

The effect of organic molecules adsorption on hydrogen absorption in relation to the hydrogen evolution reaction*

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The competitive adsorption of organic molecules (2,7-naphthalenedisulfonic acid) and adsorbed H is of interest in relation to its influence on H absorption into a Pd-Ni electro-deposited alloy. The experimental results, in acid solution, show an enhancement of the coverage of the electrode surface with adsorbed H due to the competitive adsorption of organic molecules that interfere with H atoms, through lateral attractive interactions between the adsorbed species and communal electronic effects, leading supposedly to a decreased probability of H entry into the alloy. Chemisorbed H is, on the other hand, an intermediate in the HER, so the enhancement of the electrode coverage in the presence of co-adsorbed organic molecules promotes the hydrogen evolution reaction.

Keywords: hydrogen adsorption, absorption, hydrogen evolution, lateral interactions.

INTRODUCTION

An interesting aspect of the process of cathodic evolution of hydrogen at some transition metals or alloys is the transfer of H from its adsorbed state into the metal just below the surface layer of metal and then the diffusion of H from this state into the bulk.

At the same time, it is known that the adsorption of site – blocking elements called poisons, such as: S, SH⁻, H₂S, Pb^{1–4} usually promotes the cathodic absorption of H into some metal lattices, such as Fe, Ti, Ni or related alloys. However, it is also known that the kinetics of the HER is influenced by the adsorption of such catalyst “poisons” which decrease the coverage of overpotential deposited (OPD) H,^{5,6} as well as the coverage by underpotential deposited (UPD) H.^{6,7} For these reasons the rate of the hydrogen evolution reaction is usually lowered in the presence of small amounts of poison.⁶

In the present work the influence of the competitive adsorption of organic molecules on H absorption and hydrogen evolution reaction were examined in relation to the thermodynamics of H in the adsorbed state and the role of the effects of lateral interac-

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tions on both the chemical potential of the absorbed H and the kinetics of its transfer into the electrode metal.

EXPERIMENTAL

The electrochemical measurements were performed using an electrochemically deposited Pd (mol % 63) – Ni (mol % 37) electrode⁸ in 0.5 mol dm⁻³ H₂SO₄.

The competitive adsorption effect of organic molecules was studied using 2,7-naphthalenedisulfonic acid (NDA) at a concentration of 5.0×10^{-4} mol dm⁻³.

A conventional three-compartment glass cell was used. A reversible hydrogen electrode (RHE) in the same basic solution (0.5 mol dm⁻³ H₂SO₄) as that of the working electrode was used. A platinum gauze, spotwelded onto a platinum wire, sealed into a glass tube, was used as the counter electrode.

The solution in the working electrode compartment was saturated with N₂ at atmospheric pressure, which was continuously bubbled through the solution.

RESULTS AND DISCUSSION

Steady-state measurement

The hydrogen evolution reaction was studied by steady-state measurements in 0.5 mol dm⁻³ H₂SO₄ both with and without NDA molecules.

A very positive steady-state potential [≈ 0.30 V (RHE)], stable in time, was established at the unpolarized Pd–Ni electrode, immersed in acid solution. It was recognized that this potential was set due to the possibility that a passivation process could have occurred, producing a surface oxide film at the electrode. The $E - \log j$ relationship obtained from this open circuit potential in the cathodic direction is given in Fig. 1 (curve a). The curve shows some kind of limiting current in the potential range between this potential and the potential close to the reversible hydrogen potential, which is related to the reduction of the oxide present on the electrode surface.

In order to reduce any oxide from the electrode surface, the electrode was polarized at $E = -0.300$ V (RHE) for 1 h. Starting from this potential to the new

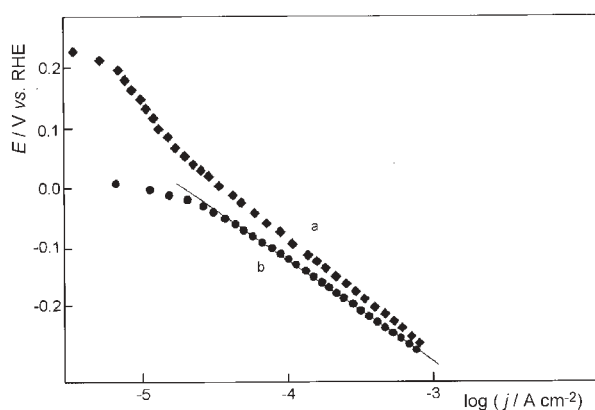


Fig. 1. Tafel plots for the HER on Pd–Ni electrode in 0.5 mol dm⁻³ H₂SO₄ solution, (a) fresh electrode (b) polarized at -0.300 V (RHE).

