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## Kinetics of Atomic Hydrogen Evolution and Hydrogen Permeability of Ag–Pd Alloys in an Alkaline Medium

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### Abstract

Homogeneous Ag–Pd alloys are effective catalysts for the cathodic evolution of hydrogen. They are characterised by high mechanical strength and are less susceptible to hydrogen embrittlement than metallic palladium. The aim of this study was to determine the kinetics of hydrogen evolution on palladium and its homogeneous alloys with silver in an alkaline aqueous solution, and to investigate their hydrogen permeability.

The behaviour of Pd and Ag–Pd alloys ( $X_{Pd} = 15–80$  at%) in a deaerated 0.1 M KOH aqueous solution was studied using cyclic voltammetry and double step anodic-cathodic chronoamperometry. Cyclic voltammograms for Pd and Ag80Pd were similar. However, when a small amount of silver ( $\leq 20$  at%) was introduced into palladium, the ionization rate of hydrogen decreased. A further increase in the concentration of silver in the alloy resulted in a complete suppression of the ionisation process. For Ag–Pd alloys with palladium concentrations below 30 at%, the voltammograms did not show any hydrogen ionization peaks. The dependencies of the peak ionisation current on the potential scan rate for all the studied alloys were linear and were extrapolated to the origin of the coordinates, which indicated that the process was complicated by solid-phase diffusion. The slopes of the lines for Ag60Pd and Ag50Pd alloys were higher than the slope for the Ag80Pd alloy, which indicated the presence of silver oxides on the surface. For all the studied electrodes the dependence of the peak current potential on the potential scan rate log linearly increased, which means that the electrochemical stage of atomic hydrogen ionization, which is complicated by solid-phase diffusion, is irreversible. The hydrogen permeability parameters of the alloys were calculated using potentiostatic cathodic and anodic current transients at different time intervals (1–10 sec.). The longer the hydrogenation time, the lower the current amplitudes on cathodic and anodic branches of the chronoamperograms. The hydrogen permeability parameters were calculated based on cathodic and anodic current transients linearised in the corresponding criteria coordinates, using the results of theoretical modelling of hydrogen injection and extraction for semi-infinite thickness electrodes. The phase-boundary exchange constant and the ionisation rate constant of atomic hydrogen were maximum for the alloy with the concentration of palladium of 80 at%. The hydrogen extraction rate constant changed linearly with the decrease in the concentration of palladium. The study determined that the values of hydrogen permeability for Ag–Pd alloys in alkaline solutions are lower than in acidic ones.

The determining stage of the hydrogen evolution reaction on Ag–Pd alloys ( $X_{Pd} \leq 40$  at%) in a 0.1M KOH solution is the electrochemical stage of atomic hydrogen ionization complicated by its diffusion in the solid phase. The hydrogen permeability parameters in Ag–Pd alloys are maximum, when the concentration of palladium is  $\sim 80$  at%. Therefore, such alloys can be used as materials for efficient hydrogen purification and storage.

**Keywords:** homogeneous Ag–Pd alloys; atomic hydrogen injection and extraction; hydrogen permeability; aqueous alkaline medium.

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## 1. Introduction

Although there are electrocatalysts for hydrogen evolution reaction (HER) highly efficient in acidic media, their application is still rather problematic. Most importantly, their application is limited due to the high corrosion susceptibility of the electrolytic cell and the fact that the obtained hydrogen gas is contaminated by acidic fog. On the contrary, an advantage of alkaline electrolytes is that they produce less vapour operating at high temperatures and have lower vapour pressure. Furthermore, non-noble electrodes are also more stable and do not corrode after a reaction [1].

In alkaline electrolytes, the kinetics and rate of HER is determined by the following factors: water adsorption and dissociation, the energy of hydrogen adsorption and desorption, and the affinity of hydroxyl ions to the catalyst's surface [2]. This means that for a catalyst to be efficient for HER in an alkaline medium, it should be able to dissociate water molecules adsorbed on its surface, and aggregate the resulting particles.

The most common catalyst with these properties is crystalline palladium. An advantage of palladium membranes is their increased ability to transport hydrogen through the metal. This happens because palladium has high hydrogen solubility at a wide range of temperatures [3]. The disadvantage that hinders the application of palladium membranes is that they are susceptible to hydrogen embrittlement, both at high concentrations of  $H_2$  and after multiple cycles of hydrogen adsorption and desorption.

