

# The plasma discharges in the anodic and cathodic regimes of plasma driven solution electrolysis for hydrogen production

**Streszczenie.** W pracy przedstawiono wyniki badań eksperymentalnych wyładowań plazmowych w anodowym i katodowym reżimie plazmowej elektrolizy (PDSE) wodnego roztworu  $\text{Na}_2\text{CO}_3$  (10% wag.). Badania ujawniły cechy powstawania wyładowań plazmowych na mniejszej elektrodzie. Wyznaczone zostały wartości napięć przebiccia i początku wyładowania dla obu reżimów pracy PDSE. Stosując szybką analizę transformacji Fouriera, przebadano charakterystyki częstotliwościowe wyładowań plazmowych. W reżimie anodowym PDSE wyładowania elektryczne występują przy znacznie wyższych częstotliwościach (kilkadziesiąt kHz), natomiast w reżimie katodowym przy dużo niższych częstotliwościach (setki Hz), ale przy wyższych amplitudach prądu i napięcia wyładowania, co skutkuje wyższą rozpraszaną mocą elektryczną. Za pomocą optycznej spektroskopii emisyjnej (OES) zarejestrowano linie emisyjne wzbudzonych rodników hydroksylowych ( $\text{OH}^*$ ), wodorowych ( $\text{H}^*$ ) i tlenowych ( $\text{O}^*$ ) powstałych w wyniku dysocjacji cząsteczek wody. Przedyskutowano otrzymane rezultaty pod kątem skuteczności produkcji wodoru metodą PDSE. (**Wyładowania plazmowe w anodowych i katodowych reżimach plazmowej elektrolizy roztworów do produkcji wodoru.**)

**Abstract.** This paper presents results of the experimental study of the plasma discharges in the anodic and cathodic regimes of plasma-driven solution electrolysis (PDSE) in 10 wt%  $\text{Na}_2\text{CO}_3$  aqueous solution. The study revealed features of the plasma discharge formation at the smaller electrode and values of the breakdown and discharge onset voltages for the anodic and cathodic regimes of PDSE. By applying the fast Fourier transformation analysis, the frequency characteristics of both plasma discharges were found. In the anodic regime of PDSE, the electrical discharge occurred at much higher frequencies (dozens of kHz), while in the cathodic regime at much lower frequencies (hundreds of Hz) but at higher amplitudes of the discharge current and voltage, resulting in higher electrical power dissipation. The applied optical emission spectroscopy (OES) showed emission lines of the hydroxyl ( $\text{OH}^*$ ), hydrogen ( $\text{H}^*$ ), and oxygen ( $\text{O}^*$ ) radicals formed as a result of the dissociation of the water molecules. The obtained results were discussed in terms of the hydrogen production efficiency by the PDSE method.

**Słowa kluczowe:** plazmowa elektroliza roztworów, wyładowania plazmowe w cieczach, charakterystyki częstotliwościowe wyładowania, linie emisyjne, rodniki, produkcja wodoru

**Keywords:** plasma electrolysis of solutions, plasma discharges in liquids, discharge frequency characteristics, emission lines, radicals, hydrogen production

## Introduction

In recent years, a new type of electrolysis, initially known as the contact glow discharge electrolysis (CGDE), and more recently as the plasma-driven solution electrolysis (PDSE), has attracted attention as an alternative method of hydrogen production [1, 2]. Literature studies showed that the Faradaic efficiency of hydrogen production in PDSE is dozens of times higher than that in Faradaic electrolysis [3, 4]

PDSE is a non-typical electrochemical process in which electric plasma is formed in the glow discharges excited by the direct or pulsed current in a gas-vapor envelope in the vicinity of the discharge electrode immersed in the electrolytic solution. The yield of chemicals in PDSE (i.e. the ratio of the moles of the product formed to the moles of electrons consumed in a chemical reaction) is several times higher than the Faradaic yield of chemicals (predicted by Faraday's law).

The current study gives a characterization of the transformation of Faradaic electrolysis to anodic and cathodic regimes of PDSE and the plasma discharges induced in 10 wt%  $\text{Na}_2\text{CO}_3$  aqueous solution using a high voltage (DC) power supply as a possible method of hydrogen production.

## Experimental setup and procedure

Fig. 1 shows a scheme of the experimental setup used to study the characteristics of the plasma discharges in the anodic and cathodic regimes of PDSE.

