

Review

A Bibliometric Analysis on Pulsed Electrolysis: Electronic Effect, Double Layer Effect, and Mass Transport

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Abstract: Pulsed electrolysis endowed merits of high current density, low energy consumption, and simple operation; thus, a booming in their publication numbers has been witnessed in recent years. In this review, we aim to summarize the state-of-the-art pulsed current/potential strategy to enhance electrochemical reactions, such as oxygen reduction reactions (ORR), CO₂ reduction (CO₂RR), CO reduction (COR), etc. It begins with historic analysis of pulsed electrolysis via a bibliometric method, aiming at providing a progress over the course of around 40 years in a quantitative way. Then, the definition along with its influence of electronic effect, double layer effect and mass transport have been reviewed based on a mechanism point of view for the first time. To sum up the review, several current challenges and future prospects of pulsed electrolysis have provided for the future smart design of electrochemical process.

Keywords: pulse electrolysis; mass transport; electrical double layer (EDL); electronic effect; electrochemical CO₂ reduction (CO₂RR)



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1. Introduction

Due to the global energy crisis and environmental pollution, the development of clean, efficient, and renewable energy systems is urgent [1–4]. Among these, electrochemical technology stands out as a novel and eco-friendly approach due to its remarkable adaptability and ease of control. This technology has garnered significant attention, particularly in the domains of water electrolysis [5–9], CO₂ reduction [10–12], H₂O₂ production via oxygen reduction reaction (ORR) [13,14], pollutant decomposition [15–17], and metal deposition [18–20], among others. However, it still suffers from high energy consumption [21,22] and low current efficiency [23]. In fact, these problems arise from a mismatch between mass transport conditions and electron transfer at the electrode/electrolyte interface, as indicated in Equation (1) [24–27]. As a recent deep understanding of the electrical double layer from in situ spectroscopic techniques and computational techniques, its dynamic structure [28], electrolyte, pH, buffer strength, and ion effects [29] in the double layer could both effect the electron transfer and mass transport as a recent deep understanding of electrical double layer from in situ spectroscopic techniques and computational techniques, which terms as double layer effect. As a consequence, the electrochemical rate is a joint action by a complex interplay among electrode surface structure, double layer effects (electrolyte, pH, buffer strength, ion effects), and mass transport conditions.

$$k = k_{het} \times [R] \quad (1)$$

where k is the reaction rate constant, k_{het} is the electron transfer rate on the surface, $[R]$ is the reagents concentration in the vicinity of the cathode.

In recent years, a series of works have concentrated on the design of functional catalysts/cathodes to boost electron transfer rate (k_{het} in Equation (1)) via electronic effect

regulation; then, the reaction rate could be improved. For reactions involving gas as reagents, such as oxygen reduction reaction, electrochemical CO₂ reduction, etc., diverse strategies have been proposed to alleviate the low mass transport limitation imposed by their low solubility in the aqueous electrolyte, including pressurized cell [30,31], rotary electrode [32], microbubble-enhanced electrode [33], etc. However, as discussed above, a joint regulation of electron transfer, double layer effect, and mass transport conditions could be a more promising way to boost reaction rate from mechanism views than the high energy consumption and low current efficiency concerns are more likely to be lessened [34]. Among the various proposed methods, pulse electrolysis has recently emerged as a promising strategy. It can regulate electronic effects [35,36], perturb the electrical double layer [37], and enhance mass transport [38]. As a consequence, it has been applied in diverse fields, like hydrogen production [39–41], CO₂ reduction [42,43], environmental pollutant removal [44,45], and electrodeposition [46]. However, a comprehensive review summarizing the impact of pulse electrolysis from a mechanistic perspective, encompassing electronic effects, double-layer phenomena, and mass transport, is still lacking. Pulse electrolysis have been extensively investigated in recent years as highlighted in Figure 1, making it is necessary to update the latest development to analyze the novel trends of the pulse electrolysis. Herein, a timely and comprehensive review is highly desired to cover the state-of-the-art advances. For the first time, in this review, we intend to summarize the advances of pulsed current/potential strategy to promote electrochemical reactions into three aspects from a mechanism perspective: electronic effect, double layer effect and mass transport effect. Prior to these aspects, a historic analysis of pulsed electrolysis via a bibliometric method is first performed, aiming at providing a progress over the course of almost 20 years in a quantitative way. Afterward, the effect of pulsed electrolysis was summarized from three approaches (electronic effect, double layer effect and mass transport) with examples in electrochemical CO₂ reduction, oxygen reduction reactions and CO reduction were used. Finally, several current challenges and future prospects are presented, in the last section along with introduction of our vision of future directions in pulse electrolysis.

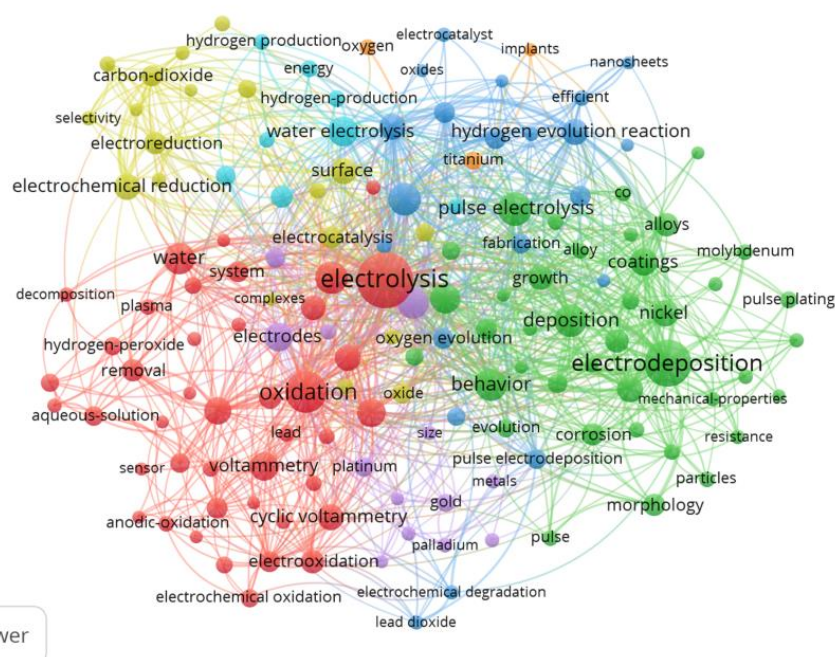


Figure 1. Cont.

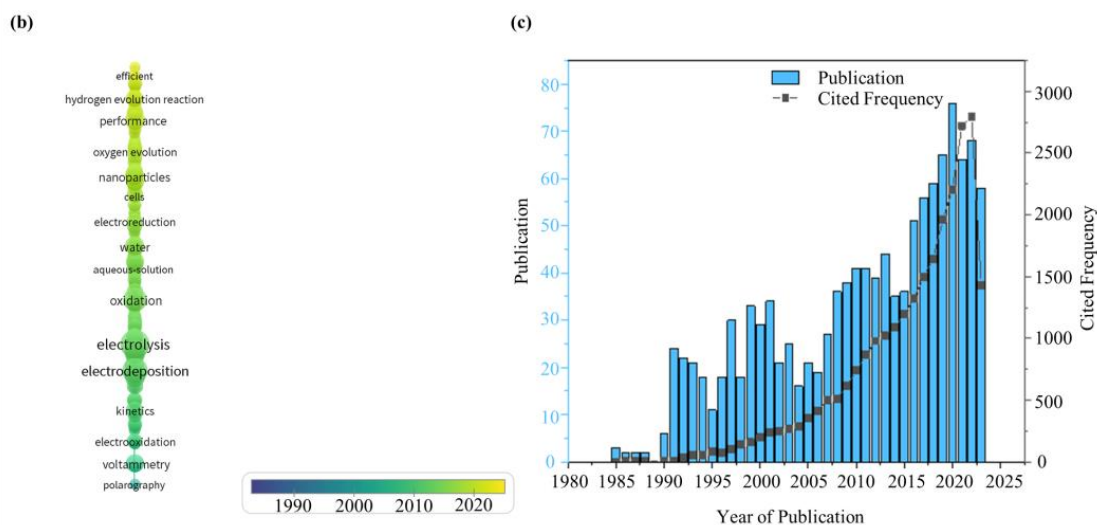


Figure 1. A meta-analysis of the literature on pulse electrolysis, where a database was extracted on 1 August 2023. Co-occurrence network (a) and year variation chart (b) of the top keywords in the pulsed electrolysis from 1985 to 2023 analyzed using VOSviewer. Statistical results (c) of pulse electrolysis literature were published annually from 1985 to 2023.

2. Historical Analysis of Pulsed Electrolysis via a Bibliometric Method

A number of 1388 publications were retrieved from the Web of Science Core Database using “pulsed electrolysis” as keywords between 1985 and 2023. It remained 1209 articles with 147 keywords extracted from publications after removing less relevance to pulsed electrolysis. Here, only the publications (reviews and scientific papers) in English were individually selected after careful analysis, while communications and conferences, along with book chapters, were excluded. Figure 1a,b was plotted via VOSviewer software (VOSviewer version 1.6.18)—a bibliometric method to provide a comprehensive understanding of the development of pulsed electrolysis research, importing database from the Web of Science core databases described. And Figure 1c showed that statistical results of pulse electrolysis literature were published annually from 1985 to 2023. With the help of bibliometric analysis, the development of pulsed electrolysis could be divided into three main stages, as given in Figure 2 and below:

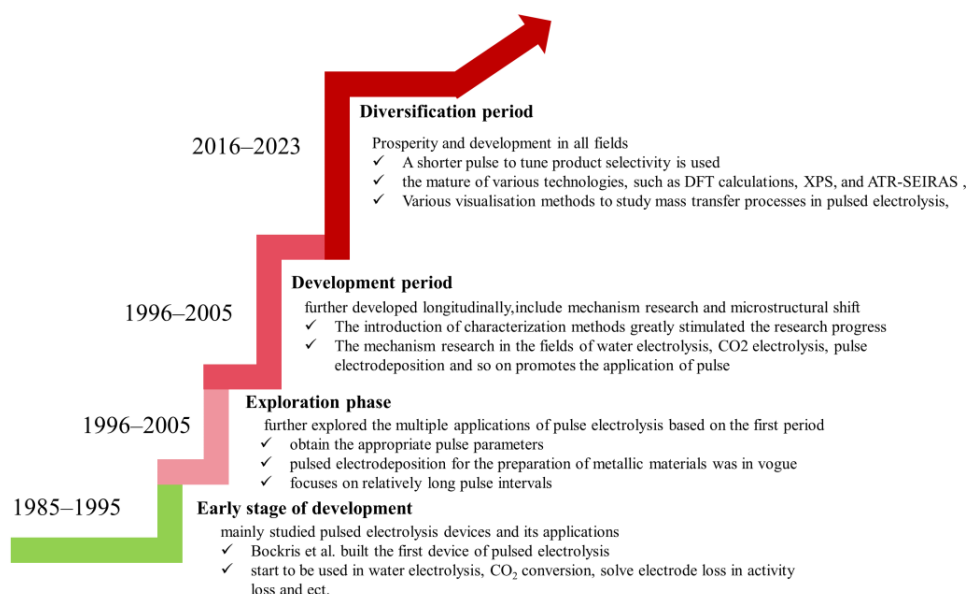


Figure 2. Historical development of pulse electrolysis between 1985 and 2023.