quasi-reversible potential close to 0.030 V (RHE), curve b (Fig. 1) was obtained. This new quasi-reversible potential established after cathodic prepolarization is considered to be a mixed potential determined by the hydrogen evolution reaction, as the cathodic reaction, and the oxidation of hydride formed during cathodic polarization at $E = -0.300$ V (RHE), as the anodic reaction. In the potential region lower than this quasi-reversible potential the Tafel plot had a slope of -0.140 V dec^{-1} . The Tafel slope remained the same at higher current densities region, but appeared to exhibit an unstable region close to the open-circuit potential.

The hydrogen evolution reaction in acid solution proceeds by a two-step reaction with adsorbed H as the intermediate either on metal or metal-hydride sites,^{7,9} so it is not clear if this change of the slope in the Tafel line in the lower current density region corresponds to a change in the reaction mechanism with two processes in series or just to a change of the coverage conditions of the adsorbed H intermediate. One should be aware that this unstable potential region could also be caused by a significant appearance of the back reaction.

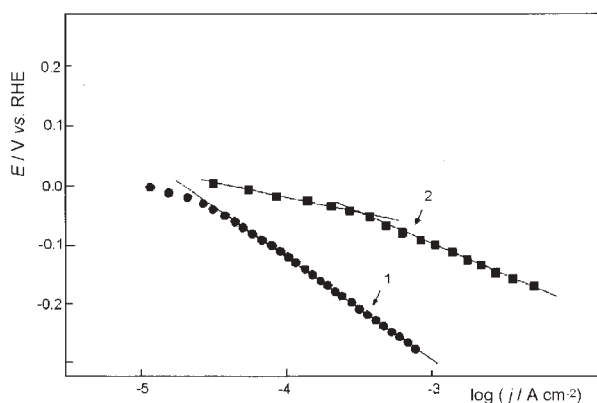


Fig. 2. Cathodic Tafel relations on Pd-Ni electrode in the base $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution and (2) in the base solution containing additionally NDA at a concentration of $1 \times 10^{-5} \text{ mol dm}^{-3}$.

In order to relate the effect of adsorption of the organic molecules on the kinetics of the HER the $E - \log j$ relation was followed in the presence of $1 \times 10^{-5} \text{ mol dm}^{-3}$ 2,7-naphthalenedisulfonic acid (Fig. 2, curve 2). Contrary to our previous results on Fe, where this organic molecule acted as inhibitor for hydrogen evolution reaction,¹⁰ this time it acted in opposite direction, improving the electrocatalytic activity of the Pd-Ni electrode. Comparing the curves 1 and 2 (Fig. 2) it can be seen that certain differences in the exchange current density exist, but the differences are more obvious when the Tafel plots are concerned. Instead of one slope in the absence of the organic molecules, the Tafel relation in the presence of organic molecules exhibits a linear region, with a slope of ≈ -0.035 V dec^{-1} , at low cathodic potentials, while the slope increases with potential at $E > -0.060$ V (RHE). This suggests that the difference is caused not only by a change of the reaction surface area, but also that they exhibit a different potential dependence of the reaction rate and thus probably different reaction mechanisms or variably mixed mechanisms.

Potential-decay measurements

Potential-decay transients were taken from constant overpotentials during steady-state polarization experiments, both in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ with and without organic molecules in a solution.

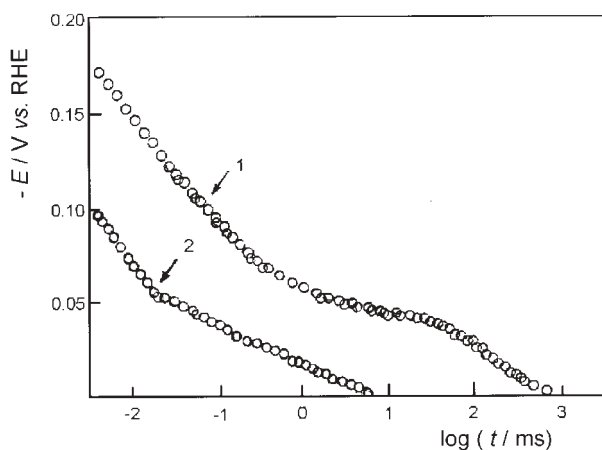


Fig. 3. Potential-decay for HER on Pd-Ni electrode in (1) the base solution and (2) the base solution containing NDA at a concentration of $1 \times 10^{-5} \text{ mol dm}^{-3}$.

