

Influence of iron impurities on the time dependence of the hydrogen evolution reaction on platinum cathodes during electrolysis of 30 w/o KOH

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The hydrogen evolution reaction (HER) on polished pure platinum cathodes in 30 w/o KOH at 70°C in the absence or presence of dissolved metallic impurities has been investigated at 100 mA cm⁻². During the first thousand seconds, the loss of efficiency for the HER, taking the form of an increase in the cathodic overpotential with time, is tentatively attributed to the penetration of atomic hydrogen into the platinum lattice. The deposition of copper and iron, observed after several hours of polarization in the presence of a non-purified electrolyte, is found to be detrimental to the hydrogen discharge. Marked improvement in the electrocatalytic activity of the cathode after 10³ s in the presence of 14 ppm dissolved iron is ascribed to the formation of small crystallites of pure iron on the cathode surface.

1. Introduction

Stable performances and low hydrogen and oxygen overpotentials are required for long operating periods in industrial water electrolysis. Time effects on both the nickel and the cobalt cathodes are reported [1-5]: in the first 3 h of polarization at high cathodic overpotentials, the deactivation process is ascribed to hydrogen absorption in the substrate while for longer times, the formation of iron deposits on the cathode surface may influence the HER, as observed by Huot and Brossard [2], for example, on a pure nickel surface after 3 h polarization in 30 w/o KOH at 70°C in the presence of 0.5 ppm dissolved iron. Under these conditions, iron deposits are detrimental to the hydrogen discharge, but in the presence of 3 ppm dissolved iron at 37°C they reduce hydrogen overpotential [5]. The influence of deposited iron on the HER in alkaline aqueous solutions is believed to depend largely on the concentration of dissolved iron and, in view of the presence of iron impurities in most industrial water electrolyzers, has aroused great interest.

The present investigation is devoted to the deactivation of polished pure platinum cathodes in 30 w/o KOH, since Pt is generally considered an excellent electrocatalyst for the HER. The experiments were performed in constant current mode with special attention to the presence of dissolved iron. The electrode surfaces were examined by scanning electron microscopy (SEM) and by X-ray microanalysis (EDX).

2. Experimental details

The electrochemical measurements were carried out in 30 w/o KOH aqueous solutions at 70°C. The cell is

described in detail elsewhere [3]. The working electrode consisted of a vertical 0.05 cm diameter platinum wire (Specialty Products 99.99%), which gave a sample surface area of 0.31 cm². The sample was not exposed to heat treatment prior to the experiments; it was polished with $\approx 0.3 \mu\text{m}$ alumina paste.

The temperature was maintained constant at 70°C by means of a Lauda M20 thermostatic bath. Polarization curves were obtained by galvanostatically decreasing the applied current from 100 mA cm⁻² where it was kept for a given period of time, to 10 mA cm⁻². The cathode potential was recorded against time at 100 mA cm⁻².

The reversible potential for the HER was measured by bubbling hydrogen against a platinized electrode immersed in 30 w/o KOH solution at 70°C. The value was -0.962 V with respect to the Hg/HgO/KOH 1 M reference electrode at 70°C. All potential values for the electrodes are given with respect to the reversible potential for HER at 70°C, unless otherwise mentioned.

The main metallic impurities measured in the fresh solutions were Al (2.5 ppm), Pb (2.3 ppm), Cr (1.3 ppm), Ni (0.6 ppm) and Fe (0.5 ppm). Some of the 30 w/o KOH solutions used were enriched with 14 ppm (0.25 mM) of Fe(II) and/or Fe(III) by anodically dissolving an iron electrode in 30 w/o KOH at 70°C at a potential of -0.900 V Hg/HgO according to the procedure described by Armstrong and Baurhoo [6].

In a different set of experiments, fresh 30 w/o KOH solutions were pre-electrolysed for ≈ 48 h to remove impurities dissolved in the electrolyte. A nickel cathode with a geometric surface area of ≈ 100 cm² was used with a 10 cm² nickel anode, while the applied current was 100 mA (1 mA cm⁻²).

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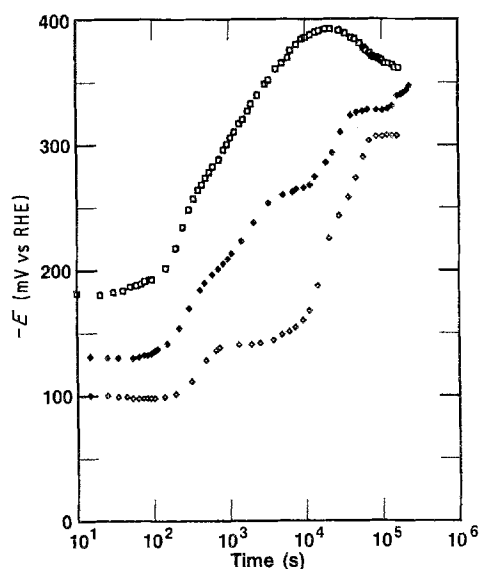


Fig. 1. Platinum cathode potential behaviour versus time under galvanostatic control in 30 w/o KOH at 70°C (purified electrolyte). Applied current density: ◇, 20 mA cm⁻²; ◆, 50 mA cm⁻²; □, 100 mA cm⁻².

