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Hydrogen Evolution Reaction on Gold Single-Crystal Electrodes in Acid Solutions

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The hydrogen evolution reaction on the low index planes of single-crystal Au electrodes has been studied in $HClO_4$ solutions with the aim of ascertaining the extent of the sensitivity of the reaction rate to the surface crystallographic structure. The use of the hanging meniscus rotating disk technique allowed to carry out all measurements under rotation, thus avoiding blocking effects produced by hydrogen bubbles and accumulation of dissolved hydrogen in the interfacial region during potential excursions into relatively high overpotentials. In contrast with previously published results showing only slight variations in activity with Au crystal face, a pronounced structural sensitivity is reported *for the first time*. The catalytic activity presents the following sequence Au(111) > Au(100) > Au(110).

1. Introduction

The hydrogen evolution reaction (HER) has been widely investigated on many different electrode materials and in a variety of electrolytic solutions and experimental conditions.[1] However, despite the large number of published papers about the HER, some fundamental aspects remain unresolved. For instance, the question of whether this reaction is sensitive to the crystallographic orientation of the electrode surface is still unclear. Although the importance of structure-sensitive data to elucidate the characteristics of the HER was recognized in the 1960s in the pioneer work of Piontelli[2] and other electrochemists, early studies of the HER on single-crystal electrodes were carried out on poorly defined surface structures. The development of surface preparation techniques that give well-defined single-crystal surfaces did not begin until the mid-1970s.[3] Unfortunately, more recent studies of the HER on well-ordered single-crystal surfaces are still relatively scarce and insufficient to establish any significant correlation between HER kinetics and surface structure.

While hydrogen adsorption on Pt single crystals has been extensively studied and found to be very sensitive to crystal plane,[4−13] only a few papers have been devoted to the HER on Pt single crystals.[14−21] Most of them reported that the kinetics of the HER is insensitive to the surface structure,[14−19] and only recently significant structural sensitivity for the HER on low-index Pt single crystals in acid as well as in alkaline solutions has been reported,[20,21] with the (110) face being the most active.

Even fewer papers have been dedicated to study the HER on single-crystal electrodes with weak catalytic activity, like Au and Ag. To our knowledge, after the two papers published some 35 years ago by Peraldo Bicelli et al.,[22,23] only three studies of the HER on gold single crystals have been reported.[24−26] Two of them were devoted to the study of the influence of surface structure on the HER rates[24,25] and the third one to temperature effects on the (111) and (210) faces.[26] A small dependence of kinetics on the crystal plane was reported, but unfortunately, the results of those investigations were found to depend on the previous potential history, were poorly reproducible, showing variations in currents up to 25% for some of the faces, and present contradictions in the order in which catalytic activity is observed.[24,25] For the HER on Ag single-crystal electrodes, only two papers were published. A structure-insensitive kinetics was found by Lorenz et al.,[27] while a recent report by Trasatti and co-workers shows significant differences in the behavior of the low index planes in perchloric acid.[28]

It is also worth mentioning that all the work that has been carried out for the HER on Au and Ag single crystals[24−28] was done using stationary electrodes, for which accumulation of hydrogen bubbles is difficult to avoid even when the applied overpotential is kept relatively low. Thus, the discrepancies among reported data and the considerable current variations found in some works could be due, at least partially, to the blocking effect of hydrogen bubbles and/or to the influence of the diffusion of dissolved hydrogen away from the interface.[29] On the other hand, the hanging meniscus rotating disk (HMRD) technique[30] makes very easy the use of cylindrical single crystals as rotating electrodes.[31,32] The use of the HMRD is very simple, requiring only a careful control of the meniscus height to avoid lateral wetting. This introduces undesired contributions to the measured current from the side of the single crystal, which present orientations different from the one being investigated and uncertainties in the evaluation of the effective electrode area.[33,34]

The small amount of published papers and the discrepancies in the reported results clearly show that a definitive correlation between the kinetics of the HER in acid media and surface structure has not yet been established unambiguously and that further research on this subject is necessary. In this work, the HER on Au single crystals is studied on rotating electrodes by using the HMRD technique, which improves the experimental conditions to study this reaction in a wider range of overpo-

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tentials. This is necessary in order to gain a better insight into the effects of surface structure on the kinetics and to clarify some of the discrepancies found in previously published works.

