The plasma discharges in the anodic and cathodic regimes of plasma driven solution electrolysis for 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 that in the Faradic electrolysis (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 (RUCELF) 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.

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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. 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.
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 Na₂CO₃ aqueous solution in the anodic regime O₂ and CO₂ gas mixture is produced at the positively charged smaller electrode, while H₂ is produced at the negatively charged larger electrode (Fig. 2a). And vice versa, in the cathodic regime (Fig. 2e) O₂ and CO₂ gas mixture is produced at the positively charged larger electrode, while H₂ 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).

**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.

![Formation of the plasma discharge at the anode](image1)

**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).

![Formation of the plasma discharge at the cathode](image2)

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. 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 10 wt% Na2CO3 aqueous solution at the applied voltage of 140 V.

In addition, the emission line observed at 589 nm is regarded as a possible method of hydrogen production. By the plasma discharges. This shows that PDSE can be used as a possible method of hydrogen production. Sergii Bespalko would like to thank the Polish National Agency for Academic Exchange (NAWA) for the funding under the Ulam Program – Seal of Excellence (the grant agreement no. PP/SEL/2020/1/00004/U/00001). Sergii Bespalko also would like to thank the Research and Innovation Center Pro-Akademia (Poland) for hosting his research activities.

REFERENCES


