SHORT COMMUNICATION

The effect of metallic impurities on the hydrogen evolution reaction rate on group-Ib metals in alkaline solution

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Received 11 September 1990; revised 20 November 1990

1. Introduction

Although the hydrogen evolution reaction (HER) has been widely studied in acidic and alkaline solutions [1], many questions remain to be answered. A particular aspect is the high sensitivity of the HER rate upon the state of the surface. For example, the rate of hydrogen evolution on Cu and Au electrodes can be considerably increased by potentiodynamic ageing of anodic films [2, 3], while Ag electrodes can be "activated" by continuous potential cycling between the hydrogen evolution and the oxide regions [4]. We have previously reported that HER rate enhancement can be promoted on Ag electrodes in alkaline solutions by prolonged polarization in the hydrogen evolution region [5]. In that work, a roughening effect was discarded and a restructuring of the surface rendering a higher concentration of active sites (Ag*) was suggested. Subsequently, the same potential perturbation was applied to Cu and Au and similar increase of the hydrogen current was observed.

The aim of this work is to present additional data to show the HER rate increase obtained in alkaline solution, after potential holding treatments, is due to chemical rather than structural modifications of the electrode surface.

2. Experimental details

All experiments were carried out in a conventional three-compartment cell. The counter electrode was a gold sheet separated by a glass frit. All potentials were measured against a Hg/HgO/NaOH (0.1 M) reference electrode. The working electrodes of Cu, Ag and Au, made from metal rods (Koch Light, 99.999%) embedded in a Teflon shroud, were mechanically polished and thoroughly rinsed before each run. Solutions were prepared from analytical grade NaOH (Merck, p.a.) and Millipore water and were continuously deareated with purified nitrogen. The supplied analysis of the reagent showed that the main metallic impurities are iron, nickel, aluminium and heavy metals such as lead (0.0005% each). Some solutions were preelectrolyzed in a polypropylene cell using a copper cathode and a gold anode at approximately 0.7 mA for several days, while being stirred and kept saturated with nitrogen.

Experiments applying potential holding treatments combined with triangular potential sweeps have been previously described [5]. After polarization, some samples were examined by X-ray microanalysis (EDAX) with an EDAX PV 9100 instrument.

3. Results and discussion

3.1. *HER rate enhancement promoted by potential holding treatment*

Significant enhancement of the HER rate on Ag electrodes in alkaline solutions can be promoted by polarization at a constant potential in the hydrogen region combined with rotation of the electrode [5]. Similar behaviour has been observed on Cu and Au electrodes. In the present work, potential holding treatments were carried out under severe conditions (for example, very negative values of holding potential, E_h, and/or high rotation rates). The j/E profiles shown in Fig. 1 were obtained for a gold electrode in 0.1 M NaOH before (curve I) and after (curve II) a 60 min polarization at -1.30 V with 3000 r.p.m. rotation. A greater HER enhancement and the presence of several current peaks in the double layer region, whose charge, relative size, shape and position changed rapidly and in a rather complex fashion during cycling, are seen. Most of the changes in the distribution of charge occurred during a few cycles and further cycling showed a steady charge distribution from which a conjugate redox couple was clearly defined (current peaks A_I and R_I). During further cycling the overall charge diminished slowly. Additionally, a small decrease of the oxygen evolution overpotential that disappeared after a few cycles was also observed. Figure 2 shows the j/E profiles obtained for an identical experiment carried out in extensively preelectrolyzed 0.1 M NaOH solution. As can be seen, HER enhancement was considerably smaller than that observed in solutions without preelectrolysis. Simultaneously, the charge associated to the processes showing up in the "double layer" region after polarization dropped so significantly that the current peaks seen in Fig. 1 are almost absent. In contrast with previously published results [5], a 10 min potential holding treatment at 550 r.p.m. carried out in a preelectrolyzed solution, produced only a slight increase of hydrogen current.

From comparison of Figs 1 and 2, it is clear that impurity species, whose bulk concentration is lowered by the preelectrolysis, are involved in the HER "acti-

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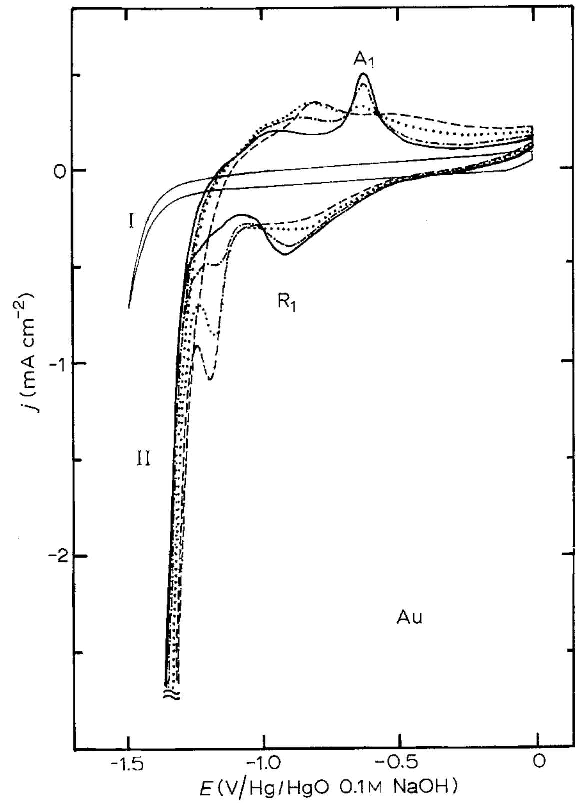