Hydrogen embrittlement comes in the form of microstructural changes caused by a significant shrinkage and expansion of the metal's crystal lattice. During the adsorption process, hydrogen atoms randomly occupy octahedral interstitial sites of the palladium crystal lattice. It was noted that with a low H/Pd atomic ratio (of about 0.06), the  $\alpha$ -phase of Pd-H remains dominant [4]. This phase is an ideal dilute palladium-hydrogen solid solution [5]. With larger quantities of the adsorbed hydrogen the  $\beta$ -phase of Pd-H, also called palladium hydride, begins to form. This phase is a saturated palladium-hydrogen solid solution and coexists with the  $\alpha$ -phase at low temperatures [5]. Nucleation and the growth of palladium hydride in the  $\alpha$  matrix of the

Pd-H solid solution sets up severe strains in the material resulting in the deformation of the crystal lattice and dislocation multiplication and hardening [6].

To reduce hydrogen embrittlement, palladium is doped with transition metals, such as Ag, Cu, Fe, Ni, Pt, and Y [3]. Of particular interest are Ag-Pd alloys. These alloys are highly selective and permeable enough towards hydrogen at room temperature, which makes them a promising material for the production of diffusion membranes [7]. It is also vital that silver and palladium form a continuous series of substitutional solid solutions within the whole concentration range with no miscibility gaps [8].

According to [9], Ag-Pd alloys with the concentrations of Ag of up to 60 % can efficiently absorb hydrogen. The hydrogen absorbed by these alloys exists in two basic phases,  $\alpha$  and  $\beta$ , analogous to pure palladium. The results of the X-ray diffraction analysis in [10] demonstrated that the lattice parameters of  $\alpha$  and  $\beta$  phases are the least different for the Ag77Pd alloy. This happens because the crystal lattice of palladium is already extended by the silver atoms and hence is less susceptible to hydrogen embrittlement. Consequently, the mechanical strength of the diffusion membranes produced from Ag-Pd alloys increases significantly [11]. It is therefore important to study the mechanism of hydrogen permeation through the alloy's electrodes in more detail. The aim of this study was to determine the kinetics of hydrogen evolution on palladium, and to investigate hydrogen permeability of palladium and its homogeneous alloys with silver in an alkaline aqueous solution.

## 2. Experimental

The object of the study were close-packed Ag-Pd electrodes with  $X_{Pd} = 15, 30, 40, 50, 60,$  and 80 at% in a 0.1M KOH (chemically pure) bidistilled aqueous solution. The surface of the electrodes was preliminary polished using MgO aqueous suspension and suede leather, degreased with ethanol, and washed in distilled water.

The experiments were conducted in a three-electrode glass cell. The auxiliary electrode was a platinized platinum electrode, and the reference electrode was a silver chloride electrode. Prior

to polarization measurements, the solution was deaerated by sparging with chemically pure argon for 30 minutes. Electrochemical measurements were performed using a computer-aided IPC-Compact potentiostat. All the potentials are given here relative to the standard hydrogen electrode, and the current values are given per single unit of the real surface area of the alloys [12].

In order to remove the trace amounts of oxides from the surface of the electrodes, the studied electrodes were held in the solution at the initial potential  $E_p = -0.60$  V for 500 seconds before obtaining cyclic voltammograms. Cyclic voltammograms were obtained in potentiodynamic mode (at a scan rate of  $v = 5$  mV/s) starting at  $E_p$  and sweeping to the cathode region. It was then swept back in the anode direction, switching potentials. Dependencies  $i, E$ -were limited by the peak currents of hydrogen and oxygen evolution.

To obtain voltammograms at different potential scan rates, the electrodes were preliminary hydrogenated with the potential being  $E_c = -0.90$  V for  $t_c = 3$  sec. and  $t_c = 5$  sec. The potential scan rate varied within the range of 0.5–100 mV/s.

To determine the parameters of extraction and injection of atomic hydrogen, double step anodic-cathodic chronoamperometry was used. Before obtaining the chronoamperograms, the working electrode was held at the potential  $E_p = -0.60$  V for 500 seconds. To standardise the state of the surface, the curve corresponding to the cathode current drop was obtained at the cathode hydrogenation potential  $E_c = -0.90$  V. The hydrogenation time  $t_c$  varied within the range of 1–10 seconds. The potential was then switched to the peak anodic potential of hydrogen ionization  $E_m^a$ , whose values were determined using the preliminary obtained  $i, E$ -dependencies. The current drop was registered before it reached its steady state value. After that, still holding the working electrode in the solution, we once more set the initial potential  $E_p$  and repeated the whole sequence for a different value  $t_c$ .