(1) Early stage of development: 1985–1995

At its very first stage, between the years 1985 and 1995, researchers mainly studied pulsed electrolysis devices and their applications [47–52]. For example, Bockris et al. (1985) installed the first pulsed electrolyzer and extended it into the application of water electrolysis [40,53]. Still, in 1989, pulsed electrolysis was further utilized for the conversion of CO₂. However, its electrode loss in catalytic activity failed to be solved until 1990 using a pulsed anodic treatment [54,55]. In 1993, Ryuichi Shiratsuchi et al. [43,56] conducted further research on pulsed electrochemical reduction in CO₂, comparing the effects of different catalysts, and Shaaban et al. [57] investigated the influence of different duty cycles. In addition, the detachment of bubble via pulsed electrolysis was also investigated during its first period [40,58,59].

(2) Exploration and development period: 1996–2015

This phase could be described as the exploration and development phase of pulse electrolysis, and it could be divided into two sub-phases. One is the exploration phase from 1996 to 2005, and the other is the rapid development phase between 2006 and 2016. From the exploration phase, the main key words derived from bibliometric analysis (Figure 1a) were electrolysis, electrodeposition, reduction, voltammetry, deposition, oxidation, pulse-radiolysis, kinetics, water, etc. However, there are relatively few links between these keywords, suggesting an infant period of pulse electrolysis. At this stage, researchers have further explored the multiple applications of pulse electrolysis based on its first periods, such as pulse electrolysis of water, CO₂, pulse-radiolysis, electrodeposition, and oxidation. Moreover, the appropriate pulse parameters in different applications have been investigated and confirmed the advantages of pulse over constant potential electrolysis [60–62]. A representative work in this stage was pulsed electrodeposition for the preparation of metallic materials [46], where the merits of accelerating the deposition of metals, improving current efficiency, and producing metallic materials with a dense structure and a smooth and bright finish have been found. The pulsed potential approach at this stage still focuses on relatively long pulse intervals (i.e., seconds to minutes), and the roles of pulsed potential in preventing catalyst deactivation were highlighted [63].

From 2006 to 2015, some new keywords emerged, for example, surface, mechanism, copper, films, nanoparticles, and microstructure, indicating a shift towards more in-depth investigations in the field of pulsed electrolysis. Additionally, both mechanism investigation and microstructural shift could be seen in this stage. Researchers began utilizing tools, such as XPS and SEM [64,65], to study microstructural changes on the pulsed coatings surface, aiming to elucidate its formation mechanism. For instance, Gao et al. [66] investigated different deposition parameters on the microstructure of Ni-Co pulse plating. Additionally, the great attention for electrochemical CO₂ reduction, particularly Cu catalyst [67], still keeps, while pulsed electrolysis is further used in water treatment [68,69], depositing metals like nickel, gold, copper and alloys using electroplating [70,71], and production of thin films [72,73].

(3) Diversification period from 2016 to 2023

The keywords in this phase are diverse, including electrolysis, performance, oxidation, degradation, water, electrodes, nanoparticles, hydrogen evolution reaction, oxygen evolution reaction, electrodeposition, degradation, etc. As shown in Figure 1a,b, a reduction in the variation in the weight of keywords and a tight link of keywords could be observed in the keyword co-occurrence diagram with a smaller diameter of the circle, indicating that pulse electrolysis presents divers directions. Notable recent discoveries are given:

- (a) A shorter pulse to tune product selectivity is used, especially for electrochemical CO₂ reduction to convert CO₂ into the high-value C₂₊ product [74]. To our knowledge, the first study on sub-second pulses was reported by Kumar et al. in 2016, who confirmed millisecond (square-wave) pulses boosted the selectivity of CO₂R on Cu electrodes [75]. The influence of adsorbed species on the electrode could be one

reason to improve selectivity when pulsed electrolysis was used [75]. Additionally, HER inhibition could be another factor in boosting selectivity during pulsed CO₂RR electrolysis. Ding et al. [76] provided a new perspective on the mechanism of pulsed electrocatalysis to promote H₂O₂ production via 2e[−]-ORR;

- (b) In the meantime, with the advancement of various technologies as the mature of various technologies, researchers used DFT calculations, XPS, and ATR-SEIRAS to study the changes in the electrode surface and electrolyte during pulsed electrolysis. For example, Zhang et al. [77] proved that the low-frequency asymmetric pulse strategy could modulate the Cu oxidation state using ex situ spectroscopy (XPS, AES and XANES) and, in situ XANES coupled with in situ ATR-FTIR/Raman and DFT calculations.
- (c) Various visualization methods have been developed to study mass transfer processes in pulsed electrolysis, such as differential electrochemical mass spectroscopy (DEMS) [78], a micromachined electrochemical cell (MEC) combined with a laser scanning confocal microscope (LSCM)-fluorescence coupled detection system (MEC-LSCM) [79].

3. Definition of Pulsed Electrolysis and Its Key Parameters

In general, pulsed electrolysis has been defined as the electrolytic process controlled using a pulsed power instead of constant current/potential. There are two types of pulsed operation: voltage pulses and current pulses [37]. In Figure 3a,b, the curves depict voltage and current over time. The on-time (t_{on}) refers to the pulse being active, while the off-time (t_{off}) is no pulse current/voltage applied. On-voltage and off-voltage represent the voltage values during the turn-on and turn-off periods. Similarly, the on-current and off-current correspond to the current during the turn-on and turn-off phases of the current pulse. Pulse period (t), which is the reciprocal of the pulse frequency (f), is the sum of on-time (t_{on}) and off-time (t_{off}). Duty cycle (r) is the ratio of pulse time to the total time, expressed by Equation (2).

The total current consists of the faradaic current (j_F) and the capacitive current (j_c) as expressed by Equation (3). The j_F is produced by the transfer of electrons through oxidation (or reduction) reactions at the electrode interface, and the current time-behavior is given as Equation (4) [49], while j_c -called “non-Faraday current” is caused by the charging or discharging of the electric double layers (EDL) (Equation (5)) [49].

$$r = \frac{t_{on}}{t}, \quad (2)$$

$$j_t = j_c + j_F, \quad (3)$$

$$j_F = j_0 \left(\exp\left(\frac{azF\eta}{RT}\right) - \exp\left(-\frac{(1-a)zF\eta}{RT}\right) \right) \quad (4)$$

$$j_c = \frac{dQ}{dt} = \frac{d\eta}{dt} C \quad (5)$$

where j_0 is the exchange current density, a is the constant in the Tafel equation, z is the ionic charge, F is the Faraday constant (96,500 C (g equiv)^{−1}), η is the overpotential, R is the constant (8.314 L·kPa/(K·mol)) and T the length of the pulse (on time). Q is the charge of the capacitor, C is the capacitance of the double layer, t is the real time in Equation (5), and the pulse period in Equation (2).

For voltage pulses, Figure 3a shows the time curves of voltage and current. The capacitive current exhibits a gradual decline to zero, while the faradaic current fraction progressively increases until it reaches the peak voltage. This phenomenon stems from the gradual charging of EDL until it reaches its full capacity. During the off-time, a distinct off-voltage threshold is evident, signifying a lack of chemical reactions. At this juncture, the

faradaic current remains constant, and the total current is solely dictated by the discharge of the EDL. There is a detailed investigation of the first applied pulse under different pulsed periods with a 50% duty cycle [80]. In Figure 3c, the reduction in the width results in an increase in the average on-current. Additionally, when the pulse width exceeds 1 ms, a shorter width leads to a decrease in the off-current during off-time. The authors calculated an EDL charging time of 3.2 ms and confirmed the dominance of capacitive processes for pulse widths ranging from 1 to 10 ms.

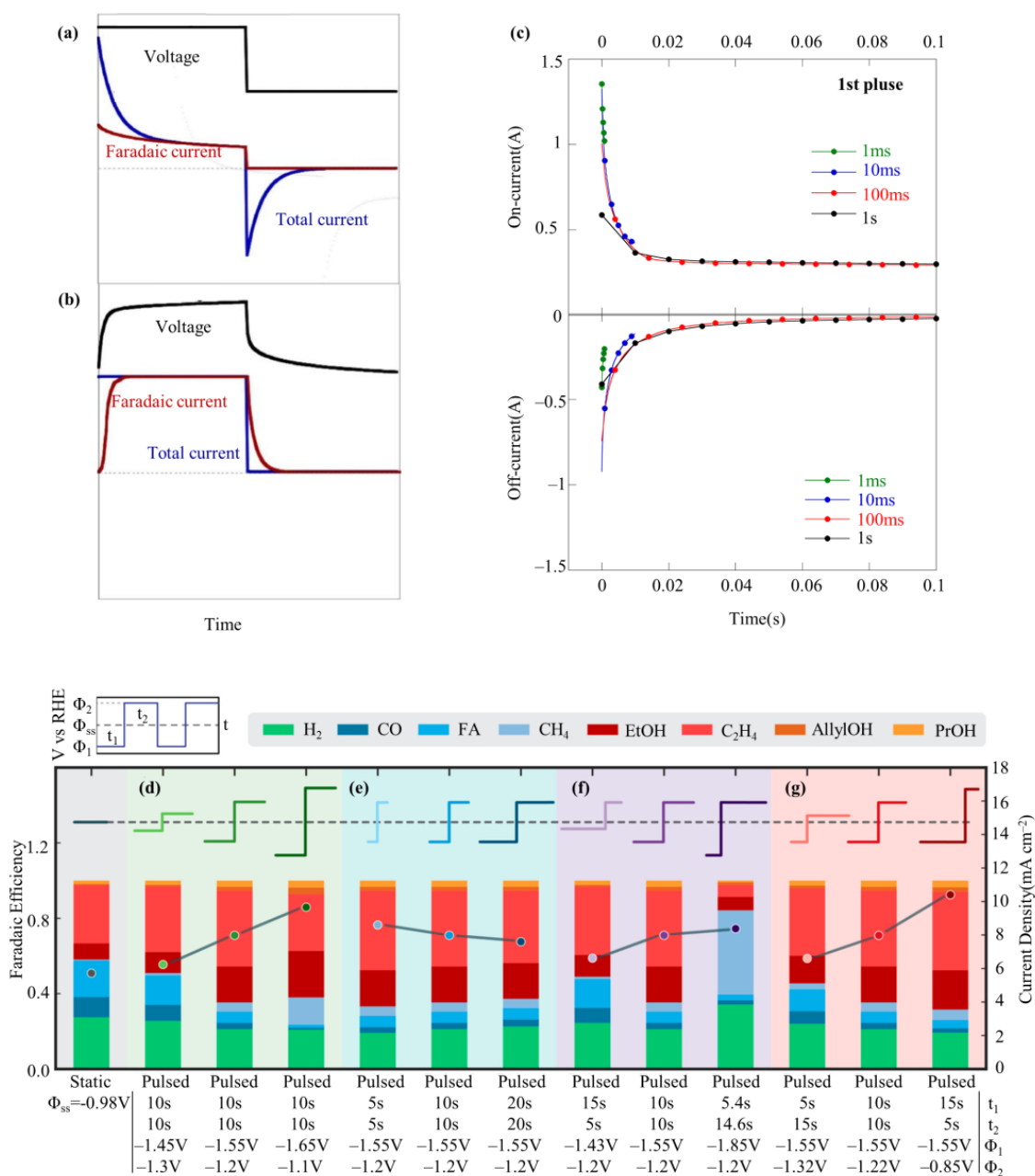


Figure 3. Time curves of voltage, faradaic current, and total current under (a) voltage pulse and (b) current pulse. Reproduced with permission from ref [37]. Copyright 2021 Elsevier. (c) Current evolution during on-time and off-time for the first applied pulse, varying pulse width with a 50% duty cycle. Reproduced with permission from ref [80]. Copyright 2021 Elsevier. The examination of the influence of pulse characteristics on pulsed CO_2 electrolysis (d–g). Reproduced with permission from ref [38]. Copyright 2021 American Chemical Society.

