Chemical Synthesis

Recent progress of enhanced bubble separation in alkaline water electrolyzer

Manuscript Draft

Manuscript ID: CS-2023-25
Manuscript Title: Recent progress of enhanced bubble separation in alkaline water electrolyzer
Manuscript Type: Review
Special Issue: 
Keywords: Alkaline water electrolyzer, bubble effect, external operation optimization, superhydrophilic and superaerophobic electrode, bipolar plates flow channel
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Funding Agency and Grant Number: National Key Research and Development Program of China, 2021YFB4000303; National Natural Science Foundation of China, 22090034

Abstract: Alkaline water electrolysis has a large industrial application and development potential in hydrogen energy owing to its high maturity and low cost. However, moderate energy efficiency, especially caused by bubble effect, inhibits their use for large-scale hydrogen production. To overcome this shortcoming, this review first analyzes the bubble effect and summarizes the external operation methods like external field intensification, fluctuation operation, and surfactant addition to the electrolyte to enhance bubble separation in the electrolyzer. Then, electrode and flow channel structure optimization, particularly superhydrophilic and superaerophobic electrodes, and flow channels with varying heights, square column arrangements, and inlet/outlet numbers are highlighted. Finally, future research directions in alkaline water electrolysis technology are suggested to advance the industrial application of large-scale alkaline water electrolysis.
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Keywords: Alkaline water electrolyzer, bubble effect; external operation optimization, superhydrophilic and superaerophobic electrode, bipolar plates flow channel

INTRODUCTION

Hydrogen energy plays a key role in the transition to a zero-carbon energy system that is cleaner, more sustainable, and lower in emissions. As a raw material for industrial production, hydrogen is widely used for oil refining, ammonia synthesis, methanol synthesis, and other chemical processes[1]. Among the world's total hydrogen production, hydrogen electrolysis accounts for only 4% due to its higher cost than fossil fuels. Nevertheless, electrolysis can reduce the cost of electrolytic water to hydrogen since it adapts to the discontinuous and unstable power supply characteristic of renewable energy systems, including wind, light, and water[2]. Connecting renewable energy to the grid by controlling the electrolytic water to hydrogen system can reduce renewable energy's intermittency, integrate multiple energy sectors, and improve energy power systems integration[3]. In this way, hydrogen production by electrolysis of water has received increasing attention.

An electrolyzer is the main production equipment of electrolytic water, which can be divided into three categories according to the electrolyte, namely alkaline water electrolyzer (AWE), proton exchange membrane electrolyzer (PEM), and solid oxide
electrolysis cell (SOEC). In terms of energy efficiency, the SOEC at 650-1000°C has the highest, but is still in the development phase\textsuperscript{[4]}. As of now, both AWE and PEM electrolyzers are commercially available, with PEM electrolyzers having an advantage in terms of operating pressures, load ranges, and footprints, while AWE electrolyzers are more cost-effective, have larger equipment sizes, and have a longer lifetime. In particular, AWE's single unit product size (MW scale) is larger than PEM's (kW scale), AWE's cost is about half that of PEM electrolyzers, and AWE lasts up to twice as long as PEM electrolyzers. Together, alkaline water electrolysis has greater industrial applicability and development due to its high maturity and low cost, and will continue to be the mainstream technology\textsuperscript{[5]}.

Despite its remarkable success, alkaline water electrolysis still faces some bottlenecks, such as energy inefficiency\textsuperscript{[6]}. One of the biggest reasons for energy inefficiency is bubbles, which produce high overpotentials and large ohmic voltage drops when they generate, cover, or disperse in the electrolyte.\textsuperscript{[7-9]} Hence, it is important to eliminate bubbles' effects and numerous studies have been undertaken to do so. To highlight the progress of bubble elimination, this review first discusses the bubble effect and external methods to aid bubble separation, such as adding external fields, fluctuating operation, and adding surfactants to the electrolyte. Following that, two key electrolyzer structures, electrodes and flow channels, are described to eliminate the bubble effect. Lastly, we discuss the perspectives that may lead to future advancements in alkaline water electrolysis.

**BUBBLE EFFECT**

The electrolysis of water produces gas at the interface of three phases: gas, liquid, and solid\textsuperscript{[8]}. Known as the bubble effect, the bubble effect leads to high overpotential and low energy efficiency. During water electrolysis, bubbles first form and adhere to electrode surfaces, and only once they reach a critical size can they be separated from
the electrode surfaces, resulting in bubble masking. As a result of the bubble masking effect, the electrode’s effective area is reduced, resulting in uneven current distribution and increased actual current density, thus increasing activation overpotential\(^9\).

Separated bubbles are dispersed in the electrolyte, increasing ion migration resistance and causing an increase in ohmic overpotential. The combined negative effects of the bubble effect inevitably increase the energy consumption of the electrolytic water.