### 3. Results and discussion

The kinetics of hydrogen evolution in a 0.1M KOH hydrogen solution was determined using cyclic voltammetry. The results are presented

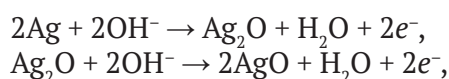
in Fig. 1. The anodic branches of the cyclic voltammograms obtained for Pd and Ag-Pd alloys with  $X_{Pd} \geq 50$  at%, show a characteristic current peak corresponding to the atomic hydrogen ionization from the electrode's surface in the potential region from  $-0.30$  to  $0.20$  V. Lower ionization rate of atomic hydrogen on pure palladium as compared to its alloys is demonstrated by a lower anodic peak amplitude. The latter can be accounted for by adsorption of hydroxide ions on the electrode's surface, or by the formation of silver compounds on the surface which block the active regions of the surface and cause anodic passivation [13]. It should be noted, that at  $X_{Pd} = 50$  at% the ionisation peak is already less prominent, and its form is distorted by the competing process of silver oxidation. For Ag–Pd alloys with low palladium concentrations ( $X_{Pd} \leq 30$  at%) no hydrogen ionization peak is observed.

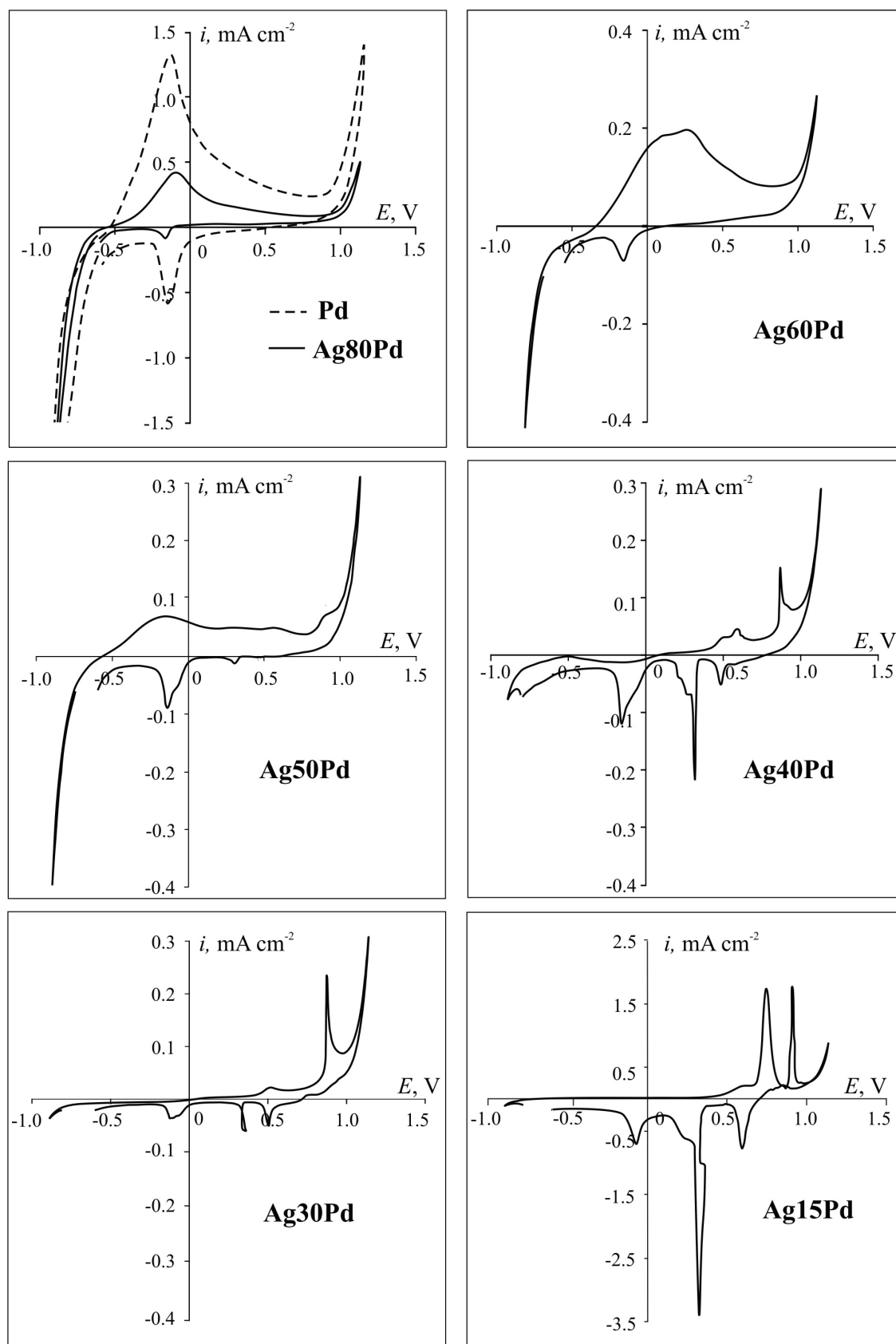
When the potential sweeps to more positive values, the region of palladium oxidation, observed at  $0.20$ – $0.80$  V, is barely visible on Pd and the Ag80Pd alloy. For alloys with  $X_{Pd} \leq 50$  at% this region is practically absent, since the process is suppressed by silver oxidation. As the potential sweeps to the cathode, both pure palladium and its alloys show a cathodic peak of reduction of PdO. For Pd, this peak is registered at  $E = -0.22$  V. However, with the decrease in the concentration of palladium, it shifts towards more positive potentials of up to  $-0.07$  V. According to [14], the formation of palladium oxide at pH  $\sim 13$  is described by the equation:



