver-plated Ni mesh to prevent corrosion [87]. A calendaring or pressing machine is then used to fix the particulate material on the current collector to form the ODC. One example for a dry process is the manufacture of electrodes according to Winsel [122]. In wet preparation processes either a paste or a suspension of the catalyst and the polymer has to be prepared. Surface active agents may be added to improve the stability of the suspensions. A paste is then fixed on the current collector either by screen printing or by calendaring, while a less viscous suspension is usually sprayed. While first ODCs used for chlor-alkali electrolysis were alkaline fuel cell electrodes, later work concentrated on the development of specialized ODCs. These electrodes can be divided into gas–liquid impermeable and gas–liquid permeable ODCs.

### 7.1 Gas–liquid impermeable ODCs

Gas–liquid impermeable cathodes are self-supporting structures for use in three compartment electrolysis cells where the ODC is in contact with a thin electrolyte film on one side while oxygen enters the porous structure from the other side (Fig. 4). These ODCs must be accessible to both reactants without permeation of gas or liquid. Gas–liquid impermeable electrodes contain either a single uniform layer (upper right hand side in Fig. 4) or separate layers for the catalytic function and for gas transport (lower right hand side). In both cases, a metallic current collector is included in the ODC, the overall thickness of which amounts to ca. 300–1000 µm.

An example for a single layer gas–liquid impermeable ODC is the so-called Silflon electrode developed by Hoechst AG. This carbon free electrode contains a silver catalyst which is deposited on PTFE using a pH controlled reductive silver precipitation [34]. The dry silver-PTFE powder obtained with a silver content in the range between