2. Experimental Section

All experimental work was performed at IQSC-USP. High-purity (99.999%) gold single crystals with the orientations (111), (110), and (100) were purchased from Metal Crystals and Oxides (Cambridge, England) with 7 mm length and 5 mm diameter. Mechanical polishing of the crystals was done in specially constructed supports using fine emery paper (Microcut 1200) and several alumina powders down to 0.05 μm from Buehler (Illinois, USA). The orientation of the surfaces was kept to better than 0.5° using procedures described elsewhere.[31]

The single crystals were mounted as HMRD electrodes as previously described.[30] To avoid lateral wetting of the electrodes, the meniscus height was carefully controlled by means of a dial gauge set at 3.1 mm for the three electrodes.

Electrochemical measurements were carried out in a conventional cell made out of Pyrex glass with a lid of Teflon. The auxiliary electrode was gold foil. In all experiments, a reversible hydrogen electrode (RHE) in the working solution was used as reference. Immediately before each experiment, the electrodes were cleaned by “flame annealing” for about 5−10 min and cooled in an Ar atmosphere. Before transferring the electrode to the cell, the surface was protected with a drop of the working solution. All experiments were done in 0.1 M $HClO_4$ (Merck, Suprapur) solutions that were deareated with pure nitrogen. The HMRD electrodes were controlled with a Pine Instruments setup and a EG&G Princeton Applied Research 273 A potentiostat.

3. Results and Discussion

This study of the HER on Au single crystals was carried out by means of slow potential sweeps (typically 10 mV s^{-1}). The currents were found to be independent of sweep rate between 5 and 20 mV s^{-1} indicating quasi-steady-state conditions in that range. Different prepolarization regimes were employed. Successive cycles to different positive potential limits, including formation and reduction of a monolayer of oxide or just within the double-layer region, as well as sequential sweeps to different negative potential limits were recorded. In all cases, results for the HER were found to be independent of the previous potential history. In contrast, it was previously reported[25] that currents were significantly sensitive to the potential cycling conditions in $HClO_4$, while in solutions containing $LiClO_4$ and $NaClO_4$, even larger variations (up to 25% for the smallest currents) were observed on some faces. Moreover, currents were found to be higher when measurements in the hydrogen region took place immediately after a cycle of oxide formation−reduction was completed than after long delay periods between the oxide formation−reduction cycle and the measurement of hydrogen evolution currents.

On the other hand, it has already been established that voltammetric curves for the formation and reduction of a monolayer of oxide, on the low-index planes of Au single-crystal electrodes in $HClO_4$ solutions, exhibit characteristic features that can be used as an indication of the general physical state of the electrode surface[35] and also serve as criterion of solution cleanliness.[31] Such curves were obtained in the working electrolyte before and after the measurements into the hydrogen evolution region and are shown in Figures 1a−3a. Essentially identical voltammetric profiles were obtained before and after several successive cycles into the hydrogen evolution region, even in the case of extended cycling involving relatively high values of current density (ca. 10 mA cm^{-2}). In contrast, it was reported by Hamelin and Weaver[25] that changes in the CV profiles of oxide formation and reduction were observed for the Au(100) face after extended potential cycling into the hydrogen region. These variations were taken as evidence of surface defects. However, it has been demonstrated that variations such as that observed in that work[25] can be associated to the removal of trace impurities from the surface.[31]