with the value of the equilibrium potential of the electrode being  $0.13$  V.

For electrodes with  $X_{Pd} \leq 40$  at%, two indistinct anodic peaks are observed in the potential ranges of  $0.43$ – $0.74$  V and  $0.89$ – $0.91$  V. These peaks correspond to the oxidation of metallic silver to  $\text{Ag}_2\text{O}$  and its subsequent postoxidation to AgO. The amplitudes of both peaks increase with larger concentrations of silver in the alloy. The equilibrium potentials  $E_{eq}$  of formation of  $\text{Ag}_2\text{O}$  and AgO on silver in the studied solution were determined by the half-reaction on the anode:

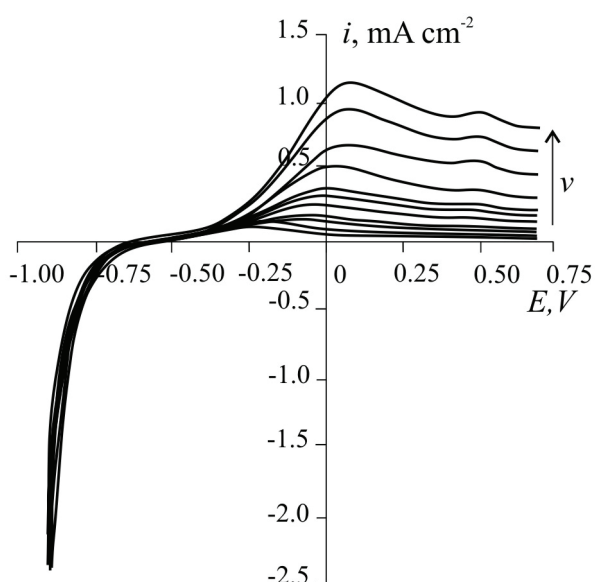




**Fig. 1.** Cyclic voltammograms obtained with a potential scan rate of 5 mV/s on Pd and Ag-Pd alloys in a 0.1 M KOH solution

and equalled to 0.40 and 0.67 V (standard hydrogen electrode) [14]. Based on the obtained data we can say that  $E_{\text{eq}}$  for silver oxidation processes are modified as compared to the calculated potentials. For 0.1M KOH they are 0.55 and 0.90 V, which was determined in [15]. Furthermore, Ag-40Pd and Ag15Pd alloys demonstrated characteristic prepeaks at 0.52 and 0.61 V respectively, which we assume to be connected with adsorption followed by AgOH oxidation [15]. The cathodic branches of the voltammograms showed peaks corresponding to the reduction of AgO (~ 0.50 V) and Ag<sub>2</sub>O (~ 0.32 V). Potentials of cathodic and anodic peaks determined for the Ag15Pd alloy are almost fully compatible with the potentials of the same peaks for pure silver [13]. The voltammogram of the Ag30Pd alloy shows a hysteresis at the potential 0.30 V, which may mean that the electrode's surface is underoxidised.