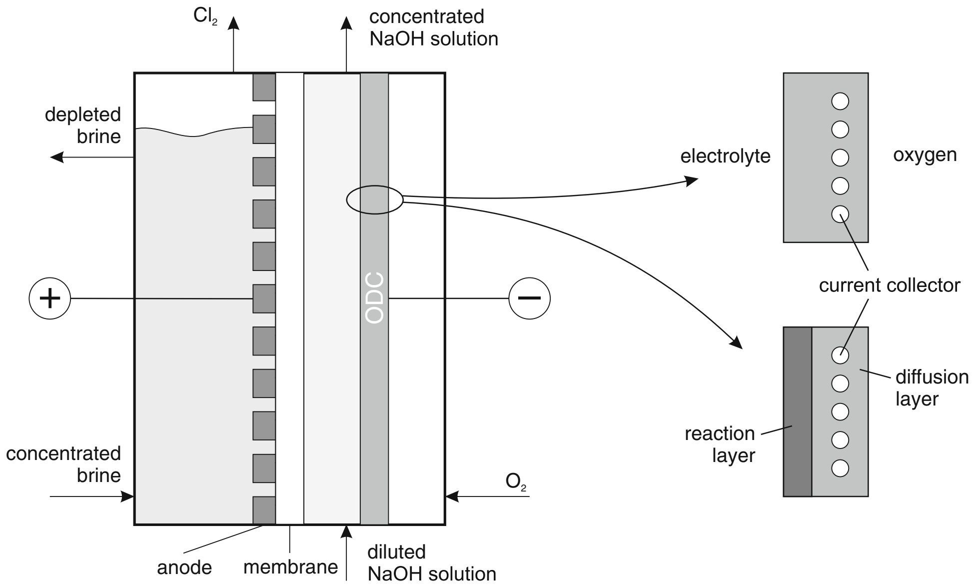

**Fig. 4** Three compartment membrane cell with gas–liquid impermeable ODCs

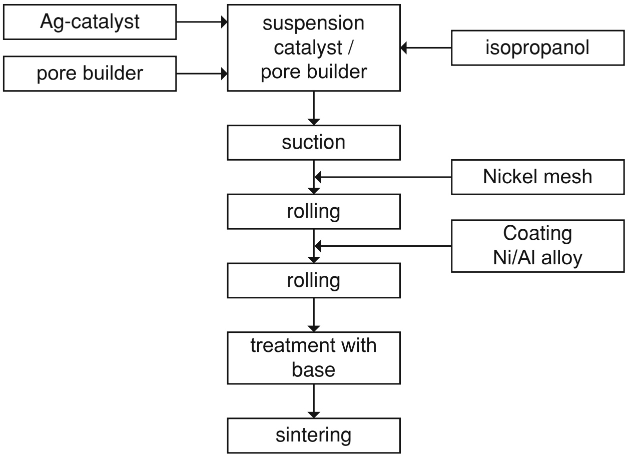

**Fig. 5** Preparation of Silflon ODCs [32]

85 and 90 wt% is mixed with an organic solvent and optionally with ammonium hydrogen carbonate as pore builder. The excess organic solvent is removed by suction to form a defined layer of the catalyst-pore builder mixture. In the next step, a nickel mesh is rolled on the remaining wet filter cake. Finally the electrode is sintered at 250 °C to obtain sufficient mechanical stability and to remove the pore builder. These electrodes may also be prepared as dual layer structure [32]. In that case the raw electrode obtained after rolling the nickel mesh is coated with nickel-aluminium alloy and again rolled out. Fine pores in the alloy are formed upon dissolving the aluminium with base. This latter version of the Silflon electrode preparation is summarized in Fig. 5. This electrode was tested in a pilot cell with an electrode area of 0.32 $m^2$ at a current density of 3 $kA/m^2$ and a cell voltage of 2.17 V [32].

A typical example of a carbon based ODC for chlor-alkali electrolysis with two layers has been described by ETEK [87]. The first layer is catalytically active, comprising a mixture of hydrophilic carbon particles (e.g. Vulcan XC-72) supporting finely dispersed Pt catalyst, and a hydrophobic binder (e.g. PTFE). This layer faces the liquid side and comprises hydrophobic channels for oxygen supply and hydrophilic channels required for removal hydroxyl ions released into the gap between membrane and electrode. The second layer is a pre-formed, porous hydrophobic electrically insulating film, bonded to the catalytic layer, required to prevent electrolyte leakage from the liquid side to the gas side that could form a liquid film able to hinder oxygen diffusion. A typical voltage for a cell fed with pure oxygen at 85 °C, operating at a current density of 3 $kA/m^2$ was around 2 V. After 60–70 days, the electrode deteriorated due to the presence of cracks filled with liquid that hindered oxygen access. In an improvement of the original ODC, an alternative diffusion layer consisting of carbon with PTFE binder was suggested.

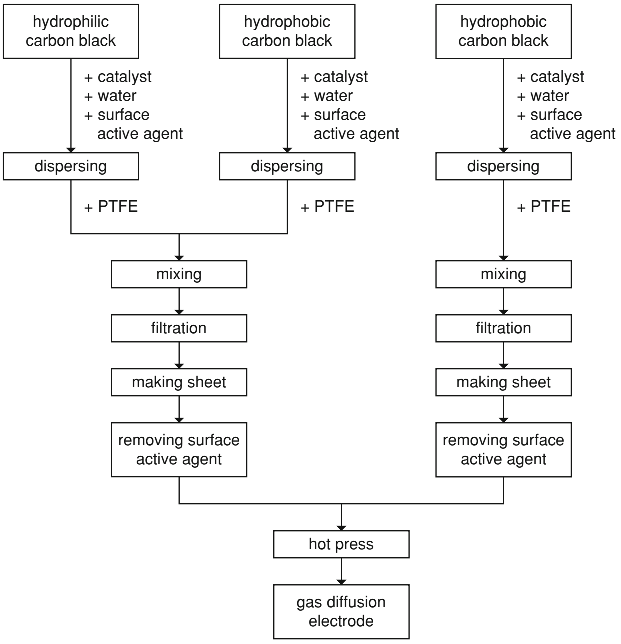

**Fig. 6** Preparation of carbon based dual layer ODCs [70]

Catalytically active and diffusion layers are then attached to a supporting conductive structure made of nickel mesh. A quite similar electrode design was described by Furuya and coworkers [70]. Here, the hydrophobicity of the reaction layer was adjusted using PTFE and a mixture of hydrophilic and hydrophobic carbons. An example of a preparation method for carbon based gas diffusion electrodes is shown in Fig. 6.