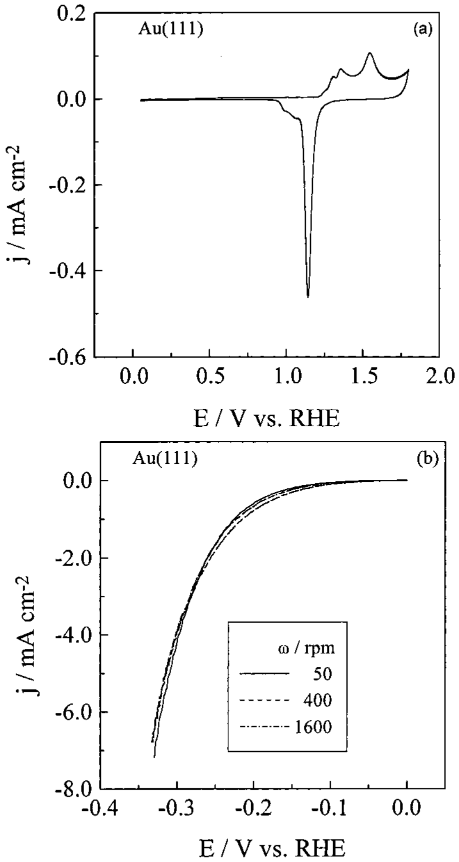

Figure 1. (a) Cyclic voltammetry for Au (111) in N_2-saturated 0.1 M $HClO_4$, sweep rate is 50 mV s^{-1}. (b) Polarization curves for hydrogen evolution at different rotation rates, sweep rate is 10 mV s^{-1}.

For all the faces, sequential sweeps into the hydrogen evolution region were also recorded at different rotation rates ranging between 50 and 1600 rpm. Several successive cycles were recorded and found to be identical for all the values of the rotation rate used and independent of potential regime. The polarization curves obtained at different rotation speeds are shown in Figures 1b−3b. Since hydrogen currents do not increase with rotation rate, it seems clear that for the experimental conditions employed (i) the HER is kinetically controlled (ii) the removal of hydrogen bubbles from the surface is efficient even at 50 rpm or, more likely, bubble formation is impeded by the lack of nucleation centers,[36] (iii) the solution is relatively free from active impurities, which otherwise would be carried to the electrode surface by convection.

However, for the (111) face, slightly lower currents are observed at higher rotation rates, probably caused by the unavoidable presence, even in the cleanest solution, of trace impurities.[31] From these results, a rotation rate of 50 rpm was selected for the kinetic measurements. It is worthwhile to note that the small decrease in the HER current for the (111) face produced by rotation is the *only effect* observed in the present work that can be associated with the influence of trace impurities

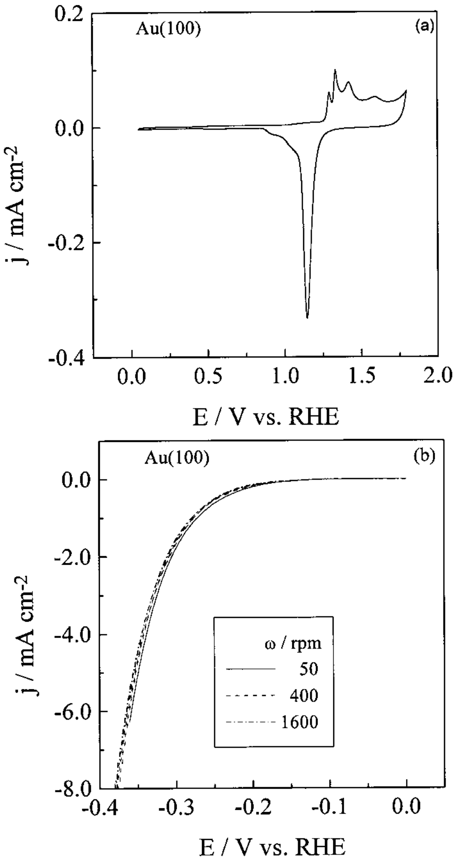

Figure 2. (a) Cyclic voltammetry for Au (100) in N_2-saturated 0.1 M $HClO_4$, sweep rate is 50 mV s^{-1}. (b) Polarization curves for hydrogen evolution at different rotation rates, sweep rate is 10 mV s^{-1}.