Moreover, the bubble effect increases the energy efficiency of the electrodes as the current density increases.

According to Figure 1, the force analysis of the bubble on the electrode surface shows that the bubble is mainly affected by the upward buoyancy force \(F_b\) and the downward adhesion force \(F_a\) (gravity cannot be ignored), described by the following two Equations (1) and (2), respectively\(^{10}\).

\[
F_a = 2\pi R_b \sin \theta = \gamma 2\pi (R \sin \theta) \sin \theta \tag{1}
\]

\[
F_b = \frac{4}{3} \pi R^3 \rho g \tag{2}
\]

where \(R\) is the bubble radius, \(R_b\) is the radius of the inactive area, \(\theta\) is the bubble-electrode contact angle, \(\rho\) is the electrolyte density, \(\gamma\) is the electrode surface tension.

In the case where \(F_b = F_a\), \(R\) is related to \(\theta\) through the following relationship Equation (3):

\[
R \propto \sqrt{\gamma} \sin \theta \tag{3}
\]

**Figure 1.** Force analysis of the bubble\(^{10}\). This figure is quoted with permission from
According to the above equations, the size of the bubble leaving the electrode surface corresponds to the force of bubble adhesion $F_a$. The bubble adhesion force can be reduced by reducing the contact angle and electrolyte surface tension, allowing the bubbles to leave the electrode surface quickly and with a very small volume. When the bubble volume leaving the electrode surface is smaller, the bubble stays on the electrode for a shorter period, the bubble coverage is smaller, and the bubble effect is less noticeable on the electrode.

Furthermore, bubbles separated from the electrode and dispersed in the electrolyte will occupy the effective volume of the electrolyte, increasing its ion migration resistance and therefore increasing its ohmic overpotential. Bruggeman equation$^{[11]}$ states that the electrolyte conductivity $\sigma_e$ (S·m$^{-1}$) depends on gas volume fraction $\Phi_g$, as follows:

\[
\sigma_e = \sigma_0 \times (1 - \Phi_g)^{1.5}
\]

where $\sigma_0$ (S·m$^{-1}$) is the conductivity of the electrolyte without the influence of the gas. Clearly, the more uniform the distribution of bubbles in the electrolyte, the less effect it has on the conductivity. Thus, it is an effective method for reducing the electrolyte's ohmic overpotential by ensuring uniform bubble distribution.

**IMPROVEMENTS TO EXTERNAL OPERATIONS**

Based on the above analysis, external operation enhancements are applied to speed up the separation of bubbles from electrode surfaces, reducing bubble-induced energy loss. Following is a description of the specific methods, including the addition of external fields, fluctuating operation, and adding surfactants to the electrolyte.
When external field enhancement is added to the water electrolysis process, the bubble separation process is accelerated, and the total system resistance is reduced, thus reducing energy consumption\cite{12}. In most cases, the electrolyzer is enhanced by a magnetic field, since obtaining a stable magnetic field is easier, and introducing a magnetic field is as simple as placing the electrode between magnets. The magnetohydrodynamic force (Lorentz force) enhances electrochemical performance, as it aligns with bubble buoyancy to improve bubble escape, reduce ohmic polarization and increase current density (Figure 2A)\cite{13-15}. In addition, magnetothermal effects\cite{16} and electron spin selectivity\cite{17} could also contribute to hydrolysis through magnetic fields. In spite of this, magnetic field enhancement has some limitations, such as low field strength and high energy input, which prevent its further application on an industrial scale.

**Figure 2.** Effect of external field enhancement on bubble separation. A: convection created by magnetic fields of different directions, A1: $F_L$ (up), A2: no magnetic field, A3: $F_L$ (down)\cite{14}; These figures are quoted with permission from Hourng et al. B: effect of supergravity length on the evolutionary process of hydrogen bubbles, B1: normal gravity conditions, B2: a supergravity field\cite{18}; These figures are quoted with permission from Wang et al. C: mechanism of bubble elimination in ultrasonic
fields\textsuperscript{[19]}. This figure is quoted with permission from Shin et al.

Separation processes involving multi-phase systems can also be accelerated by supergravity fields. In water electrolysis, supergravity fields can enhance gas-liquid phase separation and interphase slip velocity, resulting in less bubble coverage on the catalyst surface and more hydrogen production (Figure 2B)\textsuperscript{[18,20]}. It was estimated that water electrolysis would save 9\%-17\% of energy at 0.5 A cm\textsuperscript{-2}. Cavitation, an effect of ultrasonic fields, can be very significant in separating bubbles as well\textsuperscript{[21]}. Cavitation bubbles rupture periodically, causing hydrogen or oxygen bubbles to accelerate from the electrode surface and electrolyte due to the violent stirring effect, which speeds up mass transfer on the electrode (Figure 2C)\textsuperscript{[19]}. Moreover, the ultrasonic field reduces reaction overpotential through additional free radical production\textsuperscript{[22]}. The supergravity fields and ultrasonic fields, however, may require large investments in industrial electrolysis equipment, as well as cause significant damage\textsuperscript{[23]}. 

