# Hydrogen permeation through Ni layers deposited from Watts' electrolyte

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Electrochemical hydrogen permeation experiments were performed through electrodeposited Ni layers in order to study the factors affecting the entry and transport of hydrogen in such materials. The Ni layers are deposited at a different cathodic current density in a Watts' electrolyte. It was found that the layers deposited at a higher current density of 20 A·dm$^{-2}$ with a texture [100] are more permeable to hydrogen during their charging in $H_2SO_4$ solution as compared with Ni layers deposited at 0.5, 2 or 5 A·dm$^{-2}$ with a texture [110+211], [211] and [211+100], respectively. The addition of thiourea to the charging $H_2SO_4$ solution has a strong promoting effect on the permeation parameters. At one and the same conditions, the electrodeposited Ni layers show faster and more extensive hydrogenation than metallurgically obtained Ni foils.

**Key words**: hydrogen permeation, hydrogen storage, Devanathan cell, nickel.

## INTRODUCTION

Hydrogen is one of the most damaging species in metals and their alloys (hydrogen embrittlement). However, it has become clear that hydrogen is considered as important fuel in the future. This situation poses embrittlement problems with respect to transportation and storage of hydrogen. Moreover, for the production, transfer or storage of hydrogen, materials with a high permeability to hydrogen are desired.

Nickel exhibits high initial electrocatalytic activity towards hydrogen evolution reaction (HER) [1]. Industrial water electrolysis cells for the electrochemical production of hydrogen usually employ Ni-based electrodes which operate in a potassium hydroxide solution. The overall energy efficiency of electrolysis is partly related to the HER [2, 3]. Moreover, Ni-MeH system is widely used for battery applications [4]. In this case, Ni or its alloys with high hydrogen permeability are desired. In general, the following processes in a hydrogen/ metal system can be distinguished: hydrogen entry into the metal; transport (diffusion) of hydrogen inside the metal and trapping of hydrogen at structural defects and/or formation of hydride phases. Knowledge of the factors determining the solubility and transport properties of hydrogen is very important in understanding the mechanism of hydrogen permeation and storage. An extensive work has been done on the solubility and diffusivity of hydrogen in pure nickel by using a gas phase hydrogen permeation technique [5–8]. Electrochemical permeation technique of Devanathan–Stachurski [9] is widely used for studying the factors which influence the entry and transport of hydrogen in nickel and nickel alloys [10]. It is found that the kinetics of hydrogen entry depends on many environmental and metallurgical factors, such as applied potential or current density, pH of the solution, chemical composition of the solution and of the metal. In a US patent [11] a process is described for forming nickel foils with a greater hydrogen permeability than palladium by using plating bath containing an organic sulphonic acid. In our previous work [12], devoted to the hydrogen co-evolution and permeation in Ni coatings during electroplating on steel in Watts' electrolyte, it was found that the hydrogen permeation through the coatings during their charging from a $H_2SO_4$ is influenced by their fibre texture and by their grain sizes, which are a function of the presence of commonly used additives in the electroplating bath. It is also strongly affected by the addition of thiourea to the charging solution.

In the present paper, the electrolytic insertion of hydrogen into different samples of Ni deposits was investigated in order to devise conditions which would lead to extensive and reversible hydrogenation.

## EXPERIMENTAL

Nickel deposits were obtained from a Watts' electrolyte with the following composition:

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0.89 M NiSO$_4$.7H$_2$O, 0.21 M NiCl$_2$.6H$_2$O, 0.49 M H$_3$BO$_3$ (all reagents were of analytical grade).

The electrodeposition parameters were as follows: current density 0.5, 2, 5 or 20 A·dm$^{-2}$, temperature of the bath 50ºC, pH = 4.5, agitation with magnetic stirrer.

Ni deposits with a thickness of about 50 μm were obtained under a thermostatic control in a glass cell, in which Ni plate with large surface area served as an anode and a brass plate – as a cathode. The cathodic surface was preliminary treated by a very fine polishing (emery) paper and after the deposition process the Ni deposits were removed from the brass substrate. The Ni deposits were subjected to investigations of their structure as well as to hydrogen permeation tests.

The texture of the Ni layers was studied by X-ray diffractometer. The axis of the preferred orientation was identified by comparing the diffraction peak intensities with that of the ASTM data, given for a randomly oriented sample.