3. Results

Typical potential-time curves for applied constant current densities of 20, 50 and 100 mA cm⁻² at 70°C are presented in Fig. 1. At any time, the cathode half-cell potential [2] increases with the applied current density. The pattern of these curves is approximately the same, the potential plateau regions overlapping for higher current densities. Three such regions are present at 20 mA cm⁻² with $\eta \approx 100$ mV from 0 to 100 s, 140 mV from 700 to 2000 s and 310 mV over 8×10^4 s.

At 100 mA cm⁻², η shifts from 180 mV at 50 s to 390 mV at $\approx 20\,000$ s after an incubation period of approximately 50 s. The η versus log time curve is linear from 300 to 5000 s with a slope $dE/d(\log \text{ time})$ of 100 mV per decade time. In addition, η decreases slightly with time for $t > 20\,000$ s.

After electrolysis times of several days at 100 mA cm⁻², only platinum was detected on the cathode surface by EDX analysis while cyclic voltammetries performed to oxidize any metallic impurities present on the surface suggest the absence of such impurities on the substrate.

The hydrogen overpotential values during the incubation period, obtained from galvanostatic measurements, give a linear relationship when plotted against log (applied current density). The corresponding Tafel parameters are 42 mV for the Tafel slope, b , and 0.19 mA cm⁻² for the exchange current density, i_0 .

The hydrogen evolution parameters for Pt cathodes were also determined from polarization curves at various times during which the applied current was maintained constant at 100 mA cm⁻². The values of b and i_0 are summarized in Table 1. Reduction in electrocatalytic activity with time is associated with the significant increase in b from 42 mV before deactivation to 137 mV at 1000 s and 190 mV at 20 000 s.

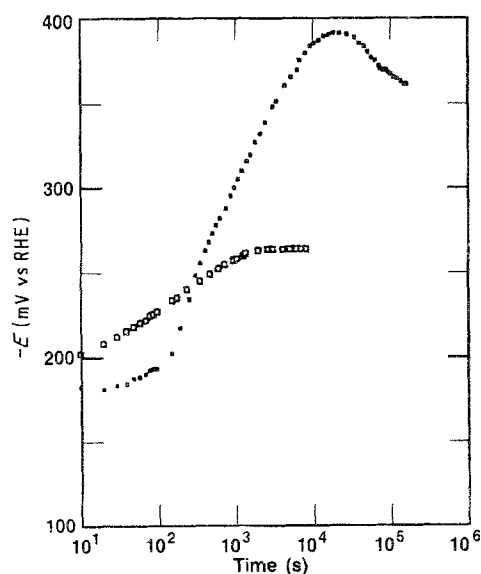


Fig. 2. η versus log time for Pt cathode at 100 mA cm⁻² after (□) a potential sweep in the anodic direction (50 mV s⁻¹) following cathodic polarization 100 mA cm⁻² during 165 000 s (■).

Stabilization of the Tafel parameters is noted from 75 000 to 165 000 s, which is consistent with the relatively constant overpotential value observed at 100 mA cm⁻² in this time range (Fig. 1).

The electrocatalytic activity of Pt cathodes was evaluated after deactivation of a fresh Pt cathode for 165 000 s at 100 mA cm⁻² followed by a potential sweep from the potential value reached at 100 mA cm⁻² to 0 mV Hg/HgO and back at a scan rate of 50 mV s⁻¹. A constant current density of 100 mA cm⁻² was applied immediately after the potential sweep. In the recording of η versus time (Fig. 2), η can be seen to decrease from 360 mV prior to the potential sweep in the anodic direction (PSAD) to approximately 205 mV immediately after the PSAD. In addition, the slope $dE/d \log t$ is only 31 mV per decade time while a potential plateau value of 270 mV is observed for $t_{100} > 2000$ s after the PSAD.

