Revisiting Chlor-Alkali Electrolyzers: from Materials to Devices

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Abstract

As an energy-intensive industry, the chlor-alkali process has caused numerous environmental issues due to heavy electricity consumption and pollution. Chlor-alkali industry has been upgraded from mercury, diaphragm electrolytic cell, to ion exchange membrane (IEM) electrolytic cells. However, several challenges, such as the selectivity of the anodic reaction, sluggish kinetics of alkaline hydrogen evolution, degradation of membranes, the reasonable design of electrolytic cell structure, remain to be addressed. For these reasons, this paper mainly reviews the research progress of the chlor-alkali industry from materials to devices, including hydrogen evolution anode, chlorine evolution cathode, IEM, and electrolytic cell system. Finally, the research directions and prospects in the chlor-alkali industry are proposed for its further improvement.

Keywords Chlor-alkali · Process · Hydrogen energy · Ion exchange · Membrane · Hydrogen evolution · Chlorine evolution

Introduction

The chlor-alkali process is one of the most basic chemical industries, mainly producing chlorine (Cl_2) and sodium hydroxide (NaOH). The global annual production of chlorine exceeds 75 million tons. Each ton of chlorine consumes about 2200–2600 kW·h of electricity, and the global chlor-alkali industry needs to consume over 150 TW·h of electricity every year, accounting for about 10% of global electricity [1]. Chlorine has been used in a variety of applications, including the production of building materials such as polyvinyl chloride, organic synthesis, metallurgy, water treatment [2], and the manufacture of titanium dioxide [3]. NaOH is also a common chemical raw material that is widely used in the production of detergents, herbicides, pesticides, medicines, plastics, and soaps. However, the current chlor-alkali process is one of the industries with high energy consumption, releasing large amounts of pollutants and causing serious environmental problems. Therefore, energy saving and

emission reduction in the chlor-alkali production process are important development directions.

The chlor-alkali industry has experienced a long development process from mercury, diaphragm electrolytic cells to ion exchange membrane (IEM) electrolytic cells. At present, membrane electrolytic cell technology accounts for approximately 81% of the global chlor-alkali capacity [4]. In mercury electrolysis cells, mercury as the liquid cathode reacts with sodium ions to form sodium amalgam ($\text{Na}^+ + \text{Hg} + \text{e}^- \rightarrow \bullet\text{NaHg}$), whereas Cl_2 is formed on the anode. Then, NaHg is transferred to another electrolytic cell to release Na^+ ($\text{NaHg} \rightarrow \text{Na}^+ + \text{Hg} + \text{e}^-$), forming NaOH in the electrolyte [5, 6]. A diaphragm is introduced to separate the anode and cathode reactions to prevent the cathode product (NaOH) and the anode product (Cl_2) from crossing over to generate sodium hypochlorite. The negatively charged membrane can inhibit the back diffusion of OH^- [7]. Therefore, in diaphragm electrolyzers, asbestos felt is often used to separate the products (Cl_2 and H_2) [8, 9], although the chemical instability of asbestos itself causes the severe swelling of pure asbestos diaphragm under a high current load [7]. Therefore, these two technologies above rely on highly toxic mercury and asbestos respectively, resulting in serious environmental pollution [1, 10].

Membrane electrolysis cells use highly conductive IEMs instead of traditional asbestos felt to separate Cl_2 and H_2 , which greatly reduces the operating voltage and pollutant emissions. Compared with diaphragm electrolytic cells, the

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membrane counterpart offers high-purity sodium hydroxide. Thus, the replacement of the diaphragm method with ion membrane technology is an inevitable trend. The perfluorinated membrane method is currently recognized as the most energy-efficient chlor-alkali process in the world. A cation-selective permeation membrane is placed between the anode and cathode compartments, and a saturated sodium chloride solution is injected into the anode compartment, which usually produces 32%–35% caustic soda (Fig. 1). This membrane rejects the passage of chloride ions (negatively charged) but allows sodium ions (positively charged) to pass through. The first-generation membrane can only work at low corrosive concentrations, whereas the state-of-the-art membrane is made of a perfluorosulfonic acid (PFSA) polymer layer, where a polytetrafluoroethylene (PTFE)-reinforced fabric and a perfluorocarboxylic acid (PFCA) polymer are bonded together. This membrane has low electrical resistance and high ion-selective permeability and can work in a highly corrosive electrolyte environment.

Hydrogen, which is usually treated as exhaust gas in the chlor-alkali industry, may become the major fuel used on a large scale in the future as the most promising clean energy. The chlor-alkali electrolyzer can be used as one of the most promising low-cost hydrogen sources in the near term, better than water electrolyzer, considering that the value of chlorine gas and chemical NaOH produced in the

former technology is notably higher than that of the oxygen gas produced in the latter. Further coupled with cheap and clean electricity generated from renewable energy, chlor-alkali electrolyzers will become a promising green hydrogen production technique.

In general, all chlor-alkali reactions include three reactions: chlorine evolution reaction (CER) at the anode, hydrogen evolution reaction (HER) at the cathode, and NaOH generation in the electrolyte. Figure 1 shows a chlor-alkali electrolysis cell. The chlor-alkali electrolyzer is mainly composed of three parts: anode, cathode, and IEM. Although the energy consumption of state-of-the-art chlor-alkali electrolyzers has been greatly reduced with technological progress, all of its structural parts still need to be further optimized.