Wang and Koda have theoretically investigated the influence of pore structure in a dual-layer impermeable ODC on electrolyte flooding, gas percolation, and electrochemical performance. According to their analysis, it should be possible to prevent breakthrough of both gas and liquid even in a vertically operated electrolyzer of 1 m height or more, provided that the electrode has uniform pores with sufficiently small diameter [89]. The electrode over-voltage calculated with the thin-film flooded agglomerate model was found to be hardly dependent on the thickness and pore structure of the diffusion layer. On the other hand, the achievable current density is limited by the low oxygen solubility and diffusion resistance in the reaction zone filled with liquid electrolyte [90]. For this reason, chlor-alkali electrolysis with ODC is usually carried out with pure oxygen at current densities of technical relevance.

## 7.2 Gas–liquid permeable ODCs

In conventional ODCs oxygen is supplied from one side of the electrode, passes through the hydrophobic porous structure and reaches the reaction layer, where it is

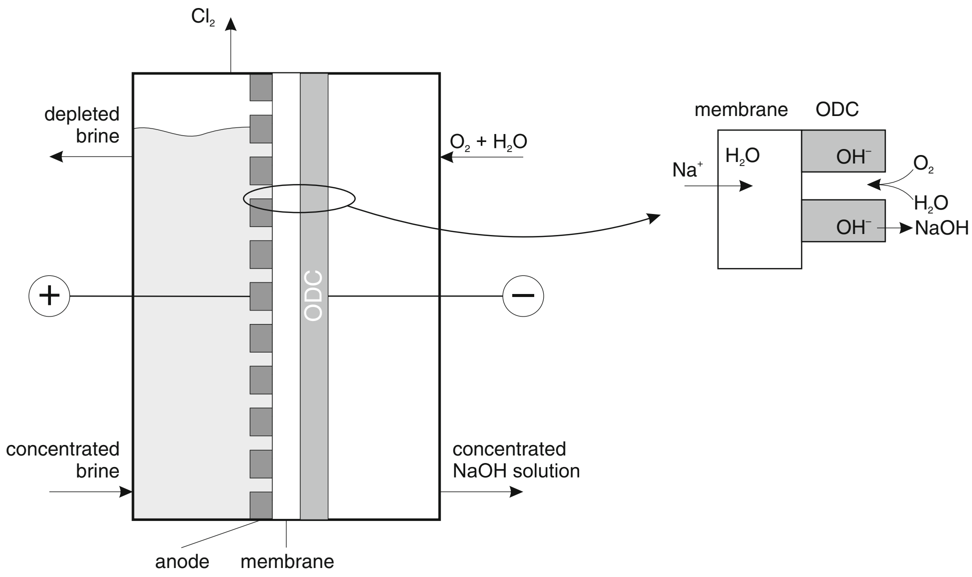

**Fig. 7** Two compartment membrane cell with gas–liquid permeable ODCs

consumed by electrochemical reduction. An ideal ODC of this type is impermeable for both gaseous oxygen and liquid electrolyte. However it is difficult to avoid leakage of the NaOH solution into the gas phase completely especially in the case of the height-dependent pressure difference in large-scale electrolyzers. To avoid these problems, a different type of oxygen depolarized cathode which is directly placed on the ion exchange membrane was proposed by several authors [20, 42, 48, 63–65, 67, 95]. This arrangement for use in two-compartment cells (Fig. 7) is called zero-gap ODC and is comparable to membrane electrode assemblies known from fuel cells.

This alternative type of cathode must have very good permeability for both gas and liquid, because oxygen requires access to the porous structure during electrolysis, while at the same time the produced sodium hydroxide is removed against the direction of oxygen flow. Furuya and coworkers have successfully operated a small-scale electrolysis cell with silver based zero-gap ODC [63, 64]. The electrode used was made of mixtures of Ag particles and PTFE suspension arranged in two layers with different porosity. The concentration of the NaOH solution produced was varied by different degrees of oxygen humidification. It was found that cell voltages strongly depended on NaOH concentration. Without humidification of oxygen, the electrode could be operated at 3 kA/m$^2$ only with low anolyte concentrations of 175 g/L. The cell voltage attained was 2.05 V at 3 kA/m$^2$. This cell could be operated stably over 700 days although the membrane had to be changed during the test due to the generation of blisters. These blisters were found on the membrane which might have been caused by condensation of the catholyte between the membrane and the attached cathode. Lipp et al. used a fuel cell type arrangement of a carbon-based zero-gap ODC with a cathode flow field for oxygen supply [95]. This publication and a related patent application [123] concentrate on the formation of and problems deriving from peroxide formation. Further results can be found in a progress report (http://www1.eere.energy.gov/industry/imf/pdfs/1797_advancedcatechnologyfinal.pdf). In a recent patent application, a novel ODC composition based on silver catalyst and containing diamond particles was used in a zero-gap chlor-alkali electrolysis cell [124].

