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Pulse electrolysis of alkaline solutions as highly efficient method of production of hydrogen/oxygen gas mixtures

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Pulse electrolysis of water solutions is a highly efficient method of production of hydrogen and hydrogen/oxygen gas mixtures, sometimes called hydroxygen. When pulse current is applied during electrolysis, the amount of hydroxygen formed is increased in comparison to the dc current regime. The aim of the present paper is to investigate the effect of ultra-short current pulses on the rate of hydroxygen gas mixture production as related to efficiency enhancement of the process by means of the reducing power consumption during electrolysis. Pulse electrolysis was carried out in a laboratory electrolysis stack consisting of nine cells featuring electrodes of 316L stainless steel at a spacing of 10 mm. Typically the experiments were carried out for 1min with current amplitudes of 1 – 1.4 A, frequencies of the signal 1 kHz and pulse saturation (duty cycle) between 1 - 5%. The volume of the produced hydroxygen gas mixture by pulse electrolysis was measured by gas flow meters and compared to the produced gas volume in the same electrolysis cell under a constant current regime of 1-5 A. On the basis of the results obtained, preliminary conclusions regarding optimization of the pulse current regime are drawn and a discussion on a possible mechanism of rate enhancement is given

Keywords: pulse electrolysis, electrical parameters, hydrogen/oxygen gas mixture, process efficiency

INTRODUCTION

The potential of hydrogen for playing an important role in future energy systems has lead researchers to investigate methods of reducing hydrogen production costs to levels that can compete with petroleum products [1-3]. Nowadays, only 4–5% [4] of total global production of this most abundant substance of the universe [5] is being done by water electrolysis. Water electrolysis is known to be one of the important assets for hydrogen production [6-11]. One of these methods is the application of pulsed current regime to a practical electrolysis system [1-5]. Electricity power demand expense constitutes the largest fraction [12] of hydrogen production costs by using electrolysis method.

At temperature of 298 K and at pressure of 1 atm, the reversible decomposition voltage for water is 1.23 V. The required voltage value of an electrolysis cell is higher than the decomposition voltage of a water molecule. No gas evolution is observed in practice until voltages of 1.65 - 1.7 V are applied [13-17]. Practical cells operate at voltages of 1.8- 2.6 V, as a result of overvoltage and ohmic losses. Overvoltage has mainly two components: (i) activation overvoltage that results from the finite rate of the electrode reactions. It varies with metal used as the electrode and its surface condition. It is reduced by operating at elevated temperatures and pressures, and increases with the current density of the electrode reaction. (ii) The concentration overvoltage arises as a result of changes in the composition of layers of electrolyte close to the electrodes. Ions are at discharged the electrode surface and hydrogen and oxygen are formed. Research results show that temperature, pressure, electrode material, electrolyte formulation and concentration, physical setup of the cell and power supply output waveform have an influence on the value of the overvoltage. In particular, when ultra-short pulses with somewhat longer pause periods between them are applied (i.e. using high-frequency pulse currents with low duty cycles), the structure of the double layer remains perturbed, the process of adsorption of intermediate products remain in a transient state and thus the overall rate of the process is expected to increase.

In that respect, the main objective of the present study is to quantify the effects of the electrical parameters of the pulse on the performance of water electrolysis for hydrogen gas mixture

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generation. First, the pulse electrolysis system employed is briefly described. Second, results of the effect of pulse electrolysis parameters on the efficiency of the process are presented and discussed. Finally, some thoughts on a possible mechanism of rate enhancement in the pulse regime are given and directions for further work are outlined.

EXPERIMENTAL

To test the influence of electrochemical parameters on the efficiency of the generator pulse electrolysis process of water tests was used generator for HHO gas mixture consists of nine series connected cells with electrodes of stainless steel 316L and area of 20 cm^2 and electrode spacing of 10 mm. During the tests were used two electrolytes with different concentration of KOH (0.1 and 0.4M) to monitor the effects of different concentrations of electrolyte. The volume of the KOH solutions used was 2 l. A laboratory made pulse generator "Electra 06" type VSDC-09/VO, 60V / 15A was used for the pulse current experiments, see **Error! Reference source not found.**. Typically the experiments were carried out for 1 min with current amplitudes of 1.0 – 1.4 A, frequencies of the pulse 1 kHz and pulse saturation (duty cycle) between 1 - 5%. The volume of the produced hydrogen/oxygen gas mixture by pulse electrolysis was measured by gas flow meters and compared to the produced gas volume of the constant current electrolysis in the same electrolyzer and applied current of 1 – 5 A, in order to achieve optimal efficiency, i.e. the highest amount of gas produced spend at a small amount of applied electrical energy.

