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A dilatometric study of nickel wire electrode electrochemically charged by hydrogen

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Abstract

The cathodic charging of nickel with hydrogen was studied with simultaneous measurements of dimensional variations within the solubility region. Relative dimensional changes as low as 3×10^{-6} could be detected which makes this measuring combination sensitive and powerful in studying the behavior of metal hydrogen systems, particularly in the low hydrogen concentration region.

The effect of current density, solution acidity and type of promoter on the extent of relative dimensional variations induced by the cathodic process is presented. Also, the process coulombic efficiency, i.e. the charge fraction converted into absorbed hydrogen atoms, is calculated and interpreted via the dimensional changes.

Keywords: Nickel–hydrogen system; Cathodic charging; Relative dimensional variations

1. Introduction

The absorption of hydrogen by nickel has in the past been thoroughly investigated, in particular under cathodic charging conditions [1–6]. The hydrogen content in nickel interacting with the gaseous phase under mild conditions is extremely low and can only be estimated via appropriate thermodynamic calculations which lead to diverse results. Thus, for 20°C and under 1 atm equilibrium pressure the values presented in the literature for the H/Ni atomic ratio range from 4×10^{-6} [1] to 6×10^{-5} [2]. However, cathodic loading of hydrogen allows the introduction of much larger hydrogen concentrations within the metal, and under these conditions it was possible to load nickel to atomic ratios in the range 0.5 to 0.7, depending on the applied current density and the thickness of the nickel sample in the direction of hydrogen penetration flux [3–5]. By adding promoters such as thiourea, AsO_2^- and SeO_3^{2-} to the solution, it was possible, under high current densities (about 20 mA cm^{-2}), to charge nickel foils to atomic ratios as high as 0.9 [6,7]. The mechanism by which these 'hydrogen charging promoters' (including some other elements of Group V and VI of the periodic table) act with nickel as well as with other metallic compounds (such as steel [8]) is not yet clear. It was postulated [9] that these promoters impede the surface recombination sites on steel and thus increase both the rate of hydrogen absorption and its steady state content.

In a previous article [10], combined electrochemical–dilatometric measurements with the Pd/H and Pd–Ni/H systems were presented and the influence of the current density on the charge efficiency as related to relative dimensional changes was discussed. The ability to monitor relative dimensional changes induced by hydrogen absorption in a highly sensitive manner provides an excellent tool for in situ study of parameters such as phase composition, absorption kinetics and mechanism, electrochemical charging efficiency, influence of surface contaminants, as well as the effect of absorption promoters, etc.

In this paper, relative dimensional changes of nickel as induced during the electrochemical charging with hydrogen are studied. It should be noted that although palladium and nickel are of the f.c.c. type, their thermodynamic and kinetic characteristics of interaction with hydrogen differ significantly [11,12]. The aim of this study is to demonstrate the sensitivity of the simultaneous electrochemical–dilatometry mea-

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surements in studying the small effects induced by hydrogen absorption as expected for nickel under ambient conditions.

It is worth mentioning that the study of hydrogen absorption into nickel is relevant to the understanding of the significance of hydrogen interaction with construction materials of nickel–metal hydride and Ni/H_2 cells. As discussed by Visintin et al. [13], a possible mechanism for the self discharge of a nickel–hydride battery is the reduction of nickel oxyhydroxide by dissolved hydrogen according to,

$$NiOOH + \frac{1}{2}H_2 \rightarrow Ni(OH)_2$$

However, under certain conditions, and particularly owing to the relatively high operating pressure (30–50 atm [13]) of these cells, penetration of hydrogen into the nickel metal lattice is also possible and the consequence of such a process to the performance of the cells should be considered.

The importance and relevance of hydrogen absorption and transport in nickel and its alloys in nuclear and fusion technology [14,15] should be mentioned too.

2. Experimental

The simultaneous measurement of dimensional, potential and charge changes were conducted in the cell shown schematically in Fig. 1.