The borosilicate glass vessel was filled with 300 g of 10 wt%  $\text{Na}_2\text{CO}_3$  aqueous solution and two metal electrodes of different shapes were immersed in it. The electrode with a larger surface area was made of a stainless-steel plate and served as a counter electrode, while the tungsten rod with a diameter of 2 mm served as the discharge electrode. Two regimes of PDSE were studied: anodic and cathodic. The anodic regime of PDSE is when the smaller electrode is

positively charged (being anode), while the counter electrode is negatively charged (being cathode). The cathodic regime is when the smaller electrode is negatively charged (being cathode), while the counter electrode is positively charged (being anode).

The LTC-300-8D (RUCSELF) variable autotransformer of 2.4 kVA nominal power equipped with a diode bridge served as the HV DC power supply and provided DC voltage in the range of 0-300 V. In the electrochemical cell, the discharge voltage was measured by a WAD-A-MAX-608 (Acon) high voltage probe (-600 V ÷ +600 V), while the discharge current was measured by a voltage drop across a resistance (the electric shunt) of 1.5 Ohm using a precision isolation amplifier WAD-A-MAX-609 (Acon) (-225 mV ÷ +225 mV). All signals from the current and voltage probes were recorded using a WAD-AD12-128H (Acon) data logger. The data acquisition frequency was set at 100 kHz for each of the probes.

Optical emission spectroscopy (OES) was carried out on the plasma discharges using a UV-Vis-NIR spectrometer LR2 (Lasertack). The light emission spectra in the range from 200 nm to 1200 nm were collected every second for 60 s in each trial. The optical probe was installed in the stainless-steel pipe outside of the electrochemical cell and placed in front of the smaller electrode. Neither focusing lens nor pinhole was applied to capture the light emitted from the discharge electrode. The exposure time was set at 10 ms. The spectra were processed using Spectra+ (Lasertack) spectroscopy software.

Two types of experiments were carried out: (1) to study the plasma discharge formation in the anodic and cathodic regimes of PDSE with increasing the applied voltage, (2) to study the characteristics of the plasma discharges in the anodic and cathodic regimes of PDSE at the applied voltage of 140 V.

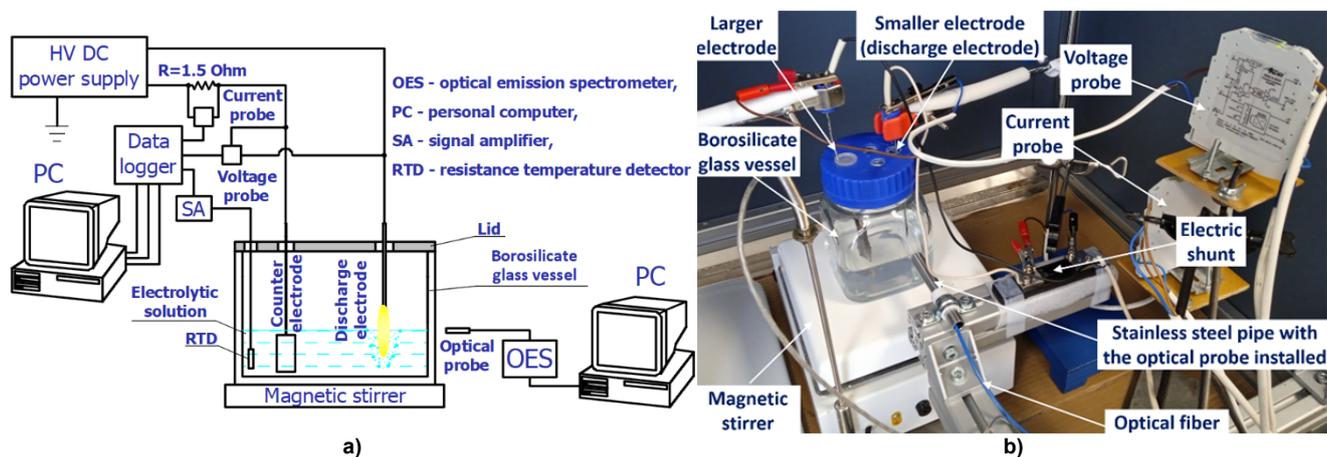


Fig. 1. The experimental setup: a) a scheme of the experimental setup, b) a photo of the experimental setup.