To determine the kinetics of hydrogen evolution on Ag-Pd alloys voltammograms were obtained for various potential scan rates and the hydrogenation time  $t_c = 3$  sec. (Fig. 2). The results show that for all the studied samples the ionisation peak increases with higher potential scan rates and shifts towards more positive values. Furthermore, the splitting of the main anodic peak into a number of smaller ones is observed, which may indicate the adsorptive



**Fig. 2.** Dependencies of the current density of hydrogen ionization on the potential scan rate on Pd and Ag-Pd alloys in a 0.1 M KOH solution obtained at  $t_c = 3$  s

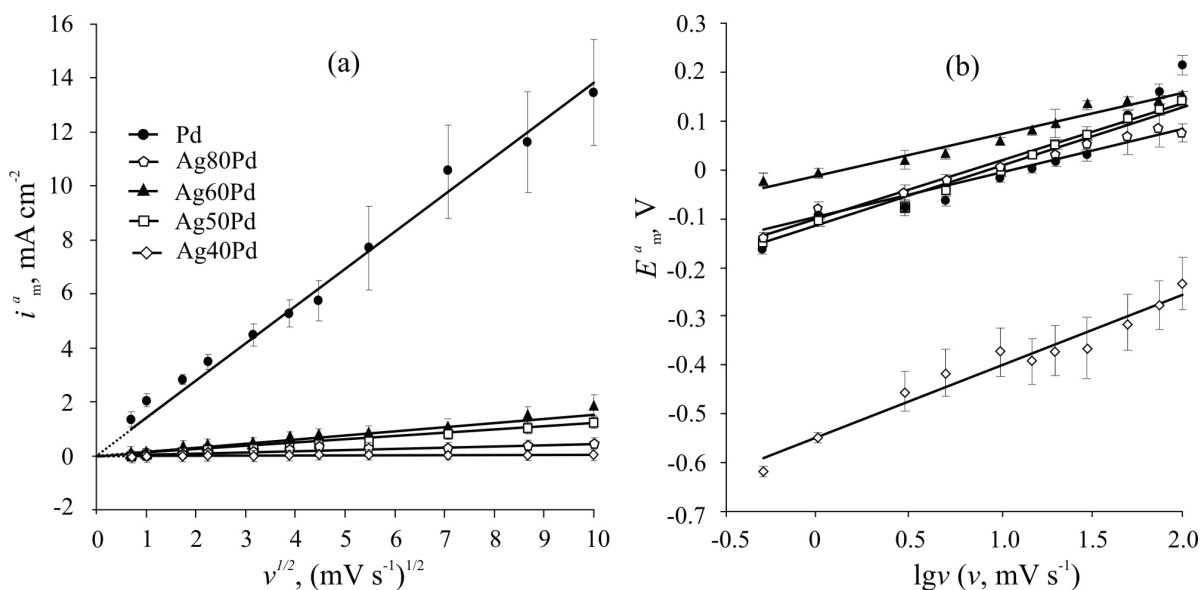
accumulation of various forms of oxygen-containing particles [16, 17]. The experimental data was processed based on the first anodic peak whose potential corresponded to the ionisation of atomic hydrogen.

The characteristic parameters of the experimental  $i, E$ -curves were replotted with some criterion coordinates. Thus, the obtained dependencies  $i_m^a - v^{1/2}$  (Fig. 3a) are easily linearized and extrapolated to the origin of the coordinates, which means that ionisation of hydrogen is complicated by solid-phase diffusion. The slopes of the graphs  $di_m^a / dv^{1/2}$  for Ag60Pd and Ag50Pd alloys are higher than that for the Ag80Pd alloy, which is most likely to be caused by silver oxidation.

The dependencies of the potential of the ionisation peak  $E_m^a$  on  $\lg v$  (Fig. 3b) are also linear for all the studied systems, which means that the electrochemical stage of atomic hydrogen ionization is irreversible. The slopes  $dE_m^a / d \lg v$ , obtained for palladium and the Ag–Pd alloy with the concentration of palladium of 80 at%, are similar, 0.049 and 0.042 V respectively, which corresponds to the single-electron charge transfer process. However, the values  $dE_m^a / d \lg v$  for the alloys with  $X_{\text{Pd}} \leq 60$  % vary within the range of 0.091–0.122 V. It is possible that in this case the kinetics of charge transfer is complicated by the formation of silver oxides. Similar dependencies are observed when the hydrogenation time is  $t_c = 5$  sec.

Using the results obtained previously on Ag–Pd electrodes in an acidic medium [18], we can assume that the kinetics of injection and ionisation of atomic hydrogen does not generally depend on the nature or the medium of the electrolyte. The complications observed in the alkaline medium are caused by silver oxidation during its dissolution from the alloys. Furthermore, as opposed to the acidic medium, in the alkaline solution atomic hydrogen is formed from the molecules of H<sub>2</sub>O. Therefore, the process of injection and ionisation of atomic hydrogen on a metal in an alkaline medium can be modelled as shown in Fig.4.

