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Effect of the indirect sonication on the plasma formation and energy parameters in the cathodic regime of the plasma-driven solution electrolysis

Streszczenie. *W artykule opisano wyniki badań wpływu sonikacji pośredniej na powstawanie plazmy oraz na parametry energetyczne plazmowej elektrolizy roztworu (PDSE) podczas pracy w reżimie katodowym. W ramach badań przeprowadzono dwa rodzaje eksperymentów. Pierwszy polegał na obserwacji wpływu sonikacji pośredniej na przebieg elektrolizy roztworu wodnego 10% (w/w) Na_2CO_3 i przejścia z reżimu faradycznego na reżim katodowy PDSE podczas zwiększania wartości napięcia stałego. Stwierdzono, że sonikacja obniża o ok. 10 % średnią moc potrzebną do wytworzenia plazmy na elektrodzie roboczej w porównaniu do elektrolizy prądem stałym bez sonikacji. Drugi eksperyment dotyczył statystycznego określenia parametrów energetycznych (gęstość prądu i zużycie energii) w reżimie katodowym PDSE przy różnych wartościach napięcia stałego. Wykazano, że dzięki sonikacji wartość napięcia potrzebna do osiągnięcia minimalnej gęstości prądu, przy której zachodzi efekt synergiczny z PDSE była niższa o 14 V, jednocześnie powodując obniżenie zużycia energii o 21,5% w porównaniu do PDSE bez sonikacji.* ***(Wpływ pośredniej sonikacji na powstawanie plazmy i charakterystykę energetyczną w reżimie katodowym plazmowej elektrolizy roztworu)***

Abstract. *The paper presents the experimental study's results on indirect sonication's effect on plasma formation and energy parameters in the cathodic regime of plasma-driven solution electrolysis (PDSE). In the study, two types of experiments were carried out. The first was to observe the effect of the indirect sonication on the transformation of the DC electrolysis of 10 wt% Na_2CO_3 aqueous solution from its Faradaic regime to the cathodic regime of PDSE with increasing the applied DC voltage. Sonication was found to decrease the average power needed to attain the plasma formation at the discharge electrode by ca. 10% compared to PDSE without sonication. The second experiment concerned the statistical determination of the energy parameters (current density and power consumption) in the cathodic regime of PDSE with varying the applied DC voltage. It was revealed that sonication reduces the applied DC voltage by 14 V to achieve the minimum current density at which sonication exhibits a synergetic effect on PDSE, reducing the power consumption by 21.5% compared to PDSE without sonication.*

Słowa kluczowe: Elektroliza, plazmowa elektroliza roztworu, wyładowania elektryczne w cieczach, wodór, charakterystyka prądowo-napięciowa, ultradźwięki, sonikacja, kawitacja akustyczna, fale akustyczne, efekt synergiczny, synergia
Keywords: Electrolysis, plasma-driven solution electrolysis, electric discharges in liquids, hydrogen, current-voltage characteristic, ultrasound, sonication, acoustic cavitation, acoustic waves, synergetic effect, synergy

Introduction

In recent years, the power of ultrasound has been reported as a promising method to increase the efficiency and rate of hydrogen production in the electrolysis process. This is because, in the combined sonoelectrochemical process, sonication provides promotion of the mass transport to the electrode surface, electrode cleaning, and surface activation, enhancing electron transport and degassing, which together results in a decrease of the overvoltage of the electrochemical reactions at the anode and cathode, and ohmic losses in the bulk of aqueous solution [1-3].

Plasma-driven solution electrolysis (PDSE) has garnered attention for the unique chemical reactions occurring at the plasma electrode. These reactions lead to Faradaic efficiencies exceeding the theoretical limit predicted by Faraday's law, making PDSE a fascinating field of study [4, 5]. The positive effect of ultrasound on the cathodic electrochemical discharge for graphene synthesis [6], plasma electrolytic oxidation process [7], and electrolyte plasma polishing [8] has already been reported. However, the influence of sonication on the current-voltage characteristics and energy parameters, especially current density and power consumption, in the cathodic regime of PDSE has not been studied yet.

Experimental setup and procedure

Fig. 1a and Fig. 1b show a photo and a schematic of the experimental setup used to study the effect of indirect sonication on the plasma formation and energy parameters (current density and power consumption) in PDSE.