\textit{Fluctuations}

Fluctuations on the electrode surface can reduce both bubble coverage and concentration polarization. Currently, pressure swings and pulsed power are primarily used to study fluctuations. According to Bakker et al.\textsuperscript{[24]}, brief pressure decreases accelerate bubble removal from electrodes and other parts, such as the diaphragm and polar plate, because bubble size rapidly increases. For pressure swings from 4 bar to 1 bar applied every 100-300 s in a rectangular electrochemical flow cell experimental rig, the voltage reduction is at most 0.1 V, increasing almost linearly with current density. A larger electrolytic system, however, requires more pressurization equipment and additional energy to pressurize the entire system.

An alternative pulsed power operation reduces or stops power energization
periodically to increase energy efficiency. By pulsing power, the diffusion layer on
the electrode surface can be reduced or eliminated, bubbles can leave the electrode
surface, and electrode surface reactants can be replenished\textsuperscript{[25]}. Using a high frequency
pulse voltage with a duty cycle, Nesrin Demir \textit{et al.}\textsuperscript{[26]} significantly increased
hydrogen production in an electrochemical water electrolyzer. A duty cycle of 50% and a frequency of 200 kHz at 6 V reduced energy consumption by 20-25%. While pulsed electrolysis improves energy efficiency, it does not sufficiently compensate for reduced productivity caused by ceasing current.

\textit{Surfactants}

When ionic or nonionic surfactants are added, the specific surface energy associated with bubble formation and growth is reduced, resulting in smaller bubbles and reduced bubble adhesion\textsuperscript{[27]}. Various surfactants, such as cetyltrimethylammonium bromide (CTAB)\textsuperscript{[28]} and isopropyl alcohol\textsuperscript{[29]}, can also enhance the adsorption of reactant ions at the electrode/electrolyte interface to improve hydrolysis. Surfactants, however, pose a problem. Organic compounds typically undergo oxidation more readily and react at lower potentials compared to water or hydroxides. This can contribute to an increase in current density and a decrease in potential upon the addition of surfactants. Furthermore, surfactants can form highly stable micro/nano-bubbles or droplets, which can make the separation of gas-liquid phases more difficult. As a result, greater input is required in the subsequent gas-liquid separator and gas scrubber to ensure complete gas-liquid separation.

\textbf{IMPROVEMENTS TO ELECTROLYZER STRUCTURES}

Although external operations can potentially improve bubble separation, there are still limitations, especially when it comes to industrial applications. Therefore, the design optimization of key components of alkaline water electrolyzers is crucial for scaling up the technology. In particular, the design optimization of electrode and bipolar plate
flow channels has received significant attention in current research. This is because these components play a crucial role in determining the performance and efficiency of the electrolyzer. By optimizing the design of these components, it is possible to improve the overall performance and reduce the cost of the electrolyzer. This is especially important for large-scale electrolyzers, where even small improvements in efficiency can have a significant impact on the overall cost and feasibility of the technology.

Electrodes

As the site where the electrolytic reaction occurs, the electrode is one of the most important components of an alkaline water electrolyzer. In electrode optimization, there are two types: structural optimization, where nickel electrodes remain active sites, and properties optimization, where nickel electrodes only serve as supports. (Note: Since space is limited, this review will only cover nickel electrodes, which are corrosion-resistant, low-cost, and have high stability, making them ideal electrode materials for industrial alkaline water electrolyzers. Although noble metal catalyst such as platinum and palladium can obtain excellent performance in electrolytic water through modulation\[^{30-32}\], their application in alkaline electrolytic water is restricted due to factors such as high cost, poor stability, and limited availability compared to nickel electrodes\[^{33}\].)

Structural optimization

To ensure sufficient active sites, fast electrochemical reactions require electrodes with a large surface area. Generally, porous electrodes are able to meet the requirement for a large surface area. Several studies have shown that nickel foam electrodes with porous structures reduce overpotential and increase current density in the electrolyzer\[^{34-36}\]. In nickel foam, however, a significant amount of bubbles is normally generated, causing significant resistance if the bubbles are not removed in a timely manner\[^{37,38}\]. According to Kim et al.\[^{39}\], the structure of a porous electrode did
influence bubble separation from the inside of the electrode. In Figure 3A1-A2, there was fabricated an asymmetric nickel foam electrode with different pore structures on each side, one having about 5 μm pores for electrochemical reaction sites, the other had about 100 μm pores for gas/electrolyte separation. On the small pore side of the electrode, hydrogen and oxygen molecules do not form bubbles at first, but they do so after diffusing through the pores to the large pore side, which makes their expulsion easier. A current density close to 0.5A cm$^{-2}$ was observed in electrochemical tests conducted at 80 °C and 1.8 V, much higher than reported in some literature and commercial devices. (Figure 3B) The method provides a new approach to optimizing the electrodes for alkaline water electrolyzers with zero gaps.