Fig. 1. Potentiodynamic j/E profiles at 0.1 V s^{-1} for a Au electrode in 0.1 M NaOH. (I) mechanically polished electrode. (II) after potential holding treatment at $E_h = -1.3$ V (60 min, ω = 3000 r.p.m.). Cycles depicted are: (– – –) first, (····) second, and those after (–·–·–·–) 5 min and (——) 10 min.

vation" as well as in peaks A_1 and R_1. From the analysis supplied for the reagent, it seems likely that metallic impurities cause the observed phenomena.

Examples of the influence of metallic impurities on the HER in alkaline solutions are found in the literature [6, 7]. For Co cathodes in base solutions, Huot and Brossard [8] have reported significant variations of Tafel parameters with time and examining these cathodes by X-ray microanalysis have found deposits of copper, iron and zinc after 60000 s polarization. Other electrochemical processes, such as oxygen evolution [9, 10] and self-discharge of chemically precipitated nickel hydroxide electrodes [11], have been found to be sensitive to iron impurities in reagent grade electrolyte.

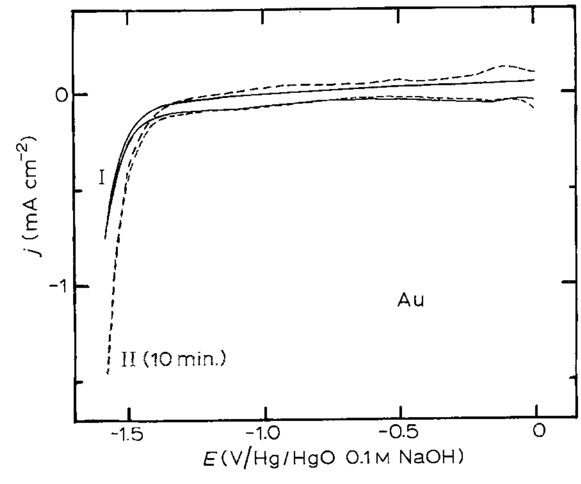

Fig. 2. Potentiodynamic j/E profiles at 0.1 V s^{-1} for a Au electrode in *preelectrolyzed* 0.1 M NaOH. (I) mechanically polished electrode. (II) As in Fig. 1. Only the profile after 10 min is shown.

In the present work, X-ray microanalysis (EDAX) was employed to analyse impurities deposited on the electrode surface. Apparently, the concentration of metallic impurities in the NaOH solution was low enough to prevent accumulation of deposited impurities in detectable amounts. However, a sample of Cu kept at -1.30 V for one week showed small amounts of iron, lead and mercury. Nickel was not detected.

Intentional addition of Fe^{2+} to the electrolyte produced an increase in the magnitude of the HER activation promoted by polarization in the hydrogen region. The j/E profiles recorded subsequently were similar to those of Fig. 1 although peaks A_1 and R_1 appeared selectively enhanced. The characteristics of A_1 and R_1 are very similar to those exhibited by the electrochemical reactions taking place in the same potential region on a colloidal film of $Fe(OH)_2$ chemically precipitated on a conducting substrate such as Au or C [12], thus indicating that the main contribution to the observed HER enhancement is due to iron impurities in the NaOH solution. However, for Ag and Cu electrodes, an "activation" effect can be obtained for E_h values more positive than the reversible potential for iron deposition. Therefore, although mainly caused by accumulation of iron onto the surface, HER enhancement can involve other metallic impurities (such as Ni, and heavy metals). This could be the cause of the complexity of the behaviour observed on group-IB metals after potentiostatic treatments.

3.2. *HER enhancement on Ag electrodes undergoing prolonged potential cycling*

The hydrogen current measured on Ag electrodes after prolonged potential cycling in alkaline solutions was found to be considerably higher than what would be expected from the increase in the electrode area caused by roughening (Figs 2 and 3 in [4]). This behaviour was interpreted as a restructuring surface effect. A set of current peaks appearing in the double layer region after prolonged cycling and an apparent $+1$ reaction order with respect to OH^- concentration for the HER were also reported in [4].

