A study of the underpotential deposited hydrogen on the nickel deposited electrode in alkaline media

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Hydrogen evolution reaction has been studied on the nickel deposited electrode. Two reduction peaks at -1 V/Ag-AgCl and -1.3 V/Ag-AgCl and one oxidation peak at -1.3 V/Ag-AgCl have been observed. Shift due to oxidation peak arises from change of cathodic limit, attributed to the two competitive reactions on the surface. The peak located on the more anodic side is due to the oxidation of Hupd and the second peak due to the oxidation of Hupd. The sodium ion has no effect on the hydrogen evolution reaction. The diffusion coefficient of hydrogen is calculated to be $D=2.88\times10^{-10} \text{ cm}^2\text{s}^{-1}$ using impedance technique.

Sodium ion participates in the hydrogen evolution reaction as an intermediate. Careful consideration of reduction potential of sodium and hydrogen, imposed some doubts about validity of the suggested mechanism. Non-stoichiometric nickel hydride formation, NiH$_x$, on the nickel electrode in the sulphuric acid have been reported by Baronowsky. The formation and presence of nickel hydride in the hydrogen evolution process has been reported by Conway and Soarose, independently. Bernardiniand et al. confirmed the formation of nickel hydride and showed the dependency of hydride formation with temperature. Baronowski suggested five different structural geometry for nickel hydride.

Two intermediates are recognized in the process of the hydrogen evolution reaction. The thermodynamic reduction potential of hydrogen is not achieved (more positive than $E^0$), all reduced hydrogens are really Hupd. When the reduction potential is more negative than $E^0$, the reduced hydrogen is actually Hupd. This behaviour is expressed by this fact that dimension of Hupd is less than 3 (ref. 10). Consequently, the surface is not totally saturated by hydrogen. As the dimension of adatom is less than 3, potential of hydrogen reduction gets more positive value than $E$, similar to platinum and palladium surfaces.

The object of the present work is an attempt to shed light on detail of HER process and explore a realistic mechanism to account properly and fit adequately the experimental results. Conventional electrochemical methods were used to obtain experimental data.

**Experimental**

All chemicals used were Analar grade (Merck) and were used without further purification. All solutions were prepared in doubly distilled water. Electrochemical studies were carried out in a conventional three electrode cell powered by a fully computerized E.G. & G and electrochemical system capable of running cyclic voltammetry and impedance spectroscopy. Nickel was deposited on the graphite electrode in solution containing NiCl$_2$·6H$_2$O (42 g/l)+NiSO$_4$·6H$_2$O (280 g/l)+HBO$_3$·3 (30 g/l) at constant current density 20 mA/cm$^2$, 50°C. This electrode was employed as the working electrode and its potential was recorded against home made Ag/AgCl electrode. The auxiliary electrode was graphite electrode. Cyclic voltammetry studies were performed using an EG & G Model 273 A potentiostat/galvanostat run by an IBM pc/value point computer through 270/250 software while impedance studies were carried out using a Solartron SI1255 frequency response analyzer supported by the Solartron S11287 potentiostat/galvanostat and run by the mentioned computer through Z plot and Z view softwares.

**Results and discussion**

The cyclic voltammogram of the nickel electrode was obtained in the alkaline solution, in the range of 0 to -1.4 V/Ag-AgCl with a scan rate of 20 mVs$^{-1}$. Two reduction peaks at -1 and -1.3 V/Ag-AgCl were identified. Hydrogen evolution was observed by naked eyes at -1.4 V/Ag-AgCl. An oxidation peak appeared at -0.9 V/Ag-AgCl. Two reduction peaks merged as only one peak at -1.2 V/Ag-AgCl and the oxidation peak shifts to a more positive value, on increasing the potential sweep rate. The current intensity increased on decreasing the pH value. The cathodic peaks shifts to more negative potential values on decreasing the
pH. It has been suggested that, the sodium ion does not play the role of an intermediate, contrary to Matsudu proposal. If the sodium ion is an intermediate according to the following mechanism:

\[
M^{n+}+ne^{-}\rightarrow M(I) \\
M(I)+nH\rightarrow nH(a)+nOH+M^{n+} \\
H(a)+H(a)\rightarrow H_2
\]

where, M(I) and H(a) stands for sodium and atomic hydrogen respectively. An enhancement of the reduction peak intensity on increasing the concentration is expected to be observed. But such a behaviour is not seen. On the other hand, Mont Karlo simulation shows that in co-adsorption of H and K, K exerts an inhibitor effect on the hydrogen adsorption. The involvement of the sodium ion as an intermediate species has been ruled out.