Basically, this is a three-electrode cell in which the normal hydrogen electrode (NHE) is a reference and a Pt slab coated with platinum black is the auxiliary electrode.

The working electrode was made of a nickel wire 99% minimum purity (Johnson Matthey), 0.0127 cm in diameter. The length exposed to the solution was 6.5 cm. The wire, used without any additional thermal or mechanical treatment, was spot welded to two pieces of platinum wire isolated from the solution by a shrinkable Teflon tubing.

The end of one platinum wire was anchored to the bottom of the cell and the end of the other one to a thin flexible steel blade fixed to a side arm stemming from the top of the cell. The steel blade kept the working electrode under constant stress, thus allowing monitoring of any longitudinal change with the tip of a Millitron No. 1306 inductive gauging head placed on it. By this unit it was possible to monitor dimensional variations as low as 0.02 μm. All length variations were measured with respect to a reference nickel wire, identical to the working electrode, installed in an identical cell and dipped in the same solution. This allowed a continuous compensation of non-desirable variations, e.g. caused by temperature changes and casual vibrations.

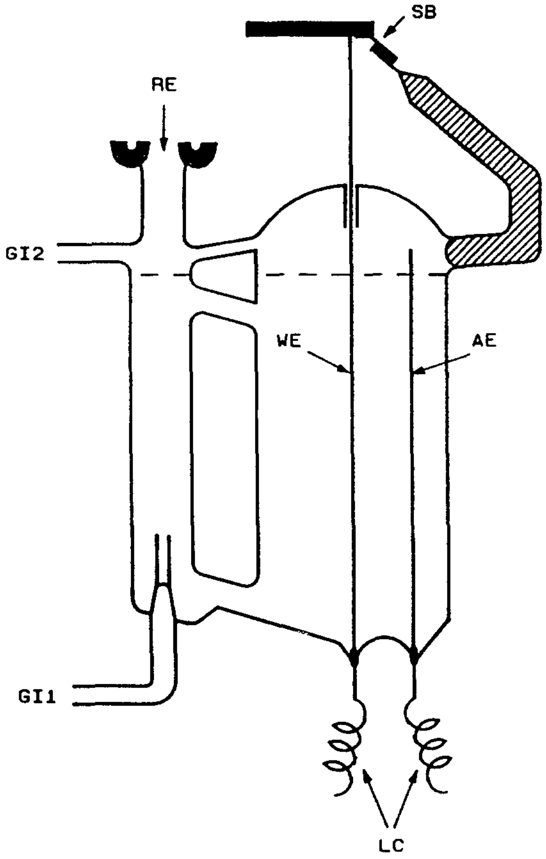

Fig. 1. Schematic representation of the electrochemical–dilatometric cell: WE, working electrode; AE, auxiliary electrode; LC, electrode leads; RE, reference electrode; SB, steel blade; GI1, GI2, purging gas inlets.

Experiments were performed in 1 N KOH and H_2SO_4. Solutions of pH 2 and 3 were made with the appropriate concentration of sulfuric acid and Na_2SO_4 was added to a total sulfate concentration of 1 N. In most of the experiments, thiourea or As_2O_3, 0.2 g l^{-1} were added to the solutions as hydrogen absorption promoters. The solutions were constantly purged with argon (99.999% grade) fed to the cell through a side inlet.

All the experiments were performed at 25 ± 2°C in galvanostatic mode using an EG&G PAR Model 273 potentiostat/galvanostat. The potential and length variation signals were monitored by a Nicolet 4094 digital oscilloscope.