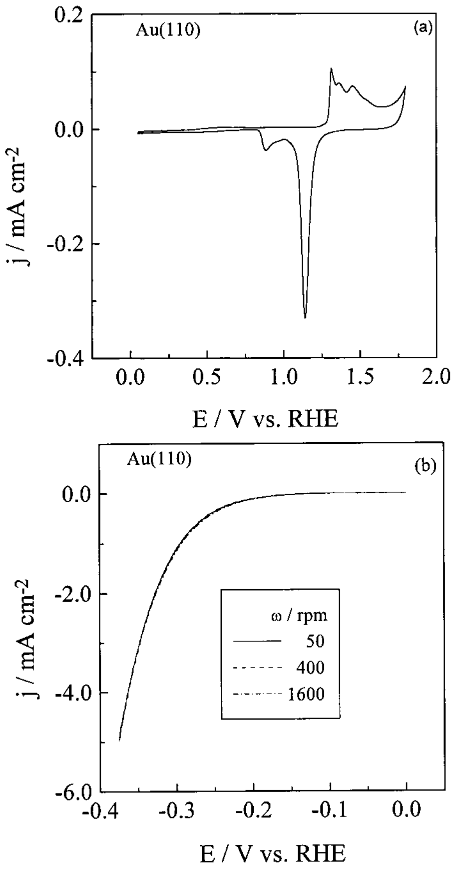

Figure 3. (a) Cyclic voltammetry for Au (110) in N_2-saturated 0.1 M $HClO_4$, sweep rate is 50 mV s^{-1}. (b) Polarization curves for hydrogen evolution at different rotation rates, sweep rate is 10 mV s^{-1}.

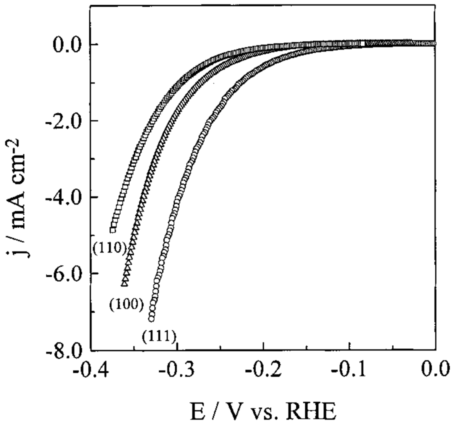

Figure 4. Polarization curves for hydrogen evolution on the low-index gold single-crystal electrodes in N_2-saturated 0.1 M $HClO_4$, sweep rate is 10 mV s^{-1}, rotation rate is 50 rpm.

on the kinetics of the HER. In contrast, it seems likely that the dependence of hydrogen currents on the prepolarization regime and the changes in the voltammetric profiles of oxide formation and reduction observed after measurements in the hydrogen evolution region reported by Hamelin and Weaver[25] could have been caused by impurities. Also, it should be mentioned that the variations reported were quite significant for some of the faces even though all data were obtained using stationary electrodes. From the comparison of the results presented here, which were independent of the potential history and showed that voltammetric curves remained unaltered after the electrode was polarized into the HER region, with those previously published,[25] it seems clear that the surfaces and solutions used in the present work were cleaner.

Figure 4 shows the polarization curves for the HER obtained at 50 rpm for the three Au low-index faces. Taking into account the results discussed, it is conclued that the influence of the surface crystallographic orientation on the HER rate is absolutely clear. Additionally, it should be stressed that such a pronounced variation of activity with the crystal face has never been reported in previous work. As it can be clearly seen in Figure 4, Au single crystals present the following sequence of activity toward the HER: (111) > (100) > (110). As discussed above, previously published data for the HER on Au single crystals seem to have been obtained using polarization regimes that could have favored contamination.[24,25] It remains difficult to explain however, why the small variation of activity with crystal face observed previously was in just the opposite order of that showed in Figure 4.

It is quite interesting to note though that a recent study of the HER on Ag single crystals in acidic solutions[28] has shown that catalytic activity is sensitive to crystallographic orientation. Even more interesting is the fact that the reported data show that catalytic activity toward the HER on Ag single crystals exhibits a sequence identical to that shown for Au in Figure 4, with the (111) face being the most active. This activity sequence for Ag was found to correlate well with the corresponding values of the potential of zero charge, and such a correlation seems to apply also for Au.[37] As pointed out by Trasatti et al.,[28] the HER rate increases with atomic density of the surface; that is, catalytic activity follows the increase of the electron work function.