In the context of current pulses, it is evident that changes in faradaic current consistently exhibit a temporal lag compared to the total current. Throughout the pulse application, the total current remains constant at its peak value, while the faradaic current gradually transitions from its baseline to the peak value, maintaining stability as depicted in Figure 3b. Once the pulse is turned off, the total current instantaneously reverts to its baseline, whereas the faradaic current gradually returns to its baseline due to the discharge of the double layer. It's important to note that the observations in Figure 3a,b are contingent on t_{on} and t_{off} durations being longer than the charge and discharge times of the double layer. If the charging process takes longer, j_F will never reach j_t , effectively halting the faradaic current during its ascent and preventing the establishment of a stable electrical double layer (EDL). Similarly, an extended discharge time will result in the initiation of the next pulse before the faradaic current reaches zero.

Pulsed electrolysis offers a broader range of independently adjustable parameters compared to DC electrolysis, including pulsed current density, duty cycle, etc. [70,81–83]. Adjusting pulse parameters can yield high instantaneous current density and negative potential, as well as trigger phenomena like adsorption, desorption, and deposit recrystallization by the introduction of t_{off} [49]. Typically, experimental methods are employed to determine optimal pulse parameters [84], while some researchers use theoretical models for guidance. For example, Justin C. Bui et al. [38] studied different pulse amplitudes, widths, and duty cycles based on their model. Their findings, illustrated in Figure 3d–g, reveal that increasing pulse amplitude and shortening pulse duration enhance current density, although this enhancement is limited when the pulse is very short (<1 s) due to double-layer charging.

4. How Pulsed Electrolysis Regulates Electrochemical Performance?

4.1. EDL Effect

After the pulse application, the efficiency of electrolysis gradually diminishes over time. This decline can be attributed to the accumulation of charge, which results in electrode and solution polarization. However, discharging the EDL while applying the resting potential proves advantageous in terms of energy conservation. This portion of current is notably efficient since it doesn't pass through the solution. Simultaneously, discharging the EDL helps prevent the accumulation of interfacial charges and ions, consequently reducing both concentration and electrode polarization [85].

4.1.1. Effect of Pulse Parameters on the EDL

Please note that t_c represents the time required for the EDL to be fully charged, and t_d is the duration for complete EDL discharge. When t_{on} is less than t_c , the double layer does not attain fully charge, preventing the faradaic current from reaching its maximum potential. In this scenario:

- (1) $t_{off} < t_d$: The bilayer is not fully discharged, leading to residual power, and EDL takes less time to fully recharge in the next pulse. After several cycles, bilayer capacitance saturates, causing alternating cycles of complete charging and incomplete discharging. It's important to note that the faradaic current becomes zero when the faradaic potential difference falls below the reaction potential.
- (2) $t_{off} > t_d$: In this case, the double layer is fully discharged, but it has not achieved complete charge, then the faradaic current with time will repeat the upward and downward trend. Consequently, the high-efficiency current from the double layer capacitor is not fully utilized, preventing the faradaic current from reaching its peak.

Additionally, when $t_{on} = t_c$ and $t_{off} = t_d$, the double layer undergoes complete charging followed by full discharge, and this cycle repeats. During this process, the faradaic current can reach its maximum value. However, it's important to note that sometimes the potential difference is lower than the electrochemical reaction's potential, indicating no electrochemical reaction occurs.

When $t_{on} > t_c$, the faradaic current remains at its peak value for a period after the EDL is fully charged. Subsequently, the response rate starts to decline due to the polarization effect of the anode passivation solution. At this point, (1) when $t_{off} < t_d$, the EDL is not fully discharged, and multiple full charges and incomplete discharges cause the bilayer to be continuously full, which is indistinguishable from the DC case. (2) When $t_{off} > t_d$, the EDL is fully charged and discharged, and there is a power-off period.

Fernando Rocha's study indirectly validated the aforementioned theoretical analysis [80]. They investigated the pulsed electrolysis process using both forced flow and natural flow methods and analyzed the difference in average pulse current after 10 s. Their findings indicated that under shorter pulse widths and 50% duty cycles, the capacitive process dominated. This conclusion was drawn from the observation that forced flow did not enhance the average current, signifying that diffusion limitation was not a significant influencing factor.

Considering the bilayer behavior, numerous studies have investigated the selection of appropriate pulse parameters [86–88]. For instance, in high-current devices characterized by substantial ohmic drop and extensive catalyst surface area, adjusting of the pulse duration becomes crucial. This adjustment is necessary because the disparity in induction time and double-layer charging rate directly correlates with the variation in electrode area.

4.1.2. Analysis of the Effect of Applied Pulses from the EDL Perspective

The variation in electric field strength within the EDL and alterations in species concentration caused by pulse electrolysis play pivotal roles in determining selectivity. In a study utilizing DFT-based first principles [76], it was demonstrated that changes in the EDL's electric field influenced the adsorption species, as depicted in Figure 4a. In the case of short pulses, where non-Faraday currents predominate, the dynamic surface energy hindered the binding of adjacent adsorbed CO species [89]. This phenomenon favored the formation of COR, enhancing the selectivity of C_1 products, and inhibiting HER, as shown in Figure 4d–f. In addition, this dynamic behavior enabled the control of the $H_2:CO$ product ratio by adjusting the pulse profile, as suggested by Kumar et al., as shown in Figure 4b,c [75]. They proposed that CO desorption was facilitated by alterations in the Helmholtz layer due to EDL charging and discharging. Other studies, such as investigation conducted by those by Blom et al. [90] on lead electrodes, have revealed that rapid reoxidation of intermediate species hindered the formation of formate compared to constant potential, primarily influencing by the high-frequency pulse period regulated using EDL charging. This finding confirmed the positive impact of continuous bilayer charging and discharging. These studies provide not only theoretical evidences but also practical applications, demonstrating that varying the EDL's electric field strength through pulses could release or transform undesired adsorbed species. It reduced catalyst poisoning caused by contaminants or by-products [43,91]. Concurrently, significant research has focused on variance in substance concentrations within the EDL. It has been observed that increasing pH or decreasing HCO_3^- concentration within the OHP reduced C_1/C_2 ratios. Thus, timely refreshing this layer, facilitated by pulse applications, mitigates the cumulative impact on product selectivity [92]. Ding et al. [76] illustrated the ORR pathway and the distribution of reactants in constant electrolysis (Figure 4g) and pulsed electrolysis (Figure 4h). They found that pulsed electrolysis facilitated the timely diffusion of reactants (O_2 , H^+) and products (H_2O_2), reducing concentration polarization. Moreover, this method enabled H_2O_2 to diffuse promptly into the bulk phase solution, inhibiting the decomposition path of H_2O_2 electro-reduction at the cathode.

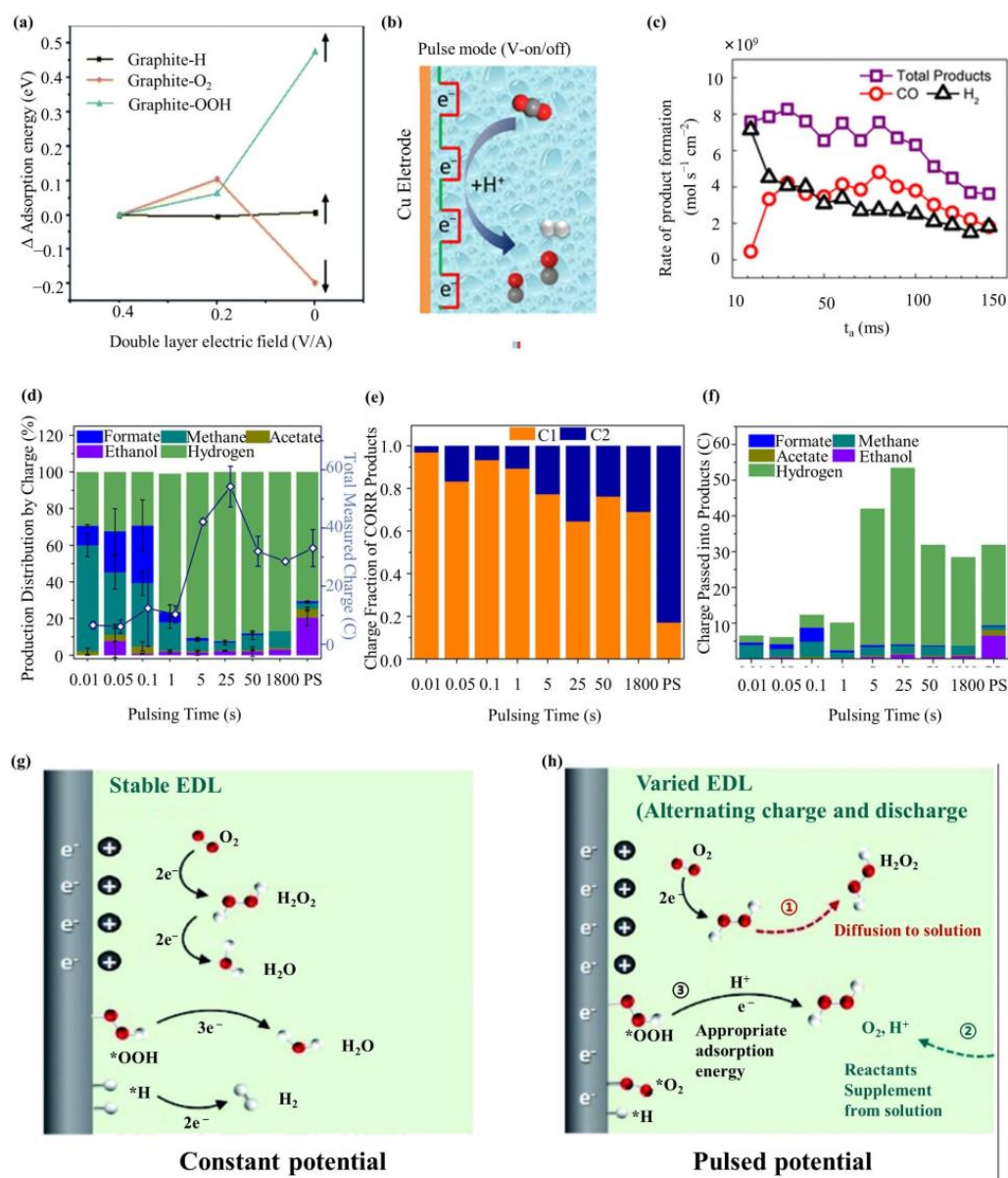


Figure 4. (a) adsorption energy evolution of ORR intermediates under different double-layer electric fields. The arrows represent the upward or downward trends. Reproduced with permission from ref [76]. Copyright 2013 Royal Society of Chemistry. (b,c) Pulse facilitates the conversion of CO₂ to CO and H₂. Reproduced with permission from ref [75]. Copyright 2016 American Chemical Society. Short pulse times increase the conversion of CO to methane and formate and inhibit HER (d–f). The charge is the charge required to produce the target products. Reproduced with permission from ref [89]. Copyright 2020 John Wiley and Sons. Oxygen reduction reaction path under constant electrolysis (g) and pulse electrolysis (h). * represents the adsorption state of the substance. Reproduced with permission from ref [76]. Copyright 2013 Royal Society of Chemistry.

4.2. Electronic Effect

Numerous endeavors have concentrated on probing the electrode interface dynamics during pulsed conditions and investigating their influence on electron behavior. As reviewed, the electronic effects of pulsed electrolysis, aimed at enhancing reactivity and selectivity, can be categorized into two main types: modifications in the adsorption energy and coverage of substances on the electrode surface and the reconfiguration of the electrode's structural arrangement. In the following discussion, we will briefly explore these fundamental aspects.