3. Results and discussion

3.1. Relative dimensional variations in acidic and alkaline solutions

Fig. 2 shows an example of the relative dimensional variations as a function of time in different acidity levels under constant current charging. Fig. 3 summarizes the relative dimensional variations as a function

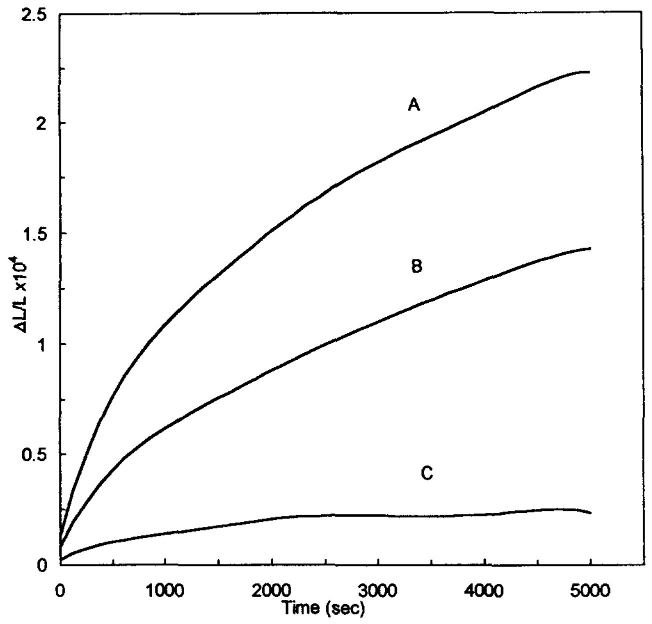

Fig. 2. Relative dimensional variations as a function of charging time at current density 2 mA cm^{-2}; solutions for A, B, C are 1 N H_2SO_4, pH 2 and 1 N KOH respectively. All solutions contained 0.2 g l^{-1} thiourea.

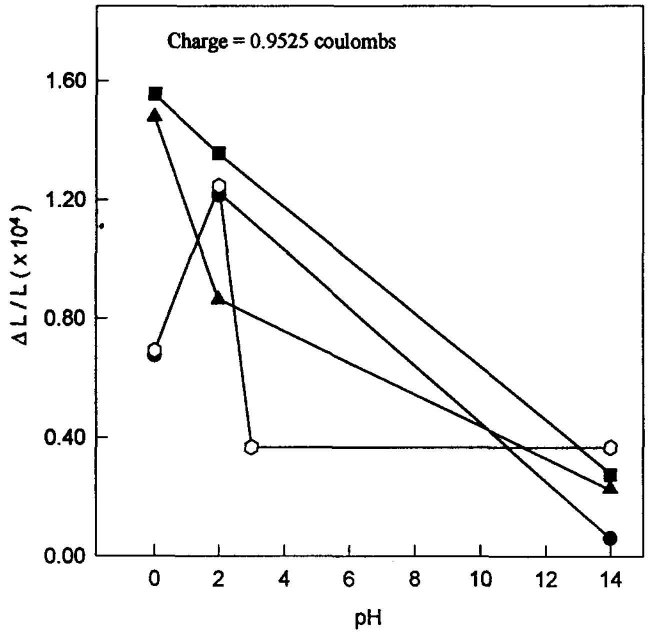

Fig. 3. Relative dimensional variations as a function of pH for different current densities at constant charge, 0.9525 C: ●, 0.5; ■, 1.0; ▲, 2.0; ○, 3.0 mA cm^{-2}. All solutions contained 0.2 g l^{-1} thiourea.

of the acidity at different current densities and at the same charge level.

The results shown in Fig. 2, as well as all other dimensional changes measurements, in fact represent an average situation. Owing to the small diffusion coefficient of hydrogen within nickel [9] it can be anticipated that the solution–metal interface will reach saturation with hydrogen atoms shortly after the current onset. Then, a radial concentration gradient of hydrogen will start to build up within the wire. It can be estimated, by means of the Einstein–Smoluchowski relationship, $\overline{X^2} = 2Dt$ (X is the random walk distance, D the diffusion coefficient and t the length of an experiment), that hydrogen atoms will reach the wire center after approximately 10^4 s, i.e. much longer than any of the experiments performed within the framework of this work. The implications are that during most of each experiment duration, a considerable portion of the wire is either partially loaded with hydrogen or not loaded at all, i.e. α, β and pure metal phases coexist within the metal. The measured relative dimensional changes are therefore an average result of transversal (assuming an axial homogeneous charging) stress and strain gradients induced by the radial concentration gradients.