3.1. Effect of 0.5 ppm dissolved iron

The hydrogen overpotential is plotted against log time in Fig. 3 for an applied constant current of 100 mA cm⁻². Curve (a) corresponds to a fresh electrolyte, i.e. containing 0.5 ppm of dissolved iron, and curve (b) to a purified electrolyte. Compared to the purified electrolyte, the presence of 0.5 ppm dissolved iron results in (i) a negligible difference of η against

Table 1. Hydrogen evolution parameters for platinum cathodes determined at various times during galvanostatic polarization in purified electrolyte

Time at 100 mA cm ⁻² (s)	b (mV decade ⁻¹)	i_0 (mA cm ⁻²)
1000	137	2.0
2×10^4	190	3.7
7.5×10^4	227	2.7
16.5×10^4	226	2.7

Table 2. Composition of the cathode surface by EDX analysis (0.5 ppm Fe, 100 mA cm⁻²)

Time at 100 mA cm ⁻² (s)	Pt (a/o)	Fe (a/o)	Cu (a/o)
10 ⁴	100	nd*	nd*
2.3 × 10 ⁴	100	nd*	nd*
7.26 × 10 ⁴	83.1	7.1	9.8
15.8 × 10 ⁴	79.7	10.4	9.9
40.6 × 10 ⁴	56.7	23.3	20.0
75.4 × 10 ⁴	25.5	40.3	34.2

*Not detected: below the limit of detection, i.e. ≈ 0.5 a/o.

time for $t < \sim 20\,000$ s and (ii) a slight increase of η for $t > 20\,000$ s. The maximum value of η is 460 mV and its corresponding time is $\approx 75\,000$ s. A linear behaviour of the cathode potential with log time was also reported for Ni [2] and Co [4] under the same experimental conditions.

The morphology and nature of the cathode surface was investigated by SEM (Fig. 4) and EDX analyses (Table 2) to determine whether metallic impurities present in the solution were deposited there. The samples were examined after a polarization time ranging from 0 to 75.4×10^4 s at 100 mA cm⁻². The following features are deduced from Fig. 4 and Table 2. From 0 to 2.3×10^4 s, the surface remains fairly smooth (Fig. 4a) and only platinum is detected. Small particles of metallic impurities are present on the platinum surface at 7.26×10^4 s (Fig. 4b), the amounts of iron and copper being 7 and 10 a/o, respectively. Both the number and size of metallic particles increase with time from 7.26×10^4 s (Fig. 4b) to 75.4×10^4 s (Figs 4e and 4f). It is consistent with the fact that a significant accumulation of iron and

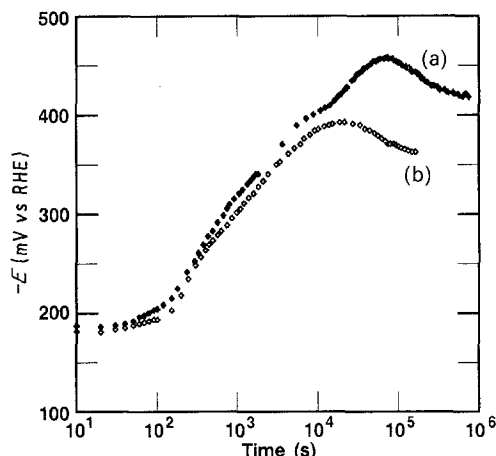


Fig. 3. Hydrogen overpotential against time at 100 mA cm⁻² in 30 w/o KOH at 70°C (a) for a non-purified electrolyte (0.5 ppm Fe) (◆) and (b) for a purified electrolyte (◇).

copper was observed by EDX analysis in this range of time. At 75.4×10^4 s, the cathode surface is almost entirely covered by iron and copper.

In the presence of 0.5 ppm dissolved iron, the deposition of impurities on the cathode surface was also evidenced by the anodic portions of a single-cycle voltammogram for Pt cathodes (Fig. 5). A constant current density of 100 mA cm⁻² was applied for times ranging from 1000 to 77.5×10^4 s.

Dependence of the shape of the voltammogram on t_{100} is observed. Two oxidation waves labelled I and II in Fig. 5b are presented for $t_{100} = 10\,000$ s, their maxima being anodic to -500 mV vs Hg/HgO. The charges associated with peaks I (Q_I) and II (Q_{II}) increase with t_{100} ; for example, from $t_{100} = 40.9 \times 10^4$ s to $t_{100} = 77.8 \times 10^4$ s, Q_I increases from 21 to 42 mC cm² while Q_{II} shifts from 45 to 89 mC cm².

