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KINETIC CHARACTERISTICS OF HYDROGEN TRANSFER THROUGH PALLADIUM-MODIFIED MEMBRANE

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The paper deals with hydrogen transfer through Pd-23%Ag *alloy membrane, the surface of which is modified by the electrolytic deposition of highly dispersed palladium. The dependence between the density of hydrogen flow and its excess pressure on the input surface of membrane is well approximated by the first-order curve. This fact indicates that the process of hydrogen permeability is defined by its dissociation on the input surface. Activation energy of this process is 47.9 kJ/mol which considerably exceeds that of the process of hydrogen transfer through palladium (22–30 kJ/mol). This confirms the fact that the chemisorption is a rate-controlling step of the hydrogen transfer through membrane.*

Keywords: palladium/silver membrane, hydrogen permeability, membrane techniques, nanopatterned surface, surface modification, hydrogen carrier, high purity hydrogen, hydrogen electrode.

INTRODUCTION

Palladium as a metal is able to reversibly absorb a significant amount of hydrogen in relatively mild conditions. Therefore, palladium and palladium alloys are used for the production of membranes capable of permeating gaseous hydrogen [1, 2]. Burkhanov *et al.* [2] also indicated that at 25°C, the pressure equilibrium over palladium (Pd) is 6 times higher than over hydrogen (H_2). Thus, when absorbing hydrogen, the palladium gaseous phase is enriched with deuterium. This enrichment reduces with the temperature growth. Therefore, during water electrolysis with the use of Pd catalyst, H_2 is mainly obtained and the liquid phase is enriched with deuterium with 3–3.3 separation factor [3]. The predominant H_2 absorption on Pd electrode results in further separation. The theoretically attainable separation factor achieves almost 9 that makes Pd-containing membranes a perspective material for separating hydrogen isotopes. Pd-containing membrane is also a promising material for manufacturing biologically active drinking water with lower deuterium content [4] and hydrogen gas diffusion electrodes applicable to diverse electrochemical devices [5, 6].

At temperatures below 200°C, the equilibrium of $H_{2(r)} = 2[H]_{Pd}$ is achieved very slowly due to the inactive or soiled membrane surface [2]. Therefore, for expediting the process of H_2 absorption, the membrane surface should be modified by the palladium black coating applied to the surface of compact Pd specimen [7].

In previous studies [8], we obtained membranes made of palladium/silver alloy modified by palladium black coating. It was demonstrated that at the excess pressure of up to 0.3 MPa, hydrogen permeability through membrane with the modified surface sharply increased as compared to membrane with a smooth surface.

This paper mainly focuses on measurements of kinetic characteristics of hydrogen transfer through a palladium/silver membrane with the modified surface.

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EXPERIMENTAL

Membranes were made of Pd-23%Ag alloy which is the most suitable material for hydrogen permeability and possesses the optimum mechanical properties. Membranes were obtained using the magnetron sputtering which utilized a composite target with the area ratio of $S(\mathrm{Ag})/S(\mathrm{Pd}) = 20.8/79.2$ [9, 10].

In order to modify the surface of Pd-23%Ag alloy membrane, it was fixed, washed with 96% ethanol and degreased with boiling in a 6 M sodium hydroxide solution for 30 min. Soon afterwards, membrane was placed in a vessel with distilled water for 10 min. Using an inert holder, membrane was then subjected to electrolytic deposition in an electrolysis cell. The holder made of 99.99% pure silver was used as a current lead. The contact was performed *via* a silver wire. Pd-23%Ag alloy membrane was then placed in a cell with a 0.1 M chlorohydric acid. Anode polarization was provided by potentiostat/galvanostat P-250I at 10–20 mA/cm^2 current density. After washing, membrane underwent cathode polarization in 0.05 M sulphuric acid at the same current density and then immersed in 2% H_2PdCl_4 solution. Palladium black precipitated at 2–6 mA/cm^2 current density during 1.5 h. The obtained black precipitate was then washed with redistilled water and subjected to cathode polarization in 0.05 M sulphuric acid.

To measure the hydrogen permeability we designed the installation based on the gas microvolumetric method. This installation comprised hydrogen generator Spektr connected to the cell *via* metal wire. Membrane was mounted in the cell situated in a bath of the liquid thermostat TZh-TS-01/100 which provided 0.1°C accuracy of temperature control within the range of 20–200°C. The bath was connected to gas analyzer and gauge tube with the uniform cross-section and scale subdivision of 0.05 ml. Prior to each experiment, the installation was subjected to helium (99.999 vol.%) pressure testing.