The situation presented in Fig. 3 is somewhat confusing, particularly at the high acidity region. At the highest and the lowest current densities applied, the relative dimensional variations have a maximum at around pH 2, whereas at other current densities the relative dimensional variations decrease gradually as the pH increases. In all the current densities applied, the relative dimensional variations attain low values as the alkalinity approaches high values. In addition, it is hard to observe a logical trend with respect to the influence of the current density on the relative dimensional variations. The behavior described above is relevant to the entire charge range that was applied to the electrode. Since the intensity of the relative dimensional variations in the nickel wire is exclusively influenced by the amount the electrolytically generated hydrogen atoms which absorb on the surface and then diffuse into the metal, the results shown in Fig. 3 should be interpreted based on the physicochemical factors governing the generation of hydrogen atoms in the present system. These factors can be summarized as follows:

(1) the current density which determines the rate of production of hydrogen atoms at the surface;
(2) the degree of surface coverage with thiourea. This is determined not only by the concentration in the bulk solution but also by the deviation of the electrical double layer potential from the potential of zero charge (pzc). It is well known [16] that in aqueous solutions neutral organic molecules show a maximum surface coverage at the pzc (which is identical to the electrocapillary maximum) of a conductive surface at which the surface binding energy of the competing polar water molecules minimizes. Under a specified solution composition, the deviation from the pzc depends on the applied electrochemical conditions, e.g. the current density;
(3) the solution pH. This factor has a broad spectrum of effects on the electrode behavior. By

shifting the pH from acidic to basic, the mechanism of hydrogen generation changes. Also, at the same time the nickel electrode is covered by a layer of $Ni(OH)_2$ which may hinder hydrogen absorption onto the metal and penetration into it. In addition, as discussed below, the chemical stability of thiourea is pH dependent, i.e. it is less stable in alkaline solutions [17].

It is evident from Fig. 3 that, under all current densities, the relative dimensional changes are least at highly alkaline solutions. Moreover, judging from the behavior under 3 mA cm^{-2}, which is the only current density that was tested at pH 3, it may be speculated that relative dimensional changes will decrease sharply at this pH for the other current densities too. According to the points made above, this may be due to a partial deactivation of the thiourea, impeding hydrogen transport by the surface hydroxide layer, and due to the smaller hydrogen discharge rate under alkaline conditions. As the pH decreases, the relative dimensional changes increase due to higher hydrogen concentration within the metal. However, for 0.127 and 0.756 mA cm^{-2}, these variations decrease again at highly acidic solution. No reasonable explanation is available at present for this behavior. A possible justification is that at the lowest and the highest current density applied at this pH range, the electrode potential is significantly shifted from the pzc, thus reducing the thiourea surface concentration. However, this point should be studied further.

3.2. The effect of the catalyzing agent

As already mentioned, the effectiveness of thiourea as a catalyzing agent for hydrogen absorption is pH dependent due to the dependence of its chemical stability on the acidity of the solution. This results from the fact that the S=C group in thiourea is more stable under acidic conditions [17]. Thus, partial deactivation and concentration reduction of the catalyzing agent at basic solutions should not be ruled out. At this point it should be noted that there are some contradicting data in the literature regarding the effectiveness of thiourea as a hydrogen absorption promoter under different acidity levels. On the one hand, Baranowski and Smialowski [18] found thiourea as a mostly effective catalyzing agent for charging nickel with hydrogen in acidic solutions, which is in accordance with the results of this work. On the other hand, Akita et al. [19] used thiourea for catalyzing charging of Pd and Pd–Rh in alkaline solutions.

Some other agents which also enhance the absorption of hydrogen are mentioned in the literature. Among them, As_2O_3, KI and Na_2S [20] are worth mentioning.