Figure 3. SEM pictures of the nickel electrode: A1: the surface with 5 μm pores, A2: the other surface with 100 μm pores$^{[39]}$; These figures are quoted with permission from Kim et al. B: current-voltage curve of the Ni electrodes$^{[39]}$; This figure is quoted with permission from Kim et al. SEM images of C1: an array of 20 μm ø Ni film and C2: an array of 20 μm ø Ni pillars$^{[40]}$; SEM images of prepared Ni micro-patterned electrodes: D1: cylindrical with large diameter, and D2: semispherical
structure\textsuperscript{[40]}; These figures are quoted with permission from Gates \textit{et al.}

Corresponding in situ optical microscope images: E1: cylindrical Ni microarray, Ni coverage: 39.9 \%, contact angle: 89.5°; and E2: semispherical Ni microarray, Ni coverage: 74.7 \%, contact angle 112.5°\textsuperscript{[41]}; These figures are quoted with permission from Wang \textit{et al.}. SEM images of the electrodeposited nickel foil and determined the PTFE coverage \textsuperscript{[42]}. G1-G4: side and H1-H4: top views of oxygen bubbles corresponding to PTFE coverage in alkaline water splitting experiments performed with porous electrodes\textsuperscript{[42]}. These figures are quoted with permission from Wang \textit{et al.}.

Alternatively, microstructures can be used to meet large surface requirements, but allow bubbles to escape as well\textsuperscript{[6]}. As an example, Paul \textit{et al.}\textsuperscript{[40]} used photolithography to fabricate hexagonal nickel electrode arrays with raised or recessed microstructures that corresponded with the size of oxygen bubbles generated by OER (Figure 3C1-C2). Compared to a flat nickel electrode, the micro-scale nickel recesses enhance mass transfer and activity, resulting in double the current density, bubble release, and a reduction in reaction overpotential. In Figure 3D1-D2, a variant of nickel electrodes with micropatterned structures was further investigated by Fujimura \textit{et al}\textsuperscript{[41]}. In situ observations of surface bubble behavior as well as contact angle measurements and electrochemical measurements (Figure 3E1-E2) indicated that micropattern coverage and shape affected the electrode surface's wettability, promoting bubble separation.

In addition to the aforementioned studies, researchers have also investigated the use of hydrophobic materials to improve electrode structures in order to control bubble formation and facilitate bubble separation and release\textsuperscript{[43]}. For instance, the use of polytetrafluoroethylene (PTFE) coatings on nickel electrodes has been found to be effective in this regard\textsuperscript{[44-46]}. The hydrophobic PTFE surfaces serve as collectors for dissolved gases, while the open nickel surfaces facilitate electrode reactions. From
Figure 3F1-F4, by increasing the coverage of PTFE on the surface of the porous nickel electrode, the surface becomes more hydrophobic, which can affect the coverage, size, and kinetics of bubbles that form on the electrode surface (Figure 3G1-G4 and H1-H4). In a 5 M KOH electrolyte with a current density of 1000 mA/cm², 20% PTFE coverage decreased the overpotential from 1.73 V to 1.58 V. This indicates that the use of hydrophobic materials can be a promising strategy for improving the performance and efficiency of alkaline water electrolysis systems.

Properties optimization

In contrast to the aforementioned strategies, properties optimization not only affect the surface structure but also act as active sites in place of nickel electrodes, with the nickel electrodes serving as support. Previous studies have reported that improvements in the performance of water electrolysis electrodes are mainly achieved by increasing the number of active sites, enhancing the activity strength of these sites, and reducing the impact of bubble effects. Gas bubble adhesion behavior can be flexibly tuned by modifying the electrode surface hydrophilicity and aerophobicity. It is also important to note that improving the hydrophilicity of electrode surfaces can enhance the contact between the electrolyte and the catalyst active center, resulting in the more efficient generation of active hydrogen and oxygen reaction intermediates. Additionally, having an aerophobic electrode surface can promote the rapid formation and release of smaller bubbles, which can prevent blockages of the catalytic active center due to smaller contact angles. These can lead to improved overall performance and efficiency of the alkaline water electrolysis system. Hence, current research on electrode design optimization focuses on developing advanced materials and surface coatings that exhibit these desirable properties.
Figure 4. The bubble behavior of superaerophobic and superhydrophilic electrodes\cite{56}. These figures are quoted with permission from Darband et al.