An in-depth understanding of the selectivity of the anode will help to further develop inexpensive, stable, and efficient chlorine evolution catalysts. The slow hydrogen evolution kinetics caused by the alkaline condition of the cathode is one of the main reasons for its high energy consumption. Therefore, the research on the alkaline HER cathode of chlor-alkali electrolysis cells is important to improve the efficiency of electric energy utilization. In addition, the use of oxygen depolarized cathodes (ODCs) to reduce the energy consumption of chlor-alkali electrolysis cells has achieved certain results, but their potential remains to be evaluated. An in-depth understanding of IEMs can not only guide specific industrial operating conditions and optimize the overall structural design of electrolytic cells to extend the service life of the membrane but also provide a basis for the design of high-performance membrane materials. In addition to the various structural units of the chlor-alkali electrolysis cell, the entire electrolysis system can still be optimized.

Fig. 1 Schematic of the working principle for a renewable electricity-powered chlor-alkali electrolyzer

Cathode

In conventional chlor-alkali electrolyzers, HER occurs at the cathode, which can be employed as one of the most promising low-cost, green hydrogen-making technology. HER is complicated in the strong alkaline solution in chlor-alkali electrolyzers compared with the reaction in acidic solutions. First, the cathode materials need to withstand the highly corrosive alkaline conditions. Moreover, the slow kinetics of HER under alkaline conditions is the main reason for the high energy consumption. Thus, the design of highly efficient electrocatalysts under strongly basic conditions is the key to achieving low-energy chlor-alkali electrolyzers for green hydrogen production.

Hydrogen Energy

Hydrogen is a clean fuel and is one of the most promising energy carriers to replace traditional fossil fuels, possessing

high heat value (120 MJ/kg) and no exhaust emissions (only produces water as by-products) at the point of use. Currently, hydrogen gas is mainly produced through petrification, such as the gasification of coal [11], natural gas steam reforming [12], and methanol cracking [13], with about 4% of global hydrogen produced from water electrolysis [14].

In a typical gasification process, coal is first gasified and then undergoes carbon monoxide vapor conversion and pressure swing adsorption purification to produce hydrogen. This process is less preferred due to the high temperature required, the pollution created, and complex operation. The most common method used in hydrogen production is the methane steam reforming process, which takes up 50% of the hydrogen produced worldwide [15]. This process is similar to the gasification of coal, and thus, the drawbacks are the same. Despite the low cost of hydrogen production from fossil fuels, the heavy carbon footprint and large investment in hardware equipment make them unattractive for future use. Three ways are used to produce hydrogen from methanol: methanol cracking, methanol-steam reforming, and partial oxidation of methanol [13]. Among these methods, methanol cracking is the most competitive due to its wider application range and single feedstock. Its advantage includes lower investment cost and less energy consumption than coal and natural gas. However, the cost of methanol feedstock is high, which results in a high unit cost of hydrogen production.

As for water electrolysis, the hydrogen production cost is the highest among different methods mainly due to the sluggish oxygen evolution reaction (OER) [16], which is estimated to be between 2.5 and 3.5 ¥/Nm³ hydrogen at the current price of electricity. Water electrolyzers can become a common method to produce hydrogen if the electricity price is decreased considerably by maturing wind and hydroelectric power supplies [17]. The chlor-alkali electrolyzer is potentially one of the most promising low-cost hydrogen-making technology, better than water electrolyzer, considering that the value of chlorine gas and chemical NaOH produced in the former technology is substantially higher than the oxygen gas produced by the latter [18, 19].

In modern chlor-alkali plants, unlike the products, namely, chlorine and sodium hydroxide, hydrogen is a by-product. In the USA, approximately 40%–50% of hydrogen from the chlor-alkali process is combusted for process heat, with 30%–40% sold to the merchant hydrogen market and the remainder (10%–30%) vented [20]. In China, nearly 1.8 billion m³ hydrogen is wasted in industrial chlor-alkali process [21]. Currently, the main applications for hydrogen produced in chlor-alkali electrolyzers include: (1) feedstock gas for the production of ammonia [22]; (2) hydrocracking and other petroleum processing industries [23]; (3) chemical and organic fine chemical synthesis; (4) production of high-purity compressed hydrogen for direct sale (for electronics, metallurgy, glass, and other industries); (5) fuel for

steam production; (6) hydrogen fuel cell technology for the construction of hydrogen power plants [24]. Several companies have bottled and marketed hydrogen gas produced in chlor-alkali plants, which is then supplied to fuel cells [25]. Hydrogen fuel cells can be well coupled with chlor-alkali plants, which can recover 20% of the electrical energy and 10% of the thermal energy consumed in chlor-alkali electrolysis [26].

HER Fundamentals

Historically, HER is the most studied, particularly in acidic solutions. By contrast, limited research has been conducted on HER in alkaline solutions, that is, the operation condition of chlor-alkali electrolyzers, mainly due to the complicated reaction mechanism. The possible pathway of HER in highly alkaline media includes the following steps: electro-reduction of water molecules and hydrogen adsorption (Volmer reaction, Step 1); electrochemical desorption of hydrogen (Heyrovsky reaction, Step 2); chemical desorption (Tafel reaction, Step 3).