The application of a pulse can induce alterations in catalyst composition and pH in the vicinity of the interface. These changes, in turn, influence the adsorption energy of species adhering to the surface, subsequently affecting their coverage. Given the pivotal role of adsorbed species in determining selectivity, extensive research efforts have been concentrated in comprehending these phenomena. For example, a great deal of attention is currently being paid to the reaction intermediates CO_{ads} , or H_{ads} , OH_{ads} . Using differential electrochemical mass spectrometry (DEMS), Chanyeon Kim et al. [78] found that the area covered by CO on the Cu surface increased linearly with more negative charge applied, and the ratio of CO to H_2 at the electrode interface was higher during pulsed electrolysis, resulting in increased selectivity of C_{2+} products and suppression of HER. Shiratsuchi et al. [56] suggested that different anodic potentials affect the degree of H_{ads} coverage, resulting in differences in product selectivity. Le Duff et al. [93] proposed that the transition to produce oxygenated hydrocarbons under pulsed conditions was caused by the reduced H_2 availability and increased OH_{ads} surface coverage, during p- eCO_2R , but there was lack of no reliable evidence to support this point. Cao-Thang Dinh et al. [94] used DFT calculations to demonstrate that copper surface hydroxides reduced the binding energy of CO and also stabilized the intermediate using stronger dipole interactions, although the charge imbalance between carbon atoms is exacerbated. Therefore, it reduced the barriers to activate the CO dimerization step. These studies have focused on the role of the adsorbing species themselves, and then, dynamic interactions between the adsorbing species failed to be considered. Kevin W. Kimura et al. [95] used a semi-empirical quadratic Langmuir isotherm model to investigate the dynamic interactions between four key intermediate sorbent species (H_{ads} , OH_{ads} , $\text{CO}_{\text{atop,ads}}$ and $\text{CO}_{\text{bridge,ads}}$). And they attributed this to the improved selectivity of the pulsed ERCO_2 reduction reaction. Figure 5a–d shows the variation of coverage for four adsorbed species and a schematic diagram of dynamic surface coverage. H_{ads} were repelled by the positively charged catalyst surface and replaced by OH_{ads} , leading to an increase in pH and then inhibiting the formation of $\text{CO}_{\text{bridge,ads}}$. They also found that OH_{ads} could prevent the inert adsorption of $\text{CO}_{\text{bridge,ads}}$ through the nearest neighbor coupling effect, promoting the adsorption of $\text{CO}_{\text{atop,ads}}$ and ultimately leading to HER inhibition.

Examining the adsorption of reactants and products is crucial, especially considering that the formation of C-C bonds represents a pivotal step in generating C_2 products from $^*\text{CO}$. In a study by Raleigh Casebolt DiDomenico and Tobias Hanrath et al. [74], they confirmed that a shift to a negative potential, coupled with an increase in interfacial charge, augmented the presence of cations at the interface, thereby stabilizing the adsorption of species containing C-C bonds. Alternating cathodic potentials had a profound effect, increasing the local concentration of CO_2 and facilitating its reaction with HER. This, in turn, notably promoted the formation of C_2^+ products [78]. Additionally, species behavior in a pulsed electrical field is subject to regulation by various factors. Ding et al. [29] disclosed that intermediates' behavior was influenced by weak interaction forces between alkali metal cations and catalyst atoms. In their research, shown in Figure 5j, vibration signals of $^*\text{O}_2^-$ and $^*\text{OOH}$ in Li^+ solution enhanced under pulsed potential. This enhancement was attributed to the coupling of cations and pulsed electrocatalysis, which activated the C- $^*\text{OOH}$ bond and effectively lowered the overall reaction energy barrier. Moreover, this coupling effect led to a more favorable $^*\text{OOH}$ formation thermodynamics.

The reconfiguration of the electrode surface structure primarily involves alterations in catalyst valence and surface composition. Changes in valence state, induced using the oxidation or reduction in the electrocatalyst, are often accompanied by shifts in composition and phase. During pulsed potential electrochemical CO_2 reduction, the state of the copper surface has been investigated extensively using techniques like in situ X-ray absorption near edge spectroscopy (XANES) [95].

Studies have revealed that the copper electrode maintained its metallic properties across a wide range of pulse potentials by employing XANES. Notably, substantial oxidation to produce $\text{Cu}(\text{OH})_2$ occurs only when the pulse potential exceeds a high oxidation

limit (>0.6 V vs. RHE). The coexistence of Cu(I) and Cu(0) has been found to be advantageous for ethanol production, although there was no consensus on the underlying mechanism. Research by Janis Timoshenko et al. [96] demonstrated variance in oxidation states of Cu nanocrystals during different anodic and cathodic pulse times, led to different product selectivity. For instance, at $t_a < 1$ s and $t_c = 4$ s, ethanol production efficiency doubled, and the Cu surface exhibited a coexistence of oxidized Cu(I), Cu(II), and reduced Cu(0). This phenomenon was attributed to the differing adsorption energies of $\text{CO}_{\text{ads,atop}}$ and $\text{CO}_{\text{ads,bridge}}$ on coexisting Cu(0) and Cu(I) surfaces, facilitating the dimerization of CO_{ads} intermediates and the subsequent formation of C_2 products [97,98]. The study also identified the independence of the $\text{Cu(0)} \rightarrow \text{Cu(II)}$ and $\text{Cu(0)} \rightarrow \text{Cu(I)}$ processes. Another investigation by Sheng-Chih Lin et al. [99] utilized second-resolution X-ray absorption spectroscopy (XAS) to monitor the chemical evolution of mixed-valence copper oxide catalysts. They concluded that the coexistence of Cu^+ and Cu^0 enhanced interfacial OH_{ads} , stabilized carbonyl intermediates and prevented protonation of terminal oxygen sites, resulting in the formation of oxygenated CO_2 products. Interestingly, anodic pulses generating in more Cu^+ , favoring ethanol production without affecting ethylene production. Ara'n-Ais et al.'s experimental results [42] also demonstrated a significant increase in ethanol selectivity in the presence of Cu^0 and Cu^+ . Theoretically, it is possible to control ethylene and ethanol selectivity by managing the reduction rate of copper during cathodic pulses. Studies have explored strategies such as lowering the temperature to slow down the reduction kinetics and enhanced ethanol selectivity [42]. Indeed, it is essential to acknowledge that copper tended to be oxidized [100–103]. To accurately capture and comprehend the transformations in catalyst surface morphology, in situ operando techniques is imperative. For instance, in situ studies of Cu using attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) can provide valuable insights into the intricate CO_2 reduction mechanism [104]. These advanced techniques enable researchers to observe real-time changes in the catalyst's surface structure and composition, enhancing the understanding of the electrochemical processes.

Investigation in surface structure changes has primarily focused on the reconstruction of surface nanostructures, including alterations in crystal surfaces, defects, and roughness. Electrodeposition studies have demonstrated that specific pulse parameters, such as cathode current, average cathode current density, and the ratio of relaxation time to pulse time (T_r/T_c) enabled continuous depositions of Molybdenum (Mo) with a preferred grain orientation (110), as depicted in Figure 5e–h [105]. Engelbrecht et al. observed that a positive up-potential resulted in a rise in grain reorganization. Notably, when the up-potential surpassed the open circuit voltage, the electrode structure experienced corrosion. Conversely, applying a more negative potential preserved the surface structure [91]. In-depth studies by Simon et al. [106] revealed significant morphological changes when the pulse duration exceeded 1 s. They employed in situ electrochemical atomic force microscopy to monitor nanoscale morphological changes on the Cu (100) surface at relevant cathodic potentials. Cubic structures became visible after 1 h of pulse treatment, indicating defect healing, while passivation occurred after 1 h of constant potential treatment. However, it's important to note that morphological changes was not the only reason for the enhanced ethanol yield. The role of Cu(I) species must also be considered. Anodic treatment was found to increase surface roughness, which, in turn, elevated pH and promoted the formation of C_{2+} products due to higher current density and sharp structures [97,107–111]. Yet, mild pulses did not significantly influence C_{2+} product selectivity due to insufficient changes in electrode surface roughness [75,112–114]. Ding et al. [115] mentioned that pulse electrolysis prevented caking on the catalyst surface after constant potential electrolysis, maintaining the morphology and active sites of carbon-based catalysts and avoiding unnecessary loss of ORR performance in traditional electrocatalysis. However, understanding the reversible changes in catalyst structure or irreversible changes in catalyst morphology caused by pulsed electrolysis needs further investigation. Jeon et al. [114] explored the impact of high oxidation pulse potential followed by constant potential on copper nanocube catalysts.

They discovered different results based on applied anodic potential, as shown in Figure 5i. At $E_{an} = 0.9$ V, catalytic properties maintained, and C_2 selectivity boosted, suggesting irreversible catalyst changes. In contrast, at $E_{an} = 1.2$ V, the primary CO_2 reduction reaction products shifted from CH_4 to C_2 , indicating a dynamic and reversible process influenced by pulsed potential.

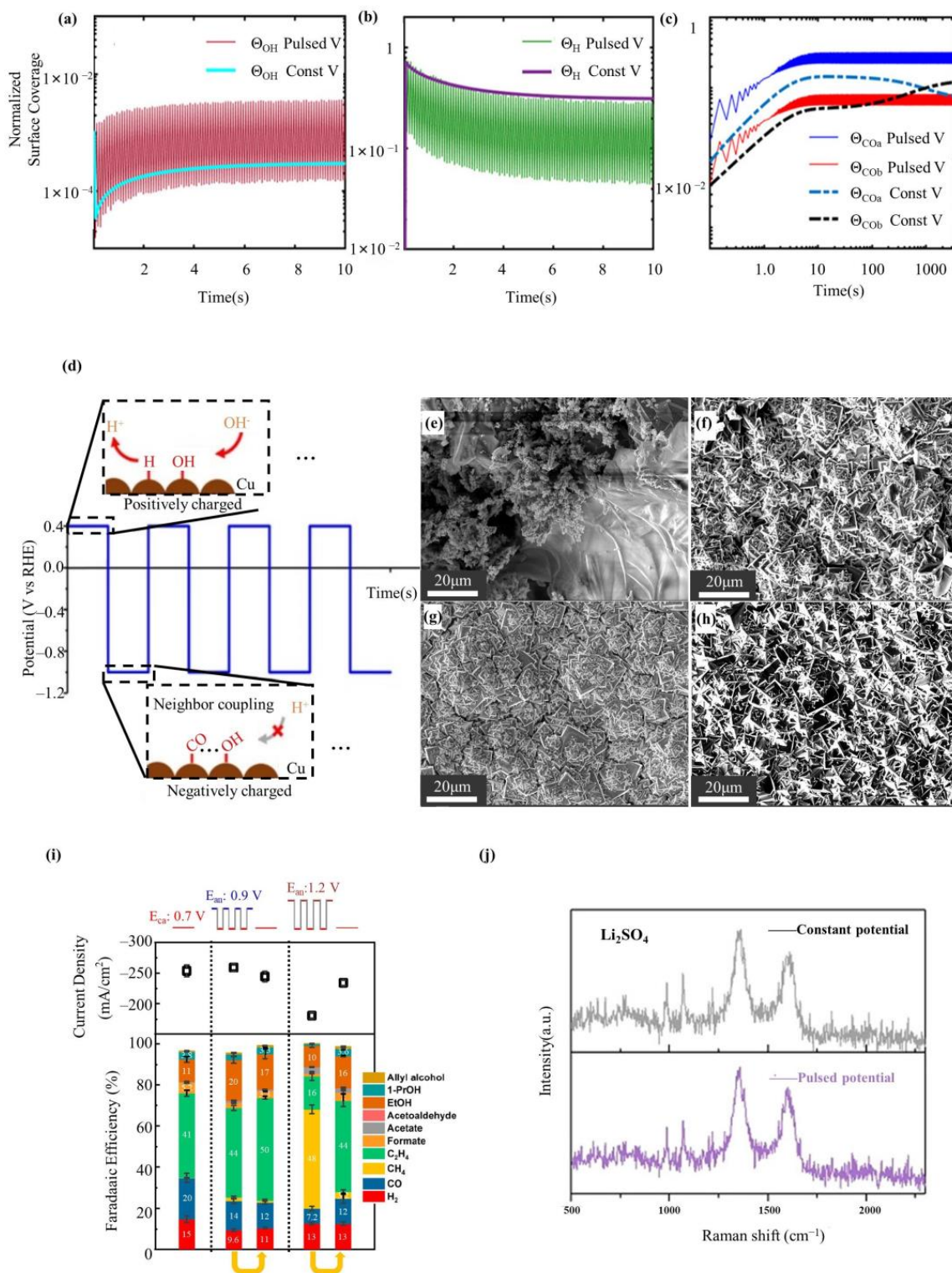


Figure 5. Relative surface coverage of (a) adsorbed OH over 10 s, (b) adsorbed H over 10 s, and (c) adsorbed CO_{atop} and CO_{bridge} over 1 h under pulsed and constant potential using a competitive quaternary Langmuir isotherm. (d) Schematic describing the dynamic surface coverage. During the