The hydrogen permeation tests of the Ni deposits were performed by the method of Devanathan–Stachurski [9]. This technique allows to charge cathodically the entry (input) side of the Ni deposits and to measure electrochemically the flow of permeating hydrogen on the exit (output) side. The Ni layers were vertically mounted between two symmetrical glass cells. Before each experiment, the membrane was degreased in acetone, rinsed, ultrasonically cleaned in ethanol and etched in a 5 M HCl solution. Pd layer with a thickness of about 0.5 μm was preliminary electrodeposited on the exit side of the membrane. The exposed area was 1 cm$^2$ on both sides. A 0.5 M NaOH solution was introduced into the ionization cell and a 150 mV (Hg/HgO) potential was applied during a time sufficiently long to get a residual anodic current density lower than 1 μA·dm$^{-2}$. Hydrogen was generated electrochemically on the input (cathodic) side of the membrane by applying a constant cathodic current of 1 A·dm$^{-2}$ in a solution of 0.5 N H$_2$SO$_4$ with or without thiourea (0.2 g/l) additive. Both cells were equipped with a platinum grid as a counter electrode. At constant positive potential, kept on the output side of the membrane (0.150 V vs Hg/HgO reference electrode), all the hydrogen diffusing through the membrane and reaching the exit side of the membrane was oxidized. The ionization current, recorded under these conditions, was a direct measure of the hydrogen permeation rate ($I_2$). The permeation current was recorded against time (transient) until reaching a steady state ($I_2^{st}$). The steady-state permeation rate gives an indication of the attainment of constant hydrogen coverage, and

also gives an idea of the permeability of the deposit. The diffusion coefficient ($D$) was calculated according to the equation of McBreen [13]. The quantity of hydrogen ($Q_H$), permeating the deposits for 30 min polarization was calculated by integrating the permeation transients $I_2$ vs $t$.

For comparison, similar permeation tests were performed with metallurgically produced Ni foils with a thickness of 50 μm (Good Fellow, 99.9%).

RESULTS AND DISCUSSION

The samples of Ni layers were subjected to investigation of their texture. The data are summarized in Table 1. The texture is different, depending on the cathodic current density, applied for the deposition of Ni layers.

**Table 1**. Texture of electrodeposited Ni layers.

| Sample | Texture |
|---|---|
| Ni layer deposited at 0.5 A·dm$^{-2}$ | mixture 110 + 211 |
| Ni layer deposited at 2 A·dm$^{-2}$ | good 211 |
| Ni layer deposited at 5 A·dm$^{-2}$ | mixture 211 + 100 |
| Ni layer deposited at 20 A·dm$^{-2}$ | good 100 |

In order to connect the texture with the permeation efficiency of Ni layers, the same samples were subjected to permeation tests in a Devanathan cell. Figure 1 shows the permeation transients during charging of Ni samples, deposited at 0.5, 2 or 20 A·dm$^{-2}$.



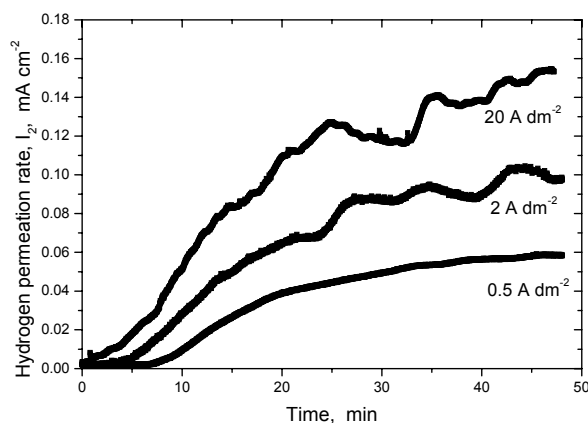Fig. 1. Permeation transients of Ni layers (50 μm), electrodeposited at 0.5, 2, 5 or 20 A·dm$^{-2}$ in Watts electrolyte, and charged with hydrogen in 0.5 N H$_2$SO$_4$.

It is observed an electrochemical noise on the permeation transients of the samples, deposited at higher current density than 0.5 A·dm$^{-2}$, due to the formation of more bubbles under these conditions. In this case, the values of $I_2^{st}$ are reached slowly. The data for $I_2^{st}$, $D$ and $Q_H$ are given in Table 2

Table 2 reveals more intensive and faster hydrogenation of the Ni layers deposited at a higher

current density, the effect being more pronounced at Ni layers, deposited at 20 A·dm$^{-2}$ with a texture [100]. Compared to the Ni foils, the $I_2^{st}$ and $Q_H$ values of Ni layers, deposited at 20 A·dm$^{-2}$ are nearly 2 times higher than those of Ni foils, i.e. the electrodeposited Ni layers have greater hydrogen permeability than the Ni foils.

