1 Highlights

- Pulsed water electrolysis is a method capable of enhancing the current/decreasing the voltage during the on period.
- Bubble removal and replenishment of ions are the main causes of this improvement, as well as the perturbation of the electrical double layer.
- Currently, the improvement in current caused by pulsed electrolysis is not high enough to compensate for the off-period. In other words, at a fixed energetic efficiency, the average production rate is lower using the pulsed method.
- Pulsed water electrolysis could be used to decrease power input while maintaining the current at a minimum
 level at which gas cross-over is not an issue.

Pulsed Water Electrolysis: a Review

F. Rocha, Q. de Radiguès, G. Thunis, J. Proost*

Université catholique de Louvain (UCLouvain), Division of Materials and Process Engineering, Place Sainte Barbe, 2, 1348, Louvain-la-Neuve,
 Belgium

5 Abstract

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The application of pulses is a promising method to enhance the efficiency of water electrolysis. In this review, we first present a historical overview with several seminal references on the topic. Then, we give an overview of the last researches. Possible reasons for the efficiency improvement are outlined, including an increase in reactant concentration at the electrode surface, the improvement of bubble detachment from the electrode, and the perturbation of the electrical double layer.

11 Keywords:

¹² hydrogen production, pulsed power, water electrolysis

13 1. Introduction

Hydrogen is widely considered to be the fuel of the future. It has the highest specific enthalpy of any known fuel: 14 142 MJ.kg⁻¹ against 55 MJ.kg⁻¹ for methane, 48 MJ.kg⁻¹ for octane and 32.8 MJ.kg⁻¹ for coke [1]. Moreover, unlike 15 burning fossil fuels, burning hydrogen does not produce any greenhouse nor acidifying gases. Burning hydrogen pro-16 duces only water and liberates a significant amount of energy [2]. The most sustainable way to produce hydrogen is by 17 water electrolysis. Additionally, this method can be used to store energy from renewable sources. The energy surplus 18 produced by these sources can be used to split water molecules, producing hydrogen. When needed, the produced 19 hydrogen can be used to produce electricity in a fuel cell supplying uninterrupted electricity, or to produce heat by 20 combustion [3]. However, the production cost remains a key issue for water electrolysis [4]. The main technology 21 used to produce hydrogen nowadays is large scale (> 90 kg.h⁻¹) steam methane reformers [5]. In 2019, hydrogen cost 22 from large projects worldwide was estimated to be between 2.5-4.5 \$/kg for green hydrogen against 1.4-2.9 \$/kg for 23 low carbon hydrogen coming from natural gas with carbon capture and storage [6]. Estimations also show a different cost per production rate (kg,h^{-1}) : while the capital expenditure (CAPEX) for large methane reformers was on the 25 order of 11200 - 33600 per kg.h⁻¹, large scale electrolyzers presented a CAPEX between 44800-56000 per kg.h⁻¹ 26 [5]. The electrolyzer lifetime is estimated to be between 60,000 and 90,000 operating hours [7]. To reduce costs, 27 efficiency needs to be enhanced and it is in this context that pulsed electrolysis becomes important. 28

Pulsed electrolysis has been studied for more than seven decades. Yet, some new studies indicate that it is a method capable of improving the efficiency of hydrogen production by water splitting, with some of the reasons being the removal of gases from the electrode during the resting time and by the increase in the concentration of reacting ions at the electrode surface.

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Another review about pulsed electrolysis can be found in [8], which also includes pulsed plasma and pulse modeling. Other reviews cite the impact of electric input fluctuation [9], the effects of the applied voltage waveform [10], and the impact of pulsating power [11] in water electrolysis. The review presented here specifically includes a historical overview and a more fundamental insight into the mechanistic details of the efficiency improvement induced by pulsed water electrolysis.

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^{*}Corresponding author (joris.proost@uclouvain.be)

There are two types of pulsed operations: voltage pulses and current pulses. In the first, voltage is changed from a base value (called off-voltage) to a peak value (called on-voltage). The sum of on-time (t_{on}) and off-time (t_{off}) is the pulse period. The ratio between on-time and pulse period is defined as the duty cycle, and the frequency is the inverse of the pulse period. The pulse amplitude is the difference between off-voltage and on-voltage. The resulting current will be the sum of a faradaic current (if the peak current is in a potential range at which water electrolysis occurs) and

⁶ a capacitive current for the charging/discharging of the double layer.

When a voltage pulse is imposed, the capacitive current can be estimated as the charge/discharge of an ideally
 polarized electrode [12]:

$$i_c(t) = \frac{\Delta E}{R_s} exp(-t/R_s C_D) \tag{1}$$

• with ΔE the amplitude of the voltage pulse, R_s the solution resistance, C_D the double layer capacitance, and t the time.

¹⁰ Note that the capacitive current decays exponentially with time. The estimation of the faradaic current, on the other

hand, can be done considering a semi-infinite linear diffusion at a planar electrode. For a quasi-reversible, one-step,

one-electron case $(O + e^- \rightarrow R)$, the current time-behavior is given as [12]:

$$i_f(t) = FA(k_f C_0^* - k_b C_R^*) \exp(H^2 t) \operatorname{erfc}(H\sqrt{t})$$
(2)

13 with:

$$k_f = k^0 exp(-\alpha f(E - E^0)) \tag{3}$$

$$k_b = k^0 exp[(1 - \alpha)f(E - E^0)]$$
(4)

$$f = \frac{F}{RT}$$
(5)

$$H = \frac{k_f}{\sqrt{D_0}} + \frac{k_b}{\sqrt{D_R}} \tag{6}$$

where erfc is the error function complement of x, defined as:

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy$$
 (7)

where k^0 is the standard rate constant; α the transfer coefficient; F the Faraday constant; A the electrode area; k_f 15 and k_b the rate constant for the forward (reduction) and backward (oxidation) reactions, respectively; C_0^* and C_R^* the 16 concentration of the reactant O and the product R in the bulk, respectively; t is the time; R the gas constant; T the 17 temperature; E voltage; E^0 the standard potential; D_0 and D_R the mass transfer coefficients for specimens O and R, 18 respectively. The graphical representation of a voltage pulse with a peak voltage at which water electrolysis occurs 19 and a base voltage at which no reaction is possible is shown in Fig. 1.a. The capacitive current was estimated using eq. 20 1 and the faradaic current using eq. 2. It can be seen that when a voltage pulse is applied, the total current starts mainly 21 capacitive and after the complete charge of the electrical double layer - EDL, it becomes mainly faradaic. When the 22 voltage returns to the base value, the EDL is discharged, giving a pure capacitive current. 23

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In the case of current pulses, the voltage-time behavior at the beginning of a pulse can be estimated considering again the ideally polarized electrode [12]:

$$E = i(R_s + t/C_D) \tag{8}$$

As the double layer is charged and the voltage reaches the reversible cell voltage, faradaic processes start to occur. Then, considering a quasireverible one-step one-electron reaction, the potential-time behavior is given by [12]:

$$-\eta = \frac{RT}{F} i \left[\frac{2\sqrt{t}}{FA\sqrt{\pi}} \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right) + \frac{1}{i_0} \right]$$
(9)

with η the overpotential and i_0 the exchange current. Additionally, when the current is off (0 A), the potential-time

² decay for a quasireversible reaction can be estimated as [12]:

$$\eta(t) = \frac{\eta(t=0)}{\epsilon - \beta} [\epsilon exp(\beta^2 t) \operatorname{erfc}(\beta \sqrt{t}) - \beta exp(\epsilon^2 t) \operatorname{erfc}(\epsilon \sqrt{t})]$$
(10)

³ with ϵ and β related to the relaxation times. Notice that the voltage relaxes to the reversible cell voltage. Olmstead [13]

 $_{4}$ proposed a method to differentiate the capacitive current from the faradaic current when current pulses are applied to $_{5}$ an electrochemical system. In this case, the ratio of the capacitive to total current density, h(y), is calculated as the numerical calution of the following equation:

6 numerical solution of the following equation:

$$\frac{1 - exp[\frac{-1}{\psi} \int_0^y h(x) \, dx]}{1 + exp[b - \frac{1}{\psi} \int_0^y h(x) \, dx]} = \sqrt{y} - \frac{1}{2} \int_0^y \frac{h(x) \, dx}{\sqrt{y - x}} \sqrt{\frac{D_O}{D_R}}$$
(11)

7 where:

$$exp(b) = \frac{C_0^*}{C_R^*} \tag{12}$$

$$\psi = \left(\frac{RT}{nF}\right) \frac{4i_T C_d}{(nFC_O^* \sqrt{\pi D_O})} \tag{13}$$

with i_T the total current and n is the stoichiometric electron coefficient. Notice that when ψ is zero, no capacitive effect

is expected. For the off-time, considering a total current of zero, the faradaic and capacitive currents can be estimated
 as follows [14]:

$$i_c = C \frac{d\eta}{dt} \tag{14}$$

$$\dot{i}_f = -\dot{i}_c \tag{15}$$

The graphical representation of these equations for a current pulse with an off-current of 0 A is shown in Fig. 1.b. In the beginning, the voltage increases linearly with time due to the charge of the EDL as predicted by eq. 8. Then, it increases with the square-root of time, following eq. 9 for the faradaic reaction. As in the voltage pulse case, the current starts mainly capacitive and then becomes faradaic as from eq. 11. During the off-period, the EDL is discharged by means of faradaic processes, which promotes a voltage decay.

There are different manners of comparing water electrolysis techniques. A simple way is to see at a constant voltage, what are the currents from each process. The one with the higher current is the most performing. Likewise, at constant current, the one with the lowest voltage is the best. Another way to compare different techniques is by the efficiency. At the same production rate, the one with the best efficiency is the greatest. Voltage efficiency is defined as [15]:

$$\eta_{voltage} = \frac{E_{th}}{E_{cell}} = \frac{1.23V}{E_{cell}} \tag{16}$$

with E_{th} the theoretical voltage value (1.23 V for water electrolysis) and E_{cell} the cell voltage. Alternatively, efficiency can be calculated using the thermal neutral voltage:

$$\eta_{voltage, thermal} = \frac{1.48V}{E_{cell}} \tag{17}$$

Another way to define efficiency is by the energetic efficiency, defined as follows [16]:

$$\eta_{energetic} = \frac{\dot{V}.\Delta H}{P_{el}} \tag{18}$$

where \dot{V} is the hydrogen production rate at standard conditions, ΔH is the heating value for hydrogen (lower or higher), and P_{el} is the consumed electric power. The lower heating value (LHV) is the energy released by the burn of hydrogen, considering water vapor as the only product and it is equal to 3.00 kW h/Nm³. The higher heating value

⁴ (HHV), on the other hand, considers liquid water as the only product and it is equal to 3.54 kWh/Nm³. Using the

⁵ Faraday law of electrolysis and the ideal gas law, one has an energetic efficiency equal to:

$$\eta_{energetic} = \frac{R.T.\Delta H}{z.F.P} \cdot \frac{i_{H_2}}{i_T} \cdot \frac{1}{E_{cell}}$$
(19)

G with R the gas constant, T the standard temperature, z the stoichiometric electron coefficient (2 for hydrogen), F the

⁷ Faraday constant, P the standard pressure, i_{H_2} the current used for hydrogen production, i_T the total current, and E_{cell}

the cell voltage. This first term is a constant. The second term is defined as Faraday efficiency and it is commonly
 100%, unless a parasitic reaction takes place. Considering no parasitic reaction, the energetic efficiency depends only

¹⁰ on the cell voltage, as in the case of voltage efficiency.

11 **2. Historical overview**

A critical summary of the historical techniques of pulsed water electrolysis is shown in Table 1. One of the first 12 studies using voltage pulses was made by Tseung et al. [17]. To study the effect of bubbles in porous electrodes, the 13 authors compared the value of the current at DC power and voltage pulses with a width of 100 μ s. In this review, 14 DC refers to the conventional non-pulsed process, which can be galvanostatic or potentiostatic. The pulse width was 15 chosen to be much higher than the electrical double layer (EDL) charging time but lower than the time for bubble 16 formation. The result was that the pulsed power presented a current value between 2-10 times higher than the DC 17 current value at the same voltage. Nevertheless, in their research, only one pulse was used. The next step would be 18 to see how much time the bubbles need to detach in the presence of a forced flux and then, apply the following pulse 19 after this time, always maintaining a high current density. The authors also argued that at low current densities, the 20 hydrogen produced can be dissolved in the electrolyte and escape the pores of the electrode by diffusion. However, at 21 higher current density, bubbles are formed. The creation of bubbles pushes the electrolyte far from the surface of the 22 electrode and reduces the active surface area and the performance of the electrode. Under this condition, the reaction 23 can still occur at the entrance of the pores, but not in their interior. Bubbles detach from the surface when the pressure 24 is equal to [17]: 25

$$P = 2\sigma \cos\theta/r \tag{20}$$

with σ the electrolyte's surface tension, θ the contact angle, and r the radius of the pores [17].