anodic pulse, the surface protons will be repelled and displaced by hydroxides. During the anodic pulse, the presence of OH^- leads to the repulsion and displacement of surface H^+ . Subsequently, during the cathodic potential, the remaining surface OH^- facilitate the coupling with nearby CO molecules, thereby promoting the process of CO_2 reduction (CO_2R). During the cathodic potential, the remaining surface OH^- will induce near neighbor coupling with CO, favoring CO_2R . This leads to the blocking of H^+ adsorption, resulting in the suppression of the hydrogen evolution reaction (HER). Reproduced with permission from ref [95]. Copyright 2020 American Chemical Society. SEM images of the Mo deposits under different pulse parameters: $i_c = 4 \text{ A/cm}^2$ and $T_c = 5 \text{ msec}$: (e) $T_r = 15 \text{ msec}$, $T_r/T_c = 3$; (f) $T_r = 45 \text{ msec}$, $T_r/T_c = 9$; (g) $T_r = 60 \text{ msec}$, $T_r/T_c = 12$; (h) $T_r = 90 \text{ msec}$, $T_r/T_c = 18$, i_c is the cathode current, and T_r/T_c is the ratio of the relaxation time to the pulse time. Reproduced with permission from ref [105]. Copyright 2023 Elsevier. (i) Current density (top) and FE (bottom bar graph) of the pulsed electrolysis with the anodic pulse $E_{\text{an}} = 0.9$ and 1.2 V and the cathodic pulse $E_{\text{ca}} = -0.7 \text{ V}$. Subsequently, the same samples, which had undergone pretreatment via pulsed electrolysis, were subjected to measurement at a constant potential of -0.7 V vs. RHE, as indicated by the arrows. Reproduced with permission from ref [114]. Open Access. (j) Operando Raman spectrum under constant and pulsed potential of $\text{CaCl}_2\text{-CO}_2\text{-CS}$ in $0.05 \text{ M Li}_2\text{SO}_4$. Reproduced with permission from ref [29]. Copyright 2023 American Chemical Society.

4.3. Mass Transport Effect

In comparison to direct current (DC) potential, pulsed electrolysis not only improved electronic and double-layer effects but also controlled its mass transport [116]. This feature proves advantageous when applied in the degradation of organic pollutants by hydroxyl radicals ($\cdot\text{OH}$). Pulsed electrolysis facilitates a thinner diffusion layer and ensures timely replenishment of reactant concentrations during the off phase (t_{off}). These factors synergistically enhance the mass transport of organic molecules, resulting in their fully attacked by free radicals in the vicinity of anode when BDD anode was used.

Moreover, pulsed electrolysis results in exceptionally high current densities. In the subsequent discussion, we will conduct a detailed examination of mass transport both spatially and temporally, supplemented by an exploration of relevant theoretical aspects. Diffusion layer forms when a rapid depletion of the substrate near the electrode and the subsequent formation of a concentration gradient at the electrode-electrolyte interface after the application of the pulse. As the boundary-layer thickness decreases, the mass transfer rate to and from the cathode surface alters; for instance, the rate of CO_2 mass transfer to the cathode increases, as does the rate of OH^- mass transfer from the cathode [117,118]. Consequently, the rate of CO_2 reduction and the distribution of the products formed are affected. Justin C. Bui et al. investigated the boundary-layer thickness to understand these mass transfer effects [38]. As depicted in Figure 6a–c, the surface CO_2 concentration increased as the reduction in boundary-layer thickness, and pH remained stable. These changes collectively reduce the efficiency of hydrogen generation through the Faradaic process.

Theoretically, the thickness of the diffusion layer is proportional to $t^{1/2}$ [39].

$$\delta_t = \sqrt{\pi D t} \quad (6)$$

where D is the diffusion coefficient of the electrolyte and t is measurement time.

Diffusion current is the current generated by the diffusion of ions from the bulk solution to the electrode for reaction. When the solution around the electrode forms the maximum concentration gradient, in other words, the reactant concentration at the electrode surface is zero, then it is termed the diffusion-limited current (I_{lim}).

$$I_{\text{lim}} = nFD \frac{c_0}{\delta} \quad (7)$$

Jae-Hoon Kim et al. [119] concluded the relationship between δ and frequency (f) and found that I_{lim} and the thickness of the diffusion layer are directly and inversely

proportional to $f^{1/2}$, respectively. This explains the small thickness of the diffusion layer for short pulses.

$$\delta = 2\sqrt{\frac{\pi D}{f}}, \quad (8)$$

However, there is a complication in that the diffusion layer must be divided into two parts when short pulses are applied. One is a stationary layer (δ_s), and the other is an inner “pulsating electrodynamic diffusion” layer (δ_p) [52]. Shorter pulses result in the formation of a thinner diffusion layer so that the outer boundary of the pulse diffusion layer can't reach the region of convective transport. Then, this leads to that there must be another diffusion layer between these two layers, i.e. stationary layer. In the pulsating electrodynamic diffusion layer, concentration changes occur due to pulsation: when a pulse is applied, the reaction persists, leading to a decrease in concentration. Conversely, without the pulse, the reaction halts, causing the concentration to rise. In contrast, the stationary layer operates hydrodynamically.

When the first pulse is applied, the concentration dissipates, and a diffusion layer begins to form. At this point, since the concentration at the outer boundary of the pulse diffusion layer is the same as that of the bulk solution, the stationary layer does not exist. When the pulse is applied again, the concentration difference between the two is generated, and the stationary layer is established.

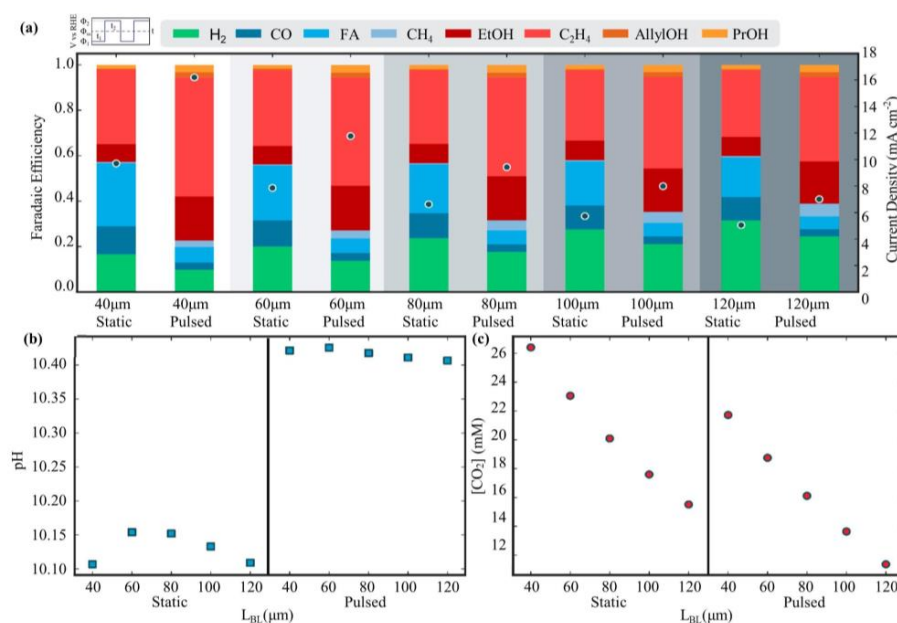


Figure 6. (a) Faradaic efficiency and total current density on different mass-transfer boundary-layer thicknesses, shown as stacked bars and markers, respectively. $\Phi_1 = -1.55$ V vs. SHE, $\Phi_2 = -1.2$ V vs. SHE, and $t_1 = t_2 = 10$ s. Effect of boundary-layer thickness on (b) surface pH and (c) surface CO_2 concentration. Reproduced with permission from ref [38]. Copyright 2021 American Chemical Society.

IBL et al. [52] proposed a concentration profile using the Nernst diffusion layer model (assuming linear concentration distribution), as shown in Figure 7a. δ_p is defined as:

$$\delta_p = 2\sqrt{(Dt_{on})/\pi}. \quad (9)$$

where δ_p is the thickness reached by the pulsating diffusion layer at the end of the pulse. In the case of a single pulse, the concentration distribution is assumed to be linear, and the following relationship is obtained [49]:

$$\delta_p = \sqrt{2Dt}. \quad (10)$$

The authors argued that the number of cations entering the growing diffusion layer from the bulk during the pulse must be taken into account if t_{off} is short enough. At this point, the current cannot drop completely to zero, so there is a small fluctuation in the current. Furthermore, the authors modify the formula as follows [49,120]:

$$\delta_p = \sqrt{2Dt_{on}(1 - \frac{t_{on}}{t_{on} + t_{off}})}. \quad (11)$$

However, the above formulas are derived from the assumption of linear concentration distribution. M. DATTA et al. [120] use the semi-empirical equation to optimize Equation (10). Thus, the problem that the limiting value of the limiting pulse current density (i_{pl}) for short pulse times and small duty cycles is different from that obtained from Siver's approximation for single pulses can be avoided [40].

$$\delta_p = \sqrt{\frac{4}{\pi}Dt_{on}(1 - \frac{t_{on}}{t_{on} + t_{off}})} \quad (12)$$

In the realm of pulsed electrolysis, the dynamic evolution of mass transfer over time holds paramount importance. This characteristic highlights the significant advantages of pulsed electrolysis, especially concerning 'cyclic renewal', when compared to traditional electrolysis. Various scholars have employed diverse methodologies to elucidate the temporal changes in concentration during pulsed electrolysis. GUPTA et al. [121] developed a detailed finite difference model to accurately estimate surface pH and CO₂ concentration at a copper electrode during CO₂ electroreduction. This model successfully demonstrated changes in local conditions around the electrode surface when a pulse was applied to mitigate copper electrode poisoning. However, it did not consider the spatial distribution of concentration and omitted the formation of copper oxides, as depicted in Figure 7b,c. Xin et al. [79] introduced a novel microfabricated electrochemical cell (MEC) combined with a laser scanning confocal microscopy (LSCM)-coupled fluorescence detection system (MEC-LSCM) to gain a detailed understanding of the mass transfer process and concentration distribution in the Nernst diffusion layer. They found changes in ion concentration with time and distance during the conversion of HCrO₄[−] to Cr₃⁺ at the cathode, as illustrated in Figure 7d,e. Results indicated that the intermittent reaction effectively suppressed the continuous decline of the HCrO₄[−] to Cr³⁺ ratio at the interface, reducing concentration polarization. Therefore, in line with previous research, the application of pulsed electrolysis facilitated cyclic renewal of the diffusion layer and effectively inhibited concentration polarization due to the increased ion diffusion rate. It's noteworthy that pulse frequency and duty cycle significantly influenced diffusion layer renewal. If substance replenishment during t_{on} was insufficient to offset consumption during t_{off} , concentration polarization accelerated.