Sun's group\cite{50} first proposed the concept of "superhydrophobicity", they synthesized MoS$_2$ nanosheet array electrodes using hydrothermal method with excellent superhydrophobicity on Ti foil as the electrode substrate. The bubbles generated on the surface of MoS$_2$ electrodes with nanoarray structure have discontinuous gas-liquid-solid three-phase contact lines, which promote the bubbles to leave the electrode surface at a later stage and significantly improve the HER performance.
Figure 5. A: air-bubble contact angles under water (top) and static-water-droplet contact angles (bottom) for CoMoSx/NF, MoSx/NF, Pt/C, and NF. B: images of bubbles released at the surface of NF, CoMoSx/NF, and Pt/C for HER at a current density of 200 mA cm$^{-2}$. C and D: overall water splitting polarization curves of four electrodes and catalytic stability of CoMoSx/NF.\cite{57} These figures are quoted with permission from Wen et al.

Then Wen et al.\cite{57} prepared a bifunctional CoMoS$_x$/NF electrocatalyst by in situ metathesis reaction using nickel foam (NF) as substrate. The hierarchical nanostructures provided the electrode superhydrophilic and superaerophobicity properties, which promote the rapid release of bubbles from the electrode surface (Figure 5A-B). The catalyst is also abundant with catalytic sites through Co doping and exhibits excellent electrochemical activity and stability at high current densities.
As shown in Figure 5C-D, it has a current density of 500 mA cm\(^{-2}\) at a low voltage of 1.89 V under alkaline conditions and can maintain its activity without decay for 100 h. It provides a guideline for the development of an efficient catalyst for large-scale water electrolysis.

Up to now, transition metal-based catalysts based on NF electrodes, such as oxides, phosphides, sulfides, carbides and nitrides, have been widely researched and show high catalytic performance in alkaline water electrolysis. Some recent studies have shown that MXene, as a new type of transition metal carbon/nitride with two-dimensional structure, possesses richer active sites, larger active surface area and good hydrophilicity, which can improve the electrode conductivity and electrochemical stability during alkaline water electrolysis, and is a promising electrocatalyst or catalyst carrier.

The poor intrinsic electrocatalytic hydrogen evolution activity of MXene requires surface property modulation or hierarchical structure design of MXene, which can assist in the preparation of highly active and durable hydrogen evolution catalysts. Recently, our group\(^{[58]}\) has prepared superaerophobic Ru/c-Ti\(_3\)C\(_2\)/NF 3D electrodes by hydrothermal methods in situ (Figure 6A). The two-dimensional material MXene (Ti\(_3\)C\(_2\)) was modified through CTAB (cetyltrimethyl ammonium bromide) to increase layer spacing and accelerate electron transport, referred to as c-Ti\(_3\)C\(_2\). As a result of the addition of modified c-Ti\(_3\)C\(_2\), the electrode surfaces of c-Ti\(_3\)C\(_2\)/NF and Ru/c-Ti\(_3\)C\(_2\)/NF were almost submerged in water, with a contact angle near zero. Meanwhile, the electrodes' bubble contact angles were 169° in the superaerophobic range, respectively. Therefore, the modified nickel electrodes were considerably improved in terms of hydrophilicity and superaerophobicity (Figure 6B1-B4). The bubble size and bubble release rate on the electrode surface was tracked in situ by a particle imaging velocimetry system and high-speed framing camera system. As can
be seen in Figure 6B1-B4, compared to the NF electrode, the bubble size decreased sharply from 300 μm to about 60 μm after deposition on the nickel foam surface with c-Ti₃C₂, and the flow field velocity near the electrode increased from 0.8 mm s⁻¹ to 3.0 mm s⁻¹, while the bubble size on the surface of the prepared Ru/c-Ti₃C₂/NF electrode was only about 40 μm, and the local flow field velocity can reach 7.0 mm s⁻¹. The main reason is that due to the introduction of the two-dimensional material c-Ti₃C₂, the superaerophobicity is improved and bubbles generated by the electrode are rapidly released into the electrolyte. In Figure 6C1-C2, the overall water splitting test was used to the Ru/c-Ti₃C₂/NF electrode, the cell voltage was only 1.53 V at a current density of 10 mA cm⁻² and no decay for 20 h, compared with 1.58 V for the commercial Pt-C/NF and RuO₂/NF coupled electrodes. Based on the above results, it is shown that the superhydrophilic and superaerophobic properties of the 3D folded structure of Ru/c-Ti₃C₂/NF electrode facilitate the wetting of the electrolyte and the timely release of bubbles at high current densities, thus improving the mass transfer of the catalytic electrode and the electrolytic water hydrogen production activity and stability.