In the following decade, researchers from Columbia University published some important articles about pulsed 28 electrolysis. Viswanathan et al. [18] inspected the ferri/ferrocyanide redox pair in a rotating disk electrode with pulses 29 in the limiting current at on-time and zero current at off-time. An increase in the limiting current was observed be-30 tween 1.43-9.10 times the one from DC electrolysis due to the reduction in the thickness of the diffusion layer. The 31 merit of this research was also the proposal of a mathematical model to estimate the limiting current during pulsed 32 electrolysis. Nevertheless, the authors did not study water electrolysis and since industrial water electrolyzers do not 33 work at limiting current conditions, the conclusion does not necessarily fit in the case of water electrolysis. After that, 34 a numerical solution was obtained for mass transfer at a rotating disk electrode (RDE) under pulsed voltage consider-35 ing a reversible reaction in excess of supporting electrolyte [19]. High current densities during on-time were reported 36 in [20] for a reversible deposition reaction with an insoluble product $(Ag_{(s)})$ from AgNO₃(aq.)) using linear sweep 37 voltammetry in an RDE. The peak current reached 3.5 times the value of the DC limiting current. 38

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Then, Viswanathan et al. proposed a numerical solution for intermittent electrolysis under mass transfer controlled 1 condition [21]. This non-DC electrolysis was defined as an electrolysis at which the surface concentration of a react-2 ing ion was always zero during the on-period, while in pulsed electrolysis the concentration arrives at zero only at 3 the end of the on-period. It was claimed that between pulsed current, pulsed voltage, and intermittent voltage, the 4 latter presented the highest electrolysis rate. Furthermore, it was concluded that the average rate of electrolysis during 5 intermittent conditions can never overcome the rate of DC electrolysis. As we will see further, the majority of the 6 paper presented here will confirm this conclusion. In other words, despite the higher on-current, the average current is lower for pulses. 8 9

Ibl et al. performed some studies about squared current pulses for electric plating [14, 22, 23]. During off-time, 10 the system was at an open circuit and the current was zero. In a study published in 1978 [22], the authors argued that 11 in pulsed electrolysis, there are two diffusion layers. The first one is close to the electrode and has pulsating concen-12 trations of ions, while the second one is far from the electrode and it is stationary after a certain number of pulses 13 were applied. Furthermore, they showed that the application of pulses yielded very high current densities. Their explanation for that was that the thickness of the diffusion layer is reduced, improving mass transport. Moreover, it was 15 concluded that the change in pulse parameters affected the surface of the electrode during electrodeposition. Finally, 16 they proposed a method to measure the capacitance by applying the equation $j_c = C \frac{\partial \eta}{\partial t}$ at the very beginning of pulse application, with j_c the capacitive current, C the double layer capacitance, $\frac{\partial \eta}{\partial t}$ the variation of overpotential with time. 17 18 19

Then, mass transport and capacitance effects in pulsed plating were evaluated [23]. The authors claimed that after a circuit interruption, the current took some time to drop to zero because of the discharge of the EDL. Thus, if offtime was short enough that the current did not have time to decrease completely, the current would slightly fluctuate around an average value. In this case, pulsed electrolysis would be very similar to DC electrolysis. Assuming a linear concentration profile, the thickness of the pulsating diffusion layer can be expressed as:

$$\delta = \sqrt{2Dt_{on} \left(1 - \frac{t_{on}}{(t_{on} + t_{off})}\right)}$$
(21)

with D the diffusion coefficient. It is independent of current density and of bulk concentration. Furthermore, the authors proposed that the time for the reactant concentration at the electrode surface to fall to zero is given by:

$$\tau = \frac{D.(C_0 nF)^2}{2i_p^2}$$
(22)

with i_p the pulse current. Finally, it was concluded that the depletion of reactants at the electrode surface can limit the rate of deposition and can cause powder formation. Equations 21 and 22 were obtained during plating, where there is the diffusion of metal ions in the electrolyte. In the case of water electrolysis, the effects of ion migration must be taken into account. Moreover, at the cathode during alkaline water electrolysis, it is difficult to talk about diffusion, since the only reactant is the water solvent itself.

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Later on, the rate of charge and discharge of the EDL using current pulses in electric plating was studied [14]. Dif-33 ferent cases were analyzed. The first one considered a negligible double layer charging time in comparison with pulse 34 time. For this situation, the faradaic current was equal to the total current. This situation was defined as an interrupted 35 DC electrolysis, without the effects of the charge/discharge of the EDL. The second case considered a double layer charging time lower than ton, but not negligible. In this situation, the Faradaic current is lower than the total current at 37 the beginning of the pulse, but after some time it reaches its maximum value. A situation close to the one presented 38 in Fig. 1.b. Finally, the third case considered a charging time longer than ton and a discharging time longer than toff. 39 As a consequence, the faradaic current neither returns to zero nor reaches the value of the total current. The authors 40 claimed that the damping decreases losses since reducing Faradaic current also reduces ohmic losses. When a pulse 41 is switched off, there is a Faradaic current, but no ohmic drop in the solution. 42 43

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Subsequently, the authors studied the capacitance of the EDL. The results showed a capacitance in the range 10-100 μ Fcm⁻², depending on the electrode. For rough nickel (Ni/H₂SO₄ 1 M) it was 80 μ Fcm⁻². Still according to this study, 50 μ Fcm⁻² is a good approximation if the real value of the capacitance is unknown [14]. Recent works talk about a specific capacitance for Ni in KOH in the order of 40 μ Fcm⁻² [24, 25] or even 20 μ Fcm⁻² [26]. To estimate the EDL charging/discharging time, besides the capacitance, the solution resistance must be known as shown in eq. 1 and eq. 8.

Chin presented some numerical methods for the analysis of mass transfer and voltage/current relation in pulsed electrolysis [27, 28]. At mass-transfer controlled processes, it was shown that short pulses with long relaxation periods could cause an instantaneous current 100-1000 times higher for the case of electrodeposition/dissolution of copper in an acid copper sulfate solution. A decrease in overpotential was also reported. This effect was attributed to the replenishment of reactants at the electrode surface and the decrease of diffusion layer thickness.

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In the 1950s, Bockris JOM published two papers studying the mechanisms of the hydrogen evolution reaction 14 (HER) in two different conditions: nickel cathodes in aqueous solutions [29], and platinum silver and tungsten in acid 15 solution [30]. In these studies, it was observed that when the applied voltage was disconnected, a significant current 16 continued to flow for a short time. This phenomenon was attributed to the discharge of ions from the electric double 17 layer in the absence of the externally applied electric field. In the book "Modern Aspects of Electrochemistry, No 15" 18 [31], Gutmann et al. explained that it is an experimental fact that "upon application of a voltage to an electrochemical 19 system, a high but short-lived current spike is observed". This conclusion was confirmed more recently by Vanags et 20 al. [32]. This would be a consequence of the EDL charging followed by the discharge of the first ionic layer, which 21 increases current. Then, the EDL would be replenished by mass transport from the bulk to the electrolyte/electrode 22 surface. As a consequence of these two phenomena, pulsed electrolysis would be capable of enhancing the overall 23 efficiency of water electrolysis. 24

In 1985, two important articles were published by the Bockris group. The first one [33] presents a review about the 26 different techniques of water electrolysis, in which also a setup for pulsed electrolysis was proposed. It consisted of a 27 homopolar generator like the one conceived by Michael Faraday. The idea was to put a disk to rotate in contact with 28 an electrolyte solution and under the effect of a magnetic field, as shown in Fig. 2a. This would create a difference in 29 electrical potential between the inner and the outer part of the disk. As a consequence, oxygen would be produced at 30 the center and hydrogen at the periphery of the disk. Moreover, to reduce viscous losses due to the disk rotation in the 31 solution, they proposed that the homopolar generator can be used as an external power supply. To use the generator 32 in pulsed mode, a propeller with magnets at both ends was designed, as seen in Fig. 2b. The proposed configuration 33 allowed the creation of pulses of 2-3 V with a duration of about 1 ms. 34

In their following paper [34], the authors carried out some experiments in water electrolysis with triangular pulses 36 on a rotation disc in a magnetic field. The pulse width was 600 μ s and the mean cell voltage was 2.6 V. The double 37 38 layer charging time was estimated to be approximately 140 μ s. Hence, the pulse lasted five times the charging time. The authors discovered that the formation of bubbles depends on the duty cycle: for duty cycles lower than 10%, 39 no bubbles were observed, while for duty cycles higher than 30%, bubbles were visible. Nevertheless, when no 40 bubbles were observed, this was because the hydrogen was dissolved. If the experiment had continued for a longer 41 time, hydrogen saturation would be reached and after that, hydrogen bubbles would be formed. Proceeding with the 42 experiment, a model to calculate the current due to a triangular voltage pulse was proposed: 43

$$i_p(t) = i_{max} exp(-kt) \tag{23}$$

where i_p is the actual pulse current, *t* the time, *k* a time constant, and i_{max} the current peak value. This model is similar to eq. 1, with $i_{max} = E/R_S$ and $k = 1/(R_S C_D)$. If there is a succession of *n* pulses, the pulse current can be estimated as:

$$\frac{i_p}{i_{DC}} = 1 + \frac{i_{max}}{k\tau i_{DC}} [1 - exp(-k\tau)]$$
(24)

with i_{DC} the DC current value and τ the pulse width. In their experiments, the pulsed current was two times greater than the DC current. [34].

In 1985, Brandon et al. noticed that bubbles departed from the electrode immediately after the current was inter-4 rupted [35]. Following this study, Khosla et al. investigated the effect of pulsed current on the generation of hydrogen 5 bubbles [36]. The bubbles were observed with the help of a video camera. In their set-up, platinum electrodes were 6 used in a 1 M sodium sulfate solution. The solution was circulated employing pumps. At first, the applied current pulse contained a high and short peak current for bubble nucleation, followed by a steady value. However, this 8 peak has shown no difference from electrolysis carried out without the peak. As a consequence, the pulses were just 9 common square pulses. The frequency was set at approximately 30 Hz. The results showed that pulsed electrolysis 10 promotes a decrease in bubble diameter. Lower duty cycles and/or higher current densities give lower bubble sizes. 11 Furthermore, it was argued that due to the higher current in pulsed electrolysis, bubble nucleation does not take place 12 only in structural defects, but occurs homogeneously and that frequent interruptions in current causes bubble detach-13 ment. 14

Shaaban [37, 38] applied voltage pulses to 3-D electrodes made of a dispersion of spherical ultra microelectrodes. 16 3-D electrodes were used as they increase the electrode surface area. At the same cell-voltage and geometric area, 3-D 17 electrodes promoted a current in the order of 100-1000 times greater than 2-D electrodes. In this work, frequencies 18 varied from 10 Hz to 40 kHz and the duty cycle went from 10-80%. The electrolyte was a solution containing 10 wt% 19 sulfuric acid. A change in current polarity during off-time was noticed, which was attributed to a reversible reaction 20 going backward. To prevent this countercurrent, the authors used a diode. Nevertheless, the diode maintained the 21 voltage during off-time at 2.3 V instead of 0 V. On-voltage went from 3.5 V to 14 V. A phase difference between 22 current and voltage was observed with current lagging behind voltage, which indicates an inductive system. There 23 was also a high voltage drop between the applied voltage and the cell voltage, caused by inductive reactance. This 24 voltage drop was given by: 25

$$\Delta V = -L_w \frac{di}{dt} \tag{25}$$

where L_w is the wire inductance. Since $\frac{di}{dt}$ was high, the voltage drop was high as well. This voltage drop also changed the shape of the voltage pulse, going from a square in the power supply to a sinusoidal curve in the cell. Contrary to their previous works, an EDL charging current was not observed. Furthermore, it was found that DC power presented a better efficiency than pulsed power and that increasing the frequency increased efficiency. Also, efficiency was better for higher duty cycles. Finally, when a diode was used, the current continued to flow during off-time, but this phenomenon was not attributed to the EDL discharge, as in [29], but to the collapse of magnetic fluxes around the leads that connect the cell to the power supply.