The electrolytic solution was 10 wt%  $\text{Na}_2\text{CO}_3$  aqueous solution at the initial temperature of 22 °C and atmospheric pressure. The weight of the electrolytic solution was 300 grams. The electrodes: a stainless-steel plate with a thickness of 0.4 mm and 2 cm × 2cm active surface area exposed to the electrolytic solution, and a tungsten rod with a diameter of 2 mm. The stainless-steel plate was immersed in the electrolytic solution to a depth of 2 cm. The tungsten rod was immersed in the electrolytic solution to a depth of 1 cm. The ratio of the active surface area of the smaller electrode and that of the larger electrode was about 1/12.

In the first experiment when the formation of the plasma discharges was studied, the data logger recorded the discharge current and voltage at increasing the applied voltage from 0 V to the voltage at which the full glow discharge plasma appears. This experiment was accompanied by taking pictures of the electrolytic cell to capture certain moments of the plasma formation at the discharge electrode.

In the second experiment, the data logger was triggered only at the moment when the full glow discharge plasma appeared. The duration of this experiment was set at 60 seconds. Simultaneously OES was applied to get the light emission spectra of the plasma discharges in the cathodic regimes of PDSE at the applied voltage of 140 V.

After finishing the data record, MATLAB 2016b was applied for mathematical data processing and presenting the collected data in graphical representations.

By multiplication of the discharge current and voltage, and their integration, the consumed energy was calculated. Then, by dividing this energy by the integration time interval, the average value of electrical power was derived.

## Results and discussion

### Formation of the anodic and cathodic regimes of PDSE

The Faradaic electrolysis transforms into PDSE with an increase in applied voltage to a value sufficient to ionize the species in the gas-vapor envelope surrounding the discharge electrode and subsequently induce the electrical discharge plasma in the envelope.

Fig. 2a-h illustrates the transformation of the electrolysis from its Faradaic form into anodic and cathodic regimes of PDSE with increasing the applied voltage.

When the voltage is applied, first the conventional electrolysis begins. Fig. 2a and Fig. 2e show the Faradaic electrolysis for anodic and cathodic regimes, respectively, at the same applied voltage of 20 V. According to classical electrochemistry, with  $\text{Na}_2\text{CO}_3$  aqueous solution in the anodic regime  $\text{O}_2$  and  $\text{CO}_2$  gas mixture is produced at the positively charged smaller electrode, while  $\text{H}_2$  is produced at the negatively charged larger electrode (Fig. 2a). And vice versa, in the cathodic regime (Fig. 2e)  $\text{O}_2$  and  $\text{CO}_2$  gas mixture is produced at the positively charged larger electrode, while  $\text{H}_2$  is produced at the negatively charged smaller electrode. Moreover, at the same value of the electric current passing the electrolytic solution and the electrodes having their surface area equal, the number of

moles of the gas mixture generated at the cathode doubles the number of moles of the gas mixture generated at the anode. That is why more gas bubbles are generated at the larger electrode having negative polarity compared to the same electrode having positive polarity as seen in Fig. 2a and Fig. 2e, respectively. The same is about the production of the gases at the smaller electrode.

Further increase of the applied voltage leads to the onset of acoustic noise coming from the smaller electrode. It was revealed that in the case of the anodic regime this phenomenon begins at the applied voltage of 35 V (Fig. 2b), while in the cathodic regime at 42 V (Fig. 2f). This phenomenon can be attributed to achieving the breakdown point and beginning of the transitional phase when the Faradaic electrolysis terminates due to the formation of a stable gas-vapor envelope around the discharge electrode as a result of the gas and vapor bubbles coalescence. The gas and vapor bubbles are produced by the Faradaic electrolysis and by evaporation of the electrolytic solution, especially at higher electric current densities causing higher Joule heating. The value of the electric current density at which the Faradaic electrolysis terminates (i.e. the breakdown point) depends on the material of the discharge electrode, conductivity of the electrolytic solution, its temperature, and surface tension [1].

The subsequent increase of the applied voltage causes the ionization of the gas-vapor envelope around the discharge electrode leading to the formation of the plasma discharges at the tip of the smaller electrode. This phenomenon is known as the discharge onset point and the applied voltage responsible for the formation of the first glow discharges is called the discharge onset voltage. In the anodic regime (Fig. 2c), the onset of the glow discharges at the tip of the smaller electrode occurred at 60 V, whereas in the cathodic regime (Fig. 2g) at 52 V. That is to say that to form the plasma discharges in the cathodic regime of PDSE lower applied voltage is needed. This agrees with the results of other authors [5, 6].