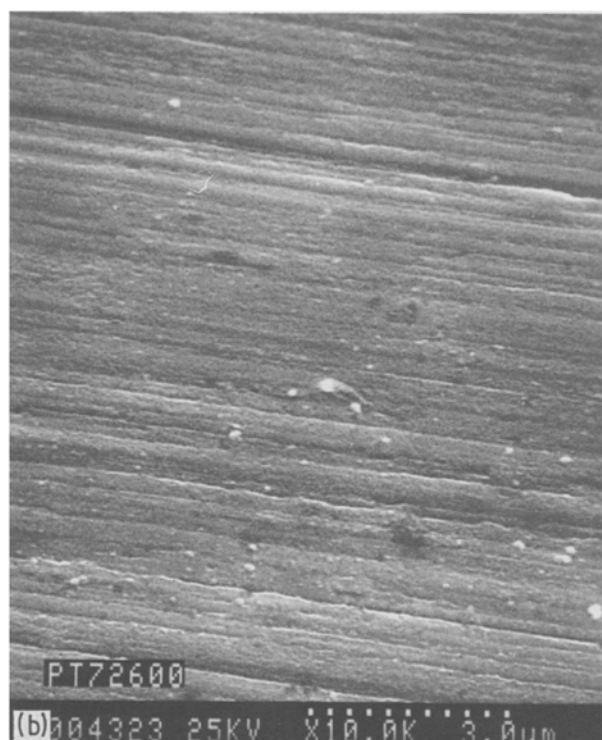
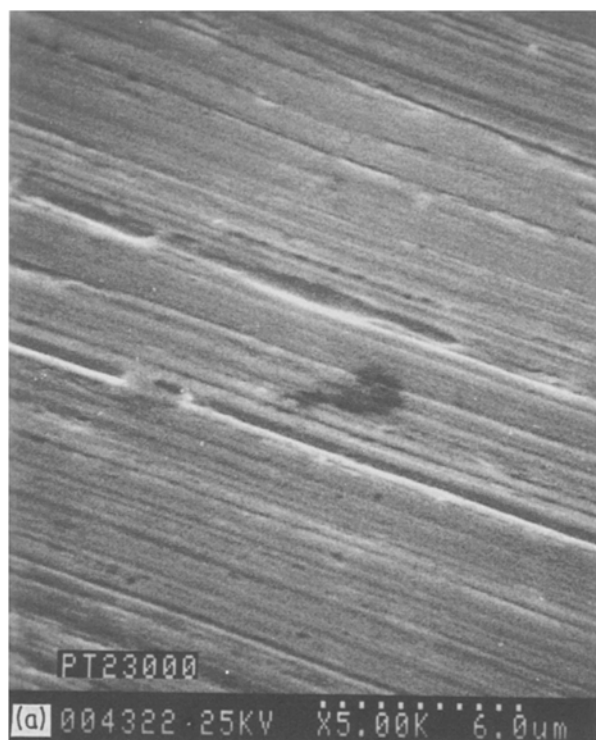


Fig. 4. Cathode surface during hydrogen discharge under the experimental conditions of Fig. 3 (0.5 ppm Fe). Removal times: (a) 2.3×10^4 s; (b) 72.6×10^4 s; (c) 15.8×10^4 s; (d) 40.6×10^4 s; (e, f) 75.4×10^4 s.