³⁴ With a different scope, but still in the domain of pulses, Hitz *et al.* used current pulses to study kinetic parameters ³⁵ of the hydrogen evolution reaction of porous nickel electrodes in alkaline solutions [39]. They estimated a double ³⁶ layer capacitance of the porous electrode on the order of 125-136 mF.cm⁻², depending on the temperature. This is ³⁷ more than a thousand times the value of 45-50 μ F.cm⁻² obtained for polycrystalline nickel electrodes and 80 μ F.cm⁻² ³⁸ obtained previously by Puippe *et al.* [14] for rough nickel. This difference shows the enormous increase in the surface ³⁹ area caused by the porous structure, as stated previously in this review.

3. Inductive pulses

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The main idea of inductive pulsed water electrolysis is the application of a very high inductive voltage as compared to the equilibrium voltage, with the double layer storing and releasing energy during pulsed operation. This affects the bubble behavior and changes the effective electrolyte resistance. With this method, the resulting current and voltage are not constant, but the power can be controlled by choosing the frequency and amplitude of the pulse in the first circuit. As a consequence, this method can be classified as a power control method. The main achievements will be presented in this section and are also critically summarized in Table 2. Shimizu *et al.* [40] studied the effect of inductive pulses with a width of 300 ns during alkaline water electrolysis. The voltage pulses were created in a primary circuit and had frequencies between 2–25 kHz, while the pulse inducted

in a secondary circuit (where the cell was inserted) had a width of 300 ns and a peak voltage of 7.9-140 V, as shown in

⁴ Fig. 3.a. The results were compared with DC power. 1 M KOH solution and platinum electrodes were the materials

⁵ used as cell constituents and a diode was placed in the secondary circuit to avoid current inversion. It was argued that

⁶ the pulse width was significantly lower than the time for the formation of the EDL and of the Nernst diffusion layer.

7 The time for the formation of the diffusion layer was estimated as:

$$t = \frac{1}{4D_O} \left(\frac{X_{ad}}{X}\right)^2 = \frac{\delta_{max}^2}{4D_O} \tag{26}$$

where D_0 is the diffusion coefficient, X_{ad} is the density of hydrogen ions on the cathode (cm⁻²), X is the concentration 8 of hydrogen ions in the bulk (cm⁻³), and δ_{max} is the thickness of the diffusion layer. The same equation was proposed previously by Bard *et al.* [12]. For proton diffusion ($D_O = 2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), 1M of KOH (X = $6.10^{20} \text{ cm}^{-3}$), and 10 a platinum electrode (X_{ad} = 1 0¹⁵ cm⁻²), the authors achieved a time of 3 μ s for diffusion layer formation. However, 11 applying this equation with the given values, a result of 30 ns is obtained. The time for the formation of a stable 12 EDL was said to be several tens of milliseconds. The results have shown that at DC power, the increase in voltage 13 also increases current and production rate, but decreases the efficiency. Contrary to DC, in the pulsed power case, the 14 production rate was decreased when the voltage at the secondary circuit was increased. In the case of relative low 15 voltages (7.9 V and 9.7 V), the efficiency increased when increasing the pulse frequency (maintaining the pulse width 16 at 300 ns). In the case of pulses with a voltage of 7.9 V and a frequency of 17 kHz, the efficiency and production rate 17 were higher than DC at the same input power (2.6 V at 0.5 A). For all the other 11 cases studied, the performance was 18 worse than conventional water electrolysis. 19

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Following the work of Shimizu et al., Dharmaraj et al. conducted some research about nano pulsed water electrol-21 ysis in the past decade. In their first publication [41], the authors used stainless steel electrodes in a NaOH solution. 22 The pulse generator was the same as the one used in [40]. They claimed to have reduced the energy consumption from 23 18 W to 0.57 W at a fixed hydrogen production rate of 0.58 ml/s. Nevertheless, their calculation of consumed power 24 for pulsed electrolysis was non-conventional. Based on another study in microwave systems [42], they measured only 25 the power consumed at on-time and not at off-time. However, this method is only valid if the current or the voltage 26 is equal to zero during off-time. Otherwise, the power should be calculated as the integral of the product of voltage 27 multiplied by the current during the entire pulse period [42]. Consequently, the efficiency of pulsed electrolysis in this 28 work may have been greatly overestimated. The energetic efficiency should be calculated using equation 18. Besides 29 the non-conventional method of power measurement, it is theoretically impossible to have such a low value of electric 30 power. A production rate of 0.58 Ncm³/s represents a current of approximately 5 A. Even if there was no overpotential 31 and the reaction occurred at the reversible cell-voltage of 1.23 V, the power consumed at this production rate would 32 be 6.15 W, way higher than the 0.57 W estimated by the authors. This reinforces the idea of a great overestimation of 33 process efficiency. 34

In their second article [43], the authors published the same research, but with some more details. The pulse frequencies varied between 0-200 kHz. It was observed that hydrogen production rate increased with frequency until 150 Hz and then it started to decrease for higher frequency values. Even though the authors did not explain the reasons for this decrease in production rate, it is possible that the different frequencies in the primary circuit created voltage pulses with different shapes in the secondary circuit. Hence, it was not only the frequency that changed but also the shape of the pulse, which would have a different effect on the resulting production rate.

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The Latvian Hydrogen Research Team also published some interesting articles about inductive pulsed water electrolysis at the beginning of the 2010s [32, 44–47]. They named their pulses inductive kickback voltage (IKV) pulses. In their first experiment [44], they used distilled water as electrolyte and steel plates as electrodes. The aim was to study resonant electrostatic phenomena. The hypothesis was that if the pulse frequency is set at the resonance frequency, the water electrolysis process will be significantly enhanced. This was attributed to the fact that the bonds between the atoms in water molecules would be disrupted and the resulting gases would evaporate out of the solution.

High voltage/short pulses were applied by induction in the configuration shown in Fig. 3b and Fig. 3c. It can be 1 seen that there were two inductors (one with variable inductivity) connected in a serial circuit with an electrolysis cell 2 (acting as a capacitor), a diode, and a transformer. Square voltage pulses with lengths between $100 - 1 \mu s$ and an 3 amplitude of 100 V were applied to the primary coil of a transformer. The winding ratio of the transformer was 1:1. 4 The space between the electrodes was filled with distilled water and the results were compared to the one achieved 5 when this space was filled only with air. When water was used (and water electrolysis occurs) a voltage fall was ob-6 served at the end of each series of pulses. This was not observed when the air was used. Electrochemical Impedance Spectroscopy analysis has found a resonant frequency at 229 kHz. They concluded that water could be split by this 8 technique and that conventional charge transfer at the electrode could be avoided. The first hypothesis made by the 9 authors was that the electrodes were working as capacitors and split water molecules by vibration of bonds. This 10 idea was abandoned in subsequent publications. Indeed, according to Stuart [48], the frequency for H-O-H bending 11 is in the order of 49 THz and the frequency for O-H stretching is in the range of 98-118 THz, which is far more than 12 the 229 kHz found before. The selection of the frequency in pulsed water electrolysis is important because different 13 frequencies affect different phenomena such as bubble removal, diffusion layer formation, and electrical double layer formation. 15

Two years after their previous paper, the group published another study in 2011 [32]. In this case, microelectrodes 17 were used to investigate preliminary stages of the hydrogen evolution reaction on tungsten and platinum electrodes 18 in a cell powered by inductive kickback voltage pulses in an alkaline solution. As before, square pulses produced 19 in the primary coil induced very sharp and high kickback pulses with opposite polarity in the secondary winding of 20 the transformer. The setup of this and the subsequent experiments of the research team is shown in Fig. 3c. The 21 pulse applied in the electrolysis cell had a high voltage of 60 V, a short width of 1 μ s, and an on-time on the order of 22 some hundreds of microseconds, as shown in Fig. 3b. A hydrogen microsensor was used to measure the dissolved 23 hydrogen concentration at the cathode vicinity. They observed that the phase angle between current and voltage was 24 not significant. After the application of a pulse, a tail-shaped voltage decay was observed (Fig. 3b), and it stabilized 25 at a voltage greater than zero as a consequence of the diode in the circuit. The diode is important as it forces the IKV 26 pulse to discharge in the cell, causing electrochemical reactions. They also noted a higher performance of tungsten 27 electrodes in comparison with platinum electrodes. To explain this, the authors proposed that while hydrogen ions 28 are adsorbed onto a platinum electrode, the electrons from tungsten directly discharge in hydrogen ions, forming H_2 29 molecules. Nevertheless, this study did not present a comparison with DC water electrolysis, so it is not possible to 30 say if IKV pulsed electrolysis presents better performance than the conventional method. 31

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In another article [45], the same authors applied IKV pulses to steel electrodes in an alkaline solution. The square 33 pulses in the primary circuit had a width of 50 μ s, an amplitude of 1 V, and a duty cycle of 50%. The same behavior 34 as before was reported in the secondary circuit, namely a high voltage short time pulse with a long tail stabilizing 35 with a voltage greater than zero and a current equal to zero. It was observed that the resulting voltage was decreased 36 when increasing the electrolyte concentration and decreasing the electrode spacing. The current was held constant, 37 independently of the electrolyte concentration and the electrode spacing. The authors argued that the setup presented 38 in Fig. 3c enabled the enhancement of the pulse amplitude: while on the primary side the amplitude did not exceed 39 1 V, on the secondary (and reactive) side, it exceeded 2 V. According to the authors, the reactive amplitude depends 40 on the quality factor (Q) of the capacitive element in the electrolysis cell. This happens because during the first mi-41 croseconds, the cell behaves as a capacitor with high-quality factor and the charging of the EDL takes place. The 42 more concentrated the solution was, the higher the capacitance, therefore, lowering the voltage at the same charge 43 (capacitance equals charge divided by voltage). After this step, the EDL needs to discharge. Nevertheless, the diode 44 blocks the discharge in any other way than through electrochemical reactions. As a consequence, water electrolysis 45 occurs and the voltage drops until a value at which the reaction cannot be activated. Finally, they concluded that with 46 the setup presented here, power consumption in water electrolysis can be lowered, since an input voltage as low as 1 47 V in the primary circuit could lead to water electrolysis. 48

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⁵⁰ Subsequently, the research team published a study [46] where the dynamics of current and voltage during the ⁵¹ application of IKV pulses with different electrolyte concentrations were analyzed. Stainless steel wires were used as ⁵² electrodes and deionized water and weak basic/acid solutions as electrolytes. As in [45], there was a decrease in the

amplitude of the pulse voltage (from 600 V to 9 V) with an increase in the electrolyte concentration (from zero to 3.6 mM). Nevertheless, the rate of EDL charging was concentration-independent. The discharge tail, on the other hand, 2 lasted longer with increasing concentration. The charge transfer to the electrolysis cell increased with concentration 3 and stabilized at a certain value. Even if both the voltage and the current changed with concentration, the power 4 remained constant. Moreover, for deionized water and very weak electrolytes (1 mM), a change in polarization (nega-5 tive current) was observed, meaning that electrons were entering the cathode from the solution. Here, since there was no reference electrode, positive current means hydrogen production at the cathode and oxygen at the anode. Negative current represents the change in polarization. To explain that, the authors proposed that after the EDL charging, elec-8 trons were emitted from the cathode into the solution. These electrons were then solvated by six water molecules in an 9 octahedral shell. Even tough $(H_2O)_6^-$ was reported previously in the literature [49–51], there are numerous low-lying 10 possible isomers. It is therefore hard to say with certainty that the structure was octahedral. Furthermore, the problem 11 is rather complex and $(H_2O)_N^-$ clusters with N up to 200 were reported [51–53]. After being solvated, Vanags et al. 12 claimed that the electrons had three scenarios to escape from the shell: 1) discharging with hydroxonium $H_3O_{(aq)}^+$; 2) 13 reacting with a water molecule, splitting it into $H_{(aq.)}^{-}$ and $OH_{(aq.)}^{-}$; 3) returning to the metal. In the case where there are sufficient hydrogen ions in the solution, the first possibility is more realistic, since this reaction has a high rate. 15 In the case where there are just a few ions, the third path is the most likely. This may explain the change in current 16 polarization observed for deionized water. 17