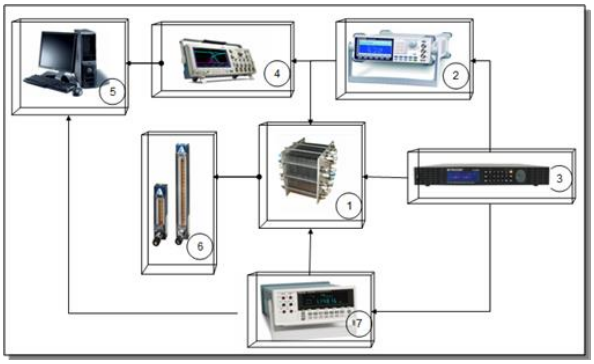

Fig. 1. Experimental setup: 1- electrolysis cell, 2- pulse generator, 60V/15 A, 3-dc power supply (100 V/15 A), 4 – digital oscilloscope, 5 - PC, 6 – flow meter (240 L/h), 7-digit multimeter.

RESULTS AND DISCUSSION

During the test runs conducted to examine the influence of different process parameters, the effects of electrolyte concentration, applied current and duty cycle are investigated. The constant current is varied from 1.0 A to 5 A, the applied current amplitude in pulsed current regime is from 1 to 1.4 A at a duty cycle from 1 to 5% for all of the experiments in 0.1 and 0.4 M KOH. The frequency of the pulse is kept constant at 1 kHz.

The electrolysis efficiency (Pυ) in constant current regime and the cell potential are shown in Fig. 2 as depending on the applied current in 0.4 M KOH electrolyte. The efficiency of the process increases with the applied current on the electrolysis cell. However, the cell potential increases together with the efficiency. For applied currents higher than I = 3 A, the efficiency of the process becomes constant.

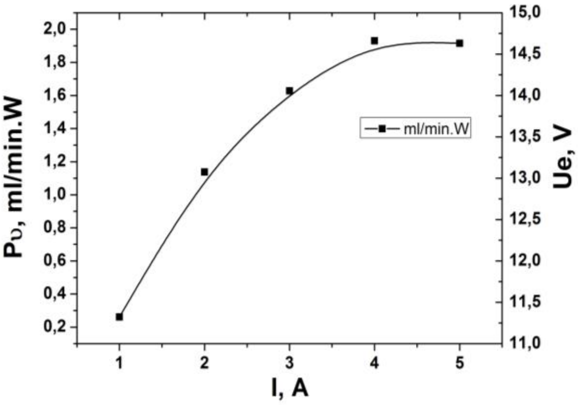

Fig. 2. Efficiency of water electrolysis in constant current regime. Electrolyte: 0.4 M KOH.

A typical test run in electrolyte of 0.1M KOH in constant current regime is show in Figure 3. The relatively high Pυ efficiency for smaller currents drastically drops with increasing currents and reaches stabilization at 4 A.

The efficiency of water electrolysis in the pulse current regime in 0.4 M KOH as depending on the duty cycle D in the range 1 – 5 % at a frequency of 1 kHz is displayed in Fig.4. The examination of the figure reveals that at lower duty cycles (smaller than D = 2%) the efficiency increases with the current, whereas a reverse trend is observed above a duty cycle of 3%. During test run with I = 1 A we obtain a maximum of Pυ at D = 3 % and stabilization after this value. Test run with I = 1.4 A efficiency is approximately constant which can be also observed in Figure 5 for experiments in 0.1 M KOH, the results being comparable. Comparable results we can observe also in bought curves of I = 1A applied current in the two different electrolytes we have used.

The efficiency of the electrolysis in pulsed current regime with duty cycle (D) of 1 to 5 % and frequencies of 1 kHz in 0.1 M KOH and applied current of 1 and 1.4 A is shown in Figure 4 . In both cases the efficiency of the process increase with applied current. An interesting observation is that at a lower current (I = 1 A) Pυ increases in a monotonous fashion with duty cycle, whereas with applied current of 1.4A, Pυ exhibits a maximum at a duty cycle of 3%, slowly decreasing at higher currents. Another observation is that the Pυ have higher values when compared to the constant current regime at applied current of 1 A, which means that at only 5% of power consumption we have a higher efficiency of the water splitting process.

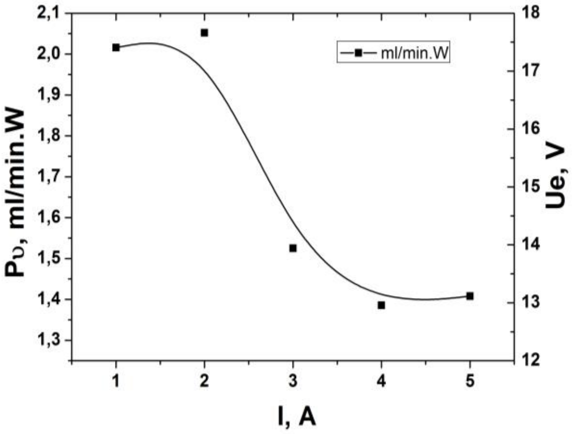

Fig. 3. Efficiency of water electrolysis in constant current regime. Electrolyte: 0.1M KOH.