HER kinetics in alkaline solution is extremely sluggish and is usually 2–3 orders of magnitude lower than that of acidic media. The pH-dependent hydrogen binding energy (HBE) derived by cyclic voltammetry is considered a reasonable descriptor. HBE is generally considered to be an inherent property of every metal and is independent of pH. However, the electrode surface is covered with water. Thus, the adsorption/desorption of hydrogen is possibly accompanied by the desorption/resorption of water. Cheng et al. [27] attributed pH dependence to the changes in water adsorption energy, given that the hydrophobicity of Pt electrodes increases as the potential becomes negative. Therefore, water adsorption or surface hydrophilicity must be tuned by alloying or introducing hydrophilic surface groups (such as OH). In addition, several uncertain properties of the interface, such as the Schottky barrier [28] or mismatched lattice space [29], can hinder electron transfer and the transfer of reaction intermediates between the two phases, causing additional kinetic obstacles.

HER Catalysts

So far, platinum offers the most superior HER performance, but its limited abundance hinders its industrial applications. In practical chlor-alkali electrolyzers, low-carbon steel is

employed as cathode material instead of platinum. Two main issues need to be addressed with the use of low-carbon steel. First, during the electrolysis process, the cathode surface becomes gradually covered by chromium oxide (Cr_2O_3), resulting in “blind current” loss. This condition will result in a large increase in overpotential and ultimately the precipitation of Ca and Mg products. Further, the steel cathode has a high corrosion rate due to the thermodynamic instability of iron in the alkaline solution. Nickel is also the most common catalyst used as cathode material in alkaline media, such as Ni foam. The complete replacement of platinum with low-cost active catalytic materials is one of the most important goals of modern electrocatalysis.

Meanwhile, numerous new materials have also been investigated for HER: (i) noble metals, such as Pd, Ir, Ru, Ag, etc.; (ii) inexpensive transition metal catalysts, including Fe, Co, Ni, Mn, Cu, Mo, and W, and their heterogamous nanostructures; (iii) non-metal catalysts, including B, C, N, P, and S [30]. These results have been summarized in the previous references [31, 32]. Nitrogen-doped transition metal materials exhibit a tunable local electronic structure and fast electron transfer capability. Lei et al. [33] developed an atomically dispersed Ni-anchored nitrogen-doped porous carbon (Ni-NC) matrix, which gave a minimum overpotential of ~ 150 mV at a current density of $10 \text{ mA}/\text{cm}^2$. Experimental observations confirmed that the strong chemical coupling between Ni nanoparticles and Ni-NC regulates the electronic structure, promotes electron transfer on the constructed interface, and optimizes the process of hydrolysis and OH^- adsorption. Nitrogen doping can effectively improve the alkaline HER activity. This atomic-level modulation strategy opens up a new way for the development of practical electrocatalysts using three-dimensional metal oxides in alkaline environments. Sun et al. [34] used N atoms to regulate ReS_2 . As shown in Fig. 2, the injection

of N atoms can effectively promote electron transfer from Re to S atoms, leading to the redistribution of electrons, rendering Re atoms in an electron-deficient state, and increasing the hydrophilicity of O. The preferential sites of adsorption activation optimize the H adsorption/desorption process, increase the electronic state near the Fermi level of the material, and improve the charge transfer.

ODC

One of the important developments in the chlor-alkali industry is the introduction of ODC, which introduces oxygen into the electrolysis chamber through a porous cathode. Figure 3 shows the ODC electrolysis cell. If the oxygen reduction reaction (ORR) [35] at the ODC cathode is used to replace the HER in the traditional process, the electrical energy demand can theoretically be reduced by up to 30% [36], and the operating voltage can be reduced by approximately 1.0 V, as shown in Eqs. (4) and (5). The ODC process has also been widely used in the HCl electrolysis scenario, which consumes downstream HCl by-products to achieve chlorine recovery [37].

$$E^0 = 0.00 \text{ V vs. RHE}$$

$$E^0 = 1.23 \text{ V vs. RHE}$$

Fig. 2 Schematic of the HER mechanism of **a** ReS_2 and **b** N-ReS_2 under alkaline conditions (reprinted from [34] with permission from RSC)

Fig. 3 Comparison of chlor-alkali electrolysis with different active cathodes. **a** Hydrogen evolving cathode. **b** ODC (reprinted from [38] with permission from ACS)

ODC Electrode Structure and Working Principle

ODC is a gas diffusion electrode (GDE) that can significantly increase the reaction current densities [39]. The industrial ODC consists of a porous structure of silver particles and a PTFE supporting layer. The typical operating conditions include 10 M NaOH, temperature range from 80 °C to 90 °C [40], and current density of 400–600 mA/cm² [41].

