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The influence of carbon monoxide on the voltammetric behaviour of nickel in acid solutions

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The voltammetric behaviour of nickel in acid solutions is considerably modified by the presence of CO. As in plain acid the voltammogram also exhibits two main anodic peaks, but in this case, the adsorption of CO on the nickel surface shifts the metal electrodissolution to more positive potentials, and increases the contribution of the second electrooxidation current peak at the expense of the first one. The latter is the main peak in CO-free acids. The presence of CO adsorbates also decreases the charge of the $Ni(OH)_2/NiOOH$ redox couple in alkaline solutions. The potential shift of the nickel electrooxidation reaction in acids follows the trend which is expected from the energy difference between CO and H_2O adsorption on nickel in the gas phase.

1. Introduction

The interaction of CO with metal electrode surfaces is of interest in electrocatalysis as adsorbed CO on noble metals appears as a poison in the course of simple organic fuel electrooxidation reactions, and also in the stability of other metal surfaces in contact with CO-containing aggressive media. For the latter the metal–CO interactions have a considerable influence on the corresponding metal corrosion rates.

The study of nickel electrodes in CO-containing aqueous media deserves special attention for the potential use of nickel, a relatively low cost material, in electrocatalysis. Much work in the area of heterogeneous catalysis [1–4] has been devoted to the strong CO(gas)–Ni interaction. The mechanism of nickel corrosion and passivation in CO-free aqueous solution has also been extensively considered in both acid and alkaline solutions [5–10]. The presence of CO in acid solutions acts as an inhibitor on the anodic electrodissolution of nickel, and the hydrogen evolution reaction on this metal [11]. The increase in nickel passivation was explained by an increase in the adsorption of CO preferentially occupying the most active surface centers, the kinetics of nickel passivation being described by the Elovich adsorption rate equation [11].

Data on the influence of CO on metal corrosion can be related to the participation of either coadsorption or competitive adsorption phenomena in the kinetics of the reactions. This paper provides new results and a different interpretation for the behaviour of nickel in CO-saturated acid solutions, derived from voltammetry run in a microflow cell to avoid the interference of CO readsorption, paying particular attention to the adsorption potential and the adsorption time.

2. Experimental details

Nickel wire working electrodes ($0.31\,cm^{-2}$), a platinum counter electrode ($\sim 2\,cm^2$) and a reversible hydrogen electrode (RHE) were mounted in a conventional microflow electrochemical cell [12]. The following deaerated electrolyte solutions were employed: 0.5 M H_2SO_4; 0.5 M $HClO_4$; and 5×10^{-3} M H_2SO_4 + 0.495 M Na_2SO_4. Conventional voltammetry combined with different preset potential steps was applied. Repetitive potential sweeps between −0.15 and 0.9 V either in a CO-free or a CO-saturated solution were made at $0.1\,V\,s^{-1}$. Occasionally, the adsorption potential, E_{ad}, was held at a preset value in the range $-0.15\,V \leqslant E_{ad} \leqslant 0.1\,V$ for a certain time, t_{ad} and immediately afterwards the potential scan was begun from E_{ad} up to 0.9 V. In another set of experiments the value of t_{ad} was systematically changed by keeping E_{ad} constant. The amount of Ni dissolved after the potential cycling, either for CO-free or CO-containing solutions, was determined by atomic absorption. Runs were made at 25° C.

3. Results

The repetitive voltammograms of nickel run in CO-containing acid solutions change considerably from those obtained in CO-free solutions (Fig. 1). In both solutions the voltammograms show two anodic peaks (I and II) at ~ 0.2 V and ~ 0.5 V, respectively. The influence of CO is reflected by the enhancement of peak II at the expenses of peak I. Under certain conditions (not shown in the figure, but described later in the text) peak I splits into peaks Ia and Ib.