In the next step, cyclic voltammetry was performed in order to differentiate and identify the two reduction peaks in the range 0 to -0.6 V, with a scan rate of 20 mVs⁻¹. The cathodic limit was gradually increased up to -1.4 V. The oxidation peak which was already detected at -0.4 V in the first cyclic voltammogram, now moved to -0.8 V. Such a trend was observed in all concentrations of NaOH solutions. This experiment was performed again with a scan rate of 100 mVs⁻¹. The oxidation peak did not shift in contradiction to the cyclic voltammogram obtained at 20 mVs⁻¹. The possible reactions in the solution can be written as:

a) reduction and hydrogen evolution reactions

\[
\text{M}+\text{H}_2\text{O}+e^{-}\rightarrow \text{MH}_{\text{ads}}+\text{OH} \\
\text{MH}_{\text{ads}}+\text{H}_2\text{O}+e^{-}\rightarrow \text{M}+\text{H}_2+\text{OH} \\
\text{MH}_{\text{ads}}+\text{MH}_{\text{ads}}\rightarrow \text{H}_2
\]

b)nickel electrode reactions

\[
\text{Ni}+\text{OH}^{-}\rightarrow \text{Ni(OH)}_2+cE^\circ=-0.7V/\text{SHE} \\
\text{Ni(OH)}_2+2\text{OH}^{-}\rightarrow \text{NiO}_2+2\text{H}_2\text{O}+2e^-E^\circ=-0.49V/\text{SHE}
\]

The thermodynamic potential of hydrogen reduction, in 6 M NaOH solution was calculated, using the following equations:

\[
E = -0.06\,pH = -0.06 \times 14 = -0.84\,V
\]

The value of the calculated potential is found to be -0.84 V for normal hydrogen electrode and -1.06 for Ag/AgCl electrode. Considering the hydrogen electrode potential over the nickel electrode, the second reduction peak can be attributed to hydrogen reduction. The first reduction peak has no relation with sodium ion, due to its thermodynamic potential, lack of any dependency with sodium ion concentration and the intensity of the reduction peak. Two scenarios could be proposed. In the first one, the first peak is due to hydride formation and in the second one, a possible pathway may exist for Hupd formation. However in both the cases, hydrogen ions are reduced, which can be written as:

\[
\text{M}+\text{H}_2\text{O}+e^{-}\rightarrow \text{(MH)}+\text{OH}^\cdot
\]

where (MH) stand for either NiH₄ (hydride), or Ni-H_ads. (MH) phase is stable until hydrogen evolution potential is not provided. When the cathodic limit was shifted to more negative values (-1.3 V), the oxidation peak shifted to more negative values. When hydrogen was liberated, this peak was removed and oxidation peak appeared at -0.8 V, arising from Hupd. The oxidation peaks are independent of oxidation of Ni to Ni(OH)₂ or following reaction, Ni(OH)₂ to NiO₂, since their potentials do not match with observed peak potentials. Perhaps one may try to relate the second oxidation potential to Ni(OH)₂ to NiO₂. But such a assumption is totally wrong, since there is no Ni(OH)₂ on the surface, due to the presence of atomic hydrogen.

Two competing reactions take place. As far as the potential of the hydrogen evolution is not applied, the reaction (1) plays the dominant role, and the oxidation peak which shifts to negative value belongs to it. As we enter the region of Hupd, the region with over potential more negative in respect to the thermodynamic potential of hydrogen reduction, the second reaction begins to run, as follows:

\[
\text{(MH)}+\text{H}_2\text{O}+e^{-}\rightarrow \text{M}+\text{H}_2+\text{OH}^\cdot \quad \text{(2)}
\]

The slope of the Tafel line was found to be 115 mV showing electrochemical desorption. Heyrovsky mechanism account for the hydrogen evolution. In the sweep oxidizing potential, if the reverse potential is located at Hupd no (MH) is available on the surface, under this situation only Hupd is present and the oxidation peak is related to it. But at more positive value with respect to thermodynamic potential, we encounter with (MH), which is different from Hupd in respect to structure and dimension and demonstrate its own oxidation potential. When the potential sweep rate is
changed from 20 mVs\(^{-1}\) to 100 mVs\(^{-1}\), only a single oxidation peak is observed at around -0.4 V, due to higher potential sweep rate relative to rate of reaction (2), consequently (MH) phase cannot be destroyed in such a short time. The observed oxidation potential arises from oxidation of (MH) phase. This is confirmed when CV's are plotted in the range of 0.0 to -1.4V at different scan rates. Two oxidation peaks are observed at 35 and 50 mVs\(^{-1}\), due to the two competitive reactions.