The ODC performance is related to the diffusion rate of oxygen and water activity [42]. Under industrial operating conditions, ORR only occurs near the gas–liquid interface [35, 43]. Given the water consumption and hydroxide ion accumulation, the phase balance changes significantly with the current density applied and oxygen solubility in the liquid electrolyte. This effect is enhanced at high reaction rates, which leads to complete depletion of oxygen and achievement of a limiting current. Röhe et al. [44] established a dynamic three-phase model of advanced chlor-alkali electrolysis porous ODC, which proved that water transport, especially that of hydroxide ions in the liquid electrolyte, is the overall limiting factor. The oxygen concentration is rapidly consumed near the gas–liquid interface [45]. Considering the non-ideal behavior of highly concentrated water, the water activity coefficient largely depends on ion concentration [46]. As sodium hydroxide concentration increases, water activity will decrease due to the formation of a solvated shell that combines water molecules with ions. For example, the highly concentrated electrolyte binds considerable water to the solvation shell of solute molecules

and thus, decreases the abundance of free water molecules [47]. The decrease in water activity and oxygen solubility is also accompanied by the decrease in oxygen mass transport rate [48].

Research has focused on the correlation between the structural parameters of the porous gas diffusion layers (GDLs) and ORR performances. GDLs with large pores may promote gas supply and further facilitate the mass transport rate of oxygen to achieve an excellent electrode performance [49, 50]. Pore volume is another factor that determines the electrode performance [51]. Nara et al. [52] employed electrochemical impedance spectroscopy to further determine the correlation between the ODC performance and the pore structures, including the primary and secondary pores within the catalyst layer. Park and Popov [53] studied the influence of PTFE content of ODC on electrode activity and observed the volcanic dependence of PTFE content in the ODC performance.

ODC Electrode Materials

1. Carbon-supported transition metal catalysts

Pt/C (usually 20 wt%) is a commonly used catalyst in fuel cells and has good activity and stability in acidic media [54–56]. However, metallic Pt is easily corroded by Cl[−] ions; thus, a large amount of noble Pt will dissolve in the highly corrosive saturated Cl₂ electrolyte [57]. The carbon-based rhodium-based chalcogenide Rh_xS_y/C developed by E-TEK is the only ODC catalyst that main-

tains activity under concentrated Cl_2 electrolyte, but this catalyst has low intrinsic activity [58]. Most of the existing carbon materials are dual-functional catalysts for ODC and chlorine evolution in hydrochloric acid electrolysis, such as CN_x [59], Co-NSC_x [60], Fe-N-C [58], etc. The main goal is to improve the tolerance to Cl^- ions. However, overall activity still needs to be improved.

2. Silver catalysts

Under the harsh operating conditions of chlor-alkali electrolysis, carbon materials are easily corroded and suffer from low stability. Alternatively, silver exhibits an oxygen reduction activity similar to that of platinum under strongly alkaline conditions [61]; thus, silver can be used as a suitable substitute for noble platinum catalysts.

Optimizing silver-based GDEs will reduce energy consumption and enhance the long-term stability of chlor-alkali electrolyzers. GDEs are composed of silver particles, a complex pore system around them, and PTFE at the boundaries of the silver particles [62]. Figure 4 shows the three-phase interface and GDE electrode. When the hydrophilic silver particles support the penetration of the electrolyte, the pore channels containing hydrophobic PTFE keep the gas phase unobstructed. The existing GDE electrode is improved mainly through the increase in the three-phase interface (catalyst material, alkaline electrolyte, and O_2 -rich gas phase), thereby increasing the utilization rate of the catalyst. However, adjusting the three-phase boundary can be a complex task because the distribution of the electrolyte in the porous structure is still unknown. To address this issue, Paulisch et al. [48] used X-ray computed tomography to study the

electrolyte infiltration and distribution during electrolysis. The results showed a potential-dependent electrolyte transport in the ODC and droplet formation on the gas diffusion side. Given the importance of determining the electrolyte distribution inside the porous structure, further research on in situ imaging technology is needed to accurately link the structural and electrochemical performances.

Anode

Anode Reaction

In chlor-alkali electrolyzers, CER is the desirable reaction at the anode. The current efficiency of chlorine is the main measure of anode selectivity, whereas the OER is a side reaction that competes with CER. OER occurs directly at the anode, where water is oxidized to generate oxygen [16, 63]. The selectivity of chlorine and oxygen evolution is related to the inherent selectivity of anode materials, process conditions, and electrolyte compositions.

The anode reaction is mainly studied by conventional electrochemical techniques (such as voltammetry and polarization techniques), but theoretical methods are also used to study the intrinsic selectivity [13–15]. The composition of the evolved gas is usually determined by gas chromatography or O_2 absorption method, such as that which uses pyrogallol. The concentrations of hypochlorite, chloride, and chlorate can be determined by titration of the electrolyte. In addition, differential electrochemical mass spectrometry can be used to measure the reaction products formed on the anode with high sensitivity [64–66].