Chanyeon Kim et al. [78] employed differential electrochemical mass spectroscopy (DEMS) to describe changes in product distribution at the copper cathode over time during pulsed CO₂ electrolysis. They attributed the increase in C₂₊ products to heightened CO₂ concentration. However, considering that potential, pH, and CO₂ concentration were crucial in promoting CO₂ reduction [122], Justin C. Bui et al. [38] incorporated the effects of pH and CO₂ concentration on the kinetics of individual product formation into their model. They proposed the time-dependent continuum model and demonstrated that the increase in C₂₊ product faradaic efficiency (FE) resulted from the combined effect of all three factors, not CO₂ alone. At the same time, an increase in local CO₂ concentration did not change the C₁/C₂₊ ratio; an increase in pH reduced current densities for both C₁ and H₂ products relative to C₂₊ products. This aligns with the pH activation energies for C₁ products and H₂ current densities on the Standard Hydrogen Electrode scale [123–125]. Recognizing alkaline pH conditions as a fundamental design principle is essential for improving energy efficiency in upcoming CO₂ reduction/CO₂ oxidation applications.

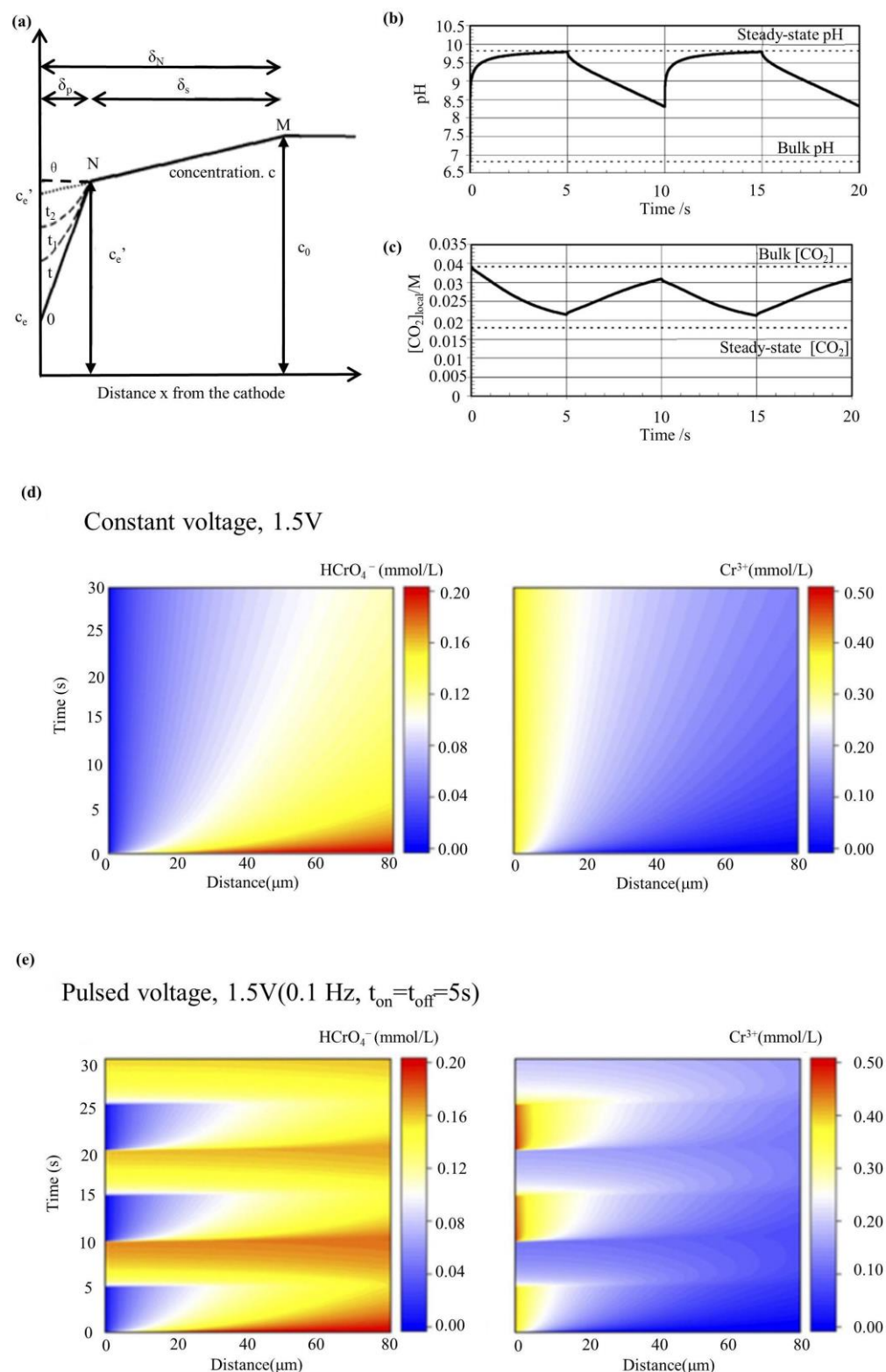


Figure 7. (a) The curve of concentration and the distance from the cathode at the end of a pulse. The dashed line shows the concentration change during the off time. ($T < t_1 < t_2 < \theta$). Reproduced with permission from ref [52]. Copyright 1978 Elsevier. Pulsed surface pH (b) and CO_2 (c) profiles by two-dimensional model. Reproduced with permission from ref [121]. Copyright 2005 Spring Nature. The spatial and temporal distribution of HCrO_4^- and Cr^{3+} at the interface of electrode solution for constant voltage (d) and pulsed voltage (e) of 1.5 V. Reproduced with permission from ref [79]. Copyright 2022 John Wiley and Sons.

5. In Situ Characterization Methods Used in the Pulsed Electrolysis

(1) In situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS)

ATR-SEIRAS is a potent surface analysis technique designed to track alterations in byproducts throughout a reaction. In the context of CO₂ reduction on a Cu catalyst, real-time monitoring of reaction intermediates, such as CO, is achievable using time-dependent in situ ATR-SEIRAS, as shown in Figure 8a–c. This method enables the observation and analysis of changes occurring at the surface during the reduction reaction, providing valuable insights into reaction kinetics and intermediate species [104].

(2) In situ X-ray absorption near-edge spectroscopy (XANES) measurements

XANES allows for the detection of the valence state of elements at the electrode surface at an atomic level. By using it, variation in the valence state of copper on the surface of Cu catalysts can be discerned. In a recent work, Kevin W. Kimura et al. [95] demonstrated that pulsed mode induces passivation with hydroxide ions without altering the bulk oxidation state of Cu(0). Moreover, using linear combination analysis (LCA) of the XANES spectra, it is possible to extract the contribution of each component. Notably, Janis Timoshenko et al. [96] found that the Cu(0) proportion in the Cu catalyst decreases in the anodic pulse and increases during the cathodic pulse, exhibiting an opposite trend to the Cu(I) ratio, as shown in Figure 8d. This sophisticated approach provides a comprehensive understanding of the dynamic changes in the surface valence states of copper during electrochemical processes.

(3) X-ray absorption spectroscopy (XAS), high-energy X-ray diffraction (XRD), and quasi-in situ X-ray photoelectron spectroscopy (XPS).

XPS serves as a tool for surface element detection, whereas XAS provides insight into the bulk characteristics. The integration of these two techniques allows for a comprehensive understanding of the structural composition of a catalyst. Employing this approach, as demonstrated by Janis Timoshenko et al., confirmed that the Cu catalyst's structure could resemble that of a core–shell. Notably, they observed that under the anodic pulse, the oxidation of the catalyst surface surpasses that of the inner core [96]. In the assessment of catalyst oxides, XRD exhibits lower sensitivity compared to XPS. This disparity arises because the XRD signal predominantly arises from ordered phases, while actual samples often include disordered phases.

(4) Selected-Ion Flow Tube Mass Spectrometry (SIFT-MS)

For the analysis of intermediates or reaction products, a choice can be made between HPLC or GC testing. Kevin W. Kimura et al. [36] employed these techniques to analyze the composition of reaction products, detecting H₂, CO, CH₄, C₂H₄, and HCOOH under different pulsed parameters. However, conventional testing methods and real-time analysis of gaseous and liquid products face limitations, with analysis times typically in the order of minutes. These limitations are addressed using Selected-Ion Flow Tube Mass Spectrometry (SIFT-MS). Lily Mandal et al. highlighted the significant potential of SIFT-MS in the field of CO₂ reduction (CO₂R), enabling real-time analysis of complex multicomponent mixtures within a time scale of 0.1–10 s, except for gaseous or liquid products. It is noteworthy that while SIFT-MS can detect all hydrocarbons, it is not suitable for the detection of H₂ and CO [126,127]. In a different study, Xiangjuan Ma et al. [128] employed HPLC-TOF-MS to detect intermediates formed during the pulse electrolysis of ciprofloxacin. This approach allowed them to obtain insights into the possible pulse electrochemical degradation mechanism of ciprofloxacin.

Although in situ characterization failed to directly measure EDL structure, the diffusion layer model could be one option to describe the change of substance concentration in EDL over time. Shuzhao Pei et al. [129] used the transient diffusion models with pulsed current to illustrate the time profiles of transient local phenol concentration in EDL, as

shown in Figure 8e,f. They found that pulsed mode ensured the increase in local concentration of phenol in EDL compared with DC. Figure 8f showed that the transient local phenol concentration in EDL changed with resting time (t_R) and anodic time (t_A). Considering that the oxidation rate of phenol is proportional to the concentration, the resting time in pulsed mode facilitates EDL update; thus, pulsed mode is conducive to phenol degradation. It is important to note that the concentration changes are determined using mathematical methods, and these findings have not been effectively integrated with practical applications [121].