The electrolytic cell consisted of the borosilicate glass vessel filled with 1 kg of 10 wt% Na_2CO_3 aqueous solution and two metal electrodes of different shapes and surface areas immersed in the electrolytic solution. The electrode with a larger active surface area of 25 mm × 25 mm, made of Ni foam (Nanografi), being positively charged, served as a counter electrode (anode), while the tungsten rod with a diameter of 2 mm and length of an active surface area of 10 mm, being negatively charged (cathode), served as the discharge electrode. Since the cathode's active surface area was much smaller than the anode's, plasma formation occurred at the cathode by increasing the applied DC voltage. The electrolytic cell was membraneless and served as a batch reactor without exchanging the electrolytic solution. Argon at a flow rate of 150 smLpm (standard milliliters per minute) was used as a purge gas to evacuate all gas products from the electrolytic cell. The electrolytic cell was placed into the center of the metal basket and installed in the Sonic-10 ultrasonic bath (Polsonic), which operated continuously at 40 kHz. Before each experiment, the aqueous solution was treated for 25 minutes with an ultrasound for degassing. Due to the ultrasonic treatment, the initial temperature of the aqueous solution increased to 29 ℃.

The LTC-300-8D (RUCELF) variable autotransformer of 2.4 kVA nominal power equipped with a diode bridge and two smoothing capacitors of 16 mF (Kemet) each served as the DC power supply. The voltage between the cathode and anode was measured by a WAD-A-MAX-608 (Acon) high-voltage probe (-600 V ÷ +600 V), while the current flowing between two electrodes was measured by the voltage drop across a resistor of 1.5 mOhm using a precision isolation amplifier WAD-A-MAX-609 (Acon) (-225 mV ÷ +225 mV). A WAD-AD12-128H (Acon) data logger recorded the probe signals. Multiplication of the current and voltage determined the electric power consumed in the experiment. In parallel, the power meter EL3433 (Beckhoff) measured the electrical power consumed by the autotransformer.

In the study, two types of experiments were carried out. The first one was carried out for the purposes (i) to observe the plasma formation at the cathode and (ii) to measure the

current-voltage characteristics when the DC electrolysis transforms from its Faradaic regime to the PDSE regime with an increase of the applied DC voltage from 0 V to 125 V in the case with and without sonication. The data acquisition frequency was set at 1 Hz for the voltage and current probes. A video recording was also conducted to determine the onset time and observe the plasma formation stages.

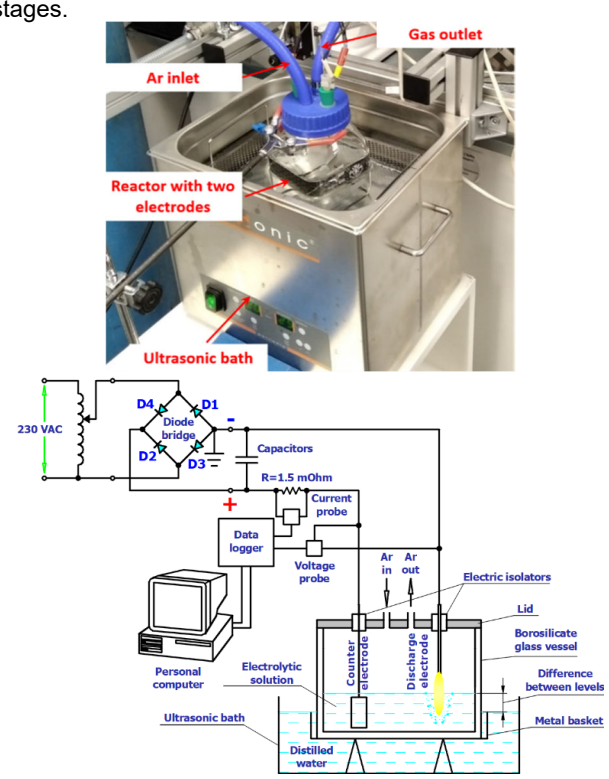

Fig. 1. The experimental setup: a) a photo of the experimental setup, b) a scheme of the experimental setup.

The distilled water volume in the ultrasound bath was 5.3 L. The mass of 10 wt% Na_2CO_3 aqueous solution in the glass vessel was 1 kg, the difference in the levels of distilled water in the ultrasound bath and 10 wt% Na_2CO_3 aqueous solution in the glass vessel was 15 mm (needed for installation of the camera to record video of the plasma formation with and without sonication). The electrodes: a Ni foam plate with 25 mm × 25 mm active surface area (anode) and a tungsten rod with a diameter of 2 mm (cathode), both immersed into the aqueous solution. The tungsten rod was immersed in the aqueous solution to a depth of 10 mm. The distance between electrodes was 60 mm.

The second experiment was carried out to statistically determine the current density and power consumption values in the range of the applied DC voltages from 85 V to 156 V when PDSE occurs with and without sonication. The duration of each measurement was 100 seconds, and n=5 measurements were conducted at each applied DC voltage. In this experiment, the data acquisition frequency was set at 100 kHz for the voltage and current probes. MATLAB 2016b was applied for mathematical data processing.