**Table 2**. Steady-state permeation rate ($I_2^{st}$), diffusion coefficient ($D$) and quantity of hydrogen permeating for 30 min polarization ($Q_H$) calculated on the basis of permeation tests of Ni deposits or Ni foils charged with hydrogen (H$_2$SO$_4$) in a Devanathan cell.

| Sample | $I_2^{st}$, μA·cm$^{-2}$ | $D \times 10^9$, cm$^2$·sec$^{-1}$ | $Q_H \times 10^7$ mol·cm$^{-2}$ |
|---|---|---|---|
| Ni layer deposited at 0.5 A·dm$^{-2}$ | 59 | 2.8 | 4.6 |
| Ni layer deposited at 2 A·dm$^{-2}$ | 100 | 2.9 | 8.4 |
| Ni layer deposited at 5 A·dm$^{-2}$ | 129 | 3.0 | 12.3 |
| Ni layer deposited at 20 A·dm$^{-2}$ | 162 | 4.9 | 13.8 |
| Ni foil (Good Fellow, 99.9 % | 86 | 3.8 | 6.8 |

Figure 2 shows the successive transients of Ni layers, deposited at 0.5 or 2 A·dm$^{-2}$. The values of $I_2^{st}$ are reached faster at the second transient, therefore, the total quantity of hydrogen $Q_H$ permeated in the Ni layers is higher at the second charging, respectively. This means that Ni layers become more permeable. Moreover, the values of $I_2^{st}$ decreases to 0, when the charging current is switched off, i.e. the hydrogenation of the Ni layers is reversible.
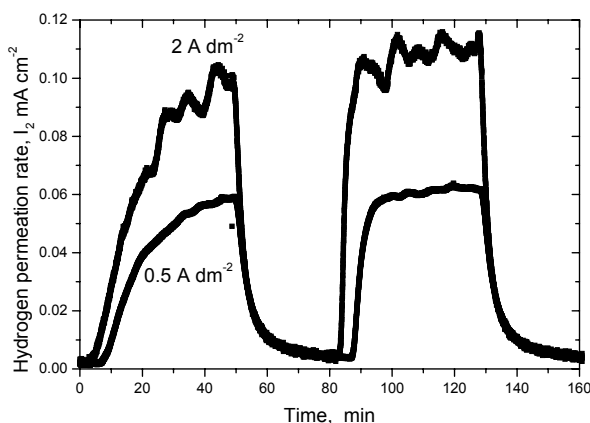
Fig. 2. Successive permeation transients of Ni layers (50 μm), electrodeposited at 0.5 or 2 A·dm$^{-2}$ in Watts electrolyte, and charged with hydrogen in 0.5 N H$_2$SO$_4$.

In Fig. 3 are compared the permeation transients of Ni layers, deposited at one and the same current density (0.5 A·dm$^{-2}$), but charged with a Tu-free solution of 0.5 N H$_2$SO$_4$ and with a solution of 0.5 N H$_2$SO$_4$ containing Tu. In the latter case, the values of $I_2^{st}$ are strongly increased as compared with the case of the absence of Tu in the charging solution. The same effect of greater hydrogen permeability in the presence of Tu in the charging solution is
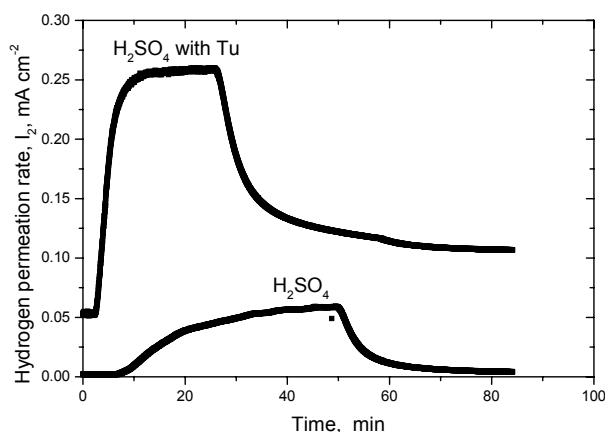
observed in the case of Ni foils (Fig. 4).