In the present work, Ag electrodes were cycled for long periods between the oxide formation and the hydrogen evolution potential regions at 0.1 V s^{-1} sweep rate in extensively preelectrolyzed 0.1 M NaOH solutions. Under these conditions, the current associated with the faradaic processes continuously increased as shown in Fig. 3. However, the ratio of the HER current increase with respect to that corresponding to oxide formation (or reduction) indicates that the "activation" of the HER is considerably smaller than that previously reported [4]. Additionally, the processes showing up in the "double layer" region involved significantly smaller charges. These current peaks and

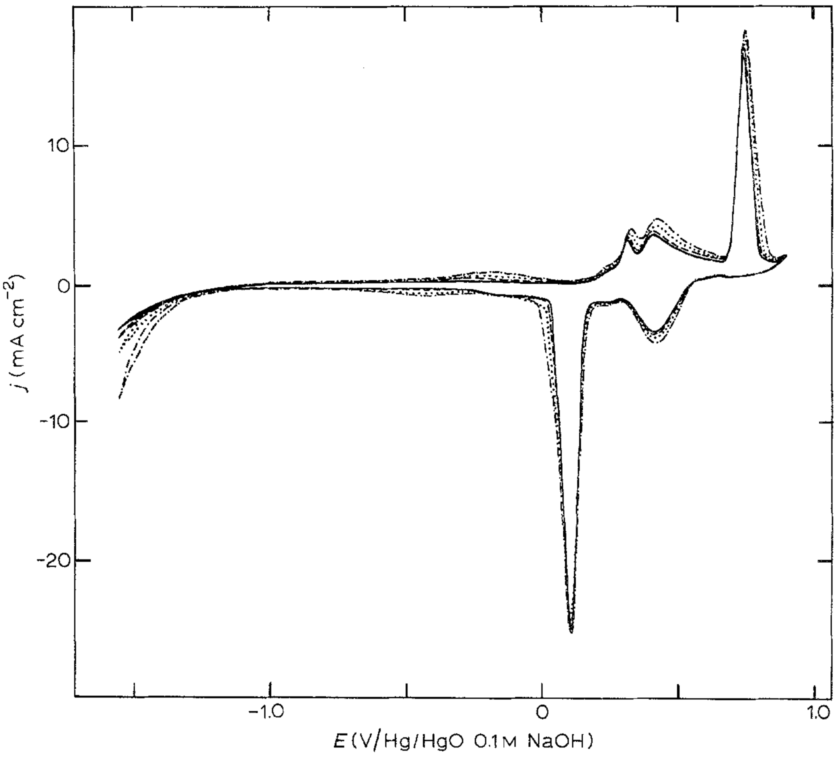

Fig. 3. Silver voltammograms run between -1.6 and 0.9 V at 0.1 V s^{-1} in *preelectrolyzed* 0.1 M NaOH. Cycles depicted are: (——) second cycle and those after (- - -) 15 min, (····) 1 h and (–·–·–) 3 h.

the HER rate enhancement seem to be intimately related and are likely to be produced by accumulation of impurities on the electrode surface. Furthermore, the apparent +1 reaction order with respect to OH^- concentration that was reported in [4] could be caused by a proportional change in impurity concentration in the working solutions.

3.3. *Preelectrolysis of alkaline solutions*

The HER enhancement obtained after potential holding experiments in preelectrolyzed solutions is very small on either Cu, Ag or Au. However, the magnitude of the HER enhancement considerably increases (some times reaching the same order as that obtained in solutions without preelectrolysis) when the preelectrolyzed solution is stored in a Pyrex glass container. Therefore, preelectrolysis, even for relatively dilute solutions, should be carried out in a polypropylene cell and preelectrolyzed solutions should be stored in polypropylene bottles [9]. Further, if the aim of a preelectrolysis of alkaline solutions is to reduce the level of metallic impurities, it will be more effective if a metal with a high overpotential for hydrogen evolution is used as cathode material [11].

Reviewing the literature on HER in alkaline solutions, Appleby has mentioned (p. 518 in [1]) that in contrast to acidic solutions, little need for preelectrolysis has been noticed. It has been pointed out that apparently, in solutions of analytical grade purity the results are reproducible on well-prepared surfaces. The results reported here showed, in general, good reproducibility. Thus, fulfilment of this requirement does not guarantee solution cleanliness, since artifacts can be quite reproducible in some cases.

4. Summary and conclusions

The HER rate enhancement obtained on group IB metals after potential holding treatments and on Ag electrodes that undergo prolonged potential cycling in alkaline solutions appears to be mainly an artifact caused by the deposition of metallic impurities onto the electrode surface. The main contribution to the hydrogen current increase seems to be due to an accumulation of iron. The results hitherto reported show the importance of preelectrolysis in alkaline solutions and could be helpful in understanding, at least partially, why the HER shows a very high sensitivity to surface pretreatment and electrolyte on most metals.

Acknowledgements

Financial support from the Consejo Nacional de Investigaciones Cientificas y Técnicas of Argentina (CONICET) and the Consejo de Investigaciones Cientificas y Tecnológicas de la Provincia de Córdoba (CONICOR) is gratefully acknowledged. We thank Dr B. Cahan for helpful discussion and Miss L. P. Falcón for language assistance.

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