Results and discussion

Formation of the cathodic regime of PDSE without and with indirect sonication

Fig. 2 shows the formation stages of the cathodic regime of PDSE at the discharge electrode without and with indirect sonication when increasing the applied DC voltage.

From Fig. 2a-b, it can be seen that a monotonic increase in the applied DC voltage from 0 V to 25 V initiates the electrochemical production of O_2 and CO_2 at the anode and H_2 at the cathode. Further increase of the applied DC voltage from 25 V to 75 V (Fig. 2c-d) develops the formation of the initial plasma discharges at the electrode with a smaller active surface area (cathode), and the cathodic regime of PDSE is attained (Fig. 2d). After getting the initial plasma discharges with the increase in the applied DC voltage, the intensive production of gases at the anode and cathode in the cell is observed, resulting in the formation of the white layer containing tiny gas bubbles in the aqueous solution (Fig. 2e). Due to this phenomenon, the anode and cathode immersed in the electrolytic solution are not visible in the photo. With the subsequent voltage increase up to 125 V, the white layer thickness is increasing (Fig. 2f).

The same stages of plasma formation at the discharge electrode in the electrochemical cell, along with the increase in the applied DC voltage, also occur (Fig. 2g-j) with indirect sonication. However, after getting the initial plasma discharges, a layer of tiny gas bubbles is not present in the electrochemical cell due to the degassing effect of the sonication. In other words, ultrasonic acoustic waves rapidly evacuate gases produced at the electrodes from the aqueous solution. This explains the absence of the white layer of tiny gas bubbles in the cell.