The primary data collected are plotted as $E - \log t$ (Fig. 3) and $E - \log(-dE/dt)$ (Fig. 4). Upon comparing these data, it can be seen that there are substantially different kinds of behaviour in the absence and in the presence of organic molecules.

So, in the absence of organic molecules, the potential decay curves (curve 1, Figs. 3 and 4) have three principal regions. The first region arises when $E < -0.060 \text{ V}$ (RHE) and corresponds to the discharge of the double-layer capacitance through the non-linear Faradaic reaction resistance.¹¹ The second region is mostly flat with "plateau" around $E = -0.060 \text{ V}$ (RHE) over the time range $\log t (t/\text{ms}) = 0$ to $\log t (t/\text{ms}) = 1.5$. The third

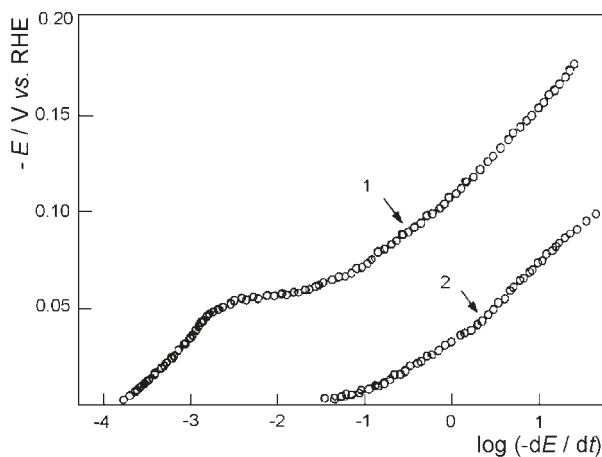


Fig. 4. Plot of $E - \log(-dE/dt)$ for the HER on Pd-Ni electrode in (1) the base solution and (2) the base solution containing NDA at a concentration of $1 \times 10^{-5} \text{ mol dm}^{-3}$.

region arises when $E \geq -0.060$ V (RHE) and corresponds to a continuing decline of E with $\log t$. The overall potential-decay process takes a relatively long time ($t \approx 1$ s) to drop to the RHE potential.

In the presence of organic molecules the potential-decay curves (curve 2, Figs. 3 and 4) have only two principal regions. In this case, in the first short time region, there is potential decay that is related to the process of discharge of the double-layer capacitance which is almost complete within a very short time, when $E < -0.060$ V (RHE). The second potential decay corresponds to the H pseudocapacitance (potential dependence of H coverage and/or extent of sorption of H). The overall potential-decay process takes a relatively short time ($t = 6.5$ ms).

The flat second region ("plateau") of the potential-decay (curve 1 Figs. 3 and 4), in the absence of organic molecules, corresponds to the existence of a high H pseudocapacitance, probably arising on account of the potential dependence of the lattice fraction X_H of the sorbed H species. Thus, the open-circuit process involves "discharge" of this C_f , which means a decomposition of the absorbed species in parallel with that of the surface pseudocapacitance,¹² according to the following equation:

$$j = C_f \frac{dE}{dt} \quad (1)$$

since $C_f \gg C_{dl}$.

Pseudocapacitance behaviour

The evaluation of the pseudocapacitance behaviour of the adsorbed OPD H species is made directly using Eq. (1), with $E - \log j$ data (Fig. 2) together with $E - t$ behaviour differentiated to give dE/dt . The obtained $C_f - E$ curves for the case with (curve 2) and without organic molecules (curve 1) present in the $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution are shown in Fig. 5.

In both cases there are variations of C_f with E , showing a maximum, as is predicted theoretically.¹³ It can be seen that the half-widths of these curves are quite different. In the case with organic molecules in solution the peak is wider than that required for Langmuir adsorption and corresponds to $g < 0$, *i.e.*, suggests that some attractive interactions are involved. When $E < -0.060$ V (RHE), C_f decreases rapidly reaching the value of C_{dl} ($\approx 40 \mu\text{F cm}^{-2}$).