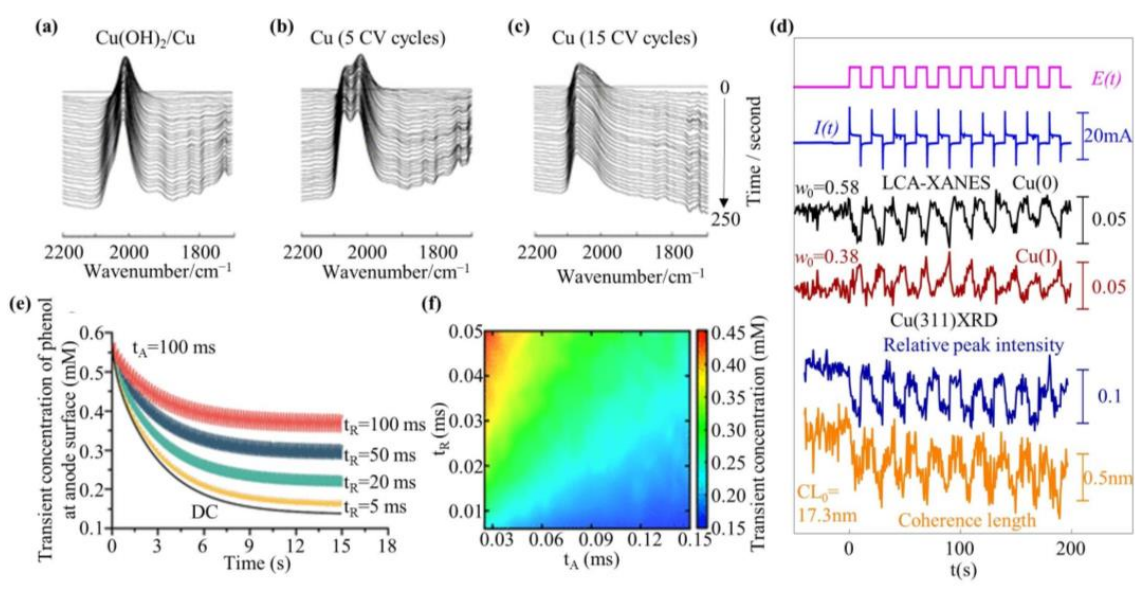


Figure 8. Time-dependent in situ ATR-SEIRAS for (a) $\text{Cu}(\text{OH})_2/\text{Cu}$ film; (b) Cu film (5 CV cycles); (c) Cu film (15 CV cycles) in the range of $1700\text{--}2200\text{ cm}^{-1}$. Reproduced with permission from ref [104]. Open Access. (d) Time dependencies of the applied potential $E(t)$ and measured current $I(t)$, the concentrations of $\text{Cu}(0)$ and $\text{Cu}(I)$ species from XANES analysis, and the relative peak intensity and coherence length from $\text{Cu}(311)$ XRD. CL_0 and w_0 are the coherence length and concentration of metallic copper species ($t = 0$), respectively. Reproduced with permission from ref [96]. Open Access. (e) Transient phenol concentration at the anode surface as a function of time under different resting times. (f) Transient phenol concentration at the anode surface under different resting times and anodic times. Reproduced with permission from ref [129]. Copyright 2021 American Chemical Society.

In summary, the utilization of in situ characterization techniques during pulse electrolysis provides a dynamic state of the system. Consequently, numerous studies have embraced time-resolved in situ characterization methods, aiming at characterizing dynamic changes. Janis Timoshenko et al. [96] found that techniques such as operando XAS, XRD, XPS, and LCA-XANES furnish valuable insights into the temporal evolution of $\text{Cu}(0)$, $\text{Cu}(I)$, $\text{Cu}(311)$, and related species, as shown in Figure 8d. These approaches primarily focus on accurately identifying the distinct electronic and geometrical structures of copper catalysts at different stages of the pulse.

Non-time-resolved characterization methods can also be employed when the impact of various pulse parameters on the catalyst is needed. For instance, in non-time-resolved XANES studies, Kevin W. Kimura et al. [95] observed that the copper electrode retained metallic properties across a broad range of pulse potentials until reaching the high oxidation limit. Hence, it depends on the specific objectives to choose between time-resolved and non-time-resolved in situ characterization techniques. Each approach offers unique advantages, allowing researchers to tailor their methods to the intricacies of the investigated processes.

6. Application of the Pulsed Electrolysis

Pulse electrolysis has a wide range of applications, such as hydrogen production using water electrolysis [39–41], H₂O₂ production by 2-e[−] ORR, CO₂ reduction [42,43,130,131], CO reduction [89], large-scale solid oxide electrolytic cells [132], environmental pollutant [44,45] and electrodeposition [46], etc. Hence, the electrode materials used in pulse electrolysis are various, but for carbon dioxide reduction, Cu-based catalysts are the main ones [95]. Because Cu is the only single metal catalyst known to be able to convert CO₂ to higher-order hydrocarbons with higher activity due to its appropriate binding energy with CO*— a key intermediate in the ECO₂RR process [133]. However, its product selectivity is low because ECO₂RR on Cu involves a polyproton-coupled electron transfer process, and hydrogen evolution reaction (HER) will also have a competitive effect on it [134]. In addition, Cu-based catalysts tend to easily passivation. Therefore, it is a hotspot to improve the CO₂RR selectivity of copper-based catalysts by means of the pulse method. Table 1 summarizes the various pulse materials and applications along with the key parameters.

Table 1. Summarizing of the application of pulsed electrolysis and their properties.

No	Year	Details for Configurations	Working Electrode	Pulse Parameters	Applications Area	Enhancement Compared to Steady State Electrolysis	References
1	2023	A three-electrode setup was used for electrolysis, consisting of counter electrode (a platinum electrode, $1.5\text{ cm} \times 1.5\text{ cm} \times 1\text{ mm}$), working electrode (graphite felt, $2\text{ cm} \times 2\text{ cm} \times 5\text{ mm}$), and reference electrode (a silver chloride electrode, Ag/AgCl, saturated potassium chloride). The electrolyte, stirred at 150 rpm, was a 0.5 M Na_2SO_4 solution saturated with O_2 .	Graphite felt	The pulse waveform was sine wave and frequency was 0.2 Hz along with the amplitude 10 mV.	H_2O_2 production by 2-e^- -ORR	When subjected to pulsed potential, H_2O_2 production rate and FE of 2-e^- -ORR increased by 1.4 times and 3.62 times compared to constant potential conditions. In addition, energy consumption reduced by 75%.	[135]
2	2023	A 10 mL-H-type cell equipped with three electrodes, using Pt foil, Ag/AgCl, $\text{Cu}_3(\text{DMPz})_3$, and 0.1 M KCl as the counter electrode, reference electrode, working electrode, and electrolyte. A nafion 117 proton exchange membrane separated the cathode and anode compartments.	Cu-dimethylpyrazole complex $\text{Cu}_3(\text{DMPz})_3$	There were two different asymmetric low-frequency pulsed strategy profiles (ALPS) to improve e selectivity of CH_4 and C_2H_4 products. (1) 30 s electrolysis at an anodic potential of 1.27 V vs. RHE, followed by 300 s electrolysis at a cathodic potential of -1.28 V vs. RHE; (2) 30 s electrolysis at cathodic potential of -0.58 V , followed by 600 s electrolysis at cathodic potential of -1.08 V , and then 30 s electrolysis at anodic potential of 0.42 V.	CO_2RR	(1) ALPS-1: High selectivity ($\text{FECH}_4 = 80.3\%$) and record-breaking stability of CH_4 . FECH_4 maintained over 76.6% within 24 h, even over 60% for 300 h. (2) ALPS-2: High selectivity ($\text{FEC}_2\text{H}_4 = 70.7\%$) and stability of C_2H_4 . FEC_2H_4 maintained over 66.8% within 24 h (3) Both systems proved better selectivity and stability than that of conventional systems for CO_2RR ($\text{FEC}_2\text{H}_4 = 34.5\%$, $\text{FECH}_4 = 5.9\%$, and low stability for less than 60 min).	[77]
3	2023	A 250 mL reactor containing a 0.1 M Na_2SO_4 electrolyte was used for electrolysis.	Ti sheet cathode and PbO_2 composite anode	Current density = 25.00 mA cm^{-2} , pulse duty cycle = 50.0%, and pulse frequency = 5000 Hz, pulse electrolysis time = 120 min.	Organic wastewater treatment	Pulse mode (21.08 kWh m^{-3}) can reduce energy consumption by 70.7% compared to DC mode (6.17 kWh m^{-3}), although the CIP removal by pulse mode (89.7%) was reduced by 2.2% compared with DC mode (91.9%). After 100 cycles of pulsed current, the voltage attenuated by 0.041% per cycle. The calculated efficiency approached 98.2%. Additionally, the total conversion rate of CO_2 was 52%, while it was about 20% with open circuit voltage. The theoretical lifespan of SOEC can exceed 500 cycles at -300 mA/cm^2 .	[128]
4	2023	The flat-tube solid oxide electrolytic cells (SOEC) include a supporting layer (NiO-3YSZ), fuel electrode (NiO-8YSZ), electrolyte (8YSZ), barrier layer ($\text{GDC}(\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta})$), and oxygen electrode (LSCF).	Fuel electrode was made of NiO-8YSZ (8 mol. % yttria-stabilized zirconia), and the oxygen electrode was made of LSCF ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$)	Pulse current = -300 mA/cm^2 .	CO_2 conversion in solid oxide electrolytic cells	Pulsed electrolysis for electrodeposition of Mo coatings from chloride molten salts shortened time to form dense deposits compared to constant current electrolysis. Optimized current density and T_r/T_c parameters increased the electrodeposition rate by a factor of 5 compared to static current electrolysis.	[132]
5	2023	Mo electroreduction is carried out in a cell with a c-axial cathode position in an argon atmosphere. The cell has a graphite container for the melt (MPG grade 8 structural graphite). The interior of the graphite container is lined with a Mo plate. Molybdenum rods are used as anode current leads for graphite containers. The electrolyte was NaCl-KCl-MoCl ₃ melt.	SY-200 grade glass carbon cathode with an area of 3 cm^2	Cathode current ranged from 2 up to 6 A/cm^2 , average cathode current density ranged from 0.286 up to 0.875 A/cm^2 , and ratio of the relaxation time to the pulse time (T_r/T_c) ranged from 6 up to 18.	Electrodeposition		[105]

Table 1. Cont.

No	Year	Details for Configurations	Working Electrode	Pulse Parameters	Applications Area	Enhancement Compared to Steady State Electrolysis	References
6	2022	CO ₂ reduction reaction was carried out in a custom-made glass two-compartment hydrogen cell, with the cathode chamber and anode chamber separated by a Nafion anion exchange membrane. The electrolyte was 0.5 M KCl. Ag/AgCl electrode was the reference electrode, and platinum mesh was the counter electrode. The electrolysis cell, constructed from plexiglass, was rectangular in shape with dimensions of 10 cm × 10 cm × 5 cm. Positioned at opposite ends of the cell, a Ti ₄ O ₇ anode (with a geometric area of 10 cm ²) and a stainless steel sheet cathode (10 cm ²) were utilized without the need for a separator.	A polycrystalline copper foil electrode	The anode pulse potential was 0.2 V, the cathode pulse potential is −1.2 V, the duty cycle was 50%, and the pulse period was 500 ms.	CO ₂ RR	A high pulse potential with positive anode current improved reaction stability and increased C ₂ selectivity (FE = 76%).	[74]
7	2021	The apparatus consisted of a counter electrode (Pt), a reference electrode (Ag/AgCl) and a working electrode (graphite felt). The electrolyte was 0.05 M Na ₂ SO ₄ , stirred at 350 rpm, and the volume was 150 mL.	Ti ₄ O ₇ anode, stainless steel sheet cathode	Pulsed-current mode adopted square current wave forms. Current density = 20 mA cm ^{−2} , reaction time = 120 min, anodic time/resting time = 100 ms.	Organic wastewater treatment	Pulsed-current mode: The rate constant for phenol oxidation was 1.48 h ^{−1} and the energy consumption was 57.1%, which was lower than the direct-current mode (0.97 h ^{−1}).	[129]
8	2021	A flow cell is composed of CO ₂ gas, cathode electrolyte, and anode electrolyte. The cathode and anode chambers were separated by an anion exchange membrane and equipped with Ag/AgCl reference electrodes, platinum-mesh counter electrodes, and the working electrode. The electrolyte solution was 1 M KOH.	Graphite felt	Pulsed width = 1 s, duty ratio = 30%, pulsed potential = −1.0 V vs. Ag/AgCl, and reaction time = 50 min.	H ₂ O ₂ production via 2-e [−] ORR	H ₂ O ₂ production increased by 138.12% using pulse potential compared to constant potential.	[76]
9	2021	A standard three-electrode setup with two compartments separated by a membrane was used for the electrolysis. The OD-Cu foil, Pt mesh, and Ag/AgCl were used as the working electrode, the counter electrode, and the reference electrode. The electrolyte was 0.1 M KOH saturated with CO.	A gas diffusion electrode sprayed with Cu NCs catalyst	The anode pulse potential = 0.9 V vs. RHE or 1.2 V vs. RHE, the cathode CO ₂ reduction pulse potential = −0.7 V vs. RHE, the duty cycle = 50%, and the pulse period = 2 s.	CO ₂ RR	Compared with a potentiostatic of CO ₂ RR at −0.7 V vs. RHE, the faraday efficiency of C ₂ H ₄ and C ₂ H ₅ OH products at an anode potential of 0.9 V vs. RHE increased from 40.9% to 43.6% and from 11% to 19.8%, respectively. Additionally, the FE _{CH₄−} was 48.3% at an anode potential of 1.2 V vs. RHE compared with the FE _{CH₄−} = 48.3% at the conventional condition.	[114]
10	2020	The setup included an Ir-MMO anode, Cu-DHP working electrode (Cu-DHP), and reference electrode (Ag/AgCl), which were separated by a Nafion membrane. The cathode electrolyte (pH = 8.5) was composed of a 0.1 M KHCO ₃ solution saturated with CO ₂ , while the anode electrolyte (pH = 8.3) was 1 M KHCO ₃ .	Oxide-derived copper (OD-Cu)	The cathodic potential = −0.35 V vs. RHE, a resting potential = 0 V vs. RHE, duty cycle = 50%, pulsing time = 10 ms, and electrolysis time = 60 min.	CO reduction	Pulsed CORR electrolysis: a product distribution by charge of approximately 70% for CORR and 29.3% for HER. The charge fraction of C ₁ products was 97% of CORR products (C ₁ and C ₂ products), while the charge fraction of C ₁ products was less than 20% for non-pulsed CORR electrolysis. Non-pulsed CORR electrolysis at −0.35 V vs. RHE: a product distribution by charge of 70.3% for HER and 29.7% for CORR.	[89]
11	2020		Deoxygenized high phosphorous copper sheets (Cu-DHP)	Working potential of −1.38 V remained 25 s, followed by the potential of −1.0 V remained for 5 s.	CO ₂ RR	Compared with constant potential electrolysis, pulse electrolysis improved stability of the catalyst. After 8 h of constant potential electrolysis, the ethylene selectivity decreased from 15% to 2%, followed by pulse electrolysis of 8 h, it recovered back to 15%.	[136]

