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HYDROGEN RELEASE FROM Pd ELECTRODES AFTER ION CURRENT IMPACT DURING ELECTROLYSIS PROCESS

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The out gassing rate of hydrogen from palladium cathode and anode after exposure to ion current during electrolysis process in the (H_2O+1wt.% $NaHCO_3$) electrolyte was measured in dependence on temperature and the duration of exposure. The activation energy of the hydrogen out gassing from the cathode was calculated to be $E \approx 46$ kJ/mole (for the anode $E \approx 18$ kJ/mole). The amount of hydrogen desorbed from the electrodes was estimated. For the Pd cathode, it was about 650 Normal (N) cm^3 H_2 (H/Pd $\approx$ 0.48). Hydrogen out gassing rate (hydrogen release) at the maximum temperature of 650 °C was 0.3 Ncm^3 H_2/s. For the Pd anode these values were much lower (0.21 Ncm^3 and 0.05 Ncm^3 H_2/s, consequently). Mass spectra of the mixtures of gases, generated during electrolysis mode, and the one, desorbed from electrodes under heating in a vacuum, were measured. Current-voltage characteristic of the electrolysis process is presented, too. It has been shown, that at electrolytes temperature of $\approx$ 50 °C and the pressure in the electrolyze chamber of 1 atm, the generated gas is hydrogen of 92 vol.%. Hydrogen desorbed in a vacuum from Pd-cathode after electrolysis process is high pure hydrogen (better than 99.99 vol.%). Physical-chemical reasons are analyze to explain hydrogen sorption and out gassing behavior in Pd electrodes during and after electrolysis.

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INTRODUCTION

Early [1-3], it has been shown the possibility to produce hydrogen in very simple electrolyzer construction, which included two Ni or Pd tube-electrodes placed in the stainless steel chamber filled with the electrolyte (H_2O + 1 wt.% $NaHCO_3$). The observed composition of the generated gas (it was measured with mass-spectrometric method) was 92…94 vol.% hydrogen. Such composition is not explosive in air and it can use as a fuel, and with addition of air or oxygen, as explosive.

During electrolysis process, large ion currents, including hydrogen ions, affect the Pd-electrodes. Palladium is the specific metal, which can absorb large amount of hydrogen [4]. Therefore, it is scientific and practice interest to study the kinetics of hydrogen interaction with Pd electrodes during electrolysis process (hydrogen absorption), and hydrogen release (desorption, out gassing) from the Pd electrodes after exposure to electrolysis ion currents. Such researches can give the useful information for improvement of electrolysis device construction and modes.

1. EXPERIMENTAL AND RESULTS

The installation used in the experiments, was similar to that in work [3] with the only difference being that one electrolysis module (Figs. 1,2) installed in the electrolyze chamber.

The general view of the electrolysis module is shown in the Figs. 1, 2. Anode in the form of Pd tube, with a diameter of 3 mm, a thickness of 1 mm and work length of 150 mm, mechanically fixed to flange through flange fitting with good electrical contact. The cathode made of Pd tubes with a diameter of 10 mm, a thickness of 0.2 mm and a work length of 150 mm, mechanically fixed to anode through fluoroplastic insulators. The distance between electrodes is about 3 mm. The Pd-electrode (Fig. 3), used in the work [3] as the cathode, exposed to ion current during five hours, but after this four months was exposure to air atmosphere, was investigated, too.