CER Fundamentals

Equations (6) and (7), respectively, list two competing reactions on the anode: CER and OER. The four-electron transfer in OER is thermodynamically more favorable and can compete with CER, although the two-electron transfer CER exhibits faster kinetics [67]. The excess oxygen and hydrogen products can possibly be combined in the cell to form an explosive gas mixture, which renders oxygen a safety hazard [68]. Therefore, chlorine selectivity must be improved.

$$E_{\text{O}_2/\text{H}_2\text{O}}^0 = 1.229 \text{ V vs. RHE}$$

$$E_{\text{Cl}_2/\text{Cl}^-}^0 = (1.358 + 0.059\text{pH}) \text{ V vs. RHE}$$

Fig. 4 Schematic of three-phase interface and GDE structure (reprinted from [62] with permission from RSC)

Numerous factors, including electrolytes, anode materials, and operating conditions, such as current densities and temperature, affect the selectivity of chlorine [68, 70]. Acidic conditions are favorable for CER, whereas alkaline conditions are favorable for OER [68]. The pH correlation between OER and CER can be represented by the phase diagram of the catalyst surface intermediates in equilibrium with Cl^- (Fig. 5). Unlike the OER, which is a pH-dependent reaction, CER is pH independent. Furthermore, increasing the current density can increase chlorine selectivity, which is related to the suppression of OER in low local pH.

Anode Electrode Material

Electrode materials with high activity for chlorine are usually also highly active for oxygen. Although these competing reactions are governed by the same factors, chlorine selectivity can still be optimized. The two reactions occur at a similar active site or form a common surface intermediate species, whereas CER and OER produce two competing intermediate products, namely, OCl and OOH , respectively [71].

Commercial Dimensionally Stable Anode (DSA) Electrodes

DSAs, which are mainly composed of noble metal Ir or Ru oxides, are currently the most advanced CER catalysts. The

innovation of DSAs is called “one of the greatest technological breakthroughs in the field of electrochemistry in the past 50 years” [72]. Commercial DSA electrodes usually contain one or more other doping materials, such as TiO_2 , SnO_2 , CoO_x , and SbO_x , to reduce the amount of precious Ir or Ru [73–75]. Modern DSAs can work at current industrial densities for more than 10 years [72]. The surface of commercial DSAs is coated with an electrocatalytic layer containing a mixture of titanium dioxide and ruthenium dioxide with an atomic ratio of about 70: 30 and a CER selectivity of about 95% [76].

To investigate the CER process at the DSA electrode, Hansen et al. [69] constructed the Pourbaix diagram of IrO_2 and RuO_2 based on density functional theory (DFT) calculations. The electrochemical and thermodynamic methods were used to construct the linear relationship of various adsorption intermediates, and a possible reaction mechanism was deduced. All material dependencies were included in one descriptor, that is, the oxygen-binding energy (Fig. 6). The unit surface has two bridge sites and two cus sites. The binding of adsorbates at a bridge site is stronger than that at a cus site. Thus, most bridge sites are occupied by oxygen. The phase diagram of IrO_2 shows that the surface is covered by OH groups at a low potential, which increases the oxidation potential of OH^- in the solution. The OH adsorbed on the bridge site is first converted to O and finally to the thermodynamically favorable OOH . The direct formation of Cl adsorbate on the cus site requires a pH less than 3, whereas the bridge site requires an even lower pH. For a high-performance chlorine evolution catalyst, the free energy of formation of Cl adsorbed species is approximately 0 at a potential close to 1.36 V. The direct binding of Cl adsorbate at Ir fails to meet these conditions, whereas the intermediate $\text{ClO}^\bullet$ is thermodynamically favorable at a potential higher than 1.5 V in the pH range from 0 to 3. Thus, the CER proceeds in two steps. $\text{O}^\bullet$ combines with Cl^- to form a $\text{ClO}^\bullet$ intermediate,

Fig. 5 Surface phase diagram for $\text{IrO}_2(110)$ in equilibrium with Cl^- , H^+ , and H_2O at 298.15 K and $a_{\text{Cl}^-} = 1$. The adsorbate phases are shown in the insets. Ir atoms are cyan, O atoms are red, H atoms are white, and Cl atoms are green (reprinted from [69] with permission from RSC)

Fig. 6 Most stable surface at pH = 0 and $a_{\text{Cl}^-} = 1$ as a function of potential, U , and the surface reactivity descriptor, $\Delta E(\text{O}^\bullet)$ (reprinted from [69] with permission from RSC)

which combines with another Cl^- to form Cl_2 . This mechanism is also known as the Volmer–Heyrovsky mechanism. The surface phase diagram of RuO_2 is complicated. A possible mechanism of the CER is that O_2^{ec} combines with Cl^- to form a $\text{Cl}(\text{O}^{\text{c}})_2$ intermediate, and $\text{Cl}(\text{O}^{\text{c}})_2$ combines with another Cl^- to form O^{c} and Cl_2 , that is, the Khrishtalik mechanism.

Exner et al. [77] used the ab initio thermodynamic method to construct the surface Pourbaix diagram of the CER on $\text{RuO}_2(110)$ based on the DFT calculations and considered the solvation effect. Under CER conditions, that is, $U > 1.36$ V, no ORR occurs on the surface of $\text{RuO}_2(110)$. All uncoordinated Ru surface atoms (Ru_{cus}) are covered by top oxygen (O_{ot}), and the adjacent $\text{Ru}_{2\text{f}}$ atoms are bridged by uncoordinated surface oxygen (O_{br}). In the ball-and-stick model, the active surface structure in CER and OER can be expressed as $\text{RuO}_2(110)\text{--O}_{\text{ot}}$.