The repetitive voltammograms show that the total anodic charge (of about $30\,mC\,cm^{-2}$ in CO-free acid)

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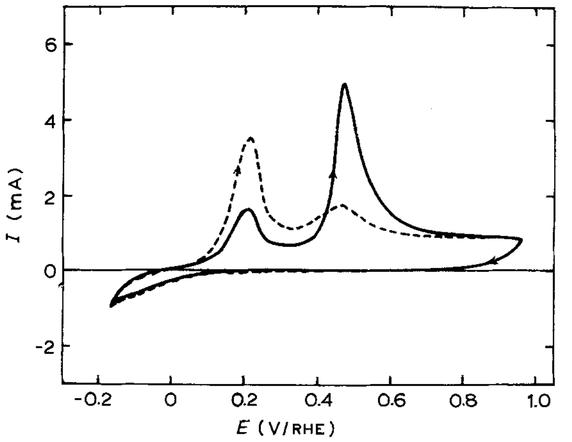

Fig. 1. Cyclic voltammograms of nickel in 0.5 M H_2SO_4. CO-free (——) and CO-saturated solution (- - -). v = 0.1 V s^{-1}. Geometric electrode area: 0.31 cm^2. 30° C.

becomes slightly greater in CO-containing solutions. Different results can be obtained by running experiments involving the systematic change of E_{ad} and t_{ad} (Fig. 2). Thus, in the absence of CO, holding the potential at −0.15 V for 1 min produces a considerable enhancement of peak I in the voltammogram run immediately afterwards. The same experiment made in CO-containing acid shows that the contribution of peak II becomes about twice as large as that of peak I, although in this case the sum of the charges related to peaks I and II, is smaller than the charge of peak I in CO-free acid. If the preceding experiment includes the washing of the nickel electrode after holding the potential at E_{ad}, the subsequent voltammogram run under comparable conditions in 0.5 M H_2SO_4 becomes slightly different from that found for the CO-containing acid without washing. According to the results depicted in Fig. 3, the increase of E_{ad} in CO-containing acid for t_{ad} = 30 s, produces the disappearances firstly of peak I, and later peak II, so that the electrochemical reaction appears to be strongly inhibited over the entire potential range.

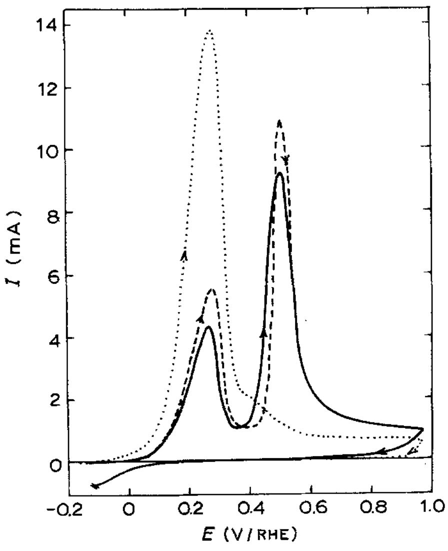

Fig. 2. Voltammograms of nickel in 0.5 M H_2SO_4 preceded by CO adsorption at E_{ad} = −0.15 V for 60 s. CO-free acid (. . .) and CO-saturated acid before (- - -) and after (——) washing. v = 0.1 V s^{-1}. Geometric electrode area 0.31 cm^2. 30° C.

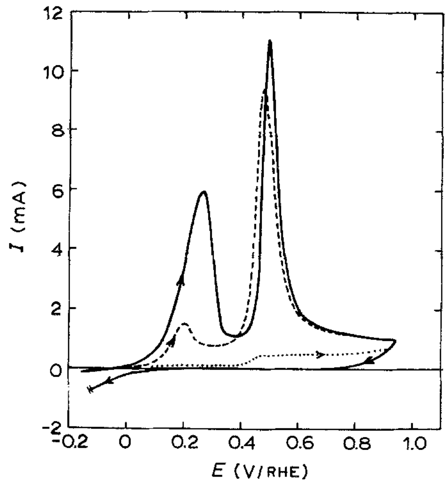

Fig. 3. Voltammograms of nickel in CO-saturated 0.5 M H_2SO_4 at different E_{ad} = 0.1 V (. . .); E_{ad} = 0.0 V (- - -); E_{ad} = −0.15 V (——). v = 0.1 V s^{-1}. Geometric electrode area 0.31 cm^2. 30° C.