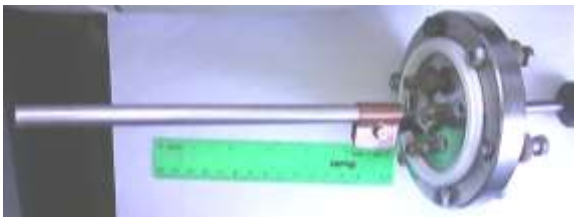

Fig. 1. General view of the E-3 electrolysis module

Fig. 2. Cathode and anode after one-hour exposure to electrolysis current

Fig. 3. Pd cathode after five hours exposure to electrolysis current

The power supply is a rectifier on two V200 diodes connected through current transformer to the autotransformer [3]. As an electrolyte, a 1 wt.% sodium bicarbonate (soda) solution in ordinary filtered water was used (mineralization measured using the TDS Meter 3 device was 157 ppm). The electrolysis process started, by switch on the constant voltage between the anode and cathode (a positive to flange, and negative,

through current lead to cathode). The current-voltage characteristic of the electrolysis process in the E-3 electrolyzer is shown in Fig. 4.

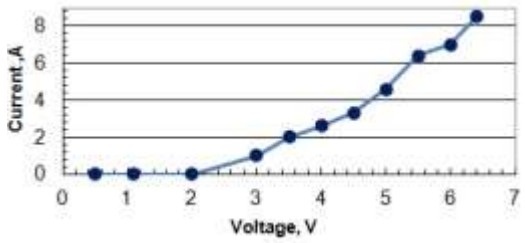

Fig. 4. The current-voltage characteristic of the electrolysis process

During the electrolysis time, the current changed in the region 6.5…7 A, and the voltage between the electrodes increased from 5.5 to 6 V (see Fig. 3). Gas pressure in electrolysis chamber was about one atmosphere. Temperature of electrolyte was about 50 °C. Mass specter of generated gases during electrolysis (Fig. 5) measured with the method similar in work [3].

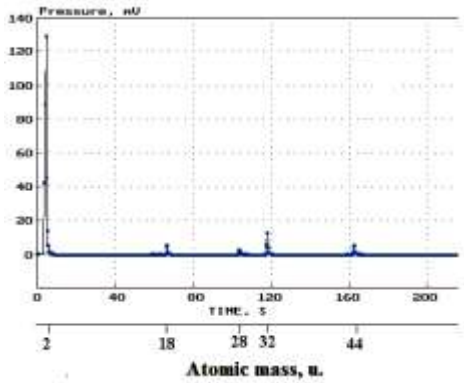

Fig. 5. Mass specter of generated gases during electrolysis

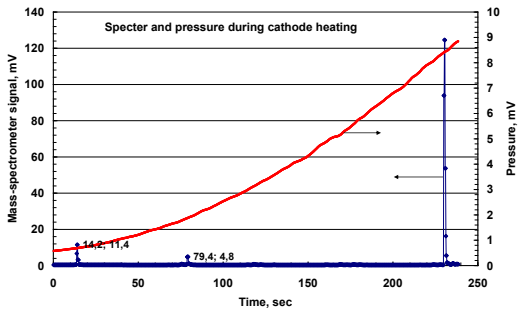

Fig. 6. Pressure time dependence and mass specter, measured during cathode heating in a vacuum

After one hour exposure to the electrolysis ion current both anode and cathode were demounted, dried out and placed into the GAS installation [3] vacuum chamber to study hydrogen out gassing behavior.

The samples (cathode or anode) heated by the direct current up to temperatures of 600…700 ºC and, at the same time, the pressure time dependence and mass-spectra of desorbed gases measured (Figs. 6–9). Apparatus curves (see Figs. 6–9) processing gives the data for estimation of hydrogen amount desorbed from a sample due to the equation $Q \cdot t = (P\text{-}P_0) \cdot S \cdot t$, where Q is out gassing rate; P – maximum pressure; P_0 – initial pressure; S – pumping speed; t – time. It taken into account, that the sensitivity of the mass spectrometer for hydrogen is approximately two times lower than for air. For the pressure measurement with a gauge PMI-10, this coefficient is four. Using the temperature dependence (see Fig. 10), the value of activation energy of hydrogen out gassing rate process was determined.