RESULTS AND DISCUSSION

Table 1 summarizes measuring parameters for hydrogen permeability both for pure palladium and palladium/silver alloy with and without the palladium black coating. Let us introduce the following notation.

1. Hydrogen volume V (l) is the gas volume which passes through the membrane having δ thickness and S area under the equilibrium conditions, T temperature, and p_1 and p_2 pressure ratios for respectively output and input membrane surfaces.
2. Hydrogen amount ν (mol) is the amount of gas transfer through the membrane.
3. Hydrogen flow Φ (mol/s) is the amount of gas transfer per unit time t.
4. Flow density J mol/(s·m^2) is the flow across the membrane.
5. Hydrogen permeability P equals the density of the flow passing through the membrane with unit thickness at $p_2 = 101.325$ кPa and $p_1 = 0$.

Figure 1 presents the dependence between the flow density (hydrogen/membrane area ratio) and excess pressure of hydrogen applied to the input surface of membrane.

At a room temperature, hydrogen permeability of palladium/silver membrane without coating is by one order higher than that of Pd-containing membrane with a smooth surface allowing to use them as a solid anode of a hydrogen-oxygen (air) cell.

According to Baichtok *et al.* [11], the process of hydrogen permeability includes the following major stages:
1) hydrogen dissociation at v_i rate on the input surface of membrane;
2) atomic hydrogen diffusion at v_d rate through membrane;
3) hydrogen atom recombination at v_o rate in molecules on the output surface of membrane.

Under the equilibrium conditions between hydrogen in gaseous phase and atomic hydrogen in the absorbed layer we have

$$v_i = k_\mathrm{d} p_1 - k_\mathrm{r} p_{1A}^2 , \tag{1}$$

$$v_\mathrm{o} = k_\mathrm{r} p_{2A}^2 - k_\mathrm{d} p_2 , \tag{2}$$

TABLE 1. Measuring Parameters for Hydrogen Permeability

Δp, MPa	V, ml	$\nu \cdot 10^6$, mol	$\Phi \cdot 10^9$, mol/s	$J \cdot 10^5$, mol/(s·m^2)	$P \cdot 10^{11}$, mol/(s·m^2) ·cm/Pa$^{0.5}$
Pure palladium					
0.1–0.3	0	0	0	0	0
0.4	0.03	1.23	2.04	2.6	1.32
0.5	0.07	2.86	4.77	6.07	2.63
0.6	0.12	4.91	8.18	10.4	3.97
Pd-23%Ag alloy with smooth surface					
0.1–0.3	0	0	0	0	0
0.4	0.02	0.82	1.36	1.73	0.88
0.5	0.055	2.25	3.75	4.77	2.07
0.6	0.09	3.68	6.13	7.81	2.98
Pd-23%Ag alloy with modified surface					
0.1	0.01	0.41	0.68	0.87	1.32
0.15	0.035	1.43	2.38	3.04	3.28
0.2	0.06	2.45	4.09	5.20	4.47
0.3	0.13	5.31	8.86	11.3	7.09
0.4	0.2	8.18	13.6	17.3	8.82
0.5	0.29	11.9	19.8	25.2	10.9
0.6	0.38	15.5	25.9	33.0	12.6

$$v_{\mathrm{d}} = D\frac{k_S\left(p_{1A} - p_{2A}\right)}{h} = D\frac{C_1 - C_2}{h}, \qquad (3)$$

where k_{d} and k_{r} are respectively dissociation and recombination constants; D is the coefficient of hydrogen diffusion in metal; k_S is the solubility factor of atomic hydrogen in metal; p_1 and p_2 are pressures of molecular hydrogen respectively on the input and output membrane surfaces; p_{1A} and p_{2A} are pressures of atomic hydrogen respectively on the input and output membrane surfaces; h is the thickness of membrane; $C_1 = k_S p_{1A}$ and $C_2 = k_S p_{2A}$ are concentrations of dissolved atomic hydrogen in the surface layer of metal respectively in the input and output membrane surfaces.