The influence of t_{ad} for a constant value of E_{ad} can be seen in Fig. 4. It is seen that for E_{ad} = −0.15 V the reaction associated with peak I, is nearly completely suppressed for t_{ad} = 5 min but, in contrast, the charge of peak II appears to be only slightly dependent on t_{ad}. A comparable effect in the voltammogram is found (Fig. 5) if it is preceded by potential cycling between −0.15 and 0.4 V for 1 min. In this case it is seen that the influence of CO on peak I is small, although presumably the potential cycling has increased the electrode roughness, a fact which is apparently reflected in the charge increase of peak II.

The voltammograms run with anodic switching potentials, $E_{s,a}$, increased stepwise (Fig. 6) show that as $E_{s,a}$ becomes more positive in both CO-free and CO-containing acid, the voltammograms exhibit a gradual decrease in the contribution of both peaks I and II. This fact seems to be a clear indication that nickel electrode passivation sets in independently of the presence of CO in the solution. Comparable behaviour can be observed in 0.5 M $HClO_4$.

By running the experiment at a higher pH by using 0.005 M H_2SO_4, for certain values of E_{ad} and t_{ad} it is seen that peak I splits into peaks Ia and Ib, whereas the voltammogram run with the CO-containing

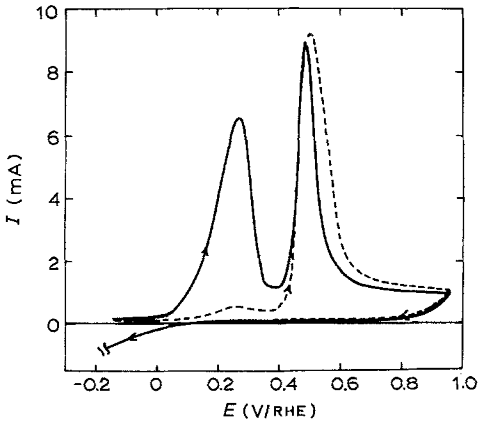

Fig. 4. Voltammograms of nickel in CO-saturated 0.5 M H_2SO_4 for E_{ad} = −0.15 V; t_{ad} = 60 s (——); t_{ad} = 300 s (- - -). v = 0.1 V s^{-1}. Geometric electrode area 0.31 cm^2. 30° C.

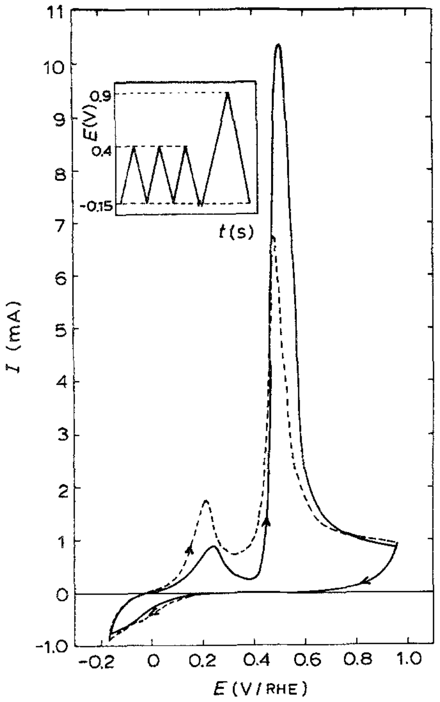

Fig. 5. Voltammograms of nickel in CO-saturated 0.5 M H_2SO_4 before (- - -) and after (——) application of the potential routine depicted in the inset. $v = 0.1\,V\,s^{-1}$. Geometric electrode area 0.31 cm^2. 30° C.

0.005 M H_2SO_4 exhibits the splitting of peak II into peaks IIa and IIb. This interesting correlation suggests that CO adsorption blocks the nickel surface within a certain potential range. Likewise after the CO-adsorbate electrochemical stripping, the electrooxidation reaction of the bare nickel surface proceeds as in CO-free acid, but in a potential range which is shifted positively.

