Influence of the Surface Structure of Metal Electrodes on the Double Layer Parameters and Reaction Kinetics.*

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I.INTRODUCTION.

Most of fundamental electrochemistry was built on experimental results obtained with liquid electrodes: mercury or amalgams. As a matter of fact, the dropping mercury electrode is renewed, its surface is maintained reproducible during the time of an experiment. On the contrary for solids the surface cannot be easily renewed.Furthermore for one solid metal electrode the surface may be:

- either covered by a disturbed layer of its atoms,
- or just a bulk termination.

In the second case if the bulk of the metal is polycrystalline, different grains and grain boundaries exist at the surface. If the bulk of the metal is only one grain (then it is a single crystal) the bulk termination has the crystallographic orientation (co) of the plane (or face) along which the metal is cut. This plane can be specified by a set of Miller indices.

Some basic crystallography is necessary for understanding the following sections. Mostly results obtained with gold and silver faces will be discussed: these two metals crystallize in the face centered cubic system (fcc). All planes of a system may be represented on a map (which is a flat sphere) (for fcc see fig.1). Pure metals have a high level of symmetry, therefore it is sufficient to consider one Unit Stereographic Projected Triangle (fig.2).

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* References will be given only for works which are not discussed in Chapter 1 ,Modern Aspects of Electrochemistry,vol.16,p.1,1985, or in Trends in Interfacial Electrochemistry, NATO ASI C179,p.83-102,1986.

Plenary lecture given at the 3rd Meeting of the Portuguese Electrochemical Society, Algarve, November, 1987.

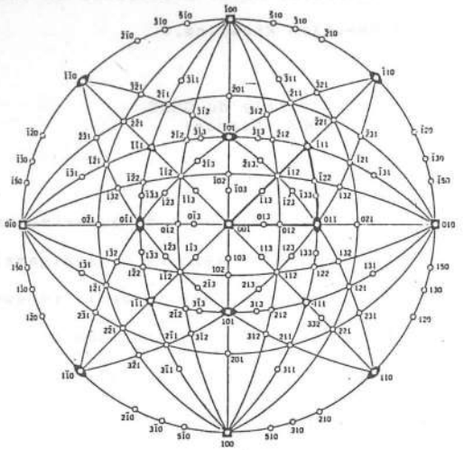


Figure 1. Standard (001) stereographic projection of poles and zones circles for cubic crystals (after E. A. Wood, *Crystal Orientation Manual*, Columbia Univ. Press, New York, 1963).

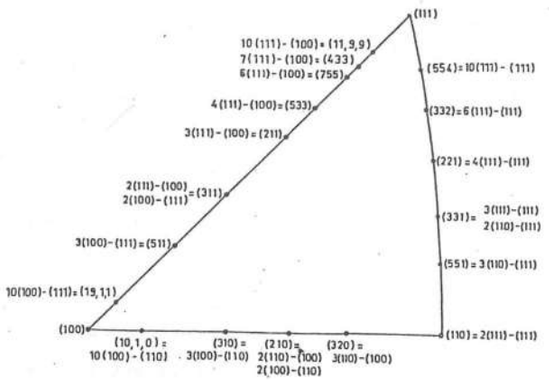


Figure 2. Unit projected stereographic triangle for the fcc structure. Miller indices and step notation are given.

II. SURFACE

Electrochemistry takes place on the outermost layer of the metal atoms of the electrode. Therefore as well the chemical state as the physical state of this top layer are responsible for the electrochemical results.

The chemical state of the surface, in electrochemical situations, depends on the quality of the metal itself, the surface preparation and the cleanliness of the interface (solvent, ions, gas, tubing of the gas, glassware). It is obvious that to observe a phenomenon which depends on the distribution of atoms , which are a few angstrom large, no large molecules of organic matters should be present at the interface. The interface has to remain clean during the observations; for mercury drops about 4 seconds were sufficient, for solids it has to remain clean for several hours. This fact makes clear why reliable results on solid electrodes are not numerous, and why some of them are still controversial.