After all these publications, the Latvian group wrote a chapter in a book entitled "Electrolysis" [47] where they 19 summarized their discoveries and proposed some new ideas. Among these, there was the hypothesis that there could 20 be oxygen production at the cathode at very low concentrated solutions, together with hydrogen production. To 21 explain that, the authors used the idea of electrons being emitted from the cathode to the solution. After that, the 22 discharge would be done according to the second mechanism proposed in [46]. Then, instead of electrons returning 23 to the metal, there would be hydroxy ions being oxidized and producing oxygen gas. To test this hypothesis, they 24 measured the concentration of dissolved oxygen near the cathode and observed that when a negative current was ob-25 served (de-ionized water and 1 mM), oxygen was indeed produced. When the current was positive, no oxygen was 26 observed. This reinforces the idea that the negative current is not caused by the return of solvated electrons to the 27 metal, but it is a result of the oxygen evolution reaction (OER). They also explained that it is possible to separate 28 EDL charging from the Faradaic process by the use of inductive voltage pulses: when the voltage pulse is on, EDL 29 is charged, when it is off, the energy is discharged and electrolysis occurs. The authors obtained a Faraday efficiency 30 of 50%, meaning that only half of the average current was used for hydrogen production. Nevertheless, this happens 31 because the capacitive charging current is also being measured. What happens indeed is that 50% of the measured 32 current is to charge the EDL and then all the stored energy is discharged in the solution, resulting in the consumption 33 of 50% of the total measured current. In other words, all the injected current is used in Faradaic processes after 34 being used to charge the EDL. Also, a low heating value (LHV) efficiency between 59-85% was obtained, which is 35 a great achievement, since the maximum LHV efficiency that can be obtained at thermoneutral conditions is 85.7%, 36 corresponding to a high heating value (HHV) efficiency of 100%. This energy efficiency was calculated by measur-37 ing the power consumption on the primary circuit and comparing it with the hydrogen production rate. Finally, they 38 argued that in pulsed electrolysis, the diffusion layer is characterized by pulsed concentrations of active ions at the 39 electrode surface and a normal diffusion layer far from the surface (as in DC), as proposed before by Puippe et al. [14]. 40 41

Encouraged by the conclusion of Vanags *et al.*, Kukhtarev *et al.* [54] proposed the use of the photogalvanic effect to create short and high voltage pulses (microseconds and kilovolts). The idea was that the illumination of ferroelectric crystal of Fe: LiNbO₃ would provoke the creation of these voltage pulses which would be used in a water electrolysis cell to produce efficiently hydrogen and oxygen. Yet, no information about neither efficiency nor production rate was given.

47 4. Voltage pulses

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48 4.1. Pulse Width Modulation

49 Concomitantly with the work of the Latvian team, Mazloomi *et al.* conducted some research about Pulse Width

Modulation (PWM) in water electrolysis [10, 55–59]. PWM is based on a semiconductor switching element that

promotes voltage pulses by cutting the circuit periodically. This is a way to control the amount of power delivered to
 an electrolysis cell. To illustrate this, an increase in the duty cycle increases the power delivered, even if the voltage
 is kept constant. An overview of the key techniques of pulse width modulation will be presented in this section and a
 critical summary is shown in Table 3.

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This system is not ideal and presents some power dissipation. These losses can be due to switching or conduction 6 losses. The latter is related to the nature of the switch, whilst the first has some other influencing variables such as control system, switching method, and power electronics circuitry. A representation of these losses can be seen in 8 Fig. 4. In their first publication [55], the authors studied the behavior of semiconductor switches (transistors) in an 9 electrolysis cell, with a special focus on the losses. They reviewed the BJT, IGBT, and MOSFET transistors technol-10 ogy and concluded that for the specifications of a water electrolysis cell, namely high current and low voltage, the 11 best transistor would be a MOSFET with soft switching methods such as zero voltage switch (ZVS) and zero current 12 switch (ZCS). The authors also proposed a parallel connection of water electrolysis cells together with semiconductor 13 switches to provide a hydrogen production plant with a wide range of production rates. 14

After that, the authors published a review [56] on the influence of different variables on the efficiency of water electrolysis. Among other things, they stated that the equivalent circuit of a water electrolysis cell contains non-linear elements. As a consequence, it was pointed out that the effect of applying other forms of voltage than DC may lead to a process improvement. They also provided a review on the effect of bubbles in water electrolysis, affirming that bubble coverage reduces conductivity and increase ohmic losses.

Bearing in mind the last statement, Mazloomi et al. conducted interesting research on the electrical impedance of 22 the water electrolysis cell [57]. Even though in this first experimental paper the authors applied current pulses and not 23 voltage ones, we choose to include it in this section for a better understanding of the whole work. The authors applied 24 current pulses by the use of PWM with a MOSFET transistor (as recommended in [56]). This setup is seen in Fig. 25 5a for different cells connected to an electrical grid. The electrodes were made of aluminum plates with surface areas 26 between 1.5 cm² and 10 cm², a thickness of 0.5 mm, and the electrolyte was potassium hydroxide with concentrations 27 between 0.1 M and 2 M at 25°C. The choice of aluminum is unconventional since among common engineering metals, 28 it is the second most reactive [60]. Singh et al. reported a corrosion rate of 15.1 mg.cm⁻².h⁻¹ for pure aluminum in a 29 1 M NaOH at 35°C [61]. At this rate, the aluminum plate would be dissolved in only a few hours. This said, it may 30 be inferred that the experiments presented by Mazloomi et al. had a short duration. Furthermore, Al has not a high 31 activity for HER, having an exchange current density for hydrogen evolution about a hundred times lower than the 32 one for commonly used Ni electrodes (at $0.5 \text{ M H}_2\text{SO}_4$) [62]. The distance between electrode plates varied between 33 5 mm and 50 mm. At a fixed DC voltage given by the power supply, pulses of different frequencies ranging from 34 20 Hz to 2 MHz were applied and the current was measured. All pulses had a duty cycle of 50%. A typical plot of 35 current versus frequency is shown in Fig. 5b. Some interesting aspects can be seen and they can be better understood 36 supposing a second-order RLC equivalent circuit shown in Fig. 5c, where R_S is equal to the internal resistance of the 37 electrolyte, C_{dl} is the cell capacitance; L_{ext} and R_{ext} come mainly from the cabling and external connections of the 38 system. The impedance of the capacitor and of the inductor is given by: 39

$$Z_c = \frac{1}{2\pi fC} \tag{27}$$

$$Z_L = 2\pi f L \tag{28}$$

where f is the pulse frequency, C is the capacitance and L is the inductance. At DC electrolysis, f=0, so that the capacitor works as an open circuit and the inductor as a short circuit. The total impedance of the system described in Fig. 5c is given by:

$$Z = Z_L + \frac{RZ_c}{R + Z_c} \tag{29}$$

with R the resistance. According to this equation, increasing the frequency decreases Z_c , and hence, the total impedance. Nevertheless, this decrease goes until a resonance frequency is reached. For frequencies higher than that, the increase in Z_L becomes more important, increasing the total impedance. As the frequency tends to infinity, the inductor acts as an open circuit and blocks the current. This behavior was observed experimentally and it is shown in Fig. 5b. Given that, the authors concluded that at the resonant frequency, the impedance is decreased and higher currents can be achieved at the same voltage.

After this first step of determination of the natural frequency, the authors compared the voltage value needed to 6 achieve the same current at DC electrolysis and at pulsed electrolysis at the resonant frequency. The results showed a decrease in the voltage value of up to 15% in the case of pulsed electrolysis at the same current. This decrease in 8 voltage would mean a decrease in power and a more efficient process. The limitation of this study is that the authors 9 did not consider the galvanic dissolution of aluminum and did not discuss the possible effects that applying voltage 10 pulses with different frequencies could have on this reaction. Thus, it is not clear whether the results are coming from 11 water electrolysis or from aluminum dissolution. Moreover, hydrogen gas was not collected, thus it cannot be stated 12 that the Faradaic efficiency was indeed 100%. Therefore, it would be useful to repeat their experiments with conven-13 tional nickel electrodes.

After that, the authors published a paper reviewing the influencing factors on the water electrolysis efficiency [10]. Pulsed voltage was included as one of the factors that can enhance efficiency, giving as an example the work done by Shimizu *et al.* [40].

Later on, Mazloomi *et al.* published another article detailing an electrochemical impedance spectroscopy analysis [58]. It was performed by applying DC sinusoidal voltage pulses (DC offset equal to AC pulse peak). The electrodes were again aluminum plates. The electrode size, distance, and KOH solution molarities were the variables. The results were similar to Fig. 5b, with a peak in the resonant or natural frequency that was in the range between 0.8 MHz and 12.2 MHz depending on the experimental conditions. Once more, the second-order RLC equivalent circuit shown in Fig. 5c was proposed to be the best representation of a water electrolysis cell. Generally, the value for the resonance frequency increased by decreasing the distance between electrodes and by increasing the molarity.

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Finally, in their last paper about pulsed water electrolysis [59], Mazloomi's team performed an experiment with 28 a similar configuration as [58]: aluminum plates in potassium hydroxide solution. Once more, the aluminum disso-29 lution in alkaline solution was not considered. The pulses applied had a frequency around 7 MHz and the voltages 30 varied between 2 V and 10 V. According to their results, the pulsed process had better efficiency and lower production 31 rate. It is easy to understand the lower production rate as a consequence of the off-period at which no production 32 is expected. This explains also the experimental observation that the lower the duty cycle, the lower the production 33 rate. Nevertheless, efficiency depends only on the voltage. Since the on-voltage was constant, the efficiency should be 34 the same. In the case of this study, the efficiency was estimated by means of energetic efficiency and the production 35 rate was measured by means of hydrogen collection. Since the dissolution of aluminum in KOH produces hydrogen 36 gas, it is expected that a percentage of the collected hydrogen was not coming from water electrolysis. As during the 37 off-period hydrogen could be coming from Al dissolution without power consumption, the efficiency would appear to 38 be better, when in reality another reaction was occurring. Hence, it is expected that both the production rate and the 39 efficiency would be lower than the calculated ones. As the effect of pulses on the aluminum dissolution is unknown, 40 it is difficult to validate the statement of better performance for pulsed water electrolysis. In any case, the authors 41 claimed that the observed improvement in efficiency resulted from the fact that neither the EDL nor the diffusion layer 42 had enough time to be fully formed. Furthermore, it was argued that immediately after a voltage application, ions 43 are attracted to the electrode with the opposite side. Nevertheless, the ionic atmosphere around these ions takes some 44 time to be rearranged. This delay, called relaxation time, is illustrated in Fig. 5d. When the ion moves and the ionic 45 atmosphere does not, an asymmetrical electric field is created, slowing the ion movement and consuming part of the 46 energy provided by the electric field. They assumed a relaxation time in the order of several hundreds of nanoseconds. 47 Since the pulse width was lower than the relaxation time, the energy for the rearrangement of the ionic atmosphere 48 49 would not be consumed, being another factor that would explain the higher efficiency of the pulsed electrolysis.

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Inspired by Mazloomi's work, Mandal *et al.* performed a study using PWM in alkaline water electrolysis [63]. The authors used graphite electrodes, potassium hydroxide as the electrolyte, and pulses in the frequency range of

0-100 kHz, voltages between 0-15 V and 50% duty cycle. The authors claimed to have achieved an improvement 1 of 34% of efficiency using pulsed electrolysis. However, looking carefully at the presented results, it is seen that the 2 on-voltage was constant: 12.65 V. Thus, the efficiency should be the same. It is not clear nor specified how the authors 3 got a value of 9.6% efficiency for DC and 12.87% for PWM electrolysis. The authors defined the efficiency as the 4 product of the theoretical voltage by the theoretical current divided by the power consumption. The theoretical voltage 5 is constant: 1.23 V. Considering that the only reactions occurring was the HER and the OER, the theoretical current 6 - measured from the collected hydrogen - should be equal to the measured current. In this case, the efficiency, as the authors defined, should depend only on the voltage. Since its value was constant and equal to 12.65 V, the efficiency 8 should be constant as well. Nevertheless, the published result shows a higher production rate for the pulsed process 9 (from 15 cm³/min to 20 cm³/min) at the same voltage of 12.65 V. This would mean an improvement of the process, as 10 to achieve the same production, the voltage could be lowered, improving efficiency. However, no information about 11 the statistical significance nor error was shown. 12

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Still using PWM, there is the work of Poláčik et al. [64]. Even though the experimental setup was not specified, the pulses appear to be in the range of 40-240 Hz. The authors claimed to have achieved a better electrolysis effi-15 ciency using pulses. The paper is mainly incomplete and it is not clear how the authors estimated efficiency. Once 16 more, since the voltage was constant, the efficiency should be constant as well. Probably the merit of this research 17 was the explanations for a possible process improvement as a consequence of pulses application. First, the authors 18 argued that if the switch was turned off fast enough, there would still be a difference in electrical potential between the 19 electrodes during off-period. Thus, even if no current could flow in the circuit (because it was interrupted), hydrogen 20 could still be formed at the interface electrode/electrolyte. The second reason was that pulsed electrolysis would be 21 more efficient in the removal of bubbles. 22

