

More information may be obtained from analysing the shape of the differential pulse voltammograms. Measurement of the peak width at half-height of the differential pulse voltammogram,  $W_{1/2}$ , and use of the formula [3]

$$W_{1/2} = 3.52RT/nF$$

enables calculation of  $n$ , the number of electrons transferred. From our voltammograms we found values of  $n$  between 0.5 and 1.0 for the different herbicides. This result suggests a degradation mechanism that includes the formation of dimers at some pH's.

The anodic oxidation mechanism of these urea herbicides leads to various products. We have evidence that the final products are not electroactive and adsorb irreversibly at the surface of the electrode: this was confirmed by bulk electrolysis where there was total blockage of the electrode surface by the products. An HPLC analysis of the products of electrochemical degradation of Fenuron show three different compounds which we are trying to identify using i.r. and n.m.r. spectroscopy. Similar studies are being carried out with the other herbicides. However it seems that a plausible explanation is that the oxidation of these ureas herbicides forms a radical that may dimerise, polimerise or cleave.

#### References

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#### O<sub>2</sub> REDUCTION ON REORGANIZED GOLD SURFACES Carlos Paliteiro *Departamento de Química, Universidade de Coimbra, Portugal*

The reduction of O<sub>2</sub> on gold was shown to be structure dependent (1,2). The (100) surface reduces O<sub>2</sub> at a lower overpotential than the (110) and (111) surfaces; moreover, in alkaline solutions and at low overpotentials, the former surface is able to reduce O<sub>2</sub> to HO<sub>2</sub><sup>-</sup> whereas the latter reduce O<sub>2</sub> only to HO<sub>2</sub><sup>-</sup>.

We found (3) that in alkaline solutions O<sub>2</sub> is reduced to HO<sub>2</sub><sup>-</sup> on polycrystalline gold and on thin films of gold deposited on graphite and platinum. The polarization curves relative to O<sub>2</sub> reduction on the above mentioned surfaces show considerable hysteresis when recorded between -50 mV and ≈1270 mV (potentials are referred to the hydrogen electrode immersed in the same solution).

If however the potential is slowly scanned from -50 mV to ≈1000 mV in alkaline solutions, the shape of the polarization curves for both thin films and polycrystalline surfaces gradually change to the characteristic shape of the polarization curves of the (100) surface (Fig.1). This change is followed by a decrease of the hysteresis.

The cycled ("100") surface is stable out of the cell, both in pyrolyzed water and in air. It is also stable in acid solutions. In 10<sup>-2</sup> M HClO<sub>4</sub>, we found the same relative activity for the "100" and the uncycled polycrystalline ("111") surfaces (Fig.2) as that reported by Jüttner (4) for the (100) and the (111) single crystal surfaces. The "100" face reverts to the "111" face when the potential is cycled

beyond a certain value: 1.2V in 1 M NaOH and 0.8V in  $10^{-2}$  M  $\text{HClO}_4$ , for example. Once the "100" surface reverts to "111" it is not possible to get it again by cycling; only an incipient maximum is got in this case.

The CV under  $\text{N}_2$  of the "111" surface shows a cathodic peak at  $\approx 825$  mV to which corresponds an incipient anodic peak centred at  $\approx 875$  mV. The peak currents of these peaks are significantly increased by cycling, as shown by the CV under  $\text{N}_2$  of the "100" surface. These peak currents vary linearly with the scan rate, which do not affect the peak potentials up to  $100 \text{ mV s}^{-1}$  (the maximum scan rate explored); this is consistent with a fast adsorption-desorption process (5). Also the peak potential varies 60 mV/pH unit and the peak current increases with the concentration of  $\text{OH}^-$ . These experimental facts strongly suggest that  $\text{OH}^-$  is significantly adsorbed on the "100" surface in the 750-950mV potential range.

Is the "100" surface a real (100) surface resulting from full restructuring or faceting of the polycrystalline surface? The experimental conditions used do not lead to faceting (6) and the capacity-potential curves recorded on the "100" surface seem to show that it is not a real (100) surface. Nevertheless, other experimental facts indicate that some reorganization of the polycrystalline surface occurs under the experimental conditions described: i) hysteresis is generally smaller for  $\text{O}_2$  reduction on "100" than on "111" surfaces, and occurs at different potential ranges; ii) change from "111" to "100" is quicker after mechanical polishing of polycrystalline surfaces or when freshly deposited

thin films are cycled. From the discussion above we infer that such reorganization favours  $\text{OH}^-$  adsorption.

The higher activity of the (100) surface in alkaline solutions relative to that of the (110) and (111) surfaces was explained in two different ways:

-the geometry of the atomic arrangement of the (100) surface favours the dissociative adsorption of  $\text{HO}_2^-$ , which is then easily reduced to  $\text{OH}^-$  (1);

-the (100) surface adsorbs OH species which, contrarily to what happens on the other two surfaces, are discharged; the adsorption of  $\text{HO}_2^-$  and other charged intermediates is therefore favoured, and reduction proceeds further to  $\text{OH}^-$  (2).