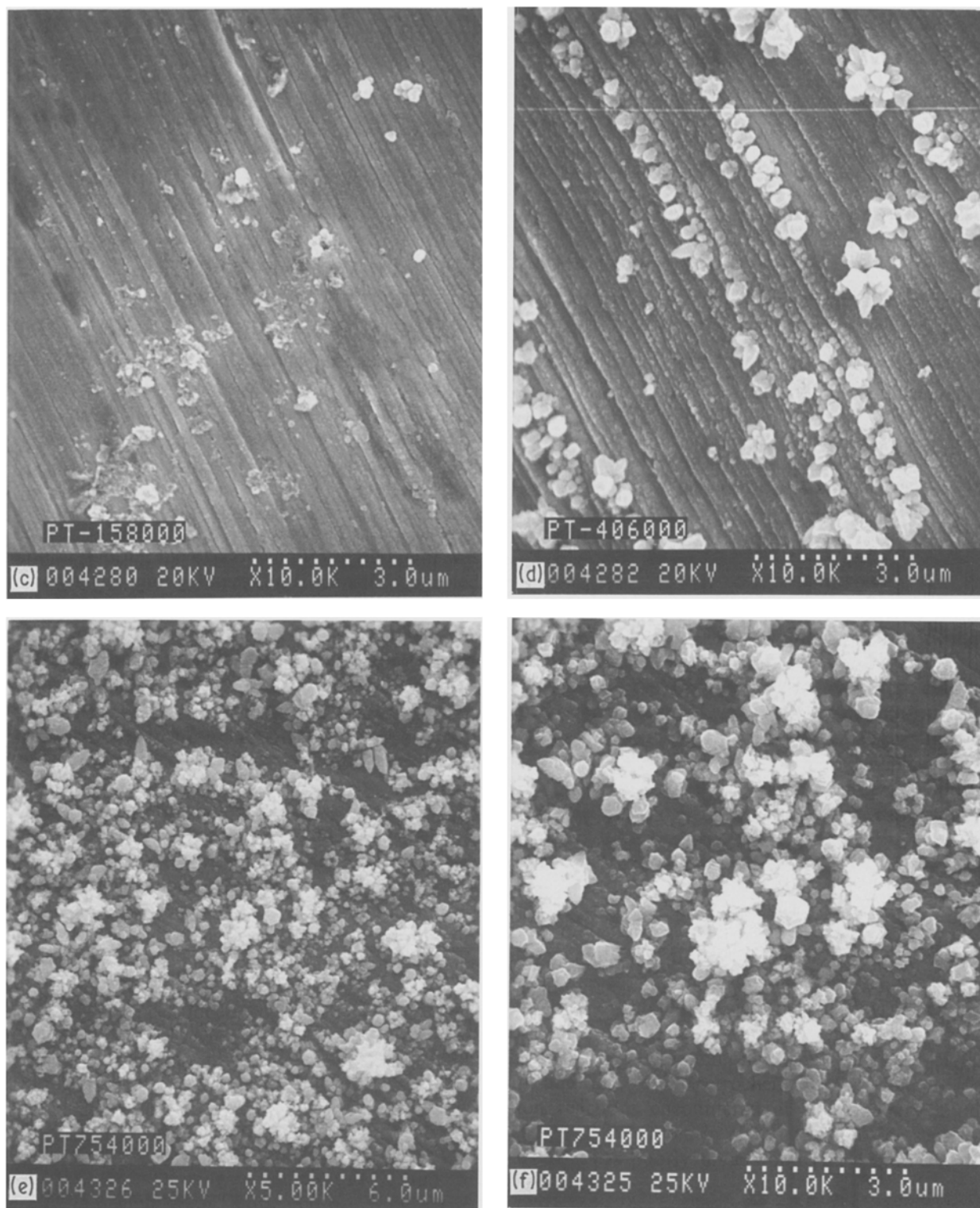


Fig. 4. Continued.

EDX analysis and SEM examination of the electrode surface after anodic sweeps show that peaks I and II correspond to the partial dissolution of both Fe and Cu accumulated during polarization at 100 mA cm^{-2} .

Hydrogen evolution parameters for Pt cathodes were determined at various times, during which the applied current was maintained constant at 100 mA cm^{-2} . The values of i_0 and b are summarized in Table 3. The loss in electrocatalytic activity with time is ascribed to the significant increase of the Tafel slope from 158 mV at 120 s to 287 mV at 7.3×10^4 s,

Table 3. Hydrogen evolution parameters for Pt cathodes determined at various times during galvanostatic polarization in 30 w/o KOH containing 0.5 ppm Fe

Time at 100 mA cm^{-2} (s)	b (mV decade ⁻¹)	i_0 (mA cm^{-2})
120	158	3.1
10^4	258	2.5
7.34×10^4	287	2.5
15.8×10^4	276	2.6
40.7×10^4	295	3.3
75.4×10^4	298	3.9

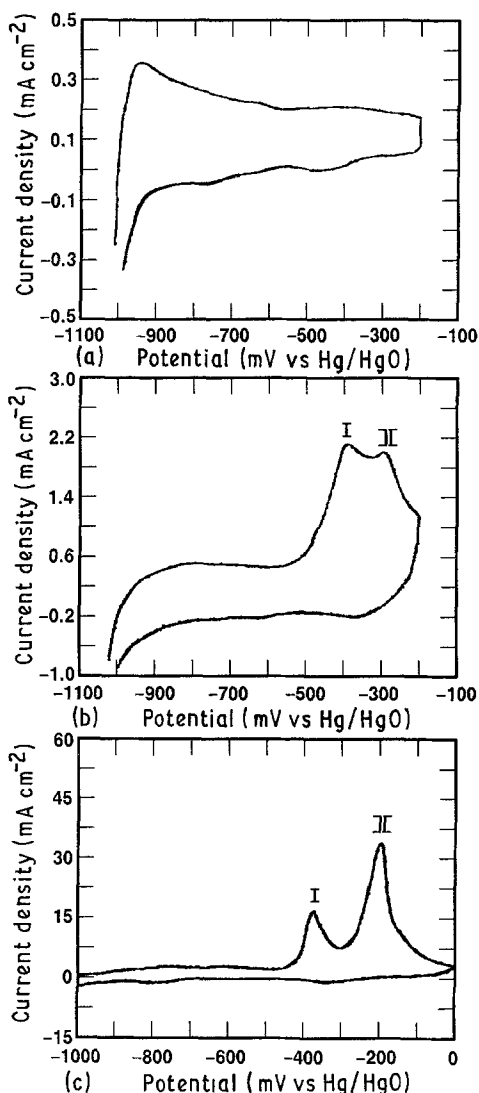


Fig. 5. Influence of the duration of the cathodic polarization at 100 mA cm^{-2} in non-purified 30 w/o KOH at the anodic portion of the single-cycle voltammogram at 50 mV s^{-1} . For (a) 10^3 s ; (b) 10^4 s ; (c) $40.9 \times 10^4 \text{ s}$.