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As in Mazloomi et al., Martiningsih et al. [65] also studied PWM in water electrolysis using a MOSFET transis-24 tor. The frequency went from 1 kHz to 16 kHz, the duty cycle went from 10% to 90%, and the voltage was set at 25 15 V. Stainless steel electrodes were immersed in 1% concentration sulfuric acid solution. For duty cycles between 26 10-50%, production rate and duty cycle were directly proportional. At 70% a decrease in the production rate was ob-27 served when compared to the rate at 50% duty cycle. After this anomaly, the production continued to increase with the 28 duty cycle in the interval 70-90%. This was observed for pulses in the frequency range of 4-12 kHz. No explanation 29 of this phenomenon was given and the error was not presented, so it is hard to say if this anomaly was statistically 30 significant. No analysis was done regarding efficiency and no comparison with conventional water electrolysis was 31 done. 32

Demir *et al.* [66] also conducted experiments with pulses during alkaline water electrolysis. The authors used platinum electrodes in 10 wt% and 15 wt% KOH solution. The applied voltage values were 6 V, 8 V, and 10 V. Two duty cycles were used: 10% and 50%. The frequencies varied between 0.1 Hz - 1200 kHz. The pulses were applied based on MOSFET transistors that cut the circuit during off-time. Using these voltage pulses, the authors claimed to have achieved an energy consumption per mole of hydrogen between 20-25% lower than the one from DC electrolysis. Nevertheless, a careful look at the results shows that this conclusion was not accurate. The way the average power consumption was calculated was as follows:

$$P = \sqrt{\frac{1}{T} \int_0^T V(t)^2} \cdot \sqrt{\frac{1}{T} \int_0^T i(t)^2 dt}$$
(30)

with *V* the cell voltage, *i* the current, and *T* the pulse period. However, this method of estimating power can bring to different conclusions from those that would be obtained using a more classical approach. Take for example the case of pulses of 6 V, 50% duty cycle, 1.2 MHz of frequency, and 15 wt% KOH, for which the authors claimed the improvement of 20-25% in efficiency. For DC, there was a hydrogen production rate in the order of 0.108 ml/s, which gives a current density of approximately 3 A/cm², considering standard conditions for temperature and pressure. For pulsed voltage, the production rate was approximately 0.042 ml/s, giving a current density during the on-period of 2.3 A/cm². This means that at a fixed cell-voltage of 6 V, DC electrolysis presented a higher current density, implying that it had the best performance. If the consumed power was estimated as the integral of the product of voltage multiplied by the current with respect to time and if the efficiency was calculated using equation 24, the efficiencies of the DC
and the pulsed process would be the same and equal to 21%. This happens because their cell-voltages were the same
and the efficiency depends only on this parameter. Since DC presented higher current densities, it means that at a
fixed production rate, DC would have a lower cell-voltage and a higher efficiency. Furthermore, since the authors used
cell-voltages much higher than the reversible cell-voltage, the LHV efficiencies were significantly low: 21%, 16%,
and 13% for 6 V, 8 V, and 10 V, respectively.

An important contribution of this work was the observation that there was a relation between the hydrogen production rate and the frequency at a fixed duty cycle. Taking as an example pulses with 50% duty cycle, 8 V, and 15 wt% KOH, an increase in production rate was observed with frequency. This improvement was attributed to the relaxation time of the bubbles on the surface of the electrode (which enhanced diffusion of dissolved gases), and to the pumping effect created by the pulsed voltage on bubbles. The authors claimed that the method also improved the lifetime of electrodes since it reduces the contact with oxygen bubbles at the anode.

Still in the domain of electrolytic hydrogen production, Huang [67] studied the effect of pulses during the elec-15 trolysis of ammonium sulfite solutions (reversible cell-voltage equal to 0.108 V). As in water electrolysis, hydrogen 16 was produced at the cathode. However, instead of oxygen, $SO_{4(aq.)}^{2-}$ was produced at the anode from the oxidation 17 of $SO_{3(aa)}^{2-}$. The author noticed that at the microsecond scale, the rate of DC electrolysis was not constant. This ob-18 servation indicated that the rate of electrolysis was controlled by the electrolyte transfer rate. Consequently, pulses 19 were applied to try to improve this transfer. In their experiment, the pulse width was 10 ms and the duty cycle was 20 between 12.5% and 50%. On-voltage was changed between 0.6-1.2 V while off-voltage was always zero. The con-21 clusion was that pulsed electrolysis can achieve the same current as DC at lower voltages. As an example, to reach 22 a current density of 180 mA.cm⁻², DC electrolysis needed a cell voltage of 1.26 V, while pulsed electrolysis needed 23 only 1.2 V. The efficiency was calculated as the product of hydrogen production rate by the heating value divided by 24 the consumed power. The improvement in electrolysis was attributed to mass transfer. Indeed, when the voltage was 25 interrupted, the $SO_{3(aq.)}^{2-}$ reactant migrated to the anode surface and its concentration was allowed to build up before 26 the next pulse was applied. Therefore, electrolysis always occurred at maximum reactant concentration on the surface 27 of the electrode, minimizing the overpotential of the electrolysis. 28

30 4.2. Other voltage pulses

Lin et al. [68] studied the effect of pulsed voltage and magnetic field in water electrolysis. Regarding the pulses, 31 their width was varied from 10-90 ms with duty cycles between 10-90%, on-voltages between 3.5-4.5 V, off-voltages 32 between 0-4.5 V, and a frequency of 10 Hz. Nickel plates were immersed in a potassium hydroxide solution. It was 33 argued that when the voltage was on, the reaction occurred and created a difference in concentration. During the 34 off-time, diffusion replenished ions that were consumed in electrolysis. This argument justifies the results obtained: 35 an increase in current density at on-time. The lower the duty cycle and/or the base voltage, the higher the on-current. 36 Looking closely at the results, it can be inferred that the increase in the on-current was not enough to compensate 37 for the off-time. In other words, at a fixed on-voltage (thus efficiency), the average current was lower for the pulsed 38 process. As an example, for an off-voltage of 0 V, on-voltage of 4.0 V, period of 100 ms, and 10% duty cycle, the 39 on-current density was 2.3 A/cm², representing an average current density of 0.23 A/cm². At 4 V, the DC process 40 produced 1.65 A/cm². Furthermore, as shown in equation 1, a capacitive charging is expected at the beginning of a 41 pulse. It is possible that part of the observed on-current was actually a capacitive charging. If so, a discharge would 42 be observed during off-time and the capacitive current could be estimated. It is not clear if the authors considered this 43 process in the analysis. With the help of a video camera, the authors observed that the pulses caused: (a) an increase 44 in the concentration of gas in both electrodes, (b) a decrease in the thickness of the gas diffusion layer, (c) a faster 45 bubble rise from the surface of the electrode. An example is shown in Fig. 8. 46

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Five years after the previous publication, Hourng *et al.* published a study about the effects of pulsed voltage in a double cell (acid-base) water electrolysis [69]. The electrodes were nickel plates and a proton exchange membrane was used. The solution at the cathode was sulfuric acid 30 wt% and the solution at the anode was potassium hydroxide

30 wt %. Two kinds of 100 Hz square voltage pulses were proposed. In the first one, the circuit was interrupted during 1 the off time. In the second, a base voltage was applied so that the voltage never felt to zero. This base voltage was 2 always higher than the reversible voltage. The tested duty cycles went from 10% to 50% in steps of 10%. The results 3 showed that pulsed voltage caused an increase in the current during on-time and a decrease in the average current (as 4 in Lin et al. [68]). As an example, at an on-voltage of 2 V and open circuit during off-period, the current for 10% 5 duty cycle was 2.4 A. At 2 V potentiostatic, the current was 1.5 A. Thus, pulsed voltage promoted a 60% increase in 6 on-current. Nevertheless, since the duty cycle was 10%, the average current for the pulsed method was only 0.24 A, more than six times lower than the potentiostatic current. The lower the duty cycle, the higher the on-current and the 8 lower the average current (related to the production rate). In other words, even if the current at on-time was higher, 9 the average production rate was lower. The effect of the base voltage was also investigated. The result was similar to 10 the one presented in [68]: the higher the base voltage, the lower the current at on-time. Nevertheless, the hydrogen 11 production rate could be increased with base voltage. In summary, pulsed water electrolysis was capable of enhancing 12 the on-current, but this benefit came along with a decrease in the production rate since the production was stopped 13 during part of the time (off-time).

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An intriguing result of this article was that using this dual-cell configuration, it was possible to arrive at an on-16 current of 0.08 A and 0.27 A for DC and pulsed electrolysis, respectively, at a cell voltage of only 1 V. Since the 17 reversible cell-voltage is a state function and does not depend on the experimental setup, there should not be current 18 for voltages lower than 1.23 V. It could be argued that this observation was only a measurement error, but this phe-19 nomenon was reported previously [70–73]. This effect was attributed to the energy liberated during the reaction of 20 water neutralization (-79.9 kJ.mol⁻¹) occurring at the membrane that separates the two electrolytes. As a consequence 21 of this energy input, the electrical requirements for water electrolysis would be lowered [70, 72–74]. In other words, 22 part of the energy used to drive water electrolysis would come from the neutralization reaction, which allowed the 23 production of hydrogen at voltages lower than 1.23 V. 24

Al-Hasnawi [75] studied the effect of different pulse variables (amplitude, frequency and waveform) on water 26 electrolysis. Even if it is not clear what were the experimental materials, it is known that the pulses had a frequency 27 between 2 Hz - 1 MHz, with amplitudes between 1.5 - 3 V, and the waveforms were square, sinus, and triangu-28 lar. In this experiment, square waveforms were the only ones to present a significant hydrogen yield. Besides, the 29 square waves presented the best efficiency. Nevertheless, the results presented for Faraday and energy efficiency were 30 strangely very close to one another, as if it was the same parameter. A higher frequency caused a decrease in pro-31 duction rate after 100 Hz and efficiency increased until 10 Hz and then arrived at a plateau, starting to decrease only 32 for frequencies higher than 10 kHz. It was not clear from the results if the efficiency was improved or not. What was 33 observed was a higher production rate for the pulses at the same current of 0.05 A (0.35 mL/min against 0.3 mL/min). 34 This would mean that a side reaction was occurring and that pulsed operation reduced its effects. However, it is dif-35 ficult to judge without knowing the electrolyzer materials. Moreover, as statistical analyses were not performed, the 36 observed difference may just be an experimental error. 37

de Radiguès et al. [76] studied the application of DC pulsed voltage for hydrogen production. The authors used 39 3-D porous electrodes made of pure nickel, an anion exchange membrane, and 1 M KOH solution. The pulses had a 40 duty cycle of 50%, frequencies varied from 2.5-250 Hz, and on-voltages were in the range of 1.3 V - 3 V. A baseline 41 voltage of 1.2 V was applied during off-time. Negative currents during off-time were observed due to transient elec-42 trical effects or to the inverse reaction taking place. The results showed that for a frequency of 250 Hz, pulses caused 43 an increase in the average current from 0.02 A/cm² to 0.05 A/cm². Moreover, the authors concluded that there was 44 a synergistic effect between 3-D electrodes, forced electrolyte flow, and pulsed voltage, which caused the current to 45 increase five times as compared to 2-D electrodes at DC operation and natural convection. 46

48 5. Current pulses

⁴⁹ Chen *et al.* [77] proposed the use of nickel hydroxide as a redox mediator to decouple hydrogen and oxygen pro-⁵⁰ duction in water electrolysis. During hydrogen production, a potential difference was imposed between a commercial

Pt-coated Ti-mesh (working as a cathode for the HER) and a nickel hydroxide electrode. Hydrogen evolution occurred 1 at the cathode and oxidation of Ni(OH)₂ occurred at the redox mediator, producing NiOOH. Then, an electrical switch 2 connected the redox mediator with an electrode made of commercial RuO2/IrO2-coated Ti-mesh for the OER. There, 3 NiOOH was reduced to Ni(OH)₂ and at the anode, OH⁻ was oxidized to O₂. Each cycle of hydrogen and oxygen pro-4 duction lasted for 10 minutes. The authors suggested that this two-step water splitting could be operated in different 5 compartments, the nickel hydroxide electrode being moved from one for H₂ production to another for O₂ production, 6 allowing the production of highly pure gases without the use of a membrane. Moreover, since the power inputs from HER and OER are different, this method allows adapting the power input according to the output from unstable power 8 sources such as wind and solar power. 9