Table 1. Cont.

No	Year	Details for Configurations	Working Electrode	Pulse Parameters	Applications Area	Enhancement Compared to Steady State Electrolysis	References
12	2018	A glass H-cell with two compartments contained a counter electrode (a platinum wire coil) and a working electrode (copper sheet), respectively. The reference electrode (Ag/AgCl, 3 M KCl) embedded in a Luggin capillary tube was placed in proximity to the working electrode. A Nafion N117 membrane separated the two compartments. The catholyte was 0.1 M KHCO ₃ (125 mL, 20 °C), and the anolyte was 1 M KHCO ₃ (125 mL, 20 °C). Ni(OH) ₂ and metal hydride MH electrodes were employed as the positive and negative electrodes. Additionally, a manganese dioxide MnO ₂ electrode served as an intermediate electrode. To ensure proper separation, a pair of polypropylene spacers with a thickness of 120 µm were placed between each electrode.	copper sheet	Cathodic time (t _c) = 25 s, anodic time (t _a) = 5 s, cathodic bias (U _c) = −1.6 V, and anodic bias (U _a) = −0.18 V.	CO ₂ RR	The long-term stability could extend 95 h under pulsed electrolysis. The faradaic efficiency of carbon containing products (CO, CH ₄ , and C ₂ H ₄) was about 40% and the efficiency of hydrogen about 20%. Potentiostatic electrolysis at −1.6 V vs. Ag/AgCl: it had very poor stability, and FE _{H2} gradually increased, and reached 70% after 16 h electrolysis.	[91]
13	2018	Two-compartment polycarbonate electrochemical cell, with the cathode chamber and anode chamber separated by an anion exchange membrane (Selemion AMV). The Ag/AgCl reference electrode was located in the cathode chamber, and the platinum mesh counterpart electrode was in the anode chamber. The electrolyte was 1.0 M HCl, and the pH value was maintained at 6.8.	Ni(OH) ₂ positive electrode, MH negative electrode, and MnO ₂ the intermediate	Current density = 0.2 A cm ^{−2} and pulse frequency = 500 Hz.	Water splitting for hydrogen production	The optimal performance was obtained at the current density of 0.2 A cm ^{−2} , and the battery voltage was 1.69 V when the pulse frequency was 500 Hz at 25 °C, which was higher than the electrochemical cycle of conventional electrolysis.	[87]
14	2016	The reactor with two graphite plates with a size of 12 cm × 5 cm × 4 mm was used for organic wastewater treatment, containing 1 L of simulated wastewater (pH 7.0 ± 0.1). The experimental setup comprised a stack of 9 electrolytic cells and a pulse generator. The electrolytes were 0.1 M and 0.4 M KOH (2 L). Electrodes with an area of 20 cm ² and a spacing of 10 mm.	Polycrystalline copper foil	The cathode pulse time = 10–80 ms, a pulse potential = −1.0 V vs. RHE was applied, anode pulse time = 50 ms, and potential = 0.61 V vs. RHE.	CO ₂ RR	A change in pulse time in the range of 10 to 80 ms produced syngas in the absence of by-products, with CO:H ₂ molar ratio ranging from ~32:1 to 9:16. No comparison with DC electrolysis.	[75]
15	2015	The reaction was carried out in a three-electrode system with saturated calomel as the reference electrode and platinum gauze used for the counter electrode. The electrolyte consisted of 3 mM CuCl ₂ , 15 mM InCl ₃ , 32 mM Ga(NO ₃) ₃ , and 75 mM H ₂ SeO ₃ at a pH of 1.5.	Graphite plates	Duty cycle = 50%, pulse frequency = 1000 Hz, and cell voltage = 3 V.	Organic wastewater treatment	Compared to DC power supply (73.2%), pulse power supply (93.2%) had a higher removal rate of sulfide.	[137]
16	2013		Stainless steel electrodes	Pulse frequency = 1 kHz, applied current = 1.4 A, and a duty cycle of 3%.	Water splitting for hydrogen production	Pulse current in water electrolysis significantly enhanced the rate of electrolysis, producing more hydrogen and oxygen than that of direct current (DC).	[69]
17	2013		A Mo coated glass substrate	The cathode pulse potential = −700 mV vs. SCE, the anode pulse potential = 180 mV vs. SCE, the pulse period = 3 s, duty cycle = 67%, and the total degradation time = 50 min.	Electrodeposition	The films prepared by pulsed electrodeposition were smoother, denser, and more uniform compared to DC electrodeposition.	[72]

Table 1. Cont.

No	Year	Details for Configurations	Working Electrode	Pulse Parameters	Applications Area	Enhancement Compared to Steady State Electrolysis	References
18	2009	The experimental setup includes deposition and counter electrodes composed of stainless steel (316 L) plates with dimensions of 2 cm × 5 cm × 0.4 mm. The reactor was filled with a 5 vol% aluminum trioxide suspension, and the pH was 4.5. The electrodes were spaced 20 mm apart, and the deposition range on the electrodes was defined as 2 cm × 2 cm. The experiment was carried out in an electrolytic cell containing electrolyte (3.4 L, 1 M KOH solution, 293 ± 2 K), anode (platinum plates), and cathode (platinum plates). The electrodes were spaced 3 cm apart. The ultra-short power supply consisted of a static induction thyristor (SITh) and an inductive energy storage (IES) circuit.	Stainless steel (316 L) plates	Applied current = 0.001 A–0.1 A. There were bubbles in the deposits above the upper limit of the pulse width and incomplete deposition below the lowest value.	Electrodeposition	There were bubble-free deposits and lower deposition yield with suitable pulse parameters, and bubbly deposits and higher deposition yield with the corresponding DC current.	[138]
19	2005	Conventional H-type gas-tight glass cell filled with CO ₂ -saturated 0.1 M KHCO ₃ buffer solution (pH 6.8) at 10 °C. The counter electrode (platinum) and the working electrode (CuAg alloy) were separated by an ion exchange membrane (Nafion 417). The reference electrode was an Ag/AgCl electrode.	Platinum plates	Voltage pulse-width = 300 ns, the secondary peak voltage ranged from 7.9 to 140 V, the frequency = 2–25 kHz, and input power changed by increasing the pulse frequency.	Water splitting for hydrogen production	Ultra-short-pulse electrolysis alleviated the issue of decreasing efficiency while increasing power under DC electrolysis.	[139]
20	2000		CuAg alloy electrodes with the atomic ratios (Cu/Ag) of 28/72	An anodic bias = −0.4 V, a cathodic bias = −2.0 V vs. Ag/AgCl. Cathodic period (T _c)/anodic period (T _a) = 5 s.	CO ₂ RR	The total value of faradaic efficiencies for these C ₂ compounds was 54.2% under the pulsed CO ₂ electroreduction. No comparison with the DC case.	[63]

7. Conclusions and Perspectives

The emergence of pulse electrolysis technology marks a promising paradigm shift, offering new methods to rise product selectivity, improve efficiency, and reduce consumption when compared to the conventional constant electrolysis. In this comprehensive review, we employ bibliometric methodologies to describe the influence of pulse electrolysis on three distinct aspects, including double electrical layer, electronic influences, and mass transport processes. Concerning the double electrical layer, we summarized the effect of various parameters on its the formation. This understanding is crucial as it impacts the discharge process, enabling energy conservation, high-efficiency current generation, and the reduction of concentration polarization and electrode polarization phenomena. Although surface changes have been reported during pulse processes, the exact mechanisms behind these remain unknown, requiring further investigation. In the domain of electronic influences, we discern how pulse operations impact the adsorption energy and surface coverage of species on electrodes, as well as the structural rearrangement of electrode surfaces. Notably, despite surface changes observed during pulse processes, the possible mechanisms driving these enhancements failed to be revealed. As for mass transport, the diffusion layer theory has been well-established, yet characterizing substance concentrations at the electrode-solution interface with simulation methods is an ongoing challenge. Bridging this gap with real-world conditions and advancing *in situ* detection technologies are important directions for future research.

Based on an extensive bibliometric analysis of pulse electrolysis literature, several key findings have emerged that will significantly influence the future direction of its development:

- (1) **Temporal and Spatial Substance Concentration:** It becomes clear that obtaining precise temporal and spatial distribution data of substance concentrations in close vicinity to the electrode surface during both ' t_{on} ' and ' t_{off} ' phases is significant. At present, the primary focus is on simulation techniques. Bridging the gap between simulation and real-world electrolysis conditions is now a top priority. In addition, further exploration of mass transfer phenomena within the microenvironment of the electrode is necessary.
- (2) **Adsorption Species, Reaction Path, and Product Selectivity:** There is a noticeable gap in our knowledge concerning adsorption species coverage, reaction pathways, and product selectivity on the electrode surface during pulsed electrolysis. Creating micro-dynamic models is crucial in clarifying these processes, as it plays a pivotal role in unraveling the mechanisms involved in pulsed electrolysis.
- (3) **Double Layer:** At present, there is a scarcity of studies that examining the microenvironment and theoretical characterization of the double layer. Understanding the factors that influence changes in the double electric layer under pulsed conditions remains an unexplored frontier.
- (4) **In Situ Detection Techniques:** To achieve a comprehensive understanding of the changes occurring at the electrode-solution interface during pulsed electrolysis, the development of more in situ detection techniques is essential. The utilization of non-in situ characterization methods in many current studies hinders our ability to gather real-time information during pulse electrolysis.

In summary, pulse electrolysis technology holds great promise in electrolysis. However, its practical application in engineering remains limited and calls for further optimization and wider adoption in various applications.

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