Under stationary conditions, the rates v_{i} and v_{o} are equal and correspond to the rate of hydrogen permeability v:

$$v = v_i = v_{\mathrm{o}} = v_{\mathrm{d}}.$$

Equations (1) and (2) demonstrate that

$$p_{1A} - p_{2A} = \frac{k_{\mathrm{d}}\left(p_1 - p_2\right) - 2v}{k_{\mathrm{r}}\left(p_{1A} + p_{2A}\right)},$$

$$C_1 - C_2 = \frac{k_S^2}{2k_{\mathrm{r}}C_{\mathrm{av}}}\left(k_{\mathrm{d}}\left(p_1 - p_2\right) - 2v\right),$$

where $C_{\mathrm{av}} = (C_1 + C_2)/2$. Substitution of this in Eq. (3) yields

$$v = D\frac{k_S^2}{2hk_{\mathrm{r}}C_{\mathrm{av}}}\left(k_{\mathrm{d}}\left(p_1 - p_2\right) - 2v\right)$$

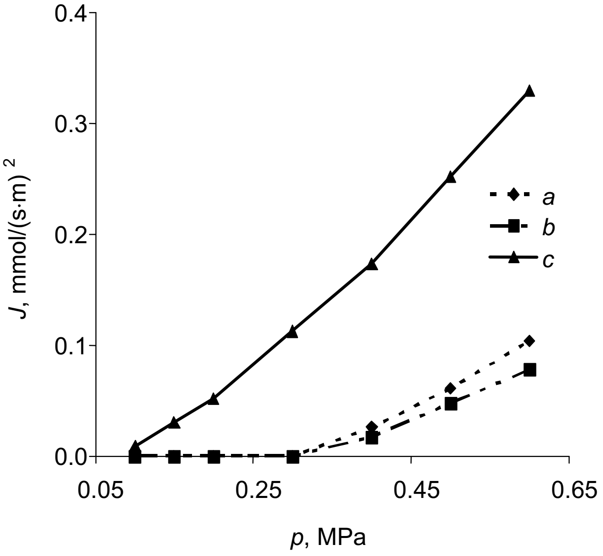

Fig. 1. Dependence between hydrogen flow density and excess pressure applied to the input surface of membrane: *a* – pure palladium; *b* – palladium/silver alloy without coating; *c* – electrolytically-treated surface.

or

$$v = k\left(p_1 - p_2\right),$$

where $k = \dfrac{1}{1/\alpha_{\text{dif}} + 2/k_{\text{d}}}$, $\alpha_{\text{dif}} = \dfrac{Dk_S^2 K_p}{2hC_{\text{av}}}$, $K_p = \dfrac{k_{\text{d}}}{k_{\text{r}}}$.

The resistance to hydrogen mass transfer through the metal membrane is composed of the diffusional resistance α_{dif} and chemical resistance. Diffusional resistance depends on the membrane thickness δ, coefficients of hydrogen diffusion and dissolution which, in turn, depend on temperature, and the pressure-dependent concentration of dissolved hydrogen.

If the hydrogen diffusion is a rate-controlling step of the process, the dissociation constant k_{d} is much more than the diffusional resistance α_{dif}. From now on we assume that

$$k = \alpha_{\text{dif}} = \frac{Dk_S^2 K_p}{2hC_{\text{av}}}.$$

When the equilibrium state is achieved on the surface ($v_i = v_{\text{o}} = 0$), the following equations are obtained:

$$p_{1A} = \sqrt{K_p p_1},$$

$$p_{2A} = \sqrt{K_p p_2},$$

$$C_{\text{av}} = \frac{k_S\sqrt{K_p}}{2}\left(\sqrt{p_1}+\sqrt{p_2}\right).$$

$$k = \frac{Dk_S\sqrt{K_p}}{h\left(\sqrt{p_1}+\sqrt{p_2}\right)},$$

$$v = \frac{Dk_S\sqrt{K_p}}{h}\left(\sqrt{p_1}-\sqrt{p_2}\right).$$

Thus, the rate of the hydrogen permeability is proportional to the square root of the gaseous hydrogen pressure that, as a whole, satisfies the Richardson equation [12]:

$$v = k\left(\sqrt{p_1}-\sqrt{p_2}\right)e^{-\frac{E_A}{RT}}.$$

If hydrogen dissociation is a rate-controlling step of the process, the dissociation constant k_{d} is much less than the diffusional resistance α_{dif}. From now on we assume that

$$k = \frac{k_{\text{d}}}{2},$$

$$v = \frac{k_{\text{d}}}{2}\left(p_1 - p_2\right).$$

Thus, the rate of the hydrogen permeability is proportional to the gaseous hydrogen pressure.