It is, therefore, interesting to study the effects of the catalyzing agent on the hydrogen absorption on nickel through the relative dimensional variations occurring while exposing to cathodic currents. This is shown in Figs. 4 and 5 for thiourea and As_2O_3 in acidic and basic solutions respectively. It is evident that in acidic solution thiourea is much more effective compared with arsenic trioxide; both the rate and the extent of relative dimensional variations are much larger for thiourea. This situation is reversed for the alkaline solution. In Fig. 5, results for the case where no catalyzing agent is added, are also presented for comparison. In this case, the electrode was coated with

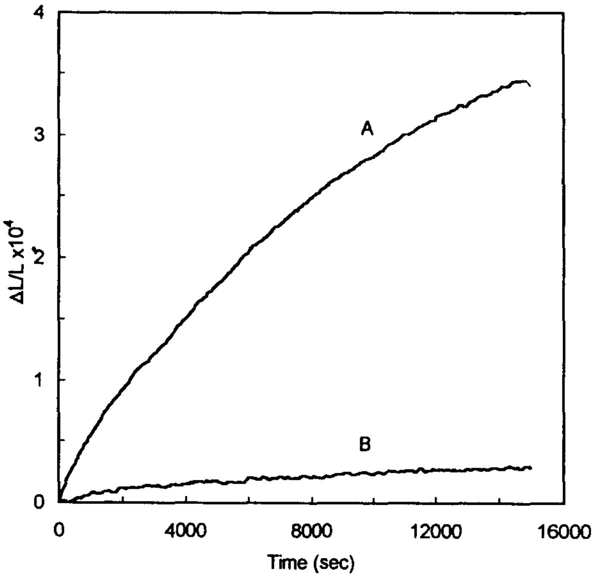

Fig. 4. Relative dimensional variations as a function of charging time for 1 mA cm^{-2} and 1 N H_2SO_4: A, with thiourea; B, with As_2O_3.

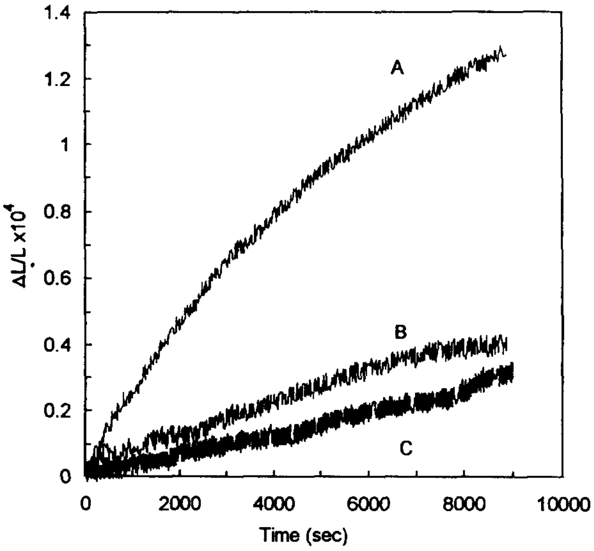

Fig. 5. Relative dimensional variations as a function of charging time for 1 mA cm^{-2} and 1 N KOH: A, with thiourea; B, with As_2O_3; C, no promoter added.

Pd in order to prevent the influence of an hydroxide layer on the absorption rate of hydrogen. It is evident that albeit with the Pd protecting layer, the dimensional changes in this case are smaller compared with the cases where promoters are present.

It can also be seen that relative dimensional variations after 1500 s for the solutions containing thiourea are about 35 times more in acidic solutions compared with alkaline solution. In solutions containing arsenic trioxide, relative dimensional variations are almost the same for acidic and alkaline solutions.

It is generally accepted [20] that thiourea enhances the absorption of hydrogen by retarding the Tafel recombination reaction which is pH independent. On this basis, the difference between the effect of thiourea on the relative dimensional variations in the alkaline and acidic solutions should be interpreted by means of the differences in its stability in the two solutions as discussed above.