The study of injection and extraction of atomic hydrogen, as well as calculation of the hydrogen permeability parameters was performed by processing double step anodic-cathodic



**Fig. 3.** Values of the current ( $i_m^a$ ) and potential ( $E_m^a$ ) of the anodic peak on voltammograms for Pd and Ag–Pd alloys in a 0.1 M KOH solution obtained at various potential scan rates; ( $t_c = 3$  s).

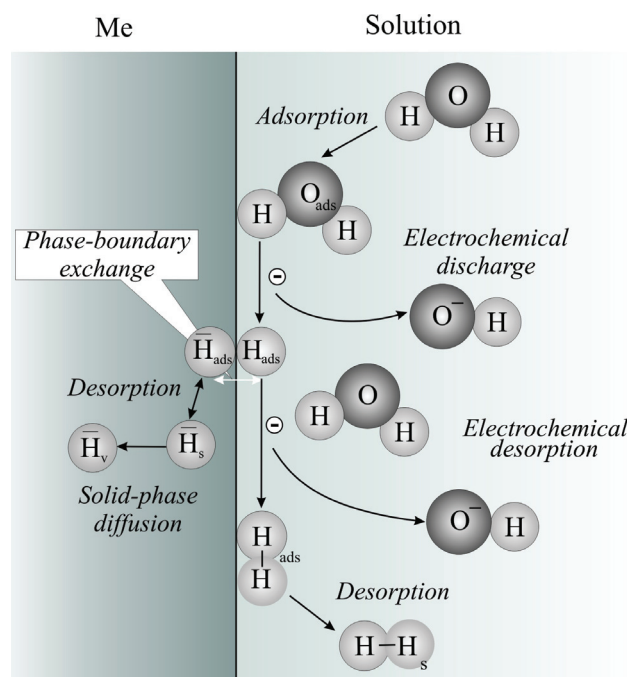
chronoamperograms obtained on palladium and its alloys. Thus, with longer hydrogenation time,  $i, t$ -dependencies (Fig. 5) show an expected decrease in the amplitudes of the cathodic and anodic branches of the chronoamperograms. This may be caused by the adsorption of oxygen-containing particles, primarily OH, which hinder the ionisation of atomic hydrogen from the surface. Indeed, while obtaining a series of chronoamperograms for different hydrogenation time, we did not polish the electrode surface between the cycles. This must have caused the accumulation of adsorbed particles and hence slowed down the ionisation process and hydrogen injection.

To see whether this assumption was correct, we obtained double step anodic-cathodic chronoamperograms only for  $t_c = 10$  sec. Cathodic and anodic current amplitudes were significantly higher than those obtained during subsequent registration (Fig. 5b). Larger concentrations of silver in the alloy result in expected decrease in the rate of ionisation of atomic hydrogen both in the cathodic and anodic region, which complies with the voltammetric dependencies.

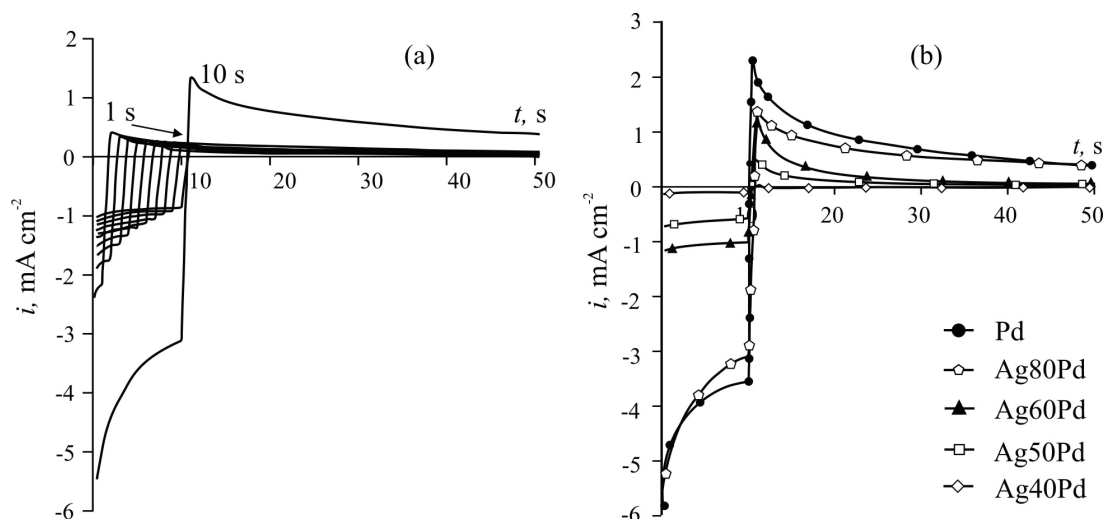
Cathodic chronoamperograms obtained for hydrogenation time  $t_c = 10$  sec., were rectified to the coordinates  $i_c-t_c^{-1/2}$  and  $i_c-t_c^{1/2}$ . For all the studied systems these dependencies are linear, but are not extrapolated to the origin of the