In the first-order reaction kinetics, the reaction mechanism of $\text{RuO}_2(110)\text{--O}_{\text{ot}}$ active surface is considered to be the Volmer–Heyrovsky pathway. The mechanism is mainly divided into the Volmer step of Cl adsorption and desorption on the $\text{Ru}_{\text{cus}}\text{--O}_{\text{ot}}$ active site and the Heyrovsky step of the adsorption of Cl on the $\text{Ru}_{\text{cus}}\text{--OCl}_{\text{ot}}$ precursor to recombine with another Cl ion to form Cl_2 [70]. This phenomenon is consistent with the recent experimental study of CER on $\text{RuO}_2(110)$ single crystal [78]. The rate-limiting step is the Heyrovsky step under a low overpotential or Volmer step under a high overpotential [79]. OER is a relatively complicated four-electron reaction. This process mainly involves the formation of OH_{ot} , O_{ot} , and OOH_{ot} adsorbates on Ru_{cus} sites.

DFT calculations showed that the formation of OOH_{ot} adsorbates is a rate-determining step. Exner et al. [80] proved this finding through experiments. Under industrial conditions, the OCl_{ot} and OOH_{ot} adsorbates control the activity of CER and OER, respectively [70]. Thus, in addition to thermodynamic properties, the kinetic-based free energy of formation of OCl_{ot} and OOH_{ot} adsorbents should also be considered in the improved design of catalysts for CER. Loading a single layer of $\text{TiO}_2(110)$ on $\text{RuO}_2(110)$ can increase the selectivity of CER, and the CER activity is also improved. Consistent with the theory above, Ti replaces the top Ru atom, which weakens the free adsorption energy of O_{ot} by about 1.5 eV.

Other Metal Oxide Electrodes

Ir, whether as a pure oxide or dopant, can maintain a long-term stability [81]. A series of iridium-based double perovskite (Ba_2BIrO_6 , where B = Pr, Nd, La, Sn, Y, Tb, Ce) has been synthesized and studied for OER selectivity and stability [82]. The results showed that CER was carried out

through the Volmer–Tafel mechanism, where the activity was strongly affected by the concentration of chloride ions, showing a stepwise negative reaction order.

Highly efficient non-noble metal catalysts have also been developed to replace expensive Ru and Ir catalysts. Among these catalysts, crystalline transition metal antimonates (TMAs) are active and stable electrocatalysts [83]. Moreno-Hernandez et al. [84] reported that crystalline TMAs, such as NiSb_2O_x , CoSb_2O_x , and MnSb_2O_x , are intermediate active catalysts for the electrochemical oxidation of chloride to chlorine under industrial chlor-alkali process conditions. The Faraday efficiencies of chlorine evolution were as follows: NiSb_2O_x ($96.0\% \pm 3.7\%$), CoSb_2O_x ($97.4\% \pm 3.0\%$), and MnSb_2O_x ($89.9\% \pm 0.8\%$). X-ray photoelectron spectroscopy showed that the valence state of the transition metal remained unchanged, whereas the valence of Sb changed from 5 to a mixed state of 5 and 3. CoSb_2O_x exhibited the best stability and selectivity, and NiSb_2O_x showed the highest intrinsic activity. Ha et al. [85] proposed that Co_3O_4 nanoparticles have better chlorine evolution selectivity and stability than DSAs. The reaction proceeds by the Khrishtalik mechanism, in which the rate-determining step is the second step, that is, the Cl atoms adsorbed on the surface of cobalt atoms are discharged to form adsorbed Cl^+ species.

Membranes

The IEM that is widely used in the chlor-alkali industry is a double-layer composite material composed of a thick sulfonic acid-based layer (PFSA) and a thin carboxylic acid-based layer (PFCA), which can be incorporated into symmetrical, dense, or non-porous membranes. Dense films are relatively void-free structures, and their permeability is inversely proportional to crystallinity. The early-aged chlor-alkali electrolysis cell employed PFSA-based IEMs, which suffered from low ion selectivity and current efficiency. By contrast, the PFCA-based IEM is usually used as proton exchange membranes in fuel cells [86–88] and has excellent current efficiency, but is only suitable for producing alkali metal hydroxides with a maximum yield of 35% by weight due to its low ion flux and high operating voltage. PFSA and PFCA are usually combined into a double-layer IEM to improve performance. Operation conditions influencing membrane performances, such as current densities and water contents, need to be optimized to advance the performance of chlor-alkali cells.

Key Parameters

The more uniform the distributions of temperature and brine concentration in the area near the IEM, the longer the service life of the IEM. A high current density can increase

production capacity and reduce production costs. However, this condition speeds up the gas generation rate and causes the accumulation of the generated gas at the top of the cell, resulting in an increase in temperature. Given the increase in local temperature of electrolyzers, the internal channels of the membrane will be damaged, a phenomenon called the “membrane pinhole effect”. In addition, a pH gradient is built on the anode side surface of the membrane, whereas the salt concentration in the tank decreases. This condition will cause IEMs to blister, delaminate, and be permanently destroyed. A high operation current density will also increase the temperature of the ion membrane surface and the interior of the electrolytic cell. When the cell temperature is higher than 90 °C, the water in the electrolytic cell will be severely vaporized, and anolyte vaporization or boiling will deteriorate the performance of the ion membrane. Therefore, information about the distribution of cell temperature, membrane anode surface concentration gradient, and brine concentration is important to the operation, design, and development of highly efficient electrolyzers.