## 8 Technical electrolysis cells applicable for ODCs

It has been already stated in the previous section that in principle two and three compartment cells may be used for chlor-alkali electrolysis with ODC. In conventional three-compartment i.e., finite-gap cells, the oxygen depolarized cathode separates the cathode chamber into the oxygen and NaOH compartments. The small gap of 1–3 mm between electrode and membrane is filled with sodium hydroxide solution. This cell type allows for independent adjustment of NaOH concentration through recycle of diluted caustic. NaOH cell concentrations are usually in the range of 30–33 wt% to ensure optimum membrane performance. The main disadvantage of this cell design is the possible pressure difference between sodium hydroxide solution and oxygen which may result in breakthrough of gas or liquid.

In alternative two compartment i.e., zero-gap cells, the ODC is directly attached to the membrane without any catholyte gap. If the electrode used is sufficiently accessible for oxygen, this design has two potential advantages. Firstly, the problem of height-dependent pressure difference is solved and secondly, the ohmic losses in the catholyte gap are minimized. On the other hand, oxygen transport may be hindered and the sodium hydroxide concentration is now mainly determined by the water permeation properties of the membrane. At an anolyte concentration of 200 g/L NaCl, membranes have a typical water transport value of 3.8 to 4.0 mol $H_2O$ per mol sodium ions [86]. With these ratios one can expect that NaOH concentrations will exceed membrane stability limits.

### 8.1 Finite-gap electrolysis cells

Although large pressure differences between catholyte and gas compartments are theoretically possible [89], real electrodes suffer from permeation of gas or liquid if the pressure difference between sides exceeds relatively low values. Even the hydrostatic pressure difference in three compartment cells with heights as low as 30 cm may be too high for optimum ODC operation [85, 87]. As this is unattractive for technical electrolyzers with element heights of 1 m or more, solutions for handling the pressure gradient in finite-gap electrolysis cells are required. Three different concepts to overcome this problem have been described. The first approach uses compartments on the oxygen side the pressure of which can be independently adjusted. The height of these compartments is sufficiently small to prevent electrode flooding or gas permeation. Compartmentalized cells for chlor-alkali electrolysis have been suggested by Eltech Systems [17] and Dow Chemical [31] in the 1980s. A more recent design by Bayer and DeNora with a pressure compensation system based on oxygen gas pockets [85] has been successfully applied on pilot and industrial scale in an electrolyzer with 2.5 $m^2$ electrode area and 16 bipolar elements [87]. Typical cell voltages obtained with pure oxygen at 85 °C using current densities of 3, 4.5 and 6 $kA/m^2$ were 2, 2.3 and 2.5 V, respectively. The principle of this system is depicted in Fig. 8.

The second concept is the use of so-called falling film electrolysis cells [38, 40, 80, 120, 125, 126]. In these falling film cells, the electrolyte is allowed to flow from the top end of the cell downward by gravity. The hydrostatic pressure is compensated by an equally high counteracted hydrodynamic pressure drop. As a result, the pressure difference between electrolyte and gas on the other side of the ODC remains constant over the whole height of the vertical electrode. Furthermore, the falling film concept allows for a very small electrolyte gap of less than 1 mm between membrane and ODC. In some cases, a porous material made of metals, metal oxides or polymers is included in the cathodic compartment of a falling film electrolyzer. The falling film concept was also suggested for highly efficient pressurized alkaline fuel cells with unprecedented power density [127]. A typical electrolyzer of the falling film design is illustrated in Fig. 9.