coordinates. This means that the registered cathodic current consists of at least two elements: the water discharge current and the maximum current of diffusion of H atoms inside the metallic phase.

Using the theoretical model for semi-infinite thickness electrodes described in [19], we performed the mathematical processing of



**Fig. 4.** Model of hydrogen evolution in an alkaline solution



**Fig. 5.** Double step chronoamperograms obtained in a 0.1 M KOH solution on the Ag80Pd alloy, with  $t_c = 1-10$  s (a), and for Pd and Ag–Pd alloys; the hydrogenation time  $t_c = 10$  s (b)

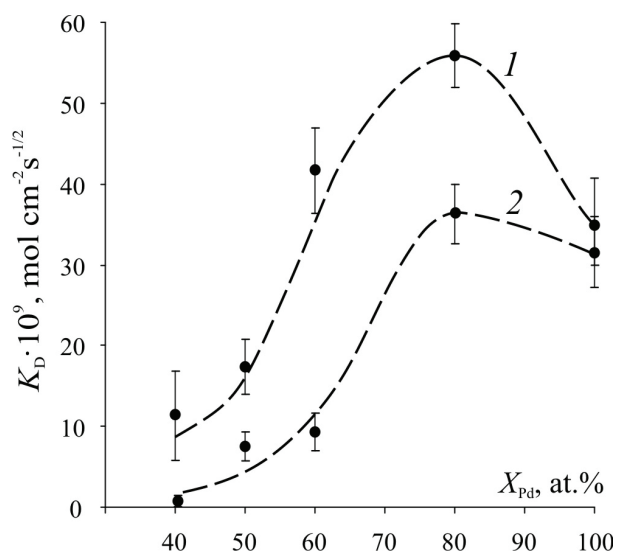
the cathodic chronoamperograms in order to determine the kinetic and diffusion parameters of the process of injection of atomic hydrogen. Mathematical modelling was used to calculate the following parameters:  $i_c(0)$  and  $i_c^\infty$  – initial and stationary cathodic current respectively, rate constants  $\bar{k}$  and  $\bar{k}$  of the reaction of injection and ionisation, and the equilibrium constant of this process  $K = \bar{k}/\bar{k}$ . The parameter characterising solid-phase diffusion, i.e. hydrogen permeability coefficient  $K_D = D^{1/2}\Delta c_{\bar{H}}$ , is integral; it is impossible to determine the diffusion coefficient  $D$  and the

magnitude of the change in the concentration  $\Delta c_{\bar{H}}$  of atomic hydrogen in the alloy separately. Hydrogen permeability parameters for Pd and Ag–Pd alloys calculated using the cathodic current transients, are given in Table 1.

All the parameters determined during our experiments, except for the hydrogen permeability coefficient  $K_D$ , decrease steadily with larger concentrations of silver in the alloy. The hydrogen permeability coefficient reaches its maximum on the Ag80Pd alloy. This can be accounted for by the maximum hydrogen permeability and hydrogen solubility in the crystal lattice of the Ag77Pd alloy determined in [10].

Comparison of the results obtained for Ag–Pd alloys in acidic [18] and alkaline media allowed us to conclude that hydrogen permeability of such alloys is lower in alkaline media than in acidic media. The dependency of hydrogen permeability coefficient  $K_D$  on the concentration of palladium is the same for the considered media. The coefficient reaches its maximum, when  $X_{Pd} = 80$  at% (Fig. 6). The hydrogen permeability coefficient for Pd and Ag–Pd alloys with  $X_{Pd} \geq 50$  at% in the alkaline medium is 1.5–4.5 times lower than in the acidic medium. For the Ag40Pd alloy the difference is even more significant.

The analysis of the results allowed us to conclude that upon transition from acidic to alkaline medium, hydrogen permeability is suppressed on all the studied alloys of the Ag–Pd system.