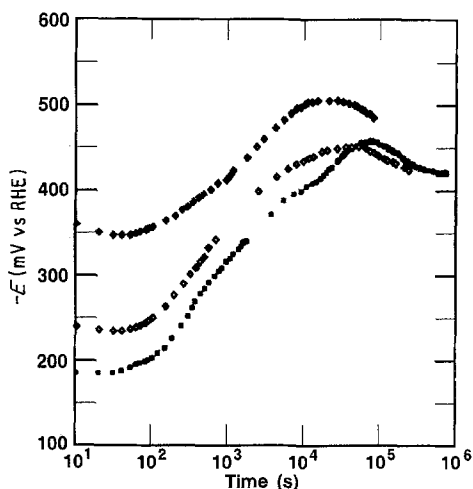


Fig. 6. Influence of the temperature on the platinum cathode potential behavior versus time for a non-purified 30 w/o KOH (0.5 ppm Fe). Applied current density: 100 mA cm^{-2} . The temperatures are 70°C (■), 50°C (◇), 30°C (◆).

since the variation of i_0 is rather small with time. At any time, b is higher in the presence of fresh electrolyte, i.e. 0.5 ppm of dissolved iron compared to the purified one (Table 1); i_0 is unaffected by the presence of dissolved iron. In both cases, the variation of b decreases with time for longer times.

The influence of the temperature on the potential behaviour of the Pt cathode versus time at 100 mA cm^{-2} is illustrated in Fig. 6. The shape of the curve remains practically unchanged from 30 to 70°C , the maximum value of η_{100} being 460 mV at 70°C , 455 mV at 50°C and 518 mV at 30°C . The times corresponding to those maxima are 75000 , 32000 and 17000 s at 70 , 50 and 30°C , respectively. In addition, a drop in temperature from 70 to 30°C results in higher values of η_{100} at any time below $\approx 10^4 \text{ s}$.

3.2. Effect of 14 ppm dissolved iron

A significant decrease of η_{100} for t_{100} longer than $\approx 10^3 \text{ s}$ is observed from 0.5 to 14 ppm dissolved iron (Fig. 7). The following features are observed with 14 ppm dissolved iron: (i) the slope $dE/d\log t$ for $t_{100} < 10^3 \text{ s}$ is 41 mV per decade time; (ii) after $7.5 \times 10^4 \text{ s}$ of polarization at 100 mA cm^{-2} the Tafel parameters are 83 mV for b and 0.21 mA cm^{-2} for i_0 and particles of iron are present on the substrate (Fig. 8). Particles only a fraction of $1 \mu\text{m}$ in diameter coexist with larger ones, i.e. $\approx 1\text{--}3 \mu\text{m}$.

The anodic portions of single-cycle voltammograms (Fig. 9) for (i) a Pt cathode after 75000 s at 100 mA cm^{-2} in the presence of 14 ppm dissolved iron and (ii) a pure Fe cathode after several seconds under cathodic polarization in the same electrolyte, show two oxidation peaks: peak I is related mainly to the formation of Fe(II) species, and peak II is ascribed to the formation of Fe(III) species [6]. The height of both peaks is significantly greater for deposited iron on a platinum substrate. In addition, the small peak generally related to the oxidation of H_{ads} on Fe and

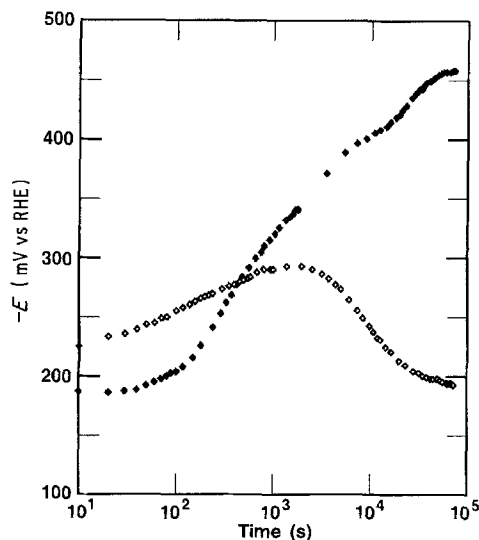


Fig. 7. Hydrogen overpotential versus time at 100 mA cm^{-2} in the presence of 14 ppm iron (◇), 30 w/o KOH, 70°C . The curve of Fig. 3 corresponding to 0.5 ppm Fe (◆) is also shown.