The water content in the membrane is determined by the nature and concentration of ion exchange groups, counterions, and the degree of cross-linking of the polymer. Two types of water absorption exist [89]: one is absorption by the film particles; the other is absorption by the combination of physical bonds and ions. The first type of water requires a very low heat; thus, it occurs at low temperatures, around 55–65 °C. The second type needs a slightly higher temperature. Structural properties, such as the equivalent weight of the polymer, free volume, the degree of aggregation of ionic clusters, or cluster size, will affect water absorption. The increase in water absorption will increase the distance

between ion groups in the cluster due to the expansion phenomenon, which weakens the membrane mechanical strength.

Mg^{2+} and Ca^{2+} impurities in the brine easily contaminate the ionic membrane, which reduces efficiency, increases energy consumption, and shortens the service life of the membrane [90]. Ca ions can combine with carbonate to form triangular CaCO_3 [9, 93]. This slow process will cause the efficiency of the electrolytic cell to gradually decrease. The state-of-the-art technology requires the use of an electrolyte containing calcium and magnesium below 20 ppb to enable the membrane function for over 4 years. Moreover, to prevent the formation of bubbles, industry operation often uses various techniques to cover a layer of mineral on the top of the membrane. However, the performance of the membrane in chlor-alkali electrolytic cells will degrade when the mineral layer detaches from the surface.

Advanced Membrane Design

Figure 7 shows the ion transport in a bilayer membrane. Under the long-term operation, particularly under abnormal conditions (such as failure of timely water supply in the cathode chamber, power interruption, reduction or interruption of brine feed, etc.), the composite membrane is easily delaminated, and blisters are formed between the two layers, resulting in increase in the operating voltage. The delamination between the sulfonic acid and carboxyl layers of the composite membrane is mainly due to the difference in their water permeability. The use of a blend of PFSA and PFCA as an intermediate layer between the sulfonic acid and

Fig. 7 Multicomponent ion transport in a bilayer cation-exchange membrane (reprinted from [91] with permission from Springer Nature)

carboxyl layers was proposed to minimize the difference in water transport between the two layers.

Wang et al. [92] studied the effect of blend layers with different ratios of PFSA to PFCA on the performance of composite membranes. The distribution morphology of the blend membrane has a great influence on its ion transport performance and water absorption capacity. The maximum amount of water absorption of PFCA is smaller than that of PFSA. However, the diffusion path of water in PFCA is straighter than that in PFSA. Thus, a large diffusion coefficient can reach equilibrium faster in the former. In addition, water absorption of the membrane in 32% sodium hydroxide solution is considerably less than that in deionized water, indicating that the highly concentrated sodium hydroxide solution significantly reduces the water absorption of the IEM in the electrolytic cell. As the content of PFCA in the blend film increases, the proton conductivity drops rapidly because the proton conductivity of sulfonate is higher than that of carbonate. The proton conductivity of PFSA is directly related to water content, and the increase in PFCA content will reduce the water content. The introduction of the blend layer can not only enhance the intermolecular binding force between PFSA and PFCA layers but also balance the water transfer. Given the different water permeabilities of the two materials, an interlayer stress will be generated due to the electro-osmotic water during the electrolysis process. The blend film can effectively reduce this interlayer stress, which increases its resistance to peeling damage and achieves long-term stability.

Electrolyzers

Membrane-Free Method

Given the above disadvantages of IEMs, membrane-less electrolysis was proposed as an alternative technology. The mercury electrolytic cell technology used in the early

chlor-alkali industry was a typical membrane-less process, but the high toxicity of mercury prevented its further development. However, the use of the previous mercury electrolysis cell implies that the reversible sodium-ion storage reaction can decouple the chlor-alkali process. Hou et al. [93] proposed the $\text{Na}_{0.44}\text{MnO}_2$ electrode for Na^+ insertion and extraction as a redox mediator (Fig. 8). The chlor-alkali process was decoupled into two separate steps: H_2/NaOH formation and Cl_2 generation. The first step is the cathodic HER ($\text{H}_2\text{O} \rightarrow \text{H}_2$) and the anode Na^+ deintercalation reaction ($\text{Na}_{0.44}\text{MnO}_2 \rightarrow \text{Na}_{0.44-x}\text{MnO}_2$), which produces NaOH in the electrolyte, as shown in Eqs. (6) and (8), respectively. The second step is the cathode Na^+ intercalation reaction ($\text{Na}_{0.44-x}\text{MnO}_2 \rightarrow \text{Na}_{0.44}\text{MnO}_2$) and the production of Cl_2 ($\text{Cl} \rightarrow \text{Cl}_2$) (Eqs. (2) and (9), respectively). Technically, the two-step reaction can be carried out in the same electrolytic cell. However, as the NaOH concentration increases, the CER process at the electrode will shift to the OER side reaction. Compared with membrane electrolysis, the Faraday efficiency of hydrogen production is higher (nearly 100%), whereas the efficiency of chlorine production is about 90.2%, which is lower than that of membrane electrolysis (97.4%).