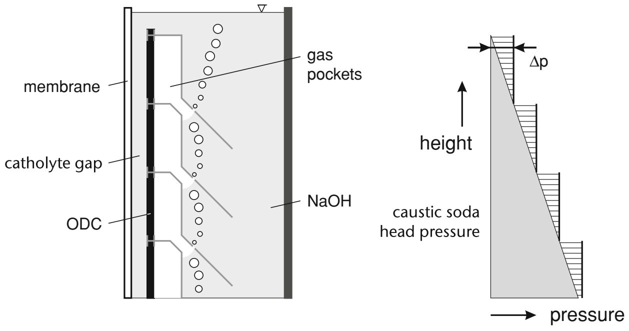

**Fig. 8** Gas pocket technology for pressure compensation in ODC chlor-alkali cells

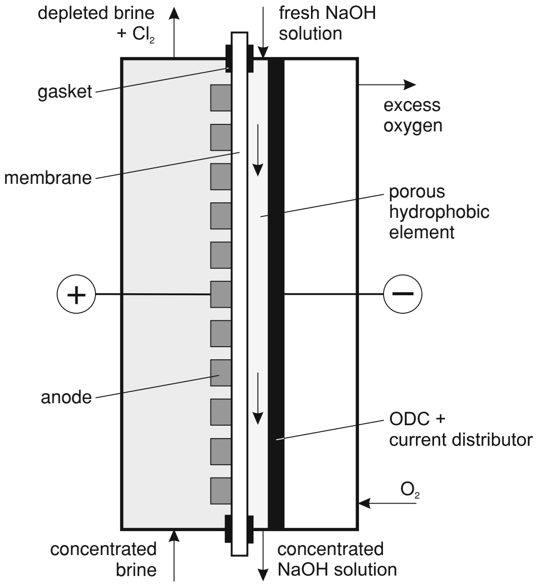

**Fig. 9** Falling film chlor-alkali cell design [120]

The third suggested concept comprises the use of electrolysis cells with horizontally disposed electrodes [37]. Hoechst described a cell (Fig. 10) where the ODC (3) rests on a grating (4) with supporting legs (2). A spacer (8) is disposed between membrane (6) and gas-diffusion cathode (3). This invention was mainly aimed at possible direct

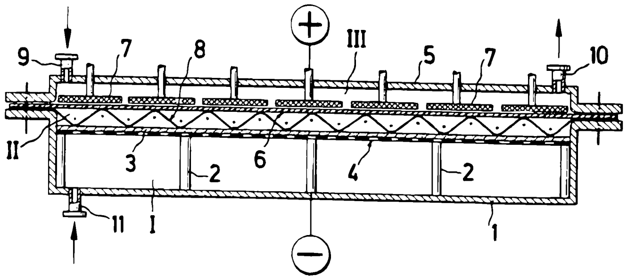

**Fig. 10** Horizontal ODC cell design [37]

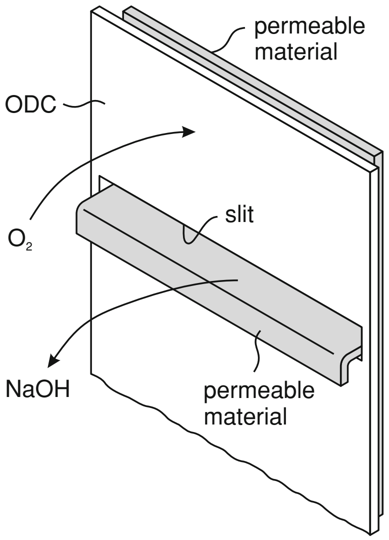

**Fig. 11** Design of ODC for zero-gap electrolysis cell ([67], modified)

conversions of existing mercury cells to membrane technology with ODC.

In a more recent application, a stacked horizontal electrolysis cell with ODC employing a cascade flow of electrolyte has been described [128].

### 8.2 Zero-gap ODC cell design

Main challenge for the construction of zero-gap chlor-alkali cells with direct contact of membrane and oxygen depolarized cathode is the counter-current flow of gaseous oxygen and liquid electrolyte through the electrode. If the sodium hydroxide solution flowing through the ODC forms a cohesive liquid film on its surface, oxygen transport to the active catalytic sites is strongly hindered. To prevent uncontrolled formation of liquid films, it has been suggested to include holes, slits or defined regions with greater hydrophilicity on the surface of the ODC to direct the flow of liquid and allow oxygen to enter the cathode [20]. In a more recent design of a zero-gap electrolysis cell an additional hydrophilic liquid-permeable material was placed between membrane and ODC [67]. As can be seen from Fig. 11, a possible configuration of the ODC in this cell has slits through which the liquid-permeable material is inserted. The liquid electrolyte is removed from the bent pieces of this material as droplets while oxygen has easy access to the ODC.