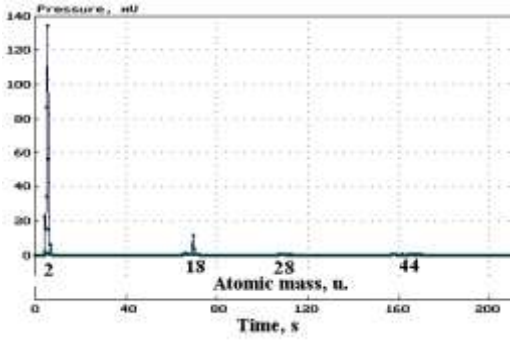

Fig. 7. Mass specter of gases, desorbed from Pd cathode during heating

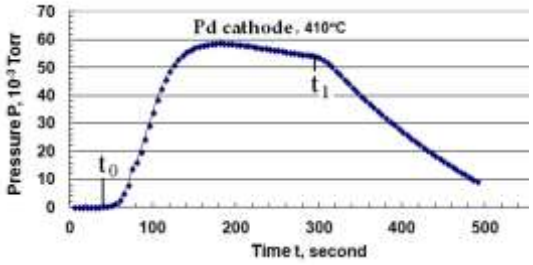

Fig. 8. Apparatus curve of pressure change in the vacuum chamber during cathode heating: t_o – switch on heating, t_1 – switch off heating

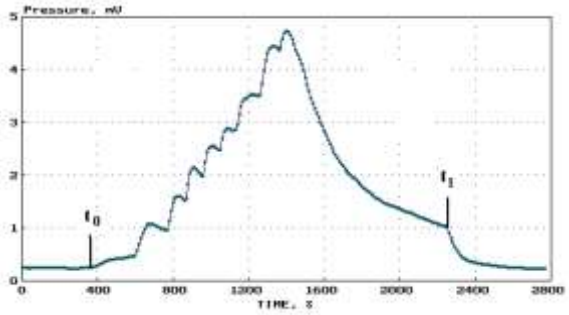

Fig. 9. Apparatus curve of pressure change in the GAS vacuum chamber during anode heating: t_o – switch on heating, t_1 – switch off heating

2. DISCUSSION

Processing of the instrumental curves shown in Figs. 6–9 and estimations with help of weight loss method gives the amount of hydrogen desorbed from the Pd cathode about 650 Ncm^3 (~10^{22} H atoms, H/Pd ≈ 0.48). It is very high value, taking into account low time of hydrogen saturation (1 h). The volume of metal cathode is ≈ 1 cm^3, so we get a compression ratio of 650 times (650 atm). Hydrogen out gassing rate at the maximum temperature 650 °C was 0.3 Ncm^3 H_2/s. For the Pd anode, this value was much less (0.05 Ncm^3 H_2/s) and amount of desorbed hydrogen was only ≈ 0.21 Ncm^3.

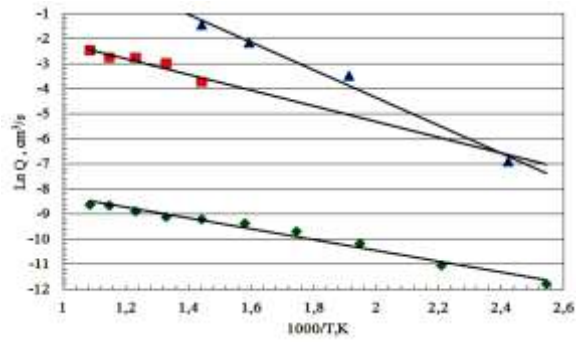

Fig. 10. Temperature dependence of hydrogen out gassing rate for the Pd electrodes: blue points – cathode after one hour exposure to electrolysis ion current, red points – Pd cathode after five hours exposure in electrolyze mode, green points – Pd anode after one-hour exposure to electrolysis ion current

For the cathode exposed to electrolysis current about five hours (see red points in Fig. 10) hydrogen out gassing rate essentially lower. The reason for this becomes clear if we take into account the fact that this cathode after exposure in the electrolysis mode kept in the air atmosphere for about 4 months. A significant amount of hydrogen could desorbed, since hydrogen in palladium has a noticeable mobility even at room temperature. As for the low activation energy of the degassing process, additional studies are required to clarify the reasons for this.