Step 1:

Step 2:

Fig. 8 Schematic of the operation mechanism of a membrane-free electrolysis cell (reprinted from [93] with permission from *Nat Commun*)

Coupling with Other Systems

The ODC electrode can be employed as the cathode to optimize the electrolysis system and improve energy efficiency. A strategy is to use bifunctional electrodes to switch between HER and ODC electrodes at any time [94]. However, a certain downtime will occur when electrode cleaning is necessary. Alternatively, chlor-alkali electrolysis cells can possibly be combined with water electrolyzers or hydrogen fuel cells [94]. The O_2 produced in water electrolyzers can be used to directly supply ODC, thereby saving part of the cost. Coupled with the H_2 fuel cell, the generated electrical energy can be used to compensate for part of the electricity consumption in chlor-alkali electrolysis cells.

The combination of the chlor-alkali process with CO_2 reduction reaction (CO_2RR) into value-added products while achieving negative carbon emissions and mitigating the greenhouse effect has also been proposed. In a single CO_2 reduction process, CO_2RR occurs at the cathode [95], and the anode undergoes the OER process. CO_2RR accepts electrons to break the $C=O$ bonds and generates a series of basic anions (OH^- , HCO_3^- , and $HCOO^-$) [96], as shown in Eqs. (10–12), whereas the anode generates acid to neutralize the cathode products [95, 97–101]. Utilizing the CO_2RR process to replace the cathode HER in the chlor-alkali electrolytic cells, CO_2 reduction products, Cl_2 , and $NaOH$ can be obtained. At present, most electrolytic cells adopt a zero-gap configuration to minimize the ohmic loss of the electrolyte. The integration of CO_2RR and chlor-alkali can be achieved in an electrolytic cell similar to the H-cell, but this process

is limited by the slow diffusion of CO_2 in saturated solutions [62], and its current density is far below that used in practical applications.

The GDE structure and flow cell have been developed to overcome the slow CO_2 transport issue. In the GDE structure [62], CO_2 is supplied in a gaseous state, and the path of CO_2 diffusion to the catalyst is extremely short. Thus, its concentration is maintained in the catalytic layer of the cathode, thereby achieving a high current density. Liu et al. [102] carried out a CO_2RR experiment in 3.5 wt% (approximately 0.6 M) NaCl electrolyte with a GDE to simulate the seawater medium used in chlor-alkali electrolyzers (Fig. 9). The high formate faradaic efficiency of over 80% and a high formate production rate of $\sim 0.5 \text{ A/cm}^2$ have been achieved within more than 0.5 V potential range. Moreover, the highest formate selectivity of 95% was achieved in saltwater because the HER side reaction was deeply suppressed along with the increased local pH.

Fig. 9 Schematic model of **a** the chlor-alkali electrolyzer coupled with CO_2RR and **b** the performance with tin oxide catalysts converting CO_2 into formate (reprinted from [102] with permission from *J Mater Chem A*)

Conclusion and Outlook

The above discussion summarizes the research progress, including those of the anode, cathode, IEM, and electrolysis system, of chlor-alkali electrolyzers. Although the chlor-alkali industry has a history of over 100 years, it remains a high-energy-consuming industry today, consuming nearly 10% of global electricity every year. This industry can be improved from the following aspects.

For the anode reaction, the mechanism of CER/OER must be further understood. For example, combining modern experimental and theoretical methods to study anode activity and selectivity can provide further insights into the structure-performance relationship. The combination of theoretical modeling and modern characterization methods (such as X-ray spectroscopy) can help explore the details of the electrode reaction process and improve the selectivity and activity of the anode. For the cathode, currently, a huge amount of hydrogen as by-products is being vented to the atmosphere directly due to the insufficient market size to consume the hydrogen produced by the chlor-alkali industry. Moreover hydrogen generated above is usually mixed with impurities (water vapor, nitrogen, oxygen, and chlorine), which limits its usage. Further purification processes, such as pressure swing adsorption, can produce high-purity hydrogen, which has a large market in electronic industry, petrochemical industry, metal smelting, scientific research, and other fields. Particularly, large amount of pure hydrogen is needed to feed fuel cells to generate clean electricity to drive future hydrogen society.

For IEMs, one can design a self-cleaning membrane to avoid the accumulation of precipitation on the surface. The service life of the membrane can be extended by optimizing the operation conditions, such as the quality of brine. Moreover, the addition of circulating electrolytes can result in the uniform distribution of the temperature and concentration of the brine in the chlor-alkali pool. This condition can be realized by a reasonable electrolytic cell design, such as the introduction of an external forced circulation or installation of an inner weir, which cannot eliminate gas accumulation at the top of the anode chamber. The passage of gas and liquid into the separation chamber must be improved to enhance liquid exhaustion. Chlor-alkali electrolyzers can be coupled with other systems (such as fuel cells and CO₂ electrolyzers). These combined technologies need to be further evaluated based on the relationship between the values of different products from CO₂ reduction and energy consumption. Moreover, hydrogen, which is usually treated as exhaust gas in the chlor-alkali industry, may become the major fuel used on a large scale in the future as a promising clean energy.

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