If the voltammograms run at $E_{ad} = -0.15\,V$ and different t_{ad} are compared, it is seen that the charge of peak II increases due to the progressive contribution of a shoulder at the positive potential side (Fig. 7). In this case peak I becomes practically suppressed.

The voltammetric changes taking place between the first and the second positive-going potential scan, with and without washing (Fig. 8), show that, in both cases, the nickel electrode attains the response of a passivated nickel electrode in acid [13].

Finally, experiments were also made initially involving CO adsorption on nickel electrodes held at the potential E_{ad} in acid, and afterward transferred into 0.1 M KOH solution to observe the voltammetric behaviour of the well-known $Ni(OH)_2/NiOOH$ redox reactions in alkaline solution (Fig. 9). The corresponding voltammograms in the presence of CO show that in this case the Ni(II)/Ni(III) redox reaction charge becomes smaller (about 50%) than that found in the blank. This result is consistent with the inhibition of the first oxidation level of nickel caused by CO adsorption. In addition, the latter hinders any roughness increase of nickel due to corrosion.

In order to demonstrate the inhibition of the nickel electrodissolution by CO adsorbates, nickel electrodes were cycled at $0.1\,V\,s^{-1}$ for 5 min in both plain and

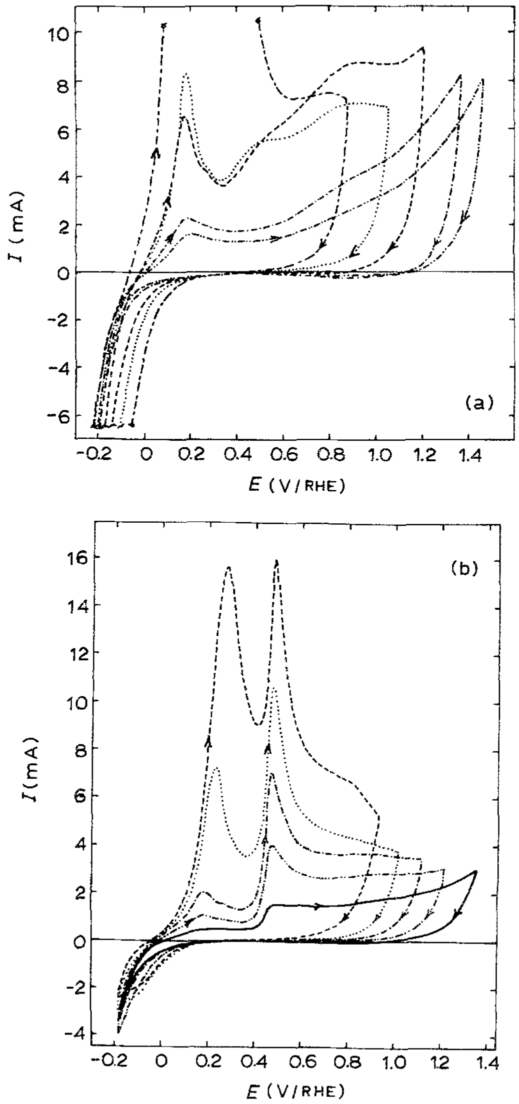

Fig. 6. Cyclic voltammograms of nickel in 0.5 M H_2SO_4 run by stepwise increasing $E_{s,a}$. (a) CO-free acid; (b) CO-saturated acid. $v = 0.1\,V\,s^{-1}$. Geometric electrode area 0.31 cm^2. 30° C.