It seen in Fig, 3, that Pd cathode after 5 h exposure to ion current changed its shape. It became curved. This effect could be explained by the phase transition $\alpha \leftrightarrow \beta$ in palladium [4–6], when the lattice parameter changes significantly and, as the result, the gradient of elastic stresses arise, leading to a change in a shape. It was observed in works [7, 8], when Pd foils of 0.2 mm thickness and 20 mm diameter, coated on the one side by 4μ W film, saturated with hydrogen for a long time (2 atm, 62/150 h, 20 ºC), to a concentration up to H/Pd≈0.6, shape changed dramatically (see Fig. 11,b,c).

Note, that after one-hour annealing at the temperature of ≈ 650 °C and removing hydrogen from the Pd cathode, its form remained bent.

The value of activation energy E of out gassing process was calculated using temperature dependence of hydrogen out gassing rate (see Fig.10) similarly to that for hydrogen permeability in works [8, 9]. It assumed that the process of gas evolution obeys the Fick diffusion laws, and the temperature dependence obeys the Arrhenius equation: $Q(T)= a\cdot e^{-E/kT}$. The activation energy of out gassing is $E = E_d + E_s$, where E_d is the activation energy of diffusion and E_s is the activation energy of desorption. In our case, the values E were determined from the slope of curves in Fig. 10 and were calculated to be ≈46 and 18 kJ/mole for Pd cathode and anode, consequently, after one-hour time of electrolysis current impact, and 26 kJ/mole for cathode after 5-h electrolysis current impact. For comparison, the activation energy of hydrogen permeability for bare Pd, measured in [9], was ≈ 15.5 kJ/mole. One can explain this difference by the fact of surface impurities, which appear after electrodes exposure to electrolysis current (see look Fig. 2). It known that rate of hydrogen sorption/desorption surface reactions highly dependents on surface conditions of palladium, especially carbon presence [10].

Fig. 11. The sample shape change after hydrogen saturation [8]: a – before saturation; b – after 62 h saturation; c – after 150 h saturation

Due to the first Faraday law [11]: $m=k\cdot I\cdot t$, where m – mass of generated gas; k – electrochemical equivalent; I – current; t – time, the mass of generated gas is proportional to current value. Estimation shows ions flow to cathode as 2.10^{19} H^+ ions/s. Summary dose was about $7.2.10^{22}$ ions, i.e. about 14% of hydrogen was absorbed with cathode and after heating was desorbed.

The gas generated during electrolysis consists of ≈ 92 vol.% of hydrogen, 4 vol.% oxygen, 1.5 vol.% each of H_2O and CO_2, and 1 vol.% of CO (see Fig. 5). It seen in Fig. 7 that hydrogen desorbed from the cathode more pure than generated gas. The water essential signal (≈4 vol.%) in Fig. 7 is explained by the release of water from the walls of the vacuum chamber. So, after hydrogen desorption from Pd, we obtain pure (better than 99.99 vol.%) hydrogen. To clarify the physicochemical reasons for this let us shortly analyze the processes of hydrogen absorption by palladium in the electrolyte and its out gassing (release) in a vacuum.

In the electrolysis mode, palladium electrodes interact with various molecules, atoms, ions, and electrons. The cathode mainly interacts with hydrogen molecules, atoms and positive hydrogen ions H^+, which are neutralized on the metal surface and the resulting atoms recombine into molecules. Molecules accumulate and form gas bubbles that emerge on the electrolyte surface. In turn, part of hydrogen molecules on the cathode surface dissociate into atoms, which with some probability dissolve in the near surface bulk of metal. Atoms and ions do not need additional energy to overcome the potential barrier at the gas-solid boundary (activation energy of solubility), so the metal under such conditions can dissolve significant amounts of hydrogen.