Figure 6. A: the synthesis process of Ru/c-Ti₃C₂/Tx/NF electrode; B1-B4: the contact angles of water droplets and underwater contact angles of gas bubbles, the digital images of bubble generation behavior and the corresponding fluid velocity vector field of the electrolyte on NF(B1), Ru/NF(B2), c-Ti₃C₂/NF(B3), and Ru/c-Ti₃C₂/NF(B4) electrodes; C1: overall water-splitting performance of Ru/c-Ti₃C₂/NF//Ru/c-Ti₃C₂/NF and RuO₂/NF//Pt-C/NF at 5 mV s⁻¹ in 1.0 M KOH; C2:
durability of Ru/c-Ti$_3$C$_2$/NF//Ru/c-Ti$_3$C$_2$/NF and demonstrated by chronoamperometry at 10 mA cm$^{-2}$[58]. These figures are quoted with permission from Zhang et al.

It was found that Ru/c-Ti$_3$C$_2$/NF 3D electrode exhibited excellent superhydrophilic performance at low current densities, while the stability of Ru/c-Ti$_3$C$_2$/NF electrode was relatively poor at high current densities (500 mA cm$^{-2}$). It is mainly because at high current density, due to the overwhelming reaction, a large number of bubbles will be generated on the electrode surface leading to catalyst detachment, increased interfacial resistance and reduced mass transfer efficiency. In order to solve the above problems, the modification process of the electrode surface needs to be improved. Therefore, we enhanced the interaction between Ti$_3$C$_2$ and nickel foam surface using electrodeposition technique in the next study[59]. The electrodeposition technology can significantly improve the interaction between the catalytic layer and the conductive substrate, which is beneficial to resist the stress generated by bubble detachment and ensure the stable performance of electrolytic water under high current density[60]. Our group Kong et al.[61] based on previous research, developed a novel and simple strategy to modulate the interaction between Ti$_3$C$_2$ and nickel foam surface using electrodeposition technique in Figure 7A and B1-C1, which can improve the stability of its deposition on nickel foam surface. When Ti$_3$C$_2$ was electrodeposited, the hydrophilic and aerophobic properties of Ti$_3$C$_2$/NF electrodes were improved with water contact angle and bubble contact angle of 90° and 149°, respectively. By further hydrothermal treatment of Ti$_3$C$_2$/NF to form Ni(OH)$_2$ nanoarrays, the corresponding water contact angle of TiO$_2$/Ni(OH)$_2$/NF and Pt/TiO$_2$/Ni(OH)$_2$/NF electrodes was close to zero, and the bubble contact angle reached 164° and 171° (Figure 7C), respectively, which obviously had superhydrophilic and superaerophobic properties. Based on the above results, it is shown that the Ti$_3$C$_2$-assisted preparation of Ni(OH)$_2$ nanoarrays can significantly improve the superhydrophilic and superaerophobic properties of the catalytic electrodes. The overpotential required for the
Pt/TiO$_2$/Ni(OH)$_2$/NF electrode is only -107, -145, and -184 mV at current densities of 500, 1000, and 1500 mA cm$^{-2}$. Meanwhile, it can operate stably for 12 h at high current densities of 500, 700, and 1420 mA cm$^{-2}$ (Figure 7D), realizing stable operation of alkaline water electrolyzer at the high current density.

**Figure 7.** A: the synthesis process of Pt/TiO$_2$/Ni(OH)$_2$/NF nanosheet arrays and B1-B2: corresponding SEM image; C: underwater contact angles of water droplets and the contact angles of gas bubbles on TiO$_2$/Ni(OH)$_2$/NF, Pt/TiO$_2$/Ni(OH)$_2$/NF as well as Pt/TiO$_2$/Ni(OH)$_2$/NF after HER stability test, respectively; D: corresponding from left to right, top to bottom: OER LSV curves and corresponding Tafel plots for NF, Ti$_3$C$_2$/NF, TiO$_2$/Ni(OH)$_2$/NF, RuO$_2$ and Pt/TiO$_2$/Ni(OH)$_2$/NF. Overall water splitting LSV curves for Pt/TiO$_2$/Ni(OH)$_2$/NF couples and commercial Pt/C and RuO$_2$ couples and stability test at 500 and 1000 mA cm$^{-2}$[61]. These figures are quoted with permission from Zhang *et al.*

These studies construct electrodes with superhydrophobic and superaerophobic properties, which greatly promote the release of surface bubbles and provide a reliable way for the contact between electrolyte and catalytic active sites, the OER and HER.
electrochemical performance can also be improved. In future studies, the effects of
different electrode surface morphology and wettability on gas kinetics need to be
further investigated to reduce the accumulation of bubbles on the electrode surface
and improve the efficiency of OER/HER.