By integration of the $C_f - E$ curves the corresponding H deposition charges are evaluated. Taking into account that the H deposition charge for a monolayer is similar to that for a Pt surface, then the apparent coverage in equivalent monolayers of H is calculated. It was found that the apparent coverage by adsorbed H species in the absence of organic molecules is about 4 monolayers, and in the presence of organic molecules it is radically different being close to 1. Since it is difficult to cover an electrode with a film of 4 monolayers in thickness, one possibility of explaining the behaviour is that the OPD H in acid solution, in the absence of organic molecules is in the form of hydride in the near surface region, on which or by means of which, proceed the elementary steps of the HER. The possibility that the anomalous OPD H capacitance, *i.e.*, apparent

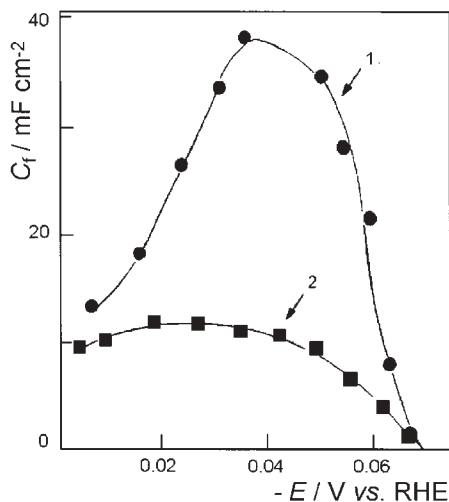


Fig. 5. Capacitance as a function of potential for the HER of Pd-Ni in (1) 0.5 mol dm⁻³ H₂SO₄ and (2) the base solution containing NDA at a concentration of 1 × 10⁻⁵ mol dm⁻³.

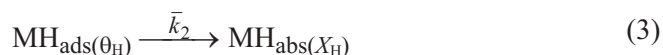
multilayer adsorption of H, could be caused by active dissociation of H₂ at Pd-Ni during the potential decay should also be considered.

One principal problem here is how site blocking elements co-adsorbed with H on Pd-Ni promote cathodic H₂ evolution and enhance the surface coverage by H.¹⁴⁻¹⁶ Since the absorption of H into the metal is closely related to the adsorption behaviour of the electrodeposited H atom intermediate involved in the steps of the H₂ evolution reaction, then a generalized scheme of the overall process could be as shown below.

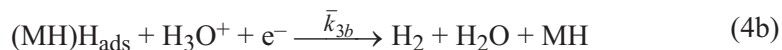
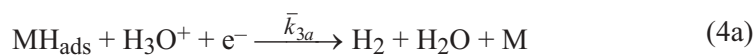
1. The primary step is proton discharge and chemisorption of H:



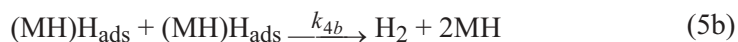
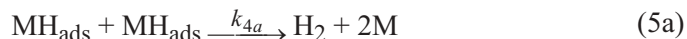
2. Phase transfer of H from the chemisorption state to the subsurface state just below the surface and from that state into the bulk by diffusion along the chemical potential gradient of H normal to the metal surface:



3. Desorption of the H adsorbed either on M or on MH as H₂ by the electrochemical desorption step:



or by the chemical recombination steps:



All experimental results show that the reaction steps in the cathodic hydrogen evolution reaction are in relation to the thermodynamics of H in the adsorbed state in terms of fractional lattice occupancy (X_H) and the role of lateral interaction effects on the chemical potential of the adsorbed H. With regard to the apparent generation of a hydride state at the boundary region of a Pd–Ni electrode in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, it is reasonable to suppose that such a surface would have a weaker affinity for chemisorbed H, which could lead to the discharge of protons and the chemisorption of H as hydride as the rate-controlling step in the hydrogen evolution reaction.

On Pd–Ni in the presence of organic molecules where θ_H was found to be close to 1 the hydrogen evolution reaction could proceed with the chemical recombination step (5a) being rate controlling. If this is the case then a Tafel slope close to -0.030 V (RHE) is to be expected, as that was found experimentally in the potential range close to the open-circuit potential. On the other hand, if this step were rate controlling then a limiting current would be expected at high cathodic potentials, which was not observed experimentally.