Owing to its chemical stability, the similarity of the effectiveness of arsenic trioxide in both solutions is not surprising. However, the mechanism by which arsenic trioxide enhances hydrogen absorption into metals is not yet clear, and several ideas are discussed in the literature. There is some evidence that it acts by enhancing the Volmer discharge reaction [21] to a small extent, hence the enhancement of relative dimensional changes.

3.3. Relative dimensional variations and charging efficiency

Cathodic reduction of hydronium ion (in acidic solutions) or water (in alkaline solutions) has been recognized as a highly efficient method for introducing hydrogen into nickel [22], as well as into many other metals. However, none of the studies dealing with this method directly discuss the matter of the coulombic efficiency of the process (in terms of the number of moles of hydrogen atoms absorbed by the metal compared with the total charge). The coulombic efficiency of the experiments made by Baranowski and Smialowski [5] in charging thin layers of nickel with a current of 20 mA cm^{-2} can be calculated from their data. Values as low as 1–2% are obtained.

This point is interesting because it can give some idea on the relationship between the rate of hydrogen diffusion into the metal and the rate of hydrogen atoms recombination on the surface via the Tafel or Herovsky mechanisms. For instance, as discussed above, for nickel it can be expected that owing to the small diffusion coefficient of hydrogen within the metal (about 2×10^{-9} cm^2 sec^{-1} [9]), surface saturation will be attained rather quickly, resulting in an increased share of the hydrogen recombination process, thereby decreasing the coulombic efficiency. The low values mentioned above support this view.

Dimensional measurements allow calculation of charging efficiency under very low hydrogen concentration levels in the metal. It was found [23] that for many f.c.c. metallic matrices, the unit cell volume change ΔV as a function of interstitial hydrogen content fell into the same linear relationship, which for concentration values up to $n = [\text{H}]/[\text{M}] = 0.7$ shows a slope of 11.428 Å^3. For nickel, with lattice parameter $a = 3.524$ Å, the relative lattice volume change for a unit change in n is, $\text{d}(\Delta V/a^3)/\text{d}n = 0.2611$. The relation between the relative volume change and the relative lattice parameter change is expressed by,

$$\frac{\Delta V}{V} = 3\frac{\Delta a}{a} + 3\left(\frac{\Delta a}{a}\right)^2 + \left(\frac{\Delta a}{a}\right)^3$$

which, for very small changes can be reduced to

$$\frac{\Delta V}{V} = 3\frac{\Delta a}{a} = 3\frac{\Delta L}{L}$$

where $\Delta L/L$ is the longitudinal change and $V = a^3$ is the lattice volume of the pure metal.

Thus, with the slope $\text{d}(\Delta V/a^3)/\text{d}n$ indicated above, it is possible to calculate the hydrogen content in the metal for the relative dimensional changes measured in this study. The coulombic efficiency in charging the metal with hydrogen could than be easily figured out.

In Figs. 6 and 7 the coulombic efficiency is shown as a function of the cathodic charging current density for different relative dimensional changes and for two acidity levels. It is evident that in both acidities the efficiency is low, i.e. in the range 0.1–20% where the