Our experiments show that  $\text{O}_2$  reduction in alkaline solutions starts at the potential of reduction of the OH layer both for the "100" and the "111" surfaces. This fact seems to support Adzic et al (2) when they relate  $\text{O}_2$  reduction on the (100) surface with adsorbed OH species. However, contrarily to Adzic views, our RDE experiments suggest that the "100" surface is more active than the "111" surface for  $\text{O}_2$  reduction in the lower potential range mainly because it is more able to disproportionate the  $\text{HO}_2^-$  formed during the  $\text{O}_2$  reducing reaction in that potential range.

#### References

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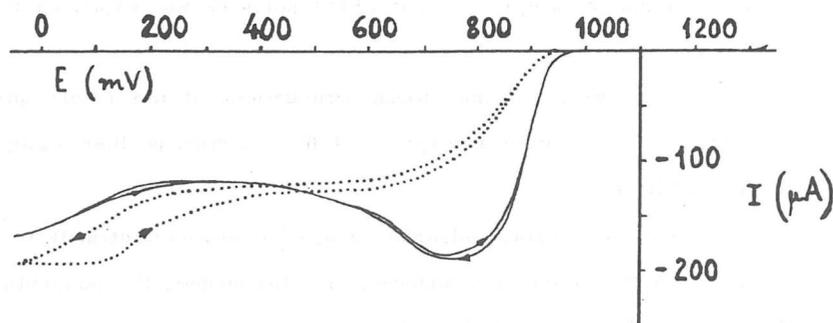


Fig. 1: Polarization curves for  $O_2$  reduction on polycrystalline gold at  $9 \text{ s}^{-1}$  and  $10 \text{ mV s}^{-1}$  in a  $O_2$ -saturated  $1 \text{ M NaOH}$  solution: (—) "100" surface, (...) "111" surface; electrode area:  $0.126 \text{ cm}^2$

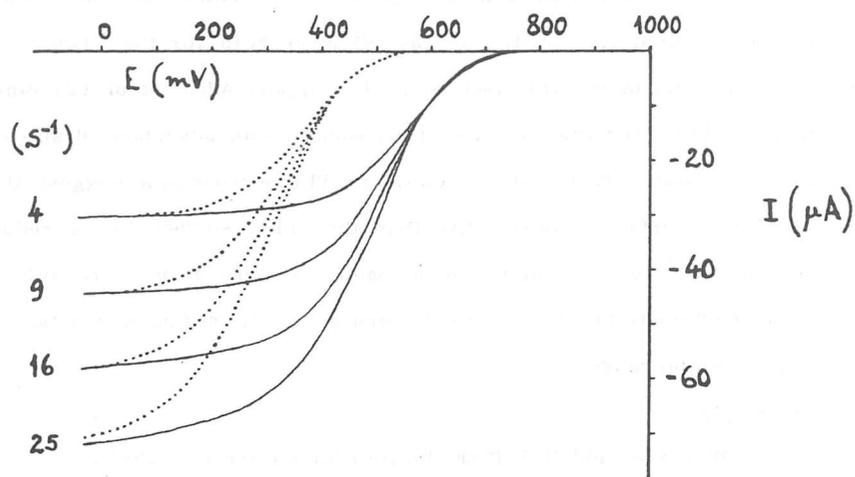


Fig. 2: Polarization curves for  $O_2$  reduction on polycrystalline gold at  $10 \text{ mV s}^{-1}$  in a  $O_2$ -saturated  $10^{-2} \text{ M HClO}_4$  solution: (—) "100" surface, (...) "111" surface; electrode area:  $0.126 \text{ cm}^2$

### Chronopotentiometric and Impedance Studies at the Nitrobenzene-Water interface in the presence of 1:2 Electrolytes

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Increasing interest have been given to interfaces between two immiscible electrolyte solutions due to their application in ion selective electrodes and electrochemically assisted ion transfer.

The interface between water and nitrobenzene have been studied in the presence of 1:1 and 2:2 electrolytes in the aqueous phase<sup>1,2</sup>. Here it is reported a study of the properties of the water nitrobenzene interface in the presence of 1:2 electrolytes in the aqueous phase and TPBTBA in the organic phase. The aqueous phase were  $0.1 \text{ M}$  solutions in  $CaCl_2$ ,  $SrCl_2$ ,  $BaCl_2$ , and  $MgCl_2$ .

Cyclic Voltammetry does not show significant dependence of the polarization potential limits on the nature of the alkaline earth cation. The influence of the nature of the cation is more visible in the chronopotentiometric data in fig. 1. The data indicates that the transference is diffusion controlled<sup>3,4</sup> but the relation between the transition times and the values of the imposed current densities is not as simple as described for other systems<sup>5</sup>.

Impedance spectra for the interface was obtained and typical results are illustrated in fig. 2. The nature of the cation is put in evidence in the semicircle observed at high frequencies. Although the semicircle observed on the impedance diagram at high frequencies is an experimental artifact due to the reference electrode circuitry<sup>1</sup> the dependence of the radius of the semicircle on the cation may be a result of the different conductivities of the solutions. From the low frequency domain the