As shown in Fig. 2, the dependence between the density of hydrogen flow and its excess pressure on the input surface of membrane is well approximated by the first-order curve. According to [13, 14], this fact indicates that the rate of hydrogen permeability is controlled by the hydrogen dissociation on the surface.

Figure 3 demonstrates the temperature dependence of the rate of hydrogen transfer through palladium/silver membrane (Pd-23%Ag alloy) with electrochemically modified surface.

According to the Arrhenius equation we obtain

$$k = Ae^{-\frac{E_A}{RT}},$$

$$-R\ln(k) = E_A\frac{1}{T} - R\ln(A).$$

Using the dependence between $R\ln(k)$ and $1/T$ presented in Fig. 4, the activation energy of this process is 47.9 kJ/mol. As the process of hydrogen permeability comprises several stages, this value is the effective (empirical) activation energy (the function of activation energies generated at individual stages) and corresponds to the rate-controlling step characteristics. The activation energy of 47.9 kJ/mol considerably exceeds that of the hydrogen transfer through palladium (22–30 kJ/mol) [14, 15], which confirms the fact that the chemisorption is a rate-controlling step of the hydrogen transfer through membrane.

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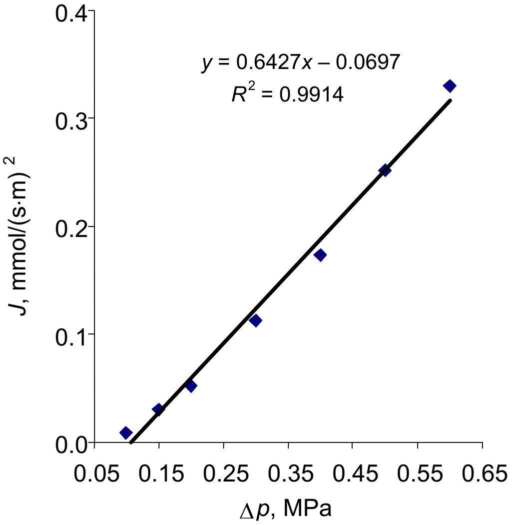

Fig. 2. Dependence between hydrogen flow density and excess pressure on the input surface of membrane.

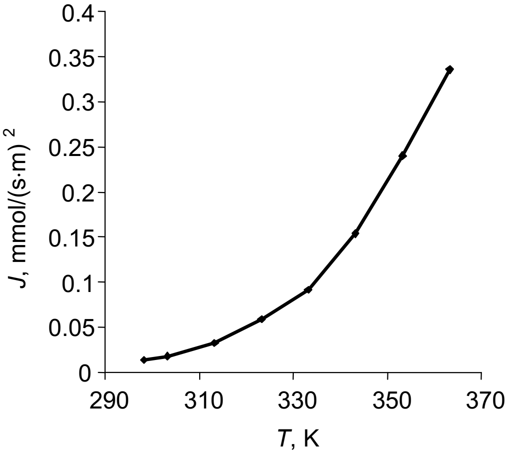

Fig. 3

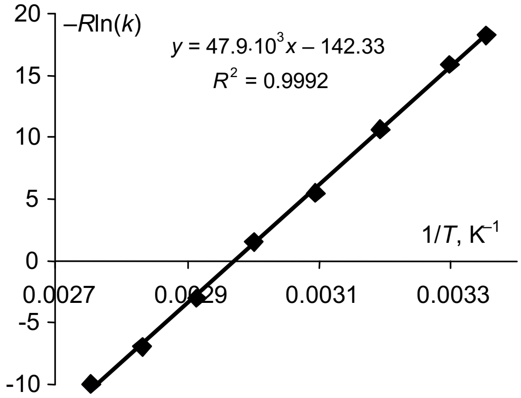

Fig. 4

Fig. 3. Temperature dependence of the rate of hydrogen transfer through palladium/silver membrane.

Fig. 4. $R\ln(k)$ and $1/T$ dependence for hydrogen transfer *via* palladium/silver membrane.

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