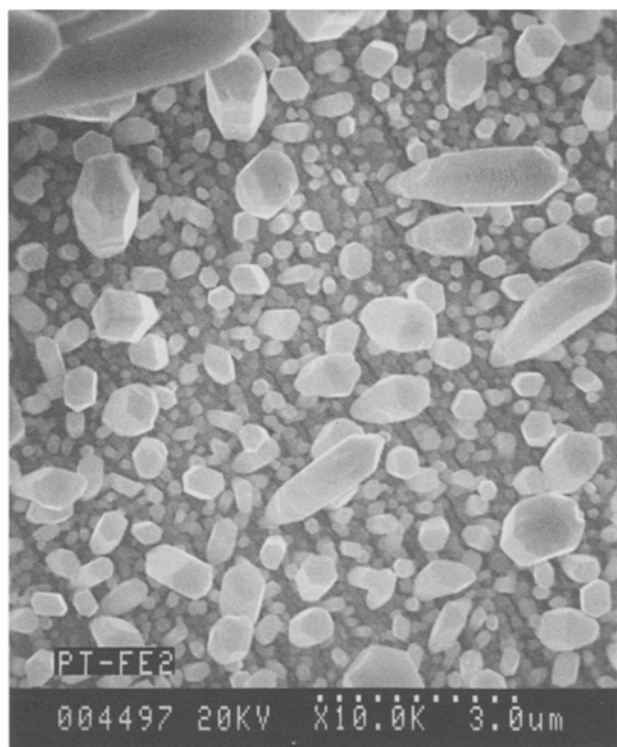


Fig. 8. Cathode surface after 75 000 s at 100 mA cm^{-2} in the presence of 14 ppm dissolved iron. The composition of the cathode surface by EDX analysis: Pt 12 a/o; Fe 88 a/o; Cu non-detected.

located close to the reversible potential for the HER [6] is absent on the potentiodynamic curves reported in Fig. 9.

4. Discussion

In the case of a purified electrolyte, or as long as the cathode surface is free from metallic impurities in the presence of the fresh electrolyte, the decay of the electrocatalytic activity up to $\approx 10^4$ s (Fig. 1) is most probably related to the penetration of atomic hydrogen into the surface region of the Pt structure under hydrogen evolution [7, 8], as suggested for bare Ni [2] or Co [4]. According to Amossé and Barbier [9], this creates a potential difference between the metal, i.e. in the first layer, and the solution, which tends to oppose current flow. The significant increase in the Tafel slope with t_{100} (Table 1) suggests that the HER reaction mechanism changes considerably with time.

It is also possible that traces of poisons present in the electrolyte are adsorbed on the electrode surface and influence the deactivation kinetics during hydrogen discharge. However, the following observations suggest that the influence of surface poisoning on the deactivation is rather marginal on the deactivation kinetics: (i) in case of a purified electrolyte or in the presence of a noticeable amount of metallic impurities dissolved in the electrolyte (e.g. 0.5 ppm Fe), the deactivation characteristics are similar in both cases for $t \approx 10^4$ s and the results are very reproducible; (ii) in both electrolytes the deactivation characteristics are unaffected by the time from 0 s to several days during which the electrode is at its open

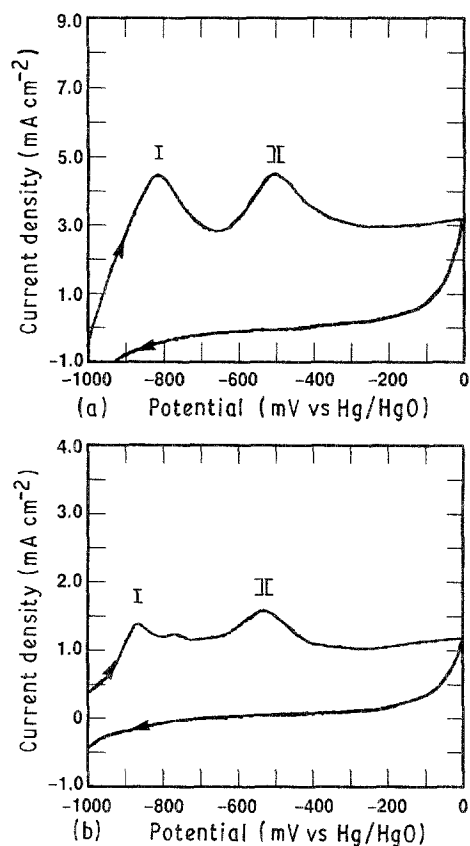


Fig. 9. Anodic portion of the single-cycle voltammogram at 50 mV s^{-1} after cathodic polarization in the presence of 14 ppm dissolved iron (30 w/o KOH, 70°C) at 100 mA cm^{-2} . Curve (a): Pt cathode polarized for 75 000 s (Fig. 8). Curve (b): Fe cathode polarized for several seconds.