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Using this idea of decoupling the HER and the OER, Vincent et al. [78] carried out an experiment with pulsed 11 alkaline water electrolysis. This time, instead of cycles of 10 minutes, cycles lasted for less than 10 seconds. An 12 electrical switch alternated the circuit between HER and OER periodically, imposing always the same current each 13 time between 0.1-0.6 A.cm⁻². This is equivalent to produce square current pulses. The resulting voltage was in the range of 1.4-3.2 V. The direction of the current was controlled by diodes. The authors stated that the frequency varied 15 from 0.05-500 Hz. Nevertheless, they affirmed that for a pulse period of 200 ms, the corresponding frequency was 16 0.5 Hz, when the real value would be 5 Hz. The same happened for 2 ms when they said that the corresponding 17 frequency was 50 Hz. When analyzing the plot of the evolution of voltage versus time that the authors provided, it can 18 be seen that the values of the pulse period are consistent and the error was in the values of the frequency. This leads 19 to a frequency between 0.5-5000 Hz. The electrode used for OER was made mainly of Ni(OH)₂ while the electrode 20 used for HER was made of a metal hydride (mainly lanthanum). The authors also used a 3-D MnO₂ electrode as an 21 intermediate electrode, meaning that it was oxidized during HER and reduced during OER. The setup can be seen in 22 Fig. 6. The idea was that during hydrogen on-time, hydrogen would be produced at the metal hydride electrode and 23 the intermediate electrode would work as an anode where the following reaction occurs: 24

$$MnO(OH) + OH^{-} \rightleftharpoons MnO_{2} + H_{2}O + 1e^{-}$$

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Then, the hydrogen production would be interrupted and the oxygen production would start, with the intermediate 26 electrode being reduced (MnO₂ \rightarrow MnO(OH)) and the oxygen being produced at the nickel electrode. This was possi-27 ble due to the electrical switch from the metal hydride electrode to the nickel electrode. The results showed that for a 28 fixed current density, the cell voltage could be lowered by the increase in the alternation frequency. This was explained 29 by the model of the pulsating diffusion layer from Ibl [23]. It was argued that in pulsed electrolysis, the thickness of 30 the diffusion layer is reduced, since it has not enough time to be completely formed and the reactants have time to 31 diffuse back to the electrode surface, enhancing the efficiency of the process by a decrease in ohmic losses caused by 32 mass transport. The higher the pulse frequency, the lower the thickness of the diffusion layer, explaining the observed 33 increase in efficiency with frequency. The results can be seen in Fig. 7, which shows that for fixed currents, when 34 on-time was lower than 2 s, the voltage was reduced. The authors explained that after this time, the diffusion layer 35 was completely formed. Finally, the Faraday efficiency was estimated to be $\sim 100\%$. 36

Vilasmongkolchai et al. [79] studied the behavior of gas bubbles during off-time in pulsed electrolysis. Stainless 38 steel electrodes in a 20 wt% KOH solution were used. An IGBT transistor created current pulses by switching the 39 circuit on and off. The frequency was in the range of 1-100 Hz and the current pulses went from 30 A to 50 A. No in-40 formation was given about the electrode area. It was pointed out that the time needed for the bubble to rise was mainly 41 dependent on bubble size and void fraction. Lower radius and/or higher void fraction gave higher rising times. As 42 the void fraction is directly proportional to the current density, higher currents mean higher rising times. The bubbles 43 were not observed by high-speed cameras but by acoustic emission analysis. The idea behind this technique is that 44 acoustic waves in the natural frequency of a bubble can break it. The natural frequency depends on the bubble size, 45 thus this method allows the prediction of bubble size and coverage. It was noticed that the efficiency was improved 46 when pulses were used and that this effect tended to increase for lower duty cycles. In other words, at a constant on-47 current, the voltage could be lowered. Nevertheless, since the pulses have an off-time, the average production rate was 48 lower than the conventional process. Furthermore, the authors observed that lower frequencies presented higher pro-49

duction rates at a fixed duty cycle. This process was explained as a consequence of bubble removal: since the resting 1 time was greater, the electrode had fewer bubbles when the voltage was turned on. Yet, as current pulses were applied, 2 the production rate at the same duty cycle should be exactly the same, except if another reaction occurs. Maybe the 3 real reason for the observed difference would be some parasitic reaction, such as the formation of oxides in the steel 4 electrode. In this case, at higher frequencies more of the current was consumed in parasitic reactions, reducing the 5 collected hydrogen. This idea was confirmed by Hristova et al. [80], as it will be shown in the next paragraph. Finally, 6 it was stated that longer off-times increased the efficiency and decreased the production rate. Additionally, it was 7 concluded that the time needed for bubbles to rise was on the order of a few hundreds of milliseconds (≈ 150 ms). 8 9

At the Bulgarian University of Chemical Technology and Metallurgy, some researches have been conducted on the 10 use of current pulses during water electrolysis. In their first study [80], the aim was to study the modification caused 11 by pulses on surface films formed on AISI 316L stainless steel electrodes. The electrolyte was a 6 M KOH solution. 12 The pulsed currents were applied with amplitudes of 12-250 mA, frequencies of 0.5-10 kHz, and duty cycles between 13 1 and 99%. The samples were analyzed after 24h of pulsed electrolysis by Electrochemical Impedance Spectroscopy, Cyclic Voltammetry, Scanning Electron Microscope, and X-ray photoelectron spectroscopic. At the cathodes, the for-15 mation of a layer of $Cr(OH)_3$ was observed, which decreased electronic conductivity. On the other hand, a decrease 16 in the normalized Cr content was noticed at the anode, causing a decrease in electronic and ionic conductivity. This 17 was attributed to Cr dissolution at the anode and its subsequent deposition at the cathode. They concluded that during 18 pulsed water electrolysis, profound surface modifications occur and they are intimately related to the pulse duty cycle 19 and frequency. At the cathode, these modifications were more significant and the number of observed crystals per 20 surface area increased with pulse duty cycle and frequency. 21

- In their second article [81], the same stainless steel electrodes were used, the current amplitude varied between 23 1-1.4 A, the duty cycle was between 1-5%, and the frequency was set at 1 kHz. 0.1 M and 0.4 M KOH solution were 24 used as the electrolyte. The method by which the power was calculated was not specified. However, there seems to 25 be some misunderstanding because they define efficiency as the ratio between the produced hydrogen and the power, 26 given in mL.min⁻¹.W⁻¹. When looking at the data provided for DC, for 1 A one finds a cell voltage of 11.3 V, hence, 27 the efficiency would be 0.66 mL.min⁻¹.W⁻¹. The authors gave 0.3 mL.min⁻¹.W⁻¹. When the current increase to 5 A, 28 the cell voltage went to 14.6 V, decreasing the efficiency to 0.51 mL.min⁻¹.W⁻¹. The authors claimed an efficiency of 29 1.9 mL.min⁻¹.W⁻¹. Thus, it was not clear from the results if pulsed electrolysis presents a higher efficiency or higher 30 hydrogen yield. 31
- 32

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Later on, a study on the surface modifications of titanium electrodes was published [82]. Again, pulsed water electrolysis was applied for 24h with current amplitudes of 12 -250 mA, frequencies in the range of 0.5-10 kHz, and duty cycles between 1 and 99%. It was seen that at the anodes, for higher duty cycles, more oxide growth is expected, which decreased the ionic and electronic conductivity.

³⁷More recently, Yang *et al.* [25] investigated how porous nickel electrodes can improve hydrogen production in an ³⁸alkaline water electrolysis cell. The authors showed that not only the surface area matters but also the structure of the ⁴⁰electrodes, especially when it comes to concerns the removal of bubbles. To study the bubble behavior, pulses with a ⁴¹width of five minutes were applied and it was noticed that at a constant current, the voltage increased with time due to ⁴²bubble formation during the on-period. During the off-period, bubbles could be removed as observed by the decrease ⁴³in pressure. With fewer bubbles, the following pulse started at lower voltages, improving the overall efficiency of the ⁴⁴process. This study shows the potential of using low-frequency pulses for improving bubble removal efficiency. ⁴⁵Table 4 provides a critical summary of the works presented above above operations.

Table 4 provides a critical summary of the works presented above about current pulses.

6. Power fluctuations

⁴⁷ Ursúa *et al.* [83] studied the effect of power fluctuations on a commercial alkaline (30 wt% KOH) electrolyzer . ⁴⁸ The authors explained that it is common for these electrolyzers to have a lower operating limit, between 25-40% of the ⁴⁹ nominal current. Below this current level, gas diffusion through the membrane becomes important and hydrogen and oxygen start to be mixed. The authors considered a 50 Hz electric AC grid and two power supplies: thyristor-based (ThPS) and transistor-based (TrPS). The first one provided a fluctuating current with a minimum of 0 A, while the

(ThPS) and transistor-based (TrPS). The first one provided a fluctuating current with a minimum of 0 A, while the
 latter provided a constant current. It was observed that the ThPS consumed more energy for the same production rate,

⁴ therefore being less efficient.

Dobó et al. [84] studied the effect of DC power fluctuations in alkaline water electrolysis. The cell was made 6 with stainless steel electrodes in 30 wt% KOH. The voltage varied in a sinusoidal shape around an average value. 7 The average voltage (DC component) was between 1.4-2.8 V, while the ripple amplitude went from 0-2 V. The pulse 8 frequency varied between 1-5000 Hz. In general, voltage fluctuations did not change the gas production rate, but 9 increased the consumed power, thus reducing the efficiency. The exception was at fluctuations of high amplitude and 10 low frequency. In this case, both the gas flow rate and the electric power were increased. Taking for example an aver-11 age voltage of 2.2 V, for pulses with 2 V amplitude and 1 Hz frequency, the gas flow rate was increased from 0.11 to 12 0.45 mL/s whilst power was increased from 1 to 5 W. Hence, since the production rate was increased only by a factor 13 4 and the electric power was increased by a factor 5, the energetic efficiency decreased. The cases at which a better efficiency was reported upon the application of voltage fluctuations were also the cases at which there was almost no 15 gas production at DC operation because the voltage level was too low (less than 1.8 V). As the production rate and 16 the current were low, imprecision in the measurement of current and flow rate may have compromised the accurate 17 estimation of the DC efficiency. 18

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Still in the domain of power fluctuations, the same authors studied the effect of current fluctuations during water electrolysis [85]. The applied current varied around a mean value in different shapes: sinusoidal, triangular, sawtooth, and square. The mean current density went from 1000 A.m⁻² to 5000 A.m⁻² (corresponding voltage between 2.1-2.9 V), with frequencies going from 1 Hz to 10 kHz. Amplitude went from zero to twice the average value. The main conclusion was that any change from steady DC power caused a decrease in energetic efficiency. This decrease occurred because the current fluctuations increased the consumed power while the hydrogen production rate was the same.