The physical state of the metal surface for single crystal faces has to be kept under control. A face is an atomically flat surface : the atomic arrangment is what it is in a plane parallel to the surface in the bulk of the metal and it should be maintained so during the electrochemical experiment. Assuming that the metal atoms are just hard sphere any face can be represented by ball models. Models for low and higher index faces are given (fig. 3,4). For the fcc system, (111) is the most close packed face and (210) the roughest on an atomic scale. Atomically flat surfaces nearly parallel to low index faces can be described by a composition of terraces (111),(100) or (110) and monoatomic steps. This model is called the TLK (terrace,ledge,kink) model. A convenient notation was proposed: $n(h_t k_t l_t)-(h_s k_s l_s)$, where $(h_t k_t l_t)$

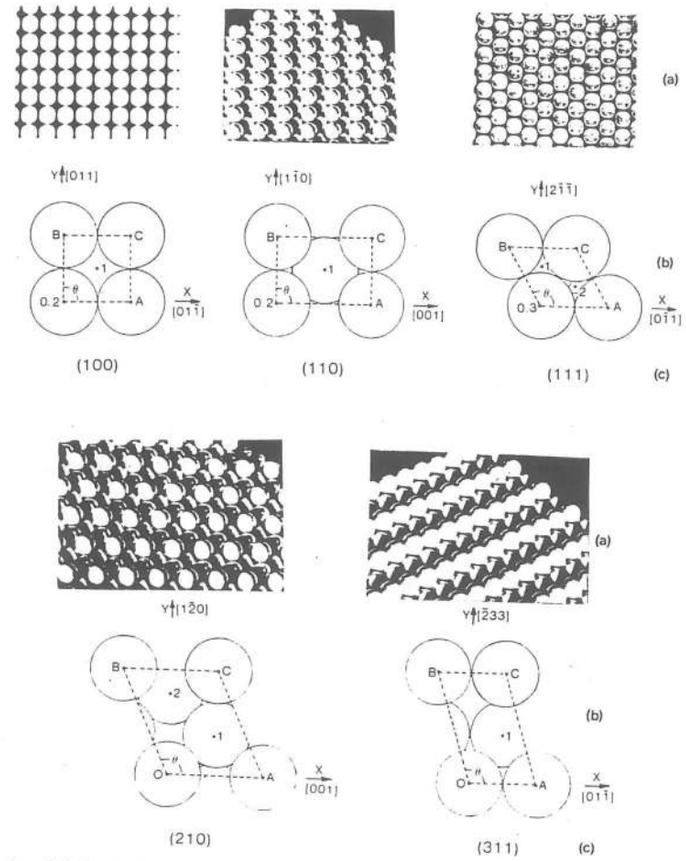


Figure 3. Ball models for five faces of the fcc system (a) Photographs. (b) Drawings looking normally at the model. The center of each surface atom which lies on, or inside, the unit-cell boundary is marked with a dot; in some cases this is all that can be shown of that atom. 0, 1, 2 are the number of the layer of atoms (0, 2 implies that one atom lies directly behind the other). (c) Miller indices.

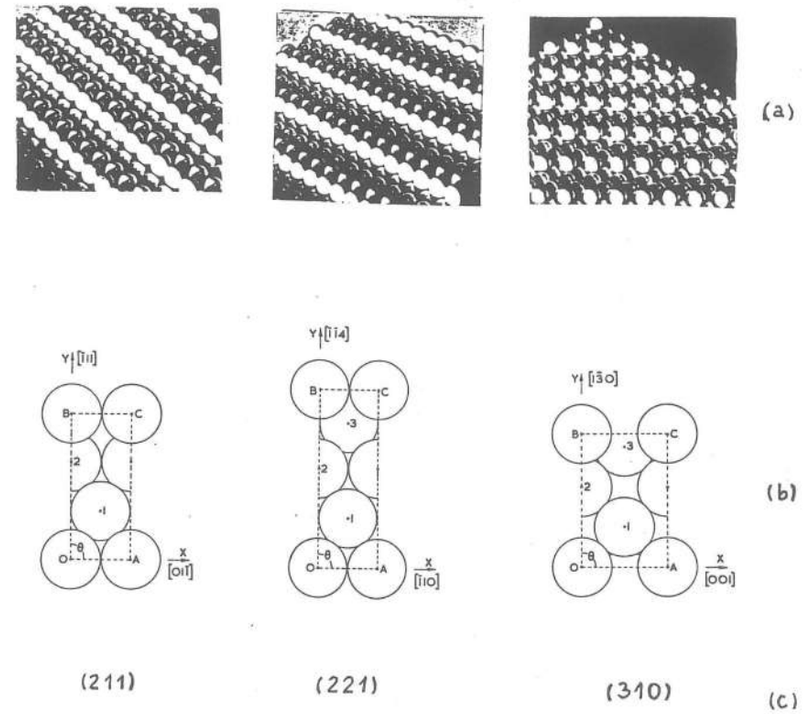


Figure 4. Models for the (221), (211), and (310) faces of the fcc system. Comments are the same as for Figure 3

represents the co of the terraces, $(h_s k_s l_s)$represents the step face and n denotes the width of the terraces in number of atoms.