The Tafel relation observed for the HER in the presence of organic molecules suggests that the recombination and the electrochemical desorption steps are involved in parallel parts and the total current density should be expressed in the form:

$$j = 2Fk_2c(\text{H}_3\text{O}^+)\theta_{\text{H}(\text{o})} \exp\left[-\frac{\beta FE}{RT}\right] + 2Fk_3\theta_{\text{H}(\text{o})}^2 \quad (6)$$

where $\theta_{\text{H}(\text{o})}$ is θ the coverage by H in the presence of organic molecules, expressed with Frumkin type of isotherm¹⁷ which takes into account the relative number of sites in the surface occupied by organic molecules:

$$\frac{\theta_{\text{H}(\text{o})}}{1 - \theta_{\text{H}(\text{o})} - \theta_{\text{o}}} = \bar{K}_{\text{H}(\text{o})} \exp[-g(\theta_{\text{H}(\text{o})} + \theta_{\text{o}})] \quad (7)$$

θ_{o} is the coverage by organic molecules, g is an interaction parameter which is > 0 for repulsive interactions and < 0 for attractive interactions and $\bar{K}_{\text{H}(\text{o})}$ is the electrochemical adsorption equilibrium constant for H when $\theta \rightarrow 0$.

It can be seen from Eq. (7) that if $g > 0$ then $\theta_{\text{H}(\text{o})}$ tends to be increased, for a given E . In term of the reaction energy profile, the Gibbs energy of activation for the transfer of H across the interface just into the metal tends to increase, which decreases the transfer rate according to:

$$\Delta G^\ddagger = \Delta G^\ddagger_{\theta(\text{o})=0} - \beta g [\theta_{\text{H}(\text{o})} + \theta_{\text{o}}] \quad (8)$$

where β is a barrier symmetry factor.

The overall effect of H transfer rate just into the metal is a combination of two effects: an increase of H coverage, and an increase of ΔG^\ddagger for H absorption (Eq. (3)), the rate of which is:

$$v_2 = k_2 \frac{\bar{K}_{\text{H}(\text{o})} \exp[-g(\theta_{\text{H}(\text{o})} + \theta_{(\text{o})})]/RT}{1 + \bar{K}_{\text{H}(\text{o})} \exp[-g(\theta_{\text{H}(\text{o})} + \theta_{(\text{o})})]/RT} \exp[-\Delta G_{\theta(\text{o})=0}] \exp[\beta g(\theta_{\text{H}(\text{o})} + \theta_{\text{o}})] \quad (9)$$

where $\theta_{\text{H}(\text{o})}$ is:

$$\theta_{\text{H}(\text{o})} \cong \frac{\bar{K}_{\text{H}(\text{o})} \exp[-g(\theta_{\text{H}(\text{o})} + \theta_{(\text{o})})]/RT}{1 + \bar{K}_{\text{H}(\text{o})} \exp[-g(\theta_{\text{H}(\text{o})} + \theta_{(\text{o})})]/RT} \quad (10)$$

according to Eq. (7) for small values of $\theta_{(\text{o})}$.

The interactions between H and organic molecules can be explained to occur through the excess of electron density, depending on the electronegativity difference of the adsorbed organic molecules and the substrate metal.

So, electron-donating lateral interactions between coadsorbed molecules and H_{ads} arise from the partial donation of a non-bonding electron pair of the coadsorbed molecule to the metal. Due to the enhanced surface “electron-gas” density the $\text{M}-\text{H}_{\text{ads}}$ bonds tend to be stronger and the bond length shortened, enhancing the absorption of H into the metal. An opposite electronic effect arises in the case of electron-withdrawing interactions between the coadsorbed molecule and H_{ads} , which will lower the “electron-gas” density at the surface metal atoms on which the H is adsorbed. This effect will weaken the $\text{M}-\text{H}_{\text{ads}}$ bonds leading to an increase of the bond length and a decrease in the rate of H absorption.

Potentiodynamic measurements

Potentiodynamic experiments were also conducted in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution both in the presence and the absence of organic molecules in the solution. The aim was another attempt to elucidate the electrochemical behaviour of hydrogen in relation to hydride formation.^{18,19}

Figure 6 shows the shape of the voltammetric response of the system in acid solution without organic molecules in the solution, after the electrode had been held at a potential of 0.00 V (RHE) for a certain time (8 min). As can be seen, a significant charge arises on the anodic side of the voltammogram (curve 1). During subsequent cycling (curves 2, 3 and 4), the anodic peak disappears showing that the quantity of charge passed in the anodic sweeps is to be associated with the oxidation of some species generated during the holding time at the potential of 0.00 V (RHE). On the cathodic side of the voltammetric profile, it is interesting to notice a small charge that is not related to the anodic peak, but probably to the reduction of some earlier adsorbed O species at potentials more positive than the anodic peak potential. Cyclic voltammetry results at various sweep rates show that the resulting anodic peak currents are dependent on $v^{1/2}$, meaning that a diffusion controlled process dominates the anodic electrochemical behaviour.