In addition, despite the fact that most of the published studies of the HER on single-crystal surfaces on several materials have not revealed any pronounced influence of structure on the reaction rate,[1,14−19,22−25,27] Horiuti and Kita[38] showed, from a

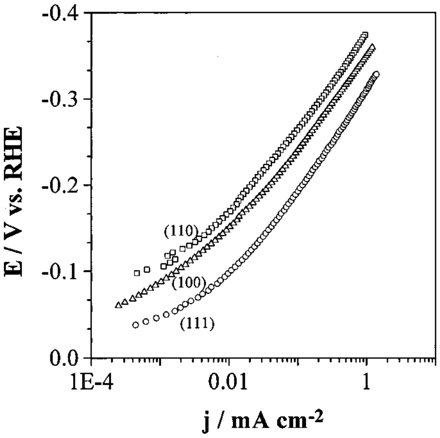

Figure 5. Tafel plots for hydrogen evolution on the low-index gold single-crystal electrodes in N_2-saturated 0.1 M $HClO_4$ obtained from data in Figure 4.

TABLE 1: Exchange Current Densities for HER in the Low-Potential Region

	jo/A cm^{-2}		
	this work, 0.1 M $HClO_4$	from ref 24,[a] 1 M $HClO_4$	from ref 25,[b] 0.1 M $HClO_4$
Au (110)	0.3×10^{-7}	1.0×10^{-7}	1.4×10^{-7}
Au (100)	0.5×10^{-7}	0.7×10^{-7}	1.0×10^{-7}
Au (111)	2.5×10^{-7}	0.8×10^{-7}	0.7×10^{-7}
Polycryst	1.4×10^{-7}		1.2×10^{-7}

[a] Calculated using empirical parameters to fit the experimental curve. [b] Estimated from Figure 3 of ref 25.

theoretical estimation of the recombination rates of adsorbed hydrogen atoms on the low-index planes of Ni, that a large effect of crystallographic structure on the reaction rate should be expected in the order (111) ≫ (100) ≫ (110).

Figure 5 shows the Tafel plots obtained from the polarization curves of Figure 4. The Tafel slope varies gradually from of ca. −0.06 at low overpotentials to −0.12 V/dec at high overpotentials, in about the same way for the three faces studied. Thus, it is apparent that the HER proceeds through the same reaction mechanism on the three crystal faces and that the differences observed in the values of the currents for the HER at any given potential are caused by the influence of surface structure on the rate of elementary steps. Identical behavior was observed for a polycrystalline electrode. Even though the Tafel slope varies continuously with electrode potential, exchange current densities were estimated for the potential region were slope is ca. −0.060 V/dec and are shown in Table 1 compared with literature values.

Despite the large amount of data for the HER on polycrystalline Au electrodes that can be found in the literature, published results are rather inconsistent. Although one value of Tafel slope has been usually reported, values are found to vary from −0.027 to −0.15 V/dec.[39−45] Kuhn and Byrne observed two Tafel slopes, $-2.3RT/2F$ at low current densities with a sharp transition to $-2 \times 2.3RT/F$ at high current densities.[46] More recently, Conway and Bai have also reported a Tafel slope of −0.06 V/dec for the HER on polycrystalline gold at relatively low overpotentials.[47] In view of this variety of reported Tafel slopes, it is surprising that although no great influence of surface structure was found in previous studies of the HER on Au single-crystal electrodes, smoothly curved Tafel plots with slopes changing from ca. −0.06 to about −0.12 V/dec were reported.[22−25] Although some mechanistic interpretation of these values has been proposed,[24,47] further studies seem to be necessary in order to get a complete understanding of the fundamental aspects of this reaction. It will clearly be of interest to perform measurements of the HER on single-crystal faces of Au and other metals using more powerful techniques such as impedance spectroscopy.[48]

4. Conclusions

A large dependence of the kinetics of the hydrogen evolution reaction on gold electrodes in $HClO_4$ solutions with the crystallographic orientation of the surface was found *for the first time*. The reaction seems to proceed through the same mechanism on the three faces studied. The catalytic activity increases with atomic density of the surface and presents the following sequence: Au(111) > Au(100) > Au(110).

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