At the applied voltage higher than that pointed out by the discharge onset point, the third phase of the electrolysis occurs. This phase is called PDSE. In the anodic regime of PDSE, the plasma forms as a thin layer around the tungsten rod (Fig. 2d). The plasma formed in the cathodic regime of PDSE (Fig. 2h) occupies a much larger volume around the tungsten rod than that in the anodic regime of PDSE (Fig. 2d). This shows that the cathodic regime of

PDSE is more efficient for steam generation. The brightness of the cathodic glow discharges is much stronger than that of the anodic glow discharges, although the

applied voltage is lower in the cathodic regime of PDSE (120 V in the cathodic regime of PDSE versus 130 V in the anodic regime of PDSE).

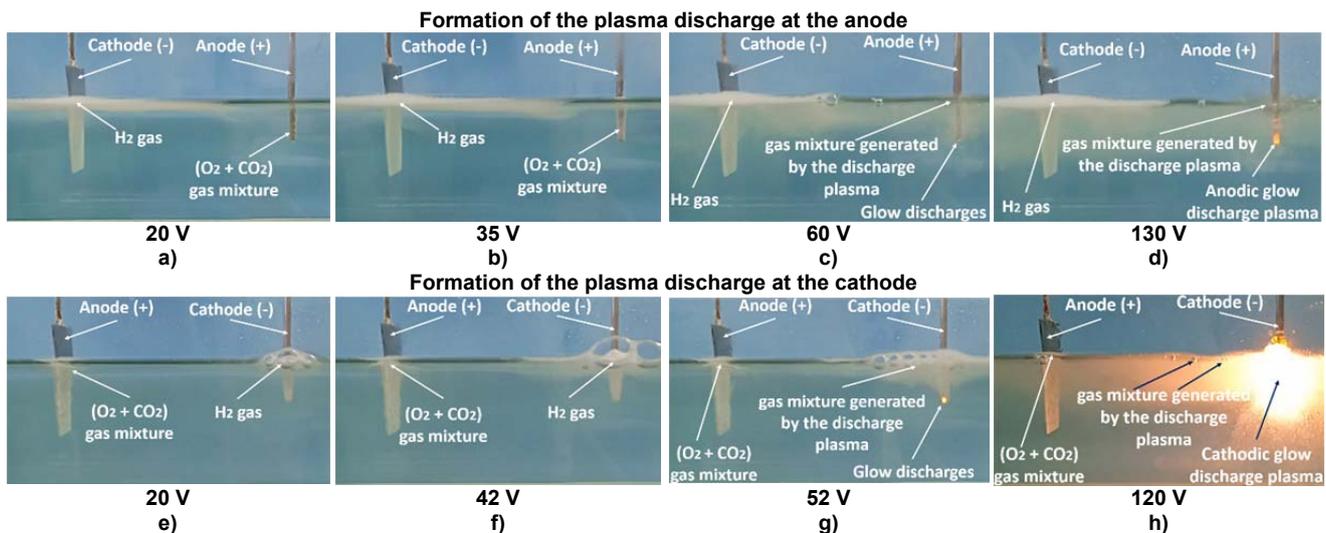


Fig. 2. Transformation of the electrolysis from its Faradaic form into the anodic and cathodic regimes of PDSE with increasing the applied voltage. The numbers below the pictures indicate the applied voltage.

- a) Faradaic electrolysis at the applied voltage of 20 V (tungsten rod served as an anode),
- b) The onset of noise from the tungsten rod at the applied voltage of 35 V (tungsten rod served as an anode),
- c) The onset of the glow discharges at the tip of the tungsten rod at the applied voltage of 60 V (tungsten rod served as an anode),
- d) The anodic mode of the PDSE at the applied voltage of 130 V (tungsten rod served as an anode),
- e) Faradaic electrolysis at the applied voltage of 20 V (tungsten rod served as a cathode),
- f) The onset of noise from the tungsten rod at the applied voltage of 42 V (tungsten rod served as a cathode),
- g) The onset of the glow discharges at the tip of the tungsten rod at the applied voltage of 52 V (tungsten rod served as a cathode),
- h) The cathodic mode of the PDSE at the applied voltage of 120 V (tungsten rod served as a cathode).