Bipolar plate flow channels

Another key component of the electrolyzer is the bipolar plate, which supports the
electrodes, conducts electrons and connects adjacent cells in the stack[62]. Moreover,
its flow channel structure promotes uniform electrolyte distribution in the electrolytic
chamber[63]. Electrolyzer performance can be adversely affected by gas accumulation
on electrodes[37,38]. Proper flow promotes the timely discharge of bubbles from the
electrode, and the uniformity of gas phase distribution affects the electrolyte’s
conductivity[62]. As a result, designing a flow channel is an extremely important part
of designing an electrolyzer.

Flow channel effects require a detailed study of the multiphase flow field within the
electrolyzer, which is not possible with common optical testing techniques because of
its hermetic nature. Consequently, multiphase flow and reaction behavior of
electrolytic cells have been simulated numerically using computational fluid
dynamics (CFD)[64,65]. Due to the strong nonlinearity of the Euler-Euler k-ε turbulence
model, the turbulent variables involved in the two-phase flow greatly increase the
degrees of freedom of the model. In a more complex three-dimensional electrolyzer
structure, the coupling of the Euler-Euler two-phase turbulent field and electric field
is more difficult to converge. Thus, little is known about the bipolar plate flow
channel structure or the combination of the bipolar plate and electrode in the zero-gap
alkaline electrolyzer. Hyunchul Ju et al.[66] and Fang et al.[67] established three-
dimensional two-phase zero-gap alkaline water electrolysis models with straight-type
(Figure 8A-C) and ring cross-type (Figure 8D-F) flow channel structures,
respectively. They evaluated the effects of two-phase flow initiation and bubble coverage. Through the simulations, it was possible to determine the effects of operating parameters such as voltage, electrolyte flow, and temperature on gas distribution and current density distribution. There was no attention paid to the effect of change in flow channel structure on electrolysis. In a study by Wong et al.\textsuperscript{[68]}, the bubble behavior in a single serpentine flow channel was investigated by simulation, and the flow state around square and rounded bends of a single serpentine flow channel was examined and compared in terms of velocity and pressure drop (Figure 8G-I). Due to its smaller low velocity region and higher pressure stability, the rounded bend provided better bubble separation from the electrode than the square bend. According to Wong et al., even small changes in flow channel structure had a large effect on electrolysis cell flow state. It is therefore very important to optimize the flow channel structure to promote bubble separation, and more in-depth research is necessary to accomplish this.
Figure 8. Straight-type flow channel[66]: A: computational domain and mesh configuration of a zero-gap AWE cell; B and C: contours of H₂/O₂ molar concentration over the plane cutting across the center: B1 and C1: $v_m=0.1\, \text{m/s}$, B2 and C2: $v_m=0.01\, \text{m/s}$; These figures are quoted with permission from Fang et al. Ring cross-type flow channel[67]: D: three-dimensional structure of the electrolyzer cell; E: distribution of hydrogen and oxygen in the flow channel of anode and cathode; F: the uneven distribution of current density of the catalyst due to the bubble-effect ($E_{\text{cell}} = 2.1\, \text{V}$); These figures are quoted with permission from Shen et al. Single serpentine flow channel[68]: G: geometry and boundary conditions of the computational domain; The flow state around square (H) and rounded (I)bends. These figures are quoted with
permission from Wong et al.

There are different types of flow channels, each with its own advantages and disadvantages. The flow channels of an industrial alkaline water electrolyzer must be easy to process and capable of handling high pressures and flows. Square column flow channels have grooves formed by protruding square columns that allow the electrolyte to flow through. As a result of this structure, high flow rates are possible in the electrolyzer, resulting in uniform distribution of the electrolyte and efficient transport of bubbles generated in the nickel foam electrodes while having a lower pressure drop\(^\text{[62]}\). As a further step toward optimizing this structure, our group evaluated the effects of different square column flow channel structures on the gas distribution and electrolysis performance of an alkaline electrolyzer. Simulating various parameters on the I-V characteristic curve and hydrodynamic characteristics allowed us to determine the optimal structural parameters. As shown in Table 1, sixteen different geometric models of alkaline electrolyzers were constructed, and their representative models were shown in Figure 9A-F. Parameters considered included flow channel height (h_ch), arrangements of square columns, and the number of flow inlets and outlets in the electrolyzer\(^\text{[69]}\).

**Figure 9.** Construction of representative geometric model of alkaline electrolyzers\(^\text{[69]}\), A: G-2.5-T-0-3-1, B: G-2.5-T-2-3-1, C: G-2.5-S-0-3-1, D: G-2.5-T-0-3-3, E: G-2.5-T-
By deepening the flow channel, we found that lye distribution is more uniform, and the gas is removed more quickly (Figure 10A-C). This resulted in a lower voltage compared to the electrolyzer with a small flow channel height (Figure 10M). After that, the number of flow inlets and outlets, as well as the arrangement of square...
columns, were examined for their impact on electrolyzer performance. There was evidence that triangular channels could result in more uniform gas distribution, which mitigated bubble effects (Figure 10I-J). To combat the inlet circulation issue and uneven fluid distribution resulting from a single inlet and outlet, a multi-port electrolyzer with high flow was used to increase the flow rate in the side chamber, reduce the dead zone in the middle flow field, and lower the cell voltage significantly (Figure 10N). It is particularly noticeable at high current densities.