**Fig. 6.** Dependence of the hydrogen permeability coefficient on the alloy composition in a 0.1 M  $H_2SO_4$  solution (1) and a 0.1 M KOH solution (2)

**Table 1.** Characteristics of the hydrogen injection in palladium and in Ag-Pd alloys in a 0.1 M KOH solution

| $X_{Pd}$ , at % | $i_c^\infty$ , mA/cm <sup>2</sup> | $i_c(0)$ , mA/cm <sup>2</sup> | $K_D \cdot 10^9$ , МОЛЬ/CM <sup>2</sup> C <sup>1/2</sup> | $\bar{k} \cdot 10^8$ , mol/cm <sup>2</sup> S <sup>1/2</sup> | $\bar{k} \cdot 10^4$ , cm/s | $K \cdot 10^5$ , mol/cm <sup>3</sup> |
|-----------------|-----------------------------------|-------------------------------|--|---|-----------------------------|--------------------------------------|
| 100             | 2.39±0.32                         | 4.95±1.21                     | 32.17±10.05  | 3.84±1.21   | 3.82±0.05                   | 11.87±4.64                           |
| 80              | 1.91±0.15                         | 3.65±0.12                     | 36.19±3.67   | 2.99±0.47   | 2.65±0.30                   | 10.40±1.41                           |
| 60              | 1.17±0.35                         | 1.36±0.31                     | 9.31±2.40  | 0.76±0.22   | 0.93±0.06                   | 2.51±0.65                            |
| 50              | 0.63±0.10                         | 0.96±0.14                     | 7.54±1.77  | 0.58±0.12   | 0.26±0.03                   | 2.23±0.32                            |
| 40              | 0.07±0.01                         | 0.13±0.02                     | 0.75±0.10  | 0.07±0.03   | 0.14±0.01                   | 0.19±0.05                            |

The anodic current drops were analysed using the same theoretical model [19]. Hydrogen permeability coefficients calculated based on the slopes of the linear regions of anodic chronoamperograms –  $K_D(i_a)$  and chronocoulograms –  $K_D(q_a)$ , are also maximum for the Ag80Pd alloy (Table. 2). It should be noted that hydrogen permeability coefficients calculated using the anodic current transients are significantly higher than those calculated based on the cathodic current transients. This may be the result of the dilatation of the crystal lattices of the alloys [18].

We can thus state that the dependency of practically all the parameters of hydrogen permeability on the composition of Ag–Pd alloys passes through the extremum observed for the Ag80Pd alloy. We can therefore conclude that 80 at% concentration of palladium in the alloy is optimal with regard to hydrogen permeability, which means that this alloy can be effectively used for hydrogen purification and storage.

#### 4. Conclusions

1. The behaviour of Ag-Pd alloys during hydrogen evolution in an alkaline solution was studied. Introduction of small quantities (up to 20 at%) of silver into the crystal lattice of palladium results in the increase in the rate of ionisation of atomic hydrogen. When  $X_{Ag} > 20$  at% the process is suppressed by silver oxidation.

2. When palladium alloys with concentrations of Ag of up to 60 at% are used, the kinetics of hydrogen evolution remains the same. The determining stage of the hydrogen evolution

reaction on Ag-Pd alloys in a 0.1M KOH solution is the electrochemical stage of atomic hydrogen ionization, which is complicated by its diffusion in the solid phase.

3. The dependency of the ionisation peak  $E_m^a$  on the potential scan rate indicates that the electrochemical stage is irreversible. For alloys with  $X_{Pd} \leq 60$  at% the kinetics of charge transfer is complicated by silver oxidation.

4. The parameters of hydrogen permeability are optimal, when the concentration of palladium in the alloy is ~80 at%. These alloys can be used as efficient materials for hydrogen purification and storage.

#### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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**Table 2.** Values of  $K_D$  for Pd and its alloys obtained using anodic current transients in a 0.1M KOH solution

| $X_{Pd}$ , at%  | 100        | 80         | 60        | 50        | 40        |
|---|------------|------------|-----------|-----------|-----------|
| $K_D(i_a) \cdot 10^8$ , mol/cm <sup>2</sup> S <sup>1/2</sup>    | 28.03±2.40 | 35.35±3.29 | 6.50±1.09 | 6.13±0.99 | 0.23±0.04 |
| $K_D(q_a) \cdot 10^{10}$ , mol/cm <sup>2</sup> S <sup>1/2</sup> | 15.21±2.23 | 19.05±1.62 | 4.61±1.02 | 3.02±0.39 | 0.12±0.04 |



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