During Pd-electrode heating in a vacuum, hydrogen atoms, dissolved in metal bulk (these could also be hydrogen ions H^+, and the state of the lattice gas in palladium can be interpreted as plasma [5], or dense non-ideal plasma [6]), diffuse to surface, recombine into molecules, and desorbs. This process and surface impurities influence on it, rather sufficiently described in literature [10, 12].

Thus, the hydrogen saturation of Pd cathodes during electrolysis and then its release by heating in a vacuum can consider, as purification of the generated gas and obtaining highly pure hydrogen compressed to high concentration. It well known that after hydrogen

penetration through Pd membranes (Pd-filters) one can obtain very pure (better than 99.999 vol.%). Note that not only palladium and its alloys can use with this point, but also other diffusion-catalytic metals, e.g., nickel, metal hydrides and titanium, which chemosorb large amounts of hydrogen, also seem promising.

CONCLUSIONS

The out gassing rate of hydrogen from palladium anode and cathode after exposure to ion current during electrolysis process in the (H_2O+$NaHCO_3$) electrolyte measured in dependence on temperature and the time of exposure.

The activation energy of the hydrogen out gassing from the cathode after one-hour exposure to electrolysis current was calculated to be E ≈ 46 kJ/mole and from the anode as 18 kJ/mole.

The amount of hydrogen desorbed from the electrodes estimated. For the Pd cathode, it was about 650 Ncm^3H_2 (H/Pd ≈ 0.48) and hydrogen out gassing rate at the maximum temperature 650 °C was 0.3 $Ncm^3 H_2$/s. For the Pd anode these values were much lower (0.21 and 0.05 $Ncm^3 H_2$/s, consequently).

Mass spectra of the mixtures of gases, generated during electrolysis and out gassing, current-voltage characteristic of electrolysis process presented.

It has been shown that at electrolytes temperature of ≈50 °C and a pressure in the electrolyze chamber of ≈ 1 atm, the generated gas is 92 vol.% hydrogen. After hydrogen absorption by Pd cathode during electrolysis, and with subsequent heating in a vacuum, we obtain pure (better than 99.99 vol.%) hydrogen.

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ВИДІЛЕННЯ ВОДНЮ З Pd-ЕЛЕКТРОДІВ ПІСЛЯ ДІЇ ІОННОГО СТРУМУ В ПРОЦЕСІ ЕЛЕКТРОЛІЗУ

Г.П. Глазунов, М.М. Бондаренко, О.Л. Конотопський

Швидкість виділення водню з паладієвого катода та анода після впливу іонного струму під час процесу електролізу в електроліті (H_2O+1 wt.% $NaHCO_3$) вимірювалась у залежності від температури та тривалості впливу. Енергія активації виділення водню з катода розрахована як E ≈ 46 кДж/моль (для анода E ≈ 18 кДж/моль). Оцінено кількість водню, десорбованого з електродів. Для Pd-катода вона становила близько 650 $см^3H_2$ (H/Pd ≈ 0,48), а швидкість виділення водню при максимальній температурі 650 °C становила 0,3 $Ncм^3$ H_2/с. Для Pd-анода ці значення були значно нижчими (0,21 $см^3H_2$ і 0,05 $Ncм^3$ H_2/с відповідно). Наведено мас-спектри сумішей газів як тих, що утворюються при електролізі, так й тих, що десорбовані під час нагрівання електродів у вакуумі, вольт-амперні характеристики. Показано, що при температурі електролітів ≈ 50 °C і тиску в електролізній камері 1 атм утворюється газ 92 об.% водню. Водень, десорбований у вакуумі з Pd-катода після процесу електролізу, є дуже чистим воднем (краще 99,99 об.%). Фізико-хімічні причини обговорюються для пояснення процесів сорбції та десорбції водню в Pd-електродах під час і після електролізу.