**Figure 10.** Effects of structural parameters on the performance of alkaline electrolyzer[^69], A: mixture velocity of G-2.25-T-0-3-1, B: mixture velocity of G-2.5-T-0-3-1, C: mixture velocity of G-3-T-0-3-1, D: mixture velocity of G-2.5-S-0-3-1, E: mixture velocity of G-2.5-T-0-3-3, F: mixture velocity of G-2.5-T-0-3-3, G: gas volume fraction of G-2.25-T-0-3-1, H: gas volume fraction of G-2.5-T-0-3-1, I: gas volume fraction of G-3-T-0-3-1, J: gas volume fraction of G-2.5-S-0-3-1, K: gas volume fraction of G-2.5-T-0-3-3, L: gas volume fraction of G-2.5-T-0-3-3, M: cell voltage of different channel height, N: cell voltage of different number of flow inlets and outlets. This figure is quoted with permission from Zhang et al.
To leverage the advantages of the multi-port design, the channel height and column spacing of the multi-port electrolyzer were further examined. There was a significant impact of the spacing between the conductive columns in multiple inlet and outlet electrolyzers. When this spacing is increased, the central flow rate of the KOH aqueous solution in the channel and the normal flow rate of the electrode surface of the cell could be effectively increased (Figure 11A-H), reducing bubble effects and lowering cell voltage. Of the various types of electrolyzers, the electrolyzer G-2.5-T-0-5-3 demonstrated the best performance in terms of improving the normal flow rate and reducing the cell voltage (Figure 11J).

The electrolyzers with conductive columns shown above demonstrated that a multi-port electrolyzer with wide spacing between conductive columns could enhance rapid bubble detachment and reduce alkaline water electrolysis voltage requirements. Future studies should investigate the scaling-up effects of different flow channel structures to provide more reliable and economical model design tools for alkaline water electrolysis.
Figure 11. Effects of channel height and column spacing on the performance of multi-port electrolyzers\textsuperscript{[69]}, A: mixture velocity of G-2.5-T-0-3-3, B: mixture velocity of G-2.5-T-0-5-3, C: mixture velocity of G-2.5-S-0-5-3, D: mixture velocity of G-2.5-S-0-7-3, E: normal velocity of electrode surface of G-2.5-T-0-3-3, F: normal velocity of electrode surface of G-2.5-T-0-5-3, G: normal velocity of electrode surface of G-2.5-S-0-5-3, H: normal velocity of electrode surface of G-2.5-S-0-7-3, I: cell voltage of multi-port electrolyzers under different channel height, J: cell voltage of multi-port electrolyzers under different column spacing. This figure is quoted with permission from Zhang et al.

CONCLUSION AND OUTLOOK

This review analyzes the negative effects of bubbles inside alkaline water electrolyzers and highlights recent research progress on improving bubble separation,
primarily by optimizing external operation and electrolyzer structure. Improvements, such as adding external fields, fluctuating operation, and adding surfactants to the electrolyte, as well as optimizing electrode structures and designing functional electrodes and flow channels, have been discussed in detail. Electrodes and flow channels are the main equipment of electrolyzers, and show some significance in improving electrolysis efficiency and electrolysis performance.

Clearly, bubble separation is progressing, but challenges remain. In order to reduce the negative effects of bubbles and make alkaline water electrolysis cost-effective and energy-saving, the following are some directions to investigate. For instance, the main focus of most researchers at present is on adjusting the wettability of electrode surfaces and designing electrode structures to separate bubbles from electrode surfaces. Nevertheless, bubbles are generated preferentially in the pores or uneven areas of the electrode surface, and the nucleation sites are specific. Observing how bubbles form on electrode surfaces would help separate bubbles by removing them from easily accessible locations. Alternatively, capillaries could produce hydrogen from alkaline water by delivering KOH solution to the porous electrode surface, without producing bubbles. Also, the flow channel structure, especially for large-scale alkaline water electrolyzers, should be studied in detail and rationally designed. There has not been much exploration of this front, which may be a promising direction for future research.

DECLARATIONS

Authors’ contributions

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Availability of data and materials
Not applicable.

Financial support and sponsorship
The work was supported by the National Key Research and Development Program of China (No. 2021YFB4000303) and the National Natural Science Foundation of China (No. 22090034).

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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