### Characteristics of the discharge current and voltage

After applying high DC voltage to the electrodes, the electrical discharges were initiated at the smaller electrode and operated in the self-pulsing mode as a result of the formation and behavior of the gas-vapor envelope around the discharge electrode. The waveforms of the discharge current and voltage measured in the anodic and cathodic regimes of PDSE at the applied voltage of 140 V are presented in Fig. 3 a-b, respectively. At the small thickness of the gas-vapor envelope around the smaller electrode, the plasma discharges are characterized by a higher amplitude of the discharge current and a lower amplitude of the discharge voltage. While at the large thickness of the gas-vapor envelope around the smaller electrode, the plasma discharges are characterized by the lower amplitude of the discharge current and higher amplitude of the discharge voltage.

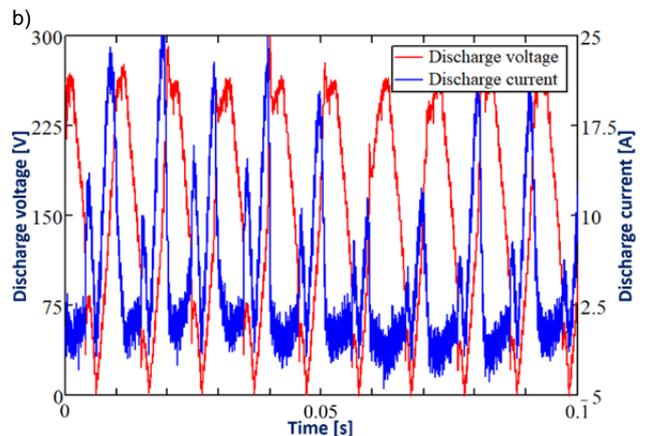
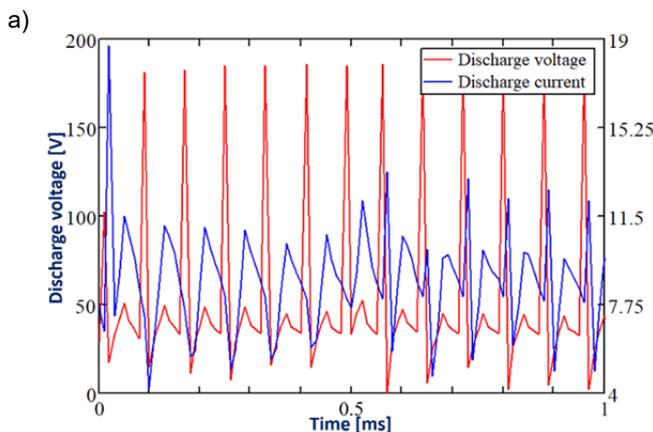


Fig. 3. Current and voltage waveforms of the plasma discharges in the anodic (a) and cathodic (b) regimes of PDSE in 10 wt%  $\text{Na}_2\text{CO}_3$  aqueous solution at the applied voltage of 140 V.

By applying a fast Fourier transformation analysis, it can be concluded that the plasma discharges superpose as the harmonic oscillations consisting of a set of frequency components. As expected, in the anodic and cathodic regimes of PDSE, one frequency of 100 Hz was identical to the frequency of the HV DC power supply corresponding to an operation of the autotransformer with a diode bridge but without smoothing capacitors. Generally, in the anodic regime of PDSE (Fig. 3a) the electrical discharges occur at much higher frequencies but lower amplitudes of the discharge current and applied voltage than those in the cathodic regime of PDSE (Fig. 3b). This results in higher electrical power dissipated in the vicinity of the discharge electrode in the cathodic regime of PDSE compared to the anodic regime at the same applied voltage (i.e. 710 W of

the electrical power dissipated in the cathodic regime versus 415 W of the electrical power dissipated in the anodic regime at 140 V of the applied voltage). That is why the cathodic plasma is much brighter than the anodic one as shown in Fig. 2d and 2h, respectively.

In the anodic regime of PDSE, the waveform of the discharge current and voltage is a result of superposing 12.5 kHz, 25 kHz, 37.5 kHz, and 50 kHz oscillations, while in the cathodic regime of PDSE the set of harmonics includes 200 Hz, 300 Hz, 400 Hz, and 500 Hz oscillations. The phenomenon of the difference in the frequencies of the self-operating electrical discharges in the anodic (Fig. 3a) and cathodic (Fig. 3b) regimes of PDSE is still not understood.