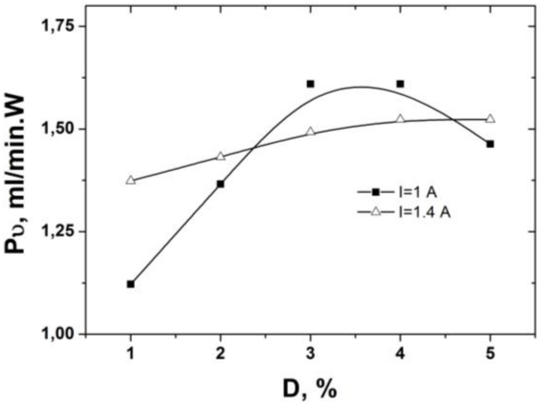

Fig. 4. Efficiency of water electrolysis in the pulsed current regime as a function of the duty cycle, f=1 kHz, 0.4M KOH.

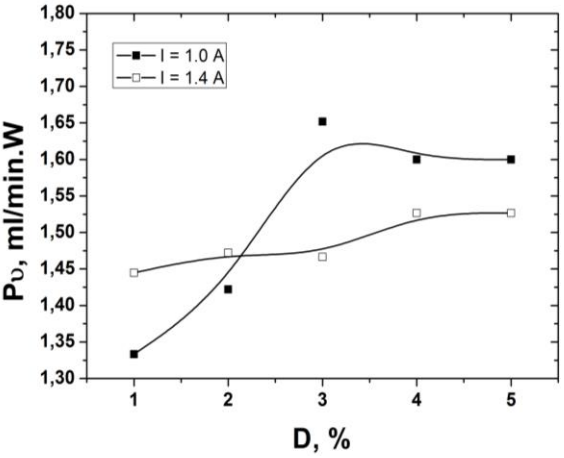

Fig. 5. Efficiency of water electrolysis in the pulsed current regime as a function of the duty cycle, f=1 kHz, 0.1 M KOH.

The interpretation of the phenomena associated with hydrogen/oxygen mixture (or hydroxygen) formation and its properties has been recently a cause of some controversy, invoking a range of explanations from the formation of new forms of matter [18-20] to that of charged water gas clusters [21]. The following mechanism of hydrogen evolution during electrolysis with inductive kickback pulses has been proposed: as no hydrogen adsorption/absorption peaks were detected for non-noble metal electrodes such as stainless steel, during the very short pulse the electrons from the metal directly discharge hydrogen ions and H_2 molecules are formed much more intensively than on Pt on which an adsorbed layer of atomic hydrogen forms [22-23]. In other words, our experiments are consistent with a picture in which the intermediate species of both the reduction and oxidation reactions of water are unstable and their rate of decomposition is much higher during pulse electrolysis when compared to conventional constant current process. Further investigations of the exact gas mixture composition are underway to try to elucidate the intimate mechanism of efficiency enhancement.

CONCLUSIONS

In conditions of pulse electrolysis of water, the rate of the process significantly increases in comparison to the dc regime.

The larges efficiency is obtained using cycles of low duty (less than 5%) as well as **higher current amplitudes.**

Results in the two employed electrolytes are comparable to each other, i.e. the effect of electrolyte concentration in the studied range is small.

A concept of the process featuring much higher decomposition rates of intermediate species during both reduction and oxidation of water is advanced, based on previous ideas in the literature. Further work is needed to quantify this concept and propose a mechanism of the process in pulse electrolysis conditions.

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ИМПУЛСНА ЕЛЕКТРОЛИЗА В АЛКАЛНИ ВОДНИ РАЗТВОРИ КАТО ВИСОКОЕФЕКТИВЕН МЕТОД ЗА ГЕНЕРИРАНЕ НА ОКСИВОДОРОДНИ ГАЗОВИ СМЕСИ

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(Резюме)

Импулсната електролиза във водни разтвори е високоефективен метод за производство на водород и водородно/кислородни газови смеси, понякога наричани оксиводород. Когато е приложен импулсен ток по време на електролизния процес, количеството получен оксиводород нараства в сравнение с електролиза при правотоков режим. Целта на тази работа е да изследва ефекта на приложени много къси пулсации на тока върху количеството на произведен газ, като се свърже с увеличаване на ефективността на процеса по отношение на намаляване консумацията на енергия по време на електролизата.

Импулсната електролиза е проведена в лабораторна електролизна клетка, съдържаща девет серии електроди от неръждаема стомана 316L с разстояние между електродите от 10 милиметра. Обемът на използвания алкален разтвор (0.5M KOH) е 2 л. Експериментите са проведени за една минута с амплитуда на тока от 0.7 до 1A, честота на сигнала от 0.4 до 1 kHz и наситеност на импулса от 2 до 95%. Обемът произведен газ/газова смес чрез импулсна електролиза е измерван чрез дебитомер и сравняван с произведеното количество газ от правотоковата електролиза, извършена в същия електролизьор при приложен ток от 5 до 10 A. На основата на получените резултати са представени предварителни изводи за оптимизация на импулсния режим и е дискутиран възможния механизъм за увеличаване на скоростта.