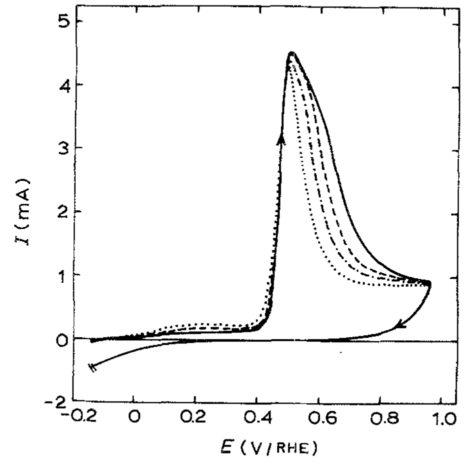

Fig. 7. Cyclic voltammograms of nickel in CO-saturated 5×10^{-3} M H_2SO_4 + 0.495 M Na_2SO_4 for different CO adsorption times; $t_{ad} = 30\,s$ (. . .); $t_{ad} = 60\,s$ (-·-·-·-); $t_{ad} = 120\,s$ (- - -); $t_{ad} = 300\,s$ (——). $v = 0.1\,V\,s^{-1}$. Geometric electrode area 0.31 cm^2. 30° C.

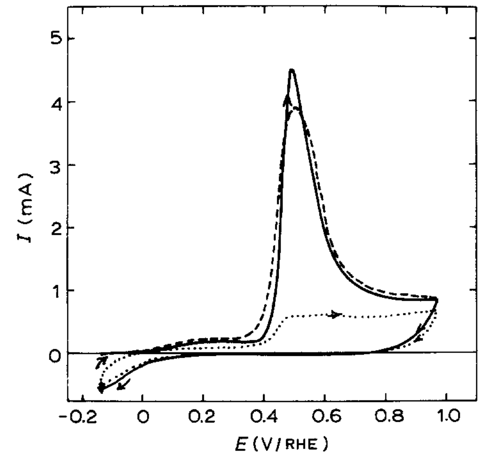

Fig. 8. Cyclic voltammograms of nickel in CO-saturated 5×10^{-3} M H_2SO_4 + 0.495 M Na_2SO_4; (——) CO-saturated solution, (- - -) 1st cycle and (. . .) 2nd cycle after washing. $v = 0.1\ V\ s^{-1}$. Geometric electrode area 0.31 cm². 30° C.

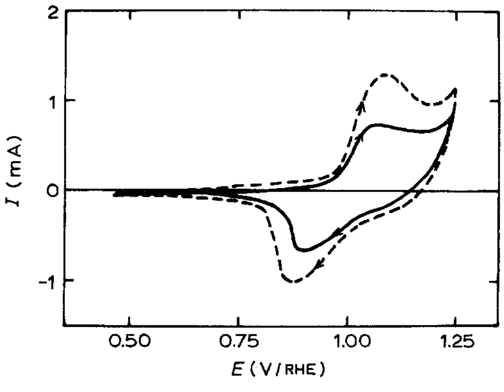

Fig. 9. Cyclic voltammograms of nickel in CO-saturated 0.1 M NaOH (——) run after the nickel electrode has been subjected to the potential routine depicted in Fig. 5 in CO-saturated 0.5.M H_2SO_4. Blank (- - -) made in 0.1 M NaOH without any previous treatment. $v = 0.1\ V\ s^{-1}$. Geometric electrode area 0.31 cm². 30° C.

CO-saturated 0.5 M H_2SO_4 by setting $E_{s,a}$ gradually at 0.34, 0.425 and 0.90 V, and $E_{s,c}$, the cathodic switching potential, at −0.15 V. Afterwards the amount of Ni(II) in solution was determined (Table 1). Voltammetric and chemical analysis data exhibit a good correlation clearly showing that, in the potential range of peak II, the electrodissolution of nickel was considerably decreased, but when the applied potential exceeded 0.9 V there was no noticeable difference between the results for the two solutions.

4. Discussion

The overall anodic reaction of nickel in acid solutions in the absence of inhibition was described in terms of three main contributions, namely, the electrodissolution of nickel yielding soluble Ni(II) species, the formation of a new phase ($Ni(OH)_2$), which constitutes the precursor of the anodic nickel oxide layer, and the chemical dissolution of the latter [6]. Voltammetric data obtained in still and stirred conditions suggests that the accumulation of the $Ni(OH)_2$ anodic layer in the potential range of peak I results from a competition between the electrochemical dissolution of nickel and the gradual growth of the anodic layer. The present results show that CO acts as an inhibitor at the first stage of nickel electrooxidation and that its greatest influence appears over the entire potential range of peaks I and II. The inhibition is caused by CO adsorption on the nickel surface.