27

A summary of the efficiencies and current densities obtained by the different methods presented in this review is 28 shown in Fig. 9. Here, the current density of a pulse is the average current density during a complete pulse period 29 e.g. for a pulse with a duty cycle of 50%, an on-current of 1 mA/cm², and an off-current of 0 mA/cm², the average 30 current would be 0.5 mA/cm². The data was extracted from Tables 1-4. The efficiencies are compared with benchmark 31 efficiencies obtained from Buttler et al. [16]. Even though it is difficult to compare works that used different setups, 32 this figure gives an idea of the range of efficiencies and current densities that the pulsed water electrolysis is currently 33 situated. For the moment, the performance is not better than the conventional methods. More research at benchmark 34 conditions should be done to prove the feasibility of the pulsed methods. The biggest challenge of the researches in 35 this field is to show an on-current higher enough to compensate for the off-time e.g. for 50% duty cycle, the on-current 36 needs to be at least two times greater than the direct current. This is not yet the case. Finally, at an LHV efficiency 37 of 87% and a current density of 50 mA/cm², there is the decoupled system from Vincent et al. [78]. Since this system 38 presented a good performance, more research about the effect of frequency on this system is encouraged. The authors 39 studied frequencies up to 5 kHz, would the cell-voltage continue to decrease for higher frequencies? 40

1 7. Conclusions

The history of pulsed water electrolysis has briefly been outlined, and previously published work in the field was 2 critically addressed. The latter was divided depending on the pulse generation technology: inductive pulses, voltage 3 pulses, and current pulses, respectively. It was seen that most of the techniques described in the literature did not use Λ industrially relevant conditions, e.g. Ni electrodes at 70°C and 30% KOH in the case of alkaline water electrolyz-5 ers. It would therefore be interesting to see to what extent the pulses can cause an improvement in efficiency when 6 more realistic operating conditions are applied. Moreover, the underlying phenomena of bubble removal could have been studied in more detail, especially when bubble entrapment is a critical issue, as is the case for 3D electrodes. 8 In general, it was seen an increase in the on-current upon the application of voltage pulses and a reduction in the 9 voltage upon the application of current pulses. Some authors, such as Vilasmongkolchai et al., Poláčik et al. [64], and 10 Demir et al. [66], explained this as a consequence of a better bubble removal, as during off-period bubbles had time 11 to leave the electrode surface. Other authors ([40, 59, 78]) attributed this results to a higher concentration of reactants 12 at the electrode surface as during off-period the surface is replenished of reactants. Vanags et al. [47] proposed that 13 during pulsed operation, the diffusion layer is characterized by pulsating concentrations of active ions. In the specific 14 case of pulse width modulation, a theory provided by Poláčik et al. [64] is that since the circuit is cut periodically, the 15 electrical double layer needs to be discharged by means of chemical reactions, which would be beneficial. Another 16 possible reason presented by Mazloomi et al. [59] is related to the relaxation time of the ionic atmosphere around 17 reactant ions. However, even though pulsed electrolysis was able to enhance performance during on-time, this im-18 provement was not high enough to compensate for the pulse behavior during off-time. For instance, for voltage pulses 19 with a 50% duty cycle, the increase in current was generally lower than two times the direct current, meaning that 20 for the same production rate, the pulsed voltage needs to be higher, hence reducing the overall efficiency. Therefore, 21 more research is needed to show the viability of this process. However, the technology could already be used today 22 in the case of low power inputs. As explained by Ursúa *et al.* [83], there is a low limit for the current below which gas 23 cross-over starts to be an issue. In this particular case of low power inputs, pulsed water electrolysis could be used to 24 reduce the input power while maintaining the current at a constant minimum level (e.g. 25% of the nominal current). 25 A study of the gas cross-over issue during pulsed water electrolysis is therefore encouraged. Moreover, a promising 26 process that is intrinsically pulsed/alternated is the decoupled process of production of hydrogen and oxygen using 27 redox mediator, as studied by Vincent et al. [78]. This appears to be a highly efficient process and an increase in 28 а the alternation frequency seems to be promising. Furthermore, the studies of surface modifications caused by pulsed 29 operations can be useful in the study of electrodeposition and pulses could be used to control the quality of electrode-30 position. Finally, the conclusions obtained in terms of enhanced mass transport during pulsed water electrolysis could 31 also be applied to refine several electroanalytical techniques, e.g. enhancing the current density in voltammetry for 32 enabling the detection of low concentration species. 33

34 List of abbreviations

- 35 DC direct current
- 36 EDL electrical double layer
- 37 HER hydrogen evolution reaction
- ³⁸ HHV high heating value
- ³⁹ IKV inductive kickback voltage
- 40 LHV low heating value
- 41 OER oxygen evolution reaction
- ⁴² PWM pulse width modulation
- 43

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Table 1: Summary of the historical discoveries in pulsed water electrolysis

YEAR	GROUP	SET-UP	CONTRIBUTIONS	LIMITATIONS	REF
1950	Bockris et al. (1952) (1957)	HER in mercury, silver, nickel, tungsten, and platinum cathodes. Acid and basic solutions.	Observed the discharge of the electrical double layer after the voltage interruption	Studied only the hydrogen evolution reaction and no pulse was applied.	29,30
1970	Tseung & Vassie (1976)	HER on Teflon bonded platinum electrodes in 5 M H_2SO_4 , 25°C. Voltage pulses were produced at 50 mV overpotential. The current was recorded after 0.1 ms. Achieved 0.5 A/cm ² at 50 mV overpotential.	Pulsed electrolysis presented an on-current 2-6 times higher than DC.	Studied only the hydrogen evolution reaction.	17
	Viswanathan et al. (1978)	Solution containing 0.01 M of ferricyanide, 0.01 M of ferrocyanide, and 1 M KCl. Platinum rotating disk electrode. 22°C. Current pulses with a duty cycle between 20-80%. Pulse periods between 0.001-5 s.	Numerical solution for mass-transfer under pulsed current conditions in a rotating disk electrode. Introduced the concept of pulsating diffusion layer. On-current between 1.4-9.5 times DC current.	Studied the redox pair ferri- ferrocyanide and not water electrolysis.	18
	(1979)	No experiment	Numerical solution for mass transfer to a rotating disk electrode under pulsed voltage conditions	Considered only a reversible reaction in excess of supporting electrode	19
	(1980)	No experiment	Numerical solution for average current at intermittent potential. Showed that even though the on-current was higher, the production rate of non-DC electrolysis cannot exceed that of DC.	No experiments were performed to verify the results. Considers a reactant in excess of supporting electrolyte and not water electrolysis.	21
	Andricacos & Cheh (1980)	Voltage pulses. Deposition of Ag from AgNO ₃ (2 mM) in a Pt rotating disk electrode. Supporting electrode was 1 M KNO ₃ .	Numerical solution for a reversible deposition reaction in a rotating disk electrode under linear potential sweep conditions. Showed that an increase on the sweep rate increases the current.	Considers a reactant in excess of supporting electrolyte and not water electrolysis.	20
	Ibl et al. (1978)	Electrodeposition of Cd from CdSO ₄ (0.75 M) + H ₂ SO ₄ (1 M) solution in a Cd substrate, 20°C. Additionally, the authors studied the electrodeposition of Au on a Cu substrate and in a solution containing KAu(CN) ₂ (15 g/l) Citric acid (80 g/l) Co (0.1 g/l), 27°C. Current pulses.	Showed that current pulses could be used to control the properties of the electrodeposition. Moreover, showed that high current densities could be applied using this method, due to the thinning of the diffusion layer.	Studied electrodeposition and not water electrolysis	22
	(1980)	Electrodeposition of Cd, Cu, and Ag from different acid solutions. Current pulses.	Model for mass transport and capacitive effect in pulsed electroplating. Showed the influence of the capacitive current.	Model for plating and not for water electrolysis	23
	(1980)	No experiment	Showed that the on and off-times are limited to the charge/discharge of the EDL. Showed that the discharge of EDL conduct chemical reactions at pulsed current.	No experiment to confirm results	14
1980	Chin (1982) (1983)	Electrodeposition of copper from 0.75 M of CuSO4 solution in a rotating disk electrode. Current pulses.	Showed that the limiting current density could be 100-1000 times greater than DC. Showed the effects of pulse reversal.	Model for plating and not for water electrolysis	27,28
	Gutmann & Murphy (1983)	Not applicable	Described a high and short-lived current spike at the beginning of a voltage pulse	No experiments performed	31
	Bockris et al. (1985)	Nickel electrodes (1 cm ²) at 35% KOH. Voltage pulses with amplitudes between 1.5-2.75 V were produced by induction caused by the rotation of a propeller (450-1150 rpm) with one magnet at each end. A loop with alternated conductive/non-conductive layers in contact with the magnets allowed the pulses creation. Pulse widths between 0.5-1 ms. The pulses had a triangular shape. Achieved peak current of 0.07 A/cm ² at 2 V.	Created one of the first set-ups for pulsed electrolyzer. On-current two times higher than DC current.	Works only when in the presence of a magnetic field.	33,34
	Brandon & Kelsall (1985)	HER and OER in Pt and Ag microelectrodes. Supporting electrolyte was Na ₂ SO ₄ 10 mM + pH variations using H ₂ SO ₄ or NaOH. Additionally, chloride ion oxidation using the same microelectrodes in a KCl (10 mM) solution + pH adjustment using HCl or NaOH.	Showed that bubbles leave the electrode surface immediately after the interruption of the current or voltage	Did not analyse pulsed electrolysis	35
1990	Khosla et al. (1991)	HER in Pt cathode (1 cm^2) in a 1 M Na ₂ SO ₄ solution, pH=10. Current pulses with an average current density between 0.5-2 A/m ² , duty cycles from 5-100%, and pulse periods of 30 ms.	Showed that pulses can be used to control bubble size, with lower duty cycles producing smaller bubbles	Did not analyse the effect of the bubbles size in the performance of HER	36
	Shaaban (1993) (1994)	Stainless steel cathode and a platinum-coated titanium anode (projected area of 64 cm ² each) in a 10 wt% H_2SO_4 solution. Naflon-membrane. Voltage pulses were producing using a waveform pulse generator and an amplifier. Pulse frequencies between 0.01-40 kHz, duty cycles between 10-80%. Base voltage was 0 V and the peak voltage was regulated to generate an average current of 240 mA/cm ² for all the pulses. Measurements were taken after 15 minutes. For 240 mA/cm ² , a power between 0.625-1.27 W/cm ² was needed for pulsed electrolysis. In the DC case, the consumed power was 0.625 W/cm ² .	Showed that a diode could be used to prevent change in current polarization during water electrolysis, even if the diode caused a relevant voltage drop in the system. Demonstrated that wires with high inductances causes a significant voltage drop when fast pulses were applied. Showed that for the same production rate, voltage pulses presented a worse efficiency (as low as 50% of the DC efficiency).	The proposed electric circuit presented a high power loss of 15%, coming from the diode and cables inductance, 4 times greater than DC electrolysis. Resulting pulses were not clean square- shaped pulses.	37,38
2000	Hitz & Lasia (2002)	HER using two different nickel electrodes: disk (geometric surface area of 0.317cm ²) and porous (0.363 cm ²). 1 M NaOH solution was used.	Mathematical model for potential-time curves during current pulses. Showed that current pulses could be used to estimate kinetic parameters and double layer capacitance.	No analysis about efficiency of current pulses. Only studied HER. Determine activation energies from the	39

Table 2: Summary of inductive pulse method

GROUP	1 SET-UP	CONTRIBUTIONS	WATER ELECTROLYSIS EFFICIENCY	LIMITATIONS	REF
Shimizu et al. (2006)	Pt plates $(3.3x9 \text{ cm}^2)$ in 1 M KOH solution at 293 ± 2 K. A thyristor and two inductors created an ultra-short pulse with a voltage pulse-width of about 300 ns and a secondary peak voltage ranging from 7.9 to 140 V. Frequencies (in pulses/second) between 2-25 kHz	Developed a method of hydrogen generation by water electrolysis using ultra-short-pulse power supply. Showed that within this method the power and production rate could be increased without a decrease in energetic efficiency.	Average current of 17.67 mA/cm ² at 1 W (for 17 kHz and peak voltage of 7.9 V)	Preliminary study. In general, this method is less efficient and has a lower production rate than conventional water electrolysis.	40
Vanags et al. (2011)	HER on tungsten and platinum wires (100 mm long with diameter 0.5 mm). Electrolytes were 0.1 M and 0.2 M KOH solutions at 22°C.	Proposed a mechanism for hydrogen generation during inductive pulses. Showed that tungsten is better than platinum for the studied method.	Not applicable (HER) and not available	Did not studied nickel electrodes. Study limited to HER.	32
(2009)	IKV pulses were applied on steel plates in a solution of distilled water.	Showed that an electrolyzer can be used as a capacitor with distilled water as dielectric material.	Not available	Did not show quantitative data and did not analyze neither efficiency nor hydrogen production rate.	44
(2011)	Stainless steel plate electrodes (2 cm ²) in 0.1-3 M KOH solution. Pulses in the primary circuit had 50% duty cycle on-voltage of 1 V and a frequency of 20 kHz.	Claimed that using the method, the EDL charges at first and then it is discharged conducting chemical reactions. Showed that it was possible to have water electrolysis even if the voltage in the first circuit was as low as 1 V.	Not available	No information about process performance or hydrogen production rate	45
(2011)	Stainless steel wire electrodes (with a diameter of 2 mm and a length of 10 cm) in very weak electrolytes (0.7 mM). Pulses with periods of 50 μ s and amplitudes of 1 V were applied at the first circuit of the IKV set-up.	Showed that the kinetics of EDL charging and the energy received by the cell did not depend on the electrolyte concentration, when IKV pulses were applied.	Not available	Studied only weak solutions. Did not study nickel electrodes. No data about efficiency or production rate.	46
(2012)	Re-published results from 26, 39, and 40. Additionally, used for the first-time microelectrodes sensors to measure the hydrogen and oxygen concentrations at the vicinity of the electrode.	More quantitative data about the previous experiments. Showed that oxygen could evolve from the cathode when IKV pulses were applied.	Average faradaic current of 1.6-2.1 mA/cm ² at 1.43-1.49 V	Did not use membrane and did not discussed how to avoid oxygen/hydrogen mixture as oxygen could be produced at the cathode. Effect of temperature was not studied.	47
Dharmaraj et al. (2012) (2016)	Stainless steel in a NaOH (0-15 g/l) solution. IKV pulses with frequencies between 0-200 kHz	Showed that there could be a decrease in production rate with an increase in frequency	Not available	No detailed information about the results. Did not explain why the production rate decreased with frequency. Did not analyze shape of the resulting pulse. It was not clear how hydrogen production rate was calculated and what was the error. Used an unconventional way to measure power.	41,13
Kukhtarev et al. (2018)	Used photogalvanic electrical discharges coming from Fe:LiNbO ₃ crystals under illumination to conduct water electrolysis. Steel electrodes in tap water.	Showed that ferroelectric materials under illumination and immersed in water solution could be used to directly conduce water electrolysis. Additionally, showed that these materials could produce pulses with high voltages (kV) in short times (ms).	Not available	No detailed information about the methods nor the results. No information about process performance or hydrogen production rate	54