According to the "jellium model" of metals , besides the positive ions there is a "gas" of electrons. At the surface, the electron density dies off gradually, the electrons spreading out perpendi_ cularly to the positive ion lattice(fig.5a). The charge density is negative on the outer side and predominantly positive just inside the metal: an electric double layer is created(fig.5b). The dipole moment of this double layer varies with the nature of the metal and with the co for one metal. The variations of the electronic work function with the co is due to this double layer. For actual faces the positive charge is not uniformly distributed; for a corrugated face (on an atomic scale), or a stepped face, the contours of constant electronic density have ridges and valleys corresponding to those of the distribution of the positive ions at the surface, but they are smoother(fig.5c). The amount by which the "smoothing" parallely to the surface,decreases the double layer moment will be the greater the rougher, on an atomic scale, the surface is. This "smoothing" makes the rougher face to have the lower work function and (111), for the fcc system, to have the highest work function.

Practically how may be obtained chemically clean and physically well defined interfaces?

Only the use of well prepared single crystal faces allows to control the physical state. As for a chemically clean interface it may be produced, for instance for gold, by flame treatment (town gas and oxygen) to burn all dirt and cooling in ultra pure water.Without any contact with the ambient air , the face is put in contact with the

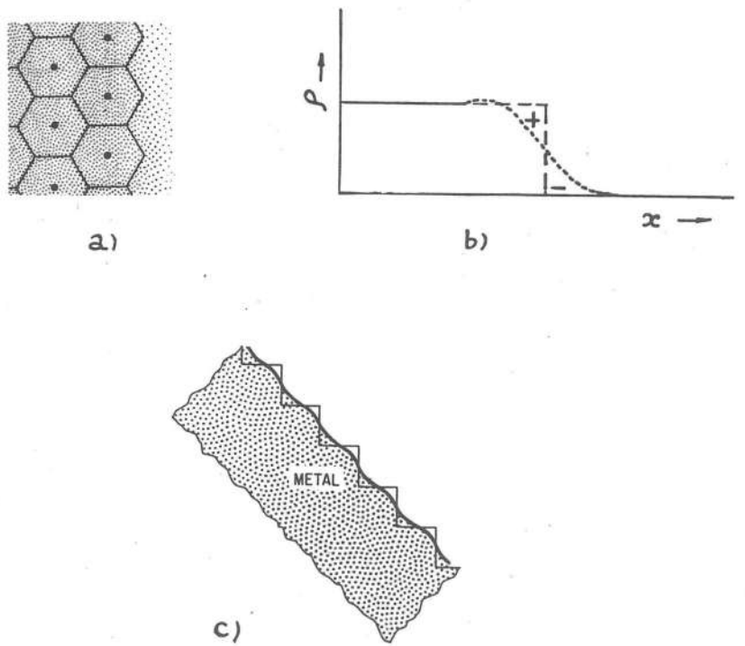


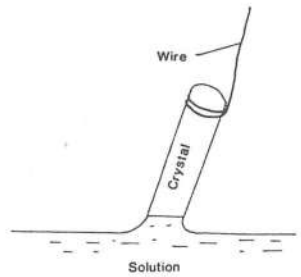
Figure 5 - a) Spreading out of the electron gas of the metal perpendicularly to the surface of the positive ions, b) an electric double layer is formed, c) smoothing of the electron gas parallely to the surface (after Smoluchowski).

solution according to the hanging electrolyte method (fig.6). This flame treatment was adapted to silver faces and to gold in non-aqueous solvent, by cooling in a flow of argon instead of water. In all cases contact with ambient air was avoided .

Ex situ checks of solid surfaces may be done in UHV. Are the surfaces observed in UHV close to the ball models? In some cases they are, but for gold, for instance, a"reconstruction"of the outermost layer of atoms was observed for low index faces. Now do these reconstructed structures exist when the surface is put in contact with the elec_ trolyte? The answer is not yet clear cut.

In situ checks of the state of the surface of the electrode and of the whole interface is necessary. For gold on CVs the profile of the current corresponding to the formation of a monolayer of oxide is considered as a"finger print"of the face (fig.7a), comparison of the first profile of current to the second,third,etc,ones is a test of the cleanliness of the interface (fig.7b).
For silver ,or for gold in the case of strong adsorption, such an observation is not possible.Then the shape of the contribution of the diffuse part of the double layer on the differential capacity-potential curves ,C(E),when working in dilute solution,is a possible check of the state of the interface (fig.7c,d).A most important check, is the stability and the reproducibility of the results, for a pre_ cise potential-time programme.

Figure 6. Only the face of interest is in contact with the solution.