### OES of the plasma discharges

As a result of the plasma discharges, in the cathodic regime of PDSE, the emission of the bright light was observed in the vicinity of the discharge electrode. Fig. 4 shows the continuous emission spectrum received in the range of 200-1200 nm in the cathodic regime of PDSE in 10wt% Na<sub>2</sub>CO<sub>3</sub> aqueous solution at the applied voltage of 140 V.

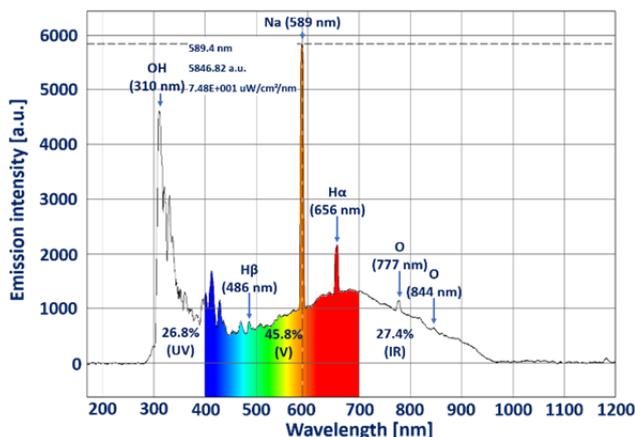


Fig. 4. The emission spectrum of the light emitted from the discharge electrode in the cathodic regime of PDSE in 10 wt% Na<sub>2</sub>CO<sub>3</sub> aqueous solution at the applied voltage of 140 V.

As seen in Fig. 4, the light spectrum has the emission lines caused by the formation of excited hydroxyl (OH\*), hydrogen (H\*), and oxygen (O\*) radicals, which can be explained by passing the following reactions [7]:

- (1)  $H_2O + e^-(9.67 \text{ eV}) \rightarrow H + e^- + OH^*, (310 \text{ nm}),$
- (2)  $H_2O + e^-(18.6 \text{ eV}) \rightarrow OH + e^- + H^*, (486 \text{ nm}),$
- (3)  $H_2O + e^-(17.8 \text{ eV}) \rightarrow OH + e^- + H^*, (656 \text{ nm}),$
- (4)  $H_2O + e^-(15.7 \text{ eV}) \rightarrow H_2 + e^- + O^*, (777 \text{ nm}),$
- (5)  $H_2O + e^-(15.9 \text{ eV}) \rightarrow H_2 + e^- + O^*, (844 \text{ nm}).$

In addition, the emission line observed at 589 nm is attributed to the excitation of sodium (Na) cations of the Na<sub>2</sub>CO<sub>3</sub> used as an electrolyte in the experiment. Thus, the collision of electrons with the water molecules causes their dissociation, which can be used to produce hydrogen.

We have also estimated the percentages of the light spectrum emitted by the plasma discharges in the ultraviolet (UV), visible (V), and infrared (IR) ranges. Thus, at the applied voltage of 140 V, 26.8% of the light spectrum is emitted in the ultraviolet range, 45.8% in the visible range, and 27.4% in the infrared range.

### Conclusions

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

A sequence of the physico-chemical and physical processes occurs with increasing the applied voltage prior to the formation of PDSE at the smaller electrode immersed in the electrolytic solution. They are Faradaic electrolysis, the Joule heating of the electrolytic solution, the solvent evaporation and formation of the gas-vapor envelope around the smaller electrode, ionization of the gas-vapor mixture within the envelope, and induction of the electrical discharge plasma in it.

In the anodic regime of PDSE in 10 wt% Na<sub>2</sub>CO<sub>3</sub> aqueous solution, the breakdown and discharge onset voltages are 35 V and 60 V, respectively. Whereas, in the cathodic regime of PDSE, the breakdown and discharge onset voltages are 42 V and 52 V, respectively.

The plasma discharges operate in the self-pulsing mode due to the formation and behavior of the gas-vapor envelope around the discharge electrode. In the anodic regime of PDSE, the electrical discharges occur at much higher frequencies (dozens of kHz), while in the cathodic regime at much lower frequencies (hundreds of Hz) but higher amplitudes of the discharge current and voltage resulting in higher electrical power dissipated.

The applied OES revealed emission lines of the hydroxyl (OH\*), hydrogen (H\*), and oxygen (O\*) radicals formed as a result of the dissociation of the water molecules by the plasma discharges. This shows that PDSE can be regarded as a possible method of hydrogen production.

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