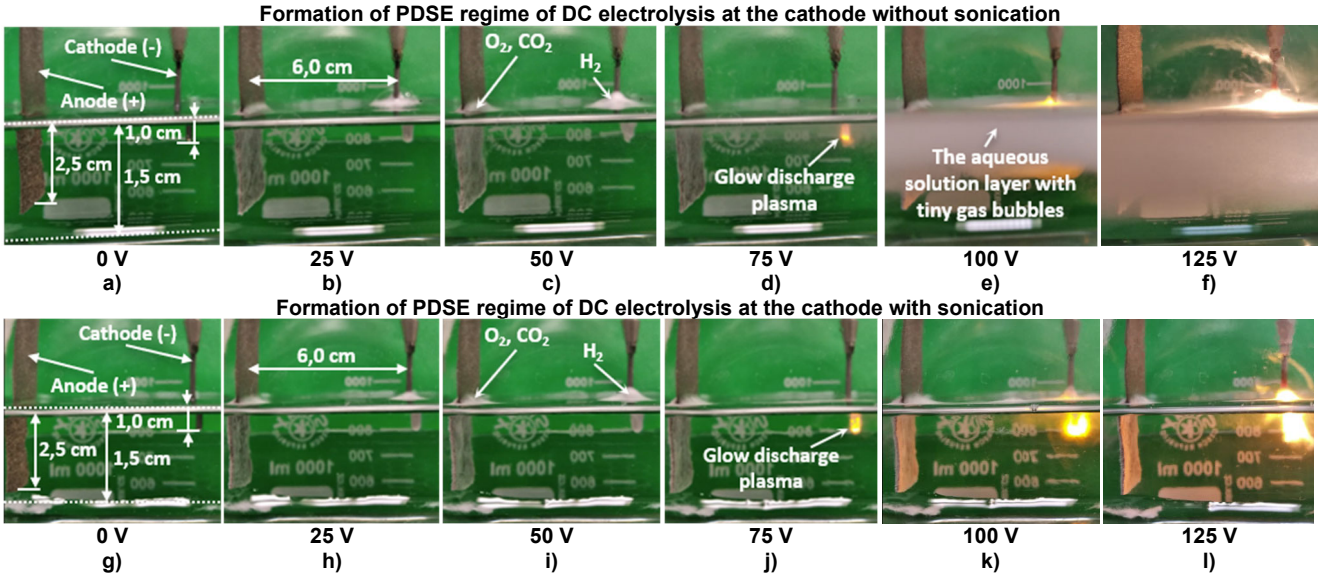

Fig. 2. Transformation of the DC electrolysis from its Faradaic regime to the cathodic regime of PDSE (without and with indirect sonication) when increasing the applied DC voltage. The numbers below the pictures indicate the applied DC voltage.
a) An Initial configuration of the electrolytic cell for conducting the DC electrolysis without sonication,
b) Faradaic electrolysis without sonication at the applied DC voltage of 25 V,
c) Faradaic electrolysis without sonication at the applied DC voltage of 50 V,
d) The cathodic regime of PDSE without sonication at the applied DC voltage of 75 V,
e) The cathodic regime of PDSE without sonication at the applied DC voltage of 100 V,
f) The cathodic regime of PDSE without sonication at the applied DC voltage of 125 V,
g) An initial configuration of the electrolytic cell for conducting the DC electrolysis with indirect sonication,
h) Faradaic electrolysis assisted with indirect sonication at the applied DC voltage of 25 V,
i) Faradaic electrolysis assisted with indirect sonication at the applied DC voltage of 50 V,
j) The cathodic regime of PDSE assisted with indirect sonication at the applied DC voltage of 75 V,
k) The cathodic regime of PDSE assisted with indirect sonication at the applied DC voltage of 100 V,
l) The cathodic regime of PDSE assisted with indirect sonication at the applied DC voltage of 125

Influence of the indirect sonication on the current-voltage characteristic

Fig. 3 shows the current-voltage characteristics measured without (red curve) and with (blue curve) indirect sonication.

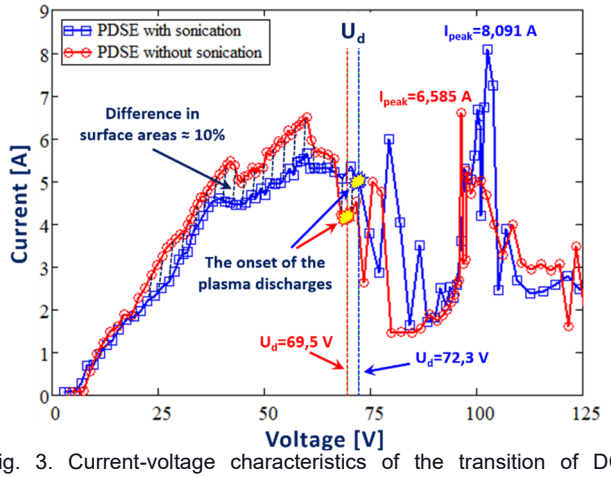

Fig. 3. Current-voltage characteristics of the transition of DC electrolysis of 10 wt% Na_2CO_3 aqueous solution from its Faradaic to the PDSE regime measured without (red curve) and with indirect sonication (blue curve). U_d is the discharge onset voltage.

From Fig. 3, it can be seen that the discharge onset voltage of 72.3 V needed to attain the initial plasma discharges at the cathode in the case with indirect sonication is higher than that of 69.5 V in the case without sonication. This is caused by the ultrasonic degassing effect shown in Fig. 2. The higher voltage is needed in the sonication case to form the stable gas-vapor envelope around the cathode tip immersed in the electrolytic solution, which is a prerequisite of the plasma formation, as shown in [4, 5, 9, 10].

However, despite the higher discharge onset voltage for the sonication case, the average power needed to attain the initial plasma discharges at the cathode tip is ca. 10% lower than that in PDSE without sonication. This can be explained by the fact that ultrasound generates the tiny acoustic cavitation bubbles in the bulk of electrolytic solution. Thus, less energy is needed for the bubbles' nucleation, which is one of the requirements for the PDSE formation around the discharge electrode [4, 5, 9, 10]. The presence of the acoustic cavitation bubbles in the bulk of the electrolytic solution also explains the lower values of electric current (by ca. 15%) measured before the onset of the initial plasma discharges at the cathode in PDSE with sonication.

It is also worth to be mentioned that due to the evident degassing effect of sonication (Fig. 2e-f and Fig. 2k-l), higher value of the electric current of 8.091 A (so-called the second current maximum [11]) is achieved with sonication compared to 6.585 A in PDSE without sonication. The average electric current is ca. 8.2% higher in the sonication case than that without sonication.

Influence of the indirect sonication on the energy parameters of the cathodic regime of PDSE

Fig. 4a and Fig. 4b show the influence of the applied DC voltage on the electric power consumption in PDSE and current densities at the discharge electrode, respectivelly.