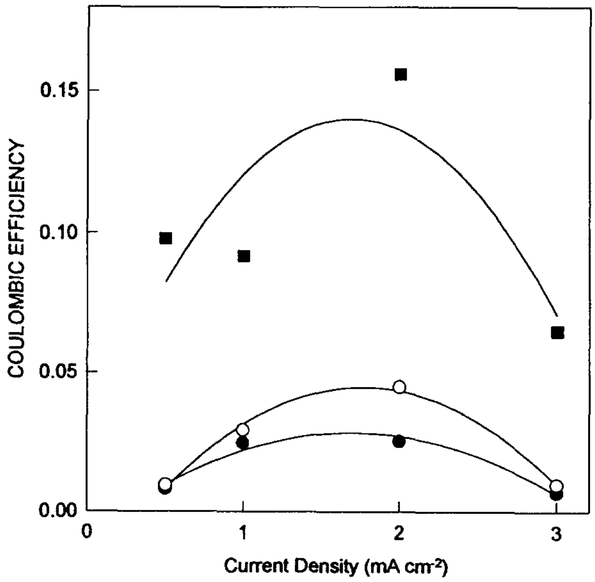

Fig. 6. Charging efficiency as a function of current density for the following relative dimensional variations: ■, 1.51×10^{-5}; ○, 7.69×10^{-5}; ●, 1.23×10^{-4}; 1 N H_2SO_4 + thiourea.

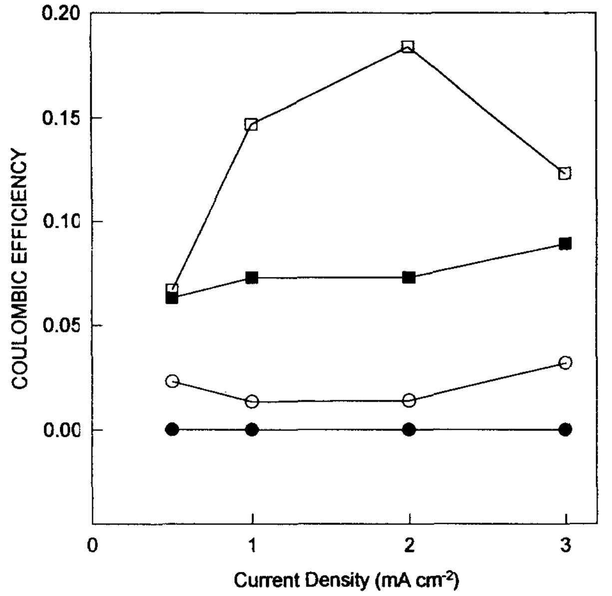

Fig. 7. Charging efficiency as a function of current density for the following relative dimensional variations: □, 7.25×10^{-6}; ■, 1.51×10^{-5}; ○, 7.69×10^{-5}; ● 1.23×10^{-4}; pH 2 + thiourea.

larger values are obtained for the highly acidic solution as expected from the Volmer mechanism. However, a striking feature in these results is the decreasing efficiency with increasing dimensional change. This can be understood on the basis of the rather slow diffusion processes within the metal which cause an increased surface concentration (and, therefore, increasing the dimensional change), resulting in an increased recombination rate, as discussed above.

On the same basis, the behavior with respect to the current density can be justified. It can be noticed that at the higher acidity, the efficiency increases at the low current densities and then declines toward the higher values at the entire relative dimensional changes studied. In the lower acidity, the same trend is evident at the larger dimensional change, whereas at the lower relative dimensional changes the efficiency is practically constant at the current density range studied. At low current densities, the production rate of atomic hydrogen via the Volmer reaction is small enough to allow for their diffusion from the surface, thus lowering the surface saturation degree and reducing the recombination rate. As the current density increases, the surface concentration increases, increasing the diffusion driving force. At much higher current densities, the surface saturation degree increases to such values in which the recombination rate exceeds that of the diffusion, resulting in a reduced coulombic efficiency. This phenomenon is more pronounced with the highly acidic solution since then, at the same current density, surface saturation degree is larger.

4. Conclusions

The combined electrochemical–dilatometric technique described in this work enables the detection of relative dimensional changes as low as 3×10^{-6}. According to Ref. [23], these variations correspond to hydrogen absorption within the nickel lattice to an atomic ratio of 3.45×10^{-5} (about 0.001 w/o ppm). Atomic ratios and hydrogen concentrations in this range can hardly be detected and analyzed by conventional methods (e.g. gas phase analysis); therefore, the effect on the system properties cannot be interpreted accurately in this range.

It is therefore evident that the present system provides a sensitive and convenient tool for analyzing the influence of minute as well as high concentrations of hydrogen absorbing into metals.

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