Fig. 3. Permeation transients of Ni layers (50 μm), electrodeposited at 0.5 A·dm$^{-2}$ in Watts electrolyte, and charged with hydrogen in 0.5 N H$_2$SO$_4$ in absence or in presence of thiourea (Tu).
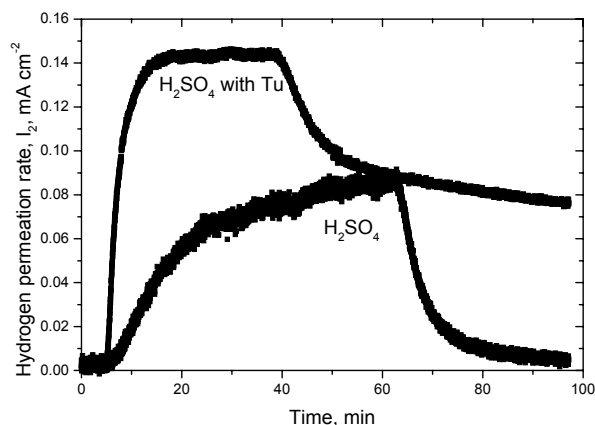
Fig. 4. Permeation transients of Ni foils (50 μm, Good Fellow, 99.9%), charged with hydrogen in 0.5 N H$_2$SO$_4$ in absence or in presence of thiourea (Tu).

Conclusion can be made that thiourea is a strong promoter of hydrogenation of the Ni material, electrodeposited Ni layers or metallurgically obtained Ni foils. This conclusion is confirmed by the data of $I_2^{st}$, $D$ and $Q_H$, given in Table 3.

**Table 3**. Steady-state permeation rate ($I_2^{st}$), diffusion coefficient ($D$) and quantity of hydrogen permeating for 30 min polarization ($Q_H$), calculated on the basis of permeation tests of Ni deposits or Ni foils charged with hydrogen (H$_2$SO$_4$ + Tu) in a Devanathan cell.

| Sample | $I_2^{st}$, μA·cm$^{-2}$ | $D \times 10^9$, cm$^2$·sec$^{-1}$ | $Q_H \times 10^7$ mol·cm$^{-2}$ |
|---|---|---|---|
| Ni layer deposited at 0.5 A·dm$^{-2}$ | 206 | 7.2 | 28.3 |
| Ni layer deposited at 2 A·dm$^{-2}$ | 160 | 9.7 | 23.9 |
| Ni layer deposited at 5 A·dm$^{-2}$ | 208 | 9.2 | 32 |
| Ni layer deposited at 20 A·dm$^{-2}$ | 266 | 13.7 | 44.8 |
| Ni foil (Good Fellow, 99.9%) | 144 | 8.2 | 20 |

CONCLUSION

It was observed that the Ni layers exhibit different texture, depending on the deposition current density. It was found that the values of $I_2^{st}$, $D$ and $Q_H$ are increased with increasing the deposition current density. The layers, deposited at a current density of 20 A·dm$^{-2}$ with a texture [100], are more permeable to hydrogen during their charging in $H_2SO_4$ solution as compared with Ni layers deposited at 0.5, 2 or 5 A·dm$^{-2}$ with a texture [110+211], [211] and [211+100], respectively. The addition of Tu to the charging $H_2SO_4$ solution has a strong promoting effect on the permeation parameters. At one and the same conditions, the electrodeposited Ni layers show faster and more extensive hydrogenation than the metallurgically obtained Ni foils. By adaptation of the Devanathan method, further investigations in a charging solution of KOH are planned.

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ПРОНИКВАНЕ НА ВОДОРОД В Ni СЛОЕВЕ ОТЛОЖЕНИ ОТ УОТСОВ ЕЛЕКТРОЛИТ

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(Резюме)

Проведени са електрохимични изследвания върху процеса на проникване на водород в електроотложени Ni слоеве с цел да се установят факторите, влияещи върху проникването и транспорта на водород в тези материали. Никеловите слоеве са отложени от Уотсов електролит при различни катодни плътности на тока. Намерено е, че отложените слоеве при сравнително висока плътност на тока 20 A·dm$^{-2}$ с текстура [100] показват по висока степен на наводородяване по време на катодна поляризация в разтвор на 0.5 N $H_2SO_4$ в сравнение с Ni слоеве, отложени при 0.5, 2 или 5 A·dm$^{-2}$ съответно с текстура [110+211], [211] и [211+100]. Добавянето на тиоуреа към разтвора на $H_2SO_4$ оказва силен стимулиращ ефект върху параметрите на проникване. При едни и същи условия, електроотложените Ni слоеве показват по-бързо и по-интензивно наводородяване в сравнение с металургично получените Ni фолия.