circuit potential prior to polarization. In addition, the use of cyclic voltammetry, impedance measurements and scanning electron microscopy do not evidence surface poisoning.

The surface rejuvenation after an anodic sweep (Fig. 2) is tentatively ascribed to the oxidation of atomic hydrogen. The slower deactivation kinetics on the rejuvenated electrode may be explained by a partially irreversible deformation owing to the hydrogen penetration into the metal lattice and which influences the penetration rate of hydrogen [10].

The penetration rate of atomic hydrogen may depend on the nature of the electrode surface [11]. Furthermore, the rate-determining step for the hydrogen discharge is generally related to the morphology and nature of the electrode material. For both these reasons, the potential-time relationship observed in the region for which the cathode surface is pure platinum is expected to differ from that in the region for which iron and copper are deposited. In the presence of a non-purified electrolyte, an additional loss in the electrocatalytic activity is observed (Fig. 3) which becomes significant as soon as the accumulation of metallic impurities is noticeable (Figs 4 and 5, Table 2). In addition, the increase of i_0 with t_{100} (Table 3) from 7.3×10^4 to 75.4×10^4 s is rather small considering the increased surface roughness resulting from the deposition of metallic impurities (Fig. 4). This agrees with the generally lower activity for HER on iron and copper as compared to Pt [12].

Comparison of the electrocatalytic activity at 0.5 and 14 ppm dissolved iron (Fig. 7) indicates it is poor when the deposit is a mixture of iron and copper. After $\approx 7.5 \times 10^4$ s at 100 mA cm^{-2} , the reaction mechanism for the HER is not the same for 0.5 as for 14 ppm dissolved iron owing to differences in the related Tafel parameters. Otherwise, the typical anodic behaviour of the deposit formed in the presence of 14 ppm dissolved iron is indicative of a pure iron deposit (Fig. 9), as confirmed by EDX analysis. Therefore it may be concluded that the activity of the metallic deposit is closely related to the morphology and nature of the deposit.

Comparison of the electrocatalytic activity and the anodic behaviour of metallic deposits from 0.5 and 14 ppm dissolved iron indicates poor activity and anodic dissolution when the iron is mixed with copper. In the presence of 14 ppm iron, high activity of the deposit and typical anodic behaviour of iron are indicative of a pure iron deposit. The electrocatalytic activity of the latter is more or less equivalent to that of pure Pt. The hydrogen overpotential of the deposit remains relatively high because of a large Tafel slope. The improved electrocatalytic activity of a deposit formed in the presence of 14 ppm dissolved iron is tentatively ascribed to the formation of small crystallites of pure iron on a Pt substrate (Fig. 8), which are known to strongly reduce the Tafel slope [13]. It is of interest to mention that in a recent investigation by Huot *et al.* [14] on an amorphous alloy containing iron, the improved electrode activity is attributed to the formation of very fine Fe particles on the amorphous matrix resulting from an electrochemical process which significantly reduces the Tafel slope and the overpotential of the hydrogen discharge.

The rate-determining step (r.d.s.) in the deposition of metallic impurities on cathodes may be mass transfer, charge transfer or surface reaction between the adsorbed hydrogen and metallic intermediate. In very dilute solutions, it is tentatively suggested that the r.d.s. is the mass transfer of metallic impurities. The stirring of the solution close to the evolving H_2 cathodes at 100 mA cm^{-2} is sufficiently strong to induce turbulent flow, affect the diffusion layer of

metallic impurities and influence the metallic deposition kinetics. However, further efforts are required to clarify this point.

5. Conclusion

The loss of efficiency for the HER on Pt cathodes takes the form of increases in the cathodic overpotential at constant current density. The overpotential increase with time depends on the applied current density and is tentatively attributed to the penetration of atomic hydrogen into the metal lattice. Iron and copper deposits observed on the cathode surface in the presence of a non-purified electrolyte are found to be detrimental to the hydrogen discharge. The significant improvement in the electrocatalytic activity of the cathode in the presence of 14 ppm iron is attributed to the formation of small crystallites of pure iron on the substrate.

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