In a recent patent application, a fuel cell type electrolysis stack has been suggested to prevent complicated cathode designs [4]. This cell design comprises flow fields for oxygen transport and caustic removal. From these examples one can see that the zero-gap design has certain advantages such as a reduction of ohmic losses in the electrolyte and avoidance of pressure differences between liquid and gas. On the other hand, however, the design of the ODC or the cell may become much more sophisticated than in finite gap electrolysis. Moreover, the caustic concentration must be adjusted by addition of water to the oxygen feed to guarantee membrane stability.

In conclusion it can be said that finite-gap falling film cells seem to be less complex than cells with pressure compensation systems. Horizontal arrangements of ODCs have to our knowledge not yet been tested on technical scale while the zero-gap cell design is elegant, but suffers from complex electrode geometries required for facile oxygen supply and requires water addition to maintain stability of common membranes.

## 9 Summary and future prospects

After intensive research and development over more than 30 years chlor-alkali electrolysis with oxygen depolarized cathodes has reached a state where little doubt about the technical feasibility of this concept remains. Relatively advanced electrode and electrolyzer designs show that, together with quite successful long-term durability tests, that large-scale implementation of the ODC technology is a viable option for energy conservation in the chlor-alkali industry. It appears that carbon free ODCs based on silver catalysts and finite-gap falling film cell designs are presently the most promising routes.

The remaining question is the economic viability of this technology. Unfortunately, there is no easy answer because on the one hand costs of electricity, new electrolysis cells, ODCs and required oxygen have to be taken into account. On the other hand, kind and degree of hydrogen usage at a certain location are of equal importance. Moreover, it has to be considered whether a new plant or the conversion of an existing amalgam or diaphragm plant is planned. Several early papers made some general remarks about economic comparison of conventional and ODC membrane electrolysis [32, 40, 60]. These authors claimed a potential benefit of ODC electrolysis, although Yeager and Bindra remained sceptical in face of the relatively low electric energy prices of these days [60]. A much more detailed economic analysis of energy conservation in the chlor-alkali industry was published by Anderson et al. in 1990 [108]. These authors investigated several fuel cell derived technologies including ODC electrolysis, utilization of hydrogen in alkaline fuel cells, a $H_2$-$Cl_2$ fuel cell for cogeneration of hydrogen chloride and electric energy and an electrochemical concentrator employing an ODC for increase of caustic concentration from 30 to 50 wt%. A net present value analysis revealed that membrane electrolysis with ODC becomes attractive at module costs below ca.

750 $/m$^2$ provided that the same current density (3.5 kA/m$^2$) as in the conventional membrane cell can be achieved. This module cost includes the price of the electrodes and the cell housing. It was furthermore shown that an alkaline fuel cell cannot compete with ODC electrolysis at the same module costs. This result is in agreement with the more general analysis of Yeager and Bindra, who pointed out that the ODC is energetically preferred because it allows for a voltage reduction of 1.0 V while the energy gain of a fuel cell system coupled to a conventional electrolysis amounts to only 0.6 V [60].

As current electric energy prices are much higher than in the 1980s and a further strong rise is generally expected, one can foresee that the economic break-even of chlor-alkali electrolysis with ODC will be reached in the relatively near future. On the other hand, the utilization of waste hydrogen in chlor-alkali plants with fuel cells has recently become quite popular (http://www.dow.com/commitments/studies/fuelcell/index.htm). This interest is understandable because the energetically more favourable ODC electrolysis is not yet available on the market and fuel cell installations at chlor-alkali plants are attractive demonstration programs for large-scale stationary applications of this new technology.

Two further aspects have to be considered for the assessment of measures for energy conservation in the chlor-alkali industry by means of avoidance or utilization of hydrogen in fuel cells. Firstly, the ongoing discussion about carbon trading and possible carbon dioxide taxes may relatively soon dramatically change the economic picture in one of the most energy intensive and, as long as electric energy is based on fossil fuels, also carbon dioxide emitting industries in the world. Secondly, a contrary situation may occur if the so-called hydrogen economy is established some day. In that case, hydrogen from chlor-alkali plants would no longer be a waste that has to be avoided or used as efficiently as possible. Instead, it would be a premium fuel easily saleable on the hydrogen market. In any case, it is evident that the economic efficiency of chlor-alkali electrolysis with ODC is closely related to the future development of world energy markets.

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