Table 1. Evaluation of Ni(II) in solution produced through repetitive cycling at $v = 1\ V s^{-1}$ between $E_c = -0.15$ V and E_a, for t_a = 5 min, (A) plain 0.5 M H_2SO_4; (B) CO-saturated 0.5 M H_2SO_4. Electrode geometric area: 0.31 cm², 30° C

Solution	*Charge passed (mC)*	*Amount of Ni (mg dm⁻³)*	E_a *(V)*
A	240	7.3	0.340
B	66	2.0	0.340
A	650	21.0	0.425
B	65	2.6	0.425
A	85	2.7	0.900
B	108	3.3	0.900

Following the previous interpretation of nickel corrosion in acids [5–10] it is likely that, below the potential range of peak I, the H_2O–Ni interactions prevail, whereas at potentials greater than that of peak II, the nickel surface becomes covered by a thin layer of $Ni(OH)_2$. Then, at low potentials, CO should be involved in a competitive adsorption as described by the equations:

$$Ni(H_2O)_{ad} + CO = Ni(CO)_{ad} + H_2O \quad (1a)$$

$$Ni + H_2O = Ni(OH)_{ad} + H^+ + e^- \quad (1b)$$

$$Ni(OH)_{ad} + CO + e^- = Ni(NO)_{ad} + OH^- \quad (1c)$$

The entire process becomes potential dependent through Reaction 1b. The adsorption of CO (Reaction 1a) occurs rather slowly as compared to Reaction 1b and is influenced by the history of the electrode. Accordingly, for sufficiently negative potentials the HER itself and the CO adsorption compete for nickel surface sites.

An extreme situation arises when the entire nickel surface is passivated through NiO layer formation [6]. In this case there is no evidence of a direct CO–NiO layer interaction, at least from the present results. Hence, as CO acts at the early stages of nickel electrodissolution, then the formation of $Ni(OH)_{ad}$ according to Reaction 1b should be largely impeded. In this case for the nickel electrodissolution reaction to proceed firstly CO must be removed from the metal surface, and once the CO stripping is finished, the nickel electrodissolution reaction apparently proceeds through a mechanism comparable to that described for plain acid solutions [6]. This conclusion is based on the fact that the voltammograms in the presence of CO appear to be only shifted positively as compared to those obtained in plain acid. Under these circumstances one can, in principle, assign the potential difference of peaks I and II to the excess of energy required for stripping the CO adsorbate from the nickel surface. This excess of energy is about

46 kJ mol^{-1}, a figure which should be related to the energy difference for producing the following reactions:

$$Ni(H_2O) + H_2O = Ni(OH)_2 + 2H^+ + 2e^- \quad (2a)$$

and

$$Ni(CO) + 2H_2O = Ni(OH)_2 + 2H^+ + CO + 2e^- \quad (2b)$$

Gas phase CO adsorption data on Ni show that the maximum CO coverage and initial heat of adsorption of CO on the low-index nickel faces are in the 111 to 150 kJ mol^{-1} range [14, 15]. These figures are consistent with the fact that for the chemisorption of CO, empty d-orbitals are required. Otherwise, the H_2O adsorption energy on Ni ranges from 37 up to about 50 kJ mol^{-1} [16, 18]. Therefore, if the energy difference involved in the electrochemical Reactions 2a and b is assigned to the reaction:

$$Ni(H_2O) + CO(g) = Ni(CO) + H_2O(g) \quad (3)$$

then, the corresponding value should be between 61 and 113 kJ mol^{-1}. Despite the fact that caution is needed in extrapolating gas phase adsorption data to electrochemical systems, it is clear that the trend of the present electrochemical results is consistent with the conclusions derivable from the corresponding, much simpler, gas phase CO–Ni and gas phase H_2O–Ni heterogeneous systems.

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