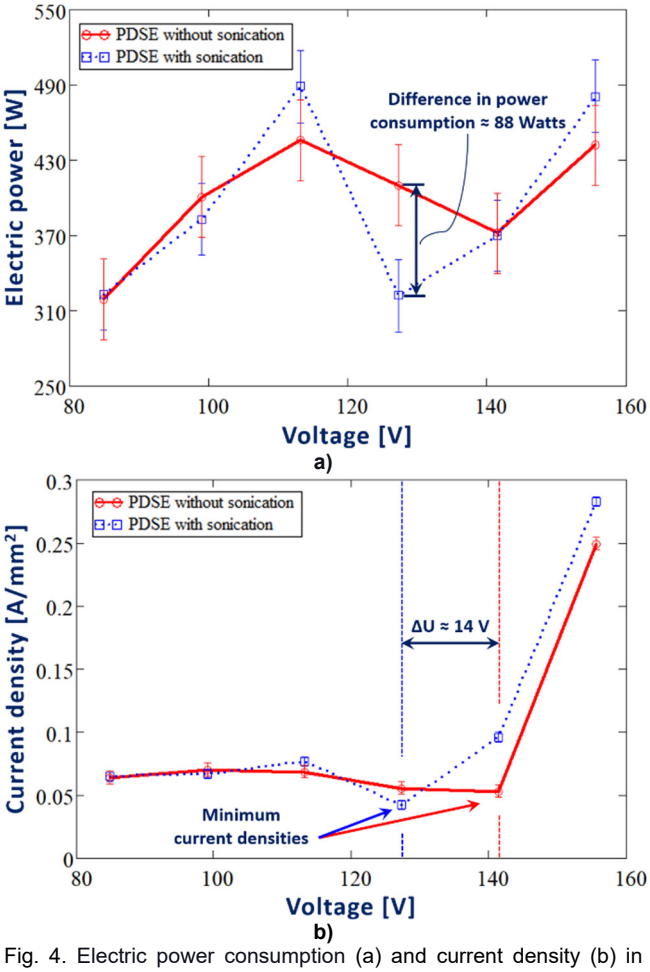

Fig. 4. Electric power consumption (a) and current density (b) in PDSE without (red curves) and with (blue curves) sonication versus applied DC voltage. Error bars are standard deviations from duplicates.

Fig. 4a shows that in PDSE with and without sonication, an increase in the applied DC voltage results in the growth of the power consumption up to its maximum of 489 W with sonication and 446 W without sonication at 113 V. After reaching its maximum, the power consumption drops up to the minimum values of 322 W in the case with sonication and 372 W without sonication. However, in the sonication case, the minimum power consumption occurs at 127 V,

while in the case without sonication at 141 V. These minimum values of the power consumption observed at 127 V and 141 V conform with the minimum values of the current densities at the discharge electrode (Fig. 4b). Thus, in the case with indirect sonication, the current density drop of up to 0.042 A/mm2 occurs at 127 V, while in the case without sonication, the drop in the current density up to 0.053 A/mm2 takes place at 141 V. Here, we can see the voltage reduction by 14 V in the sonication case to achieve this minimum current density compared to the case without sonication. This finding coincides with our previous experimental results presented in [12] on the behavior of the current densities in PDSE with an increase in the applied DC voltage.

Comparing values of the power consumption in both cases at 127 V, it can be concluded that sonication decreases the power consumption by 88 W, corresponding to ca. 21.5% of the power consumption reduction. Along with the voltage reduction by 14 V, here we can say about synergetic effect of sonication on PDSE. This suggests that there might be a potential for optimizing energy usage in PDSE assisted with sonication. However, further research is still required to delve into this phenomenon.

Fig. 4b shows that an increase in the applied DC voltage results in the slight growth of the current densities. Then, the current densities drop to the minimum values at 127 V and 141 V in the case with and without sonication, respectively. With the subsequent increase in the applied DC voltage, the current densities significantly soar up to their maximum values of 0.283 A/mm2 with sonication and 0.249 A/mm2 without sonication. It is noticeable that above the applied DC voltage of 127 V, sonication provides higher current densities compared to the case without sonication. This can also be explained by the degassing effect produced by acoustic waves.

Conclusions

Summing up the results of this experimental study, the following conclusions can be drawn:

1. Introduction of the acoustic waves into the electrochemical cell allows the evacuation of gases, which are intensively produced at the electrodes, especially when the PDSE regime is attained.

2. Indirect sonication decreases the average power needed to attain the onset of the PDSE regime by 10% compared to PDSE without sonication.

3. In the case with sonication the average electric current is ca. 15% lower in the time period before the onset of the PDSE regime, while above the discharge onset point the average electric current is ca. 8.2% higher compared to PDSE without sonication.

4. The statistical determination of the energy parameters showed that sonication provides a decrease in the applied DC voltage by 14 V to achieve the minimum current density at the discharge electrode compared to the case without sonication. In turn, it results in a decrease in power consumption by ca. 21.5% at the applied DC voltage of 127 V compared to the case without sonication. This finding on the synergetic effect of the sonication opens a new door for optimizing the energy consumption in PDSE.

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