Figure 7 shows the shape of the voltammetric response of the system with organic molecules present in the $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, which was recorded after holding the potential for the same time at 0.00 V, (RHE) as in the case without organic molecules. As can be seen, the behaviour is quite different. It should be stressed that on the anodic

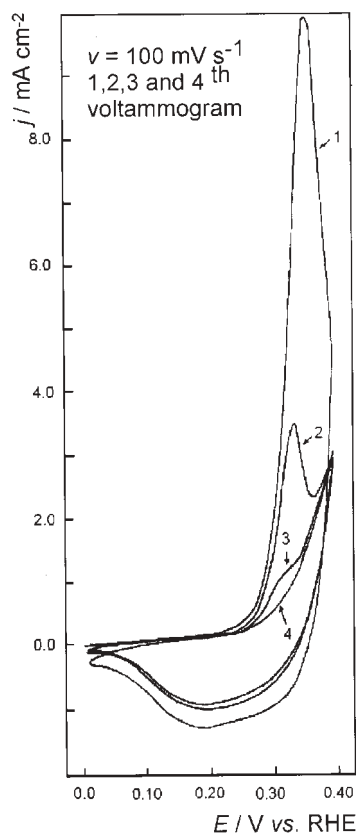


Fig. 6. Subsequent cycling of the Pd-Ni electrode, in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, after holding the potential at 0.00 V (RHE) for 8 min.

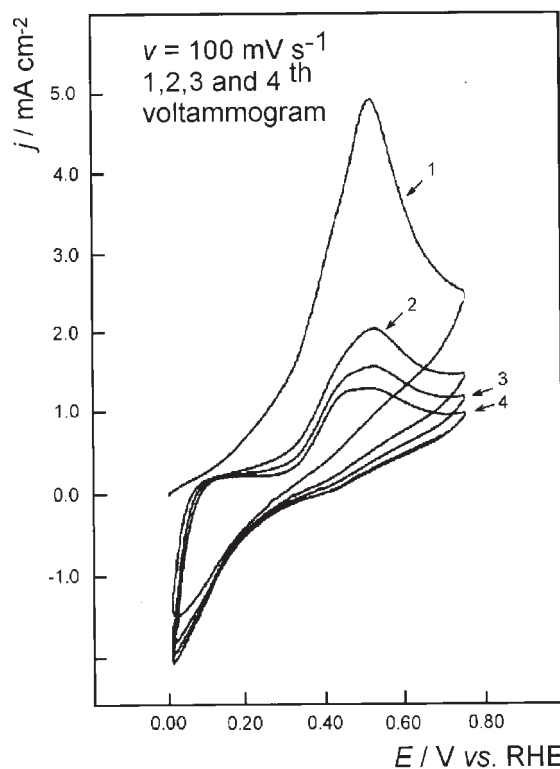


Fig. 7. Subsequent cycling of the Pd-Ni electrode, in base solution containing NDA at a concentration of $1 \times 10^{-5} \text{ mol dm}^{-3}$, after holding the potential for 8 min at 0.00 V (RHE) .

side of the voltammogram the peak appears at a more positive potential, and with a significantly lower charge under the peak. On the cathodic side of the profile, it is evident that at the potential of 0.00 V (RHE) the H_2 evolution reaction commences with significant currents. During subsequent cycling (Fig. 7, curves 2, 3 and 4), the anodic peak does not disappear and it is clear that processes in the positive-going sweep cannot be well resolved as the reoxidation of H_2 will unavoidably continue at significant currents. The dependence of the resulting anodic peak currents on the square-root of the sweep-rate shows that also in this case a diffusion controlled process dominates the anodic electrochemical behaviour in potential range where the huge anodic peak appears.

The question which first arises is what is the origin of the diffusion controlled process in both cases.

So, as there is no significant H_2 evolution at a potential of 0.00 V (RHE) in the absence of organic molecules, then a corresponding H_2 reoxidation currents are not to be

expected during the following anodic sweep. This means that diffusion and oxidation of H adsorbed within the alloy are the processes that generate the anodic profile.