Table 3: Summary of voltage pulse methods

GROUP	SET-UP	CONTRIBUTIONS	WATER ELECTROLYSIS EFFICIENCY	LIMITATIONS	REF
Mazloomi et al. (2013)	PWM. Aluminum plates as electrodes (surface areas between 2-16 cm ²) in 0.1-1 M KOH solutions at 25 °C. Frequencies between 1 Hz and 10 MHz.	Showed an increase in conductance up to 50% with the application of PWM relative to DC values	Not available	No detailed information about pulse amplitudes, process efficiency or hydrogen production rate.	58
(2013)	PWM. 8 cm ² Al plates in KOH solution (concentration not specified). On-voltages between 2-10 V and duty cycles between 10-90%	Showed that the PMW technique was more efficient at lower voltages and lower duty cycles	For 10% duty cycle, on voltage of 2 V, there was a hydrogen production rate of 1.04 ml.min ⁻¹ .cm ⁻² during on-time (against 0.88 ml/min.cm2 at DC)	Did not consider Al dissolution. No detailed information about materials or methods.	59
Mandal et al. (2012)	PWM. Graphite cylindrical and plate electrodes (212 cm^2) in KOH 0.25-1% (w/v). Frequency between 0-100 kHz and on-voltage of 12.65 V.	Showed that PWM could be used to increase current efficiency	At 12.65 V, 0.31 ml.min ⁻¹ .cm ⁻² (against 0.25 ml/min.cm ² at DC)	No information about duty cycle. Did not discuss why the current efficiency was lower for DC in comparison with PWM. Side reactions? Studied only graphite electrodes.	63
Poláčik & Pospíšil (2016)	PWM at frequencies of 40-240 kHz.	Showed a 16% increase in efficiency for PWM.	Not available	Short article without any information about materials and methods. No detailed information about results.	64
Martiningsih et al. (2017)	PWM. Carbon, stainless steel and copper electrodes on H_2SO_4 0.25-1% (surface area of 8.8 cm ² for the cathode and 6.2 cm ² for the anode). On-voltages of 15 V, duty cycles between 10-90%, and frequencies between 1-16 kHz	Showed a non-linear behavior between duty cycle and production rate	On-time production of 1.3 ml/h.cm ² at 50% duty cycle	No analyses about efficiency. No comparison with DC.	65
Demir et al. (2018)	PWM. Cylindrical Pt electrodes (0.314 cm ²) in 10-15 wt% KOH solution at room temperature. On-voltages between 6- 10 V, duty cycles between 10-50% and frequencies between 0.1 Hz and 1.2 MHz.	Showed that voltage pulsed electrolysis presented much lower hydrogen production rates.	On-current of 2.3 A.cm ⁻² at 6 V, 50% duty cycle, and 1.2 MHz of frequency, and 15 wt% KOH. DC was 3 A.cm-2 ⁻	Studied only high cell voltages (6-10 V) compared to the reversible cell voltage (1.2 V). Power consumption was underestimated.	66
Huang (2013)	PWM. Pt/carbon electrodes (5.3 cm ² each) separated by a membrane. Anolyte was 2.0 M $(NH_4)_2SO_3$ solution and catholyte was deionized water, all at 75°C. Pulse width of 10 ms and the duty cycles between 12.5% and 50%. Onvoltages between 0.6-1.2 V.	Showed an increase in the on-current by the use of pulses.	On-current of 180 mA/cm ² at on-voltage of 1.2 V and 50% duty cycle (For the same current density, DC needed 1.26 V)	More understanding about the mechanisms of the process is needed. Did not study water electrolysis, but electrolysis of aqueous $(NH_4)_2SO_3$ solution (E° _{cell} = 0.11 V).	67
Hourng et al. (2014)	Nickel plates (1 cm^2) in KOH solution (5-40 wt%). Pulse period of 100 ms, duty cycles between 10-90%, on-voltages between 3.5-4.5 V, off-voltages between 0-4.5 V.	Observed an improvement of up to 40% in on-current with the application of voltage pulses. Showed a synergistic effect between voltage pulses and the application of a magnetic field. Showed that pulses help bubbles removal.	On-current of 3 A/cm ² at 4.5 V and 10% duty cycle (against 2.1 A/cm^2 at DC)	Studied only one frequency.	68
(2019)	Ni plates (1 cm^2) separated by a proton exchange membrane. Cathloyte was a 30 wt% H ₂ SO ₄ solution and anolyte was a 30 wt% KOH solution. Pulse frequency of 100 Hz at duty cycles between 10-50% peak voltages between 1-4 V and base voltages between 0-3.5 V.	Showed a 50% increase in on-current upon the application of voltage pulses. Observed that the production rate was always lower for pulsed operations relative to DC values.	On-current of 2.4 A/cm ² at 2 V and 10% duty cycle (against 1.5 A/cm ² for DC)	Studied only one frequency. Did not analyze neutralization at the membrane.	69
Al-Hasnawi (2015)	Pulse frequency between 2Hz - 1 MHz, on-voltages between 1.5-3 V, and square, sinus and triangular waveforms.	Showed that square voltage pulses presented the best hydrogen production rate.	0.5 ml/min at on-voltage of 2 V	None information about electrolyzer materials. No proper comparison with DC.	75
de Radiguès et al. (2019)	Nickel electrodes (20 cm ²) in 1 M KOH solution at 25°C. Frequencies between 2.5-250 Hz, 50% duty cycle, base voltage of 1.2 V and peak voltages between 1.3-3 V.	Showed that voltage pulses could increase the average current by more than two times (from 0.02 A/cm ² to 0.05 A/cm ²). Showed a synergistic effect between voltage pulses, forced electrolyte flow, and 3D electrodes.	Average current of 2.17 mA/cm ² at a peak voltage of 2 V at a frequency of 250 Hz and porous electrodes (450 µm)	Studied only one pulse per condition. Did not collect the produced hydrogen.	76

Table 4: Summary of current pulse methods

GROUP	SET-UP	CONTRIBUTIONS	WATER ELECTROLYSIS EFFICIENCY	LIMITATIONS	REF
Mazloomi et al. (2012)	Aluminum plates as electrodes (surface areas between 1.5-10 cm ²) in 0.1-1 M KOH solutions at 25 °C. Frequencies between 10 Hz and 10 MHz. On-currents between 0.05-1.1 A, 50% duty cycle.	Showed that there was a resonant frequency that could decrease the cell voltage up to 15%, when the current PWM technique was applied.	3.95-11.07 V at 50 mA/cm ² (against 3.98-11.56 V at DC)	Did not consider Al oxidation in alkaline solution. Did not collect hydrogen.	57
Vilasmongkolchai et al. (2016)	Stainless steel electrodes. 20 wt% KOH solution as electrolyte under atmospheric pressure and 353 K. On- currents between 30-50 A	Showed that the method could give time for the gas bubbles to leave, improving efficiency up to 2.6 times (from 28% to 73% of energetic efficiency*method of calculation was not specified). Proposed a method to estimate gas bubbles rising time.	Not available	No information about electrodes area or about the method used to estimate efficiency.	79
Vincent et al. (2018)	Lanthanum for HER and Ni(OH) ₂ for OER (4 cm ² of each). The electrodes were separated by thin (120 um) sheets of polypropylene. Solution of 6 M KOH at 25°C. On-current between 0-0.6 A/cm ² and frequencies between 0.5 and 5000 Hz. 50% duty cycle.	Showed than on-voltage could be reduced 25% using current pulses in respect to DC. Showed that the improvement was just observable after a minimum value of frequency was achieved.	1.44 V at 0.05 A/cm ² and 5000 Hz (against 1.94 V for 0.5 Hz)	Only studied decoupled systems.	78
Tzvetkoff et al. (2013)	Stainless steel electrodes on 6 M KOH solution. Current amplitudes between 12-250 mA, pulse frequencies of 0.5-10 kHz, and duty cycles between 1 and 99%.	Observed profound modifications in the electrodes surface upon the application of current pulses	Not available	No analysis about the pulsed operation itself e.g. efficiency or cell voltage.	80
(2014)	Ti electrodes in 0.5M KOH solution. On-current between of 12 -250 mA, frequencies between 0.5-10 kHz, and duty cycles between 1 and 99%	Observed oxide growth at the electrodes surface during pulsed operation	Not available	No detailed information about the results or materials. No information about pulsed electrolysis performance.	82
Yang et al. (2020)	Ni electrodes (0.16 cm^2) in 1 M KOH. Current pulses with a peak current density of 25 A/cm ² , pulse period of 600 s and 50% duty cycle.	Showed that the interruption of current was beneficial for the bubble removal and electrolysis performance.	25 A/cm ² at 2.1 V	Studied only pulses with long periods.	25



Time

Fig. 1. Schematic representation of a) voltage pulse with an on-voltage at which a reaction occurs and an off-voltage at which no reaction occurs b) current pulse with a null total current during off-time.



Fig. 2. Schematic diagram of a) Homopolar generator b) Pulse generator [33, 34].



Fig. 3. a) Voltage-time and current-time behavior during alkaline water electrolysis using inductive pulses. Water electrolysis at Pt plates in 1 M KOH solution at 20°C [40] b) Example of an inductive kickback pulse and the resulting voltage and current. HER on Pt wire electrode immersed in 0.1 M KOH at 22°C [32] c) Experimental circuit for generation of inductive reverse voltage pulses



Fig. 4. behavior of semiconductor switch a) Power loss elements b) Command signal. Adapted from [55].



Fig. 5. a) Experimental setup for pulse width modulation [55] b) Current versus frequency plot for aluminum electrodes in 0.1 M KOH c) Equivalent circuit for a water electrolysis cell From [57] d) Relaxation time [59].



Fig. 6. Schematic view of the pulsed current supply used in [78] for two step water electrolysis with a $MnO(OH)/MnO_2$ intermediate electrode, a metal hydride (lanthanum) for hydrogen evolution reaction, and a $Ni(OH)_2$ electrode for the oxygen evolution reaction. If the switch is connected to the metal hydride electrode, HER occurs, and if it is connected to the nickel electrode, OER occurs.



Fig. 7. Pulse width-cell voltage profile at a current density of 0.1 A. cm^{-2} for (black) oxygen evolution reaction at a nickel electrode and the reduction of the intermediate MnO₂ electrode, thermodynamic cell voltage = 0.828 V; (red) hydrogen evolution reaction in metal hydride electrode and the oxidation of the MnO(OH) electrode, thermodynamic cell voltage = 0.402 V; (blue) and overall reaction i.g. sum of the two previous cell voltages, thermodynamic cell voltage = 1.229 V (blue). Adapted from [78].



Fig. 8. Oxygen and hydrogen bubbles being produced simultaneously on a different nickel electrode immersed in a KOH solution with an electrode distance of 2 mm, $E_{on} = 4.0$ V, and $E_{off} = 0$ V. Adapted from [68]



Fig. 9. Summary of pulsed water electrolysis efficiency and operational range [33, 34, 37, 38, 40, 47, 57, 59, 63, 65, 66, 68, 69, 76, 78] Comparison with PEM (blue) and AEL (green) [16]. Hydrogen production rate considers standard conditions for temperature and pressure. For [63], since the duty cycle was not given, it was estimated to be 50%. For the power-controlled pulses ([40] and [47]), the efficiencies were estimated using the mean voltage value.