Electrochemical impedance spectroscopy was employed to shed light on the data obtained by the cyclic voltammetry method. The Nyquist plots were obtained at dc offset potential equal to those potentials, preimposed on the linear voltammetry, in the range of 100 kHz to 1 mHz. As demonstrated in Fig. 1, one semicircle followed by a line is obtained. As dc offset potential changes to more negative values, the slope of the line decreases and gradually converts to a semicircle and a line. At dc offset potential equal to -1.3 V, the first semicircle combines with the second one and actually only one broad semicircle is observed. This experiment was proceeded at different concentrations. When the trend of imposing dc offset potential is reversed, the semicircle obtained at forward potential cannot be superimposed with the one obtained at reverse potential (-1.3 to -0.8 V). After -0.8 V the semicircle obtained at forward potential can be completely superimposed on the semicircle obtained at reverse potential. The observed impedance results are in agreement with the CV results. The first semicircle with the capacitance of the order \(10^{-4}\) F cannot be attributed to double layer capacitance. As a matter of fact the first semicircle originates from formation of (MH) phase and its capacitance (Fig. 1), the value of the capacitance remains constant. This behaviour may be due to the saturation of the surface. We can also add, increasing the value of this capacitance with concentration, support the (MH) phase formation, since at lower pH, more hydrogen is available. At very negative potential, the second reaction (B) proceeds, two semicircle combine and finally just one broad semicircle emerges. Such patterns are also observed in the plots of phase shift vs \(\omega\). There are two time constants at dc offset potential equal -1.3 V. At this potential only one time constant is observed. At reverse dc offset potential, up to -1.1V only one time constant is observed, and at potential more positive than -1 V, two time constants are observed again. The maximum phase shift is displaced with changing dc offset potential, and is in agreement with (MH) phase destruction upon hydrogen evolution. In the reverse dc offset potential and in the absence of (MH) phase, the second time constant can only be observed if the dc offset potential is in the suitable range, in which the (MH) phase can be formed again. Still more, the phase shift replacement reveals that the equivalent circuit is changed with changing dc offset potential and obviously the values of each circuit element is changed.

By means of the slopes of the lines in Nyquist plots and the following equations, the diffusion coefficient of hydrogen was calculated:

\[
R = \frac{R_0 - 2\sigma^2 C}{x} = \frac{RT}{(2^n^2 n^2 A D^2)} \left[ \frac{1}{C_{D}} + \frac{1}{C_{R}} \right]
\]

\[D = 2.88 \times 10^{-10} \text{ cm}^2 / \text{s}\]

Such a low value is due to the diffusion of hydrogen to the bulk of metal. Hydrogen evolution accounts for appearance of the second semicircle. Brown et al. reported \(D = 6 \times 10^{-10} \text{ cm}^2 / \text{s}\). The radius of this semicircle is reduced on increasing the dc cathodic offset potential. This conclusion is justified with hydrogen evolution reaction.

Finally the nature of (MH) should thoroughly be explored. (MH) phase is either a nickel hydride or hydrogen involved in this phase, is actually adsorbed
However, formation of palladium hydride is reported<sup>11</sup> but we cannot simply deduce the formation of nickel hydride.

Bernardini <i>et al.</i> reported that oxidation peak at -0.9 V is due to oxidation of nickel hydride β phase, at -0.48 V due to α phase and at -0.6 V due to interstitial hydrogen in nickel crystal<sup>5,6</sup>. Two broad peaks were detected at medium sweep rates. If the formation of nickel hydride is taken for granted, similar to reported<sup>*</sup> sequentially the hydrogen phase transforms. The β phase should be destroyed upon hydrogen evolution<sup>5</sup>, so the peak at -0.8 V cannot be attributed to β phase. On the other hand the peak due to the oxidation of α phase is not observed. If similar behaviour is expected, for palladium, with decrease in available hydrogen, β phase should be transformed to α phase and its peak should appear at -0.48 V<sup>5</sup>. But such expectation is not achieved and the assumption of hydride formation is rejected.

In the case of second assumption, the presence of H<sub>1</sub> on the surface, as expressed in the introduction, because i < 3 (dimension), H<sub>1</sub> is located in a place where, the potential is more positive than thermodynamic potential. As potential is moved towards negative values, more hydrogens are adsorbed and consequently increases. Thus, there is a specific E for each adatom which has its own dimension. This is clearly demonstrated by shifting oxidation potential upon increasing cathodic domain, at a scan rate of 20 mVs<sup>-1</sup>. When hydrogen evolution is observed, i = 3, and all H<sub>1</sub>'s are removed and standard oxidation potential of hydrogen is reached. As totally expressed, (MH) phase is actually MH<sub>1</sub>.

On the basis of this study the following conclusions could be obtained:

The formation of subsurface absorbed hydrogen atoms have been clearly and conclusively demonstrated. The Nyquist plots show one semicircle followed by a line to more negative values, the slope of the line was decreased, and gradually converts to a semicircle and a line. The diffusion coefficient of hydrogen was calculated to be D = 2.88 × 10<sup>-10</sup> cm<sup>2</sup>/s which shows hydrogen diffuses through the nickel.

**References**