In the presence of organic molecules, when there is a significant H₂ evolution at the potential of 0.00 V (RHE), it is to be expected that reoxidation of H₂ is the main reason for the anodic peak.

These conclusions are in agreement with steady-state and potential-decay results.

CONCLUSIONS

1. Experimental procedures based on steady-state, potential relaxation and cyclic voltammetry measurements at Pd–Ni electrochemically deposited alloy have enabled the effect of the competitive adsorption of organic molecules on H adsorption and absorption, as well as on the hydrogen evolution reaction to be evaluated.

2. All the results show that coadsorbed organic molecules promote H adsorption but inhibit H absorption and that these effects could be explained through the lateral attractive interaction between the adsorbed species, *i.e.*, including interaction effects in the θ_H function.

3. Coadsorbed organic molecules make the H coverage dependent on potential, resulting in a Tafel relation for the HER having two slopes:

a) in the lower overpotential range this slope has a value of $-0.035 \text{ mV dec}^{-1}$, where the hydrogen evolution reaction proceeds with the chemical recombination step as the rate controlling one, and

b) in the higher overpotential range this slope has a value of $-0.120 \text{ mV dec}^{-1}$, which can be explained only if the recombination and the electrochemical desorption steps are both involved in parallel parts of the hydrogen evolution reaction.

ИЗВОД

УТИЦАЈ КОАДСОРБОВАНИХ ОРГАНСКИХ МОЛЕКУЛА НА АДСОРПЦИЈУ И АПСОРПЦИЈУ ВОДНИКА

ЉИЉАНА ВРАЧАР

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Испитивање утицаја коадсорбованих органских молекула на адсорпцију и апсорпцију водоника, у киселом раствору, на легури Pd–Ni, показало је да због привлачних латералних интеракција између адсорбованих честица расте степен покривености легуре адсорбованим водоником, али расте и Гибсова енергија активације за реакцију апсорпције. Укупни ефекат промене ова два параметра одражава се на инхибирање реакције апсорпције водоника, али и на промену механизма електрохемијског издавања водоника и значајно убрзавање ове реакције.

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REFERENCES

1. R. N. Iyer, H. W. Pickering, M. Zamanzadeh, *J. Electrochem. Soc.* **136** (1989) 2463
2. R. N. Iyer, I. Takenchi, M. Zamanzadeh, H. W. Pickering, *Corrosion* **46** (1990) 360
3. F. A. Lewis, *The Palladium Hydrogen System*, Academic Press, New York, 1967
4. G. Jerkiewicz, J. J. Borodzinski, W. Chrzanowski, B. E. Conway, *J. Electrochem. Soc.* **142** (1995) 3755
5. L. Bai, B. E. Conway, *J. Electroanal. Chem.* **198** (1986) 149
6. M. Elam, B. E. Conway, *J. Electrochem. Soc.* **35** (1988) 1678
7. B. E. Conway, L. Bai, *J. Chem. Soc., Faraday Trans. 1*, **81** (1985) 1841
8. Lj. Vračar, M. Stojanović, *J. Serb. Chem. Soc.* **61** (1996) 67
9. M. Elam, B. E. Conway, *J. Appl. Electrochem.* **17** (1987) 1841
10. D. M. Dražić, Lj. Vračar, V. J. Dražić, *Electrochim. Acta* **39** (1994) 1165
11. B. V. Tilac, B. E. Conway, *Electrochim Acta* **21** (1976) 745
12. Lj. Vračar, B. E. Conway, *J. Electroanal. Chim.* **277** (1990) 253
13. B. E. Conway, P. L. Bourgault, *Trans. Faraday Soc.* **58** (1962) 593
14. E. Protopopoff, P. Marcus, *J. Electrochem Soc.* **135** (1988) 3073
15. P. Marcus, E. Protopopoff, *J. Chim. Phys.* **88** (1991) 1423
16. E. Protopopoff, P. Marcus, *Surf. Sci.* **169** (1986) L273
17. J. H. Barber, B. E. Conway, *J. Chem. Soc., Faraday Trans.* **92** (1996) 367
18. M. Enyo, T. Maoka, *J. Electroanal. Chem.* **108** (1980) 277
19. F. G. Will, K. Cedzynska, D. C. Linton, *J. Electroanal. Chem.* **360** (1993) 161.