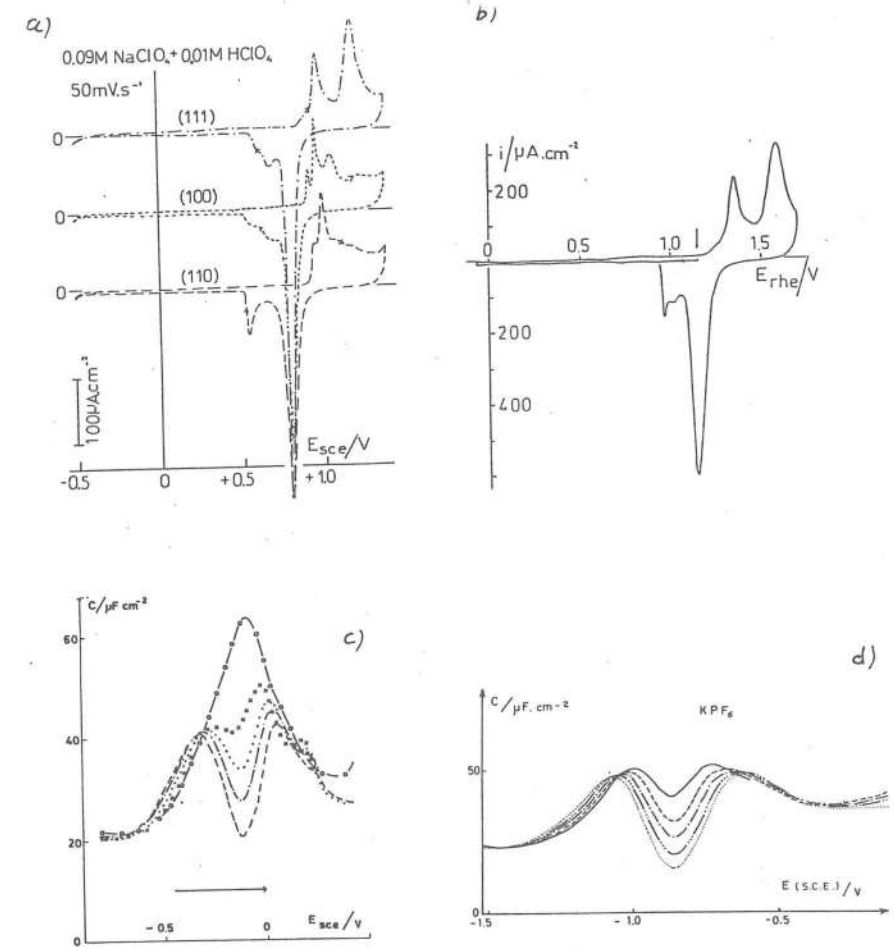


Figure 7.a) Cyclic voltammograms for the three low index faces of gold [1]; b) CV for gold (111) in 10 mM perchloric acid (80 mV/s), put in contact with the solution at +1.15 V vs RHE,first second and tenth cycles are superimposed [2] ;c) C(E) for gold (210) in NaF solutions (20 Hz,22°C): (- - -)0.01,(.-.-) 0.02,(....)0.04,(+ + +) 0.1 and (-°-°-) 0.5 M [3] ;d) C(E) for Ag(100) in KPF6 solutions:(——) 0.1,(- - -) 0.04,(-.-.-)0.02 ; (-...-...)0.01 ; (.....)0.005 M (20 Hz) [4]

III.STABILITY OF FACES AND INTERFACES:

The stability of the surface of metal faces at the electrochemical interface has now to be contemplated. Double layer studies are done in a range of potential in which there is no faradaic reaction. Exploration beyond the limits of this range of potential can alter the interface: the face of the metal,solvent,ions interactions. Let us examine a few cases.

For Au(111) in 10 mM perchloric acid (fig.7b) from 0 V vs RHE (at which thermodynamically reduction of solvated protons may begin) to +1.15 V, only the capacitive current is visible on the cyclic voltammogram; for more positive potentials a monolayer of oxide is formed and subsequently reduced. A few years ago it was understood from the change of the potential of the capacity minimum corresponding to the contribution of the diffuse part of the double layer,E min,and the change of the capacity values(fig.8a,b) that the interface or the top layer(s) of gold could possibly be altered reversibly by the formation of a monolayer of oxide and could come back to the former state electrochemically. Formation of a monolayer of oxide and its reduction is not just a mean to maintain clean the gold surface.For Au(111),alteration of the interface is even clearer when looking at the influence of the temperature of the interface (vide infra).

For Au(100) the situation is more complicated. The influence of the negative limit of the range of potential explored for dilute and concentrated solutions, and of the time when the potential is fixed, was clearly demonstrated (fig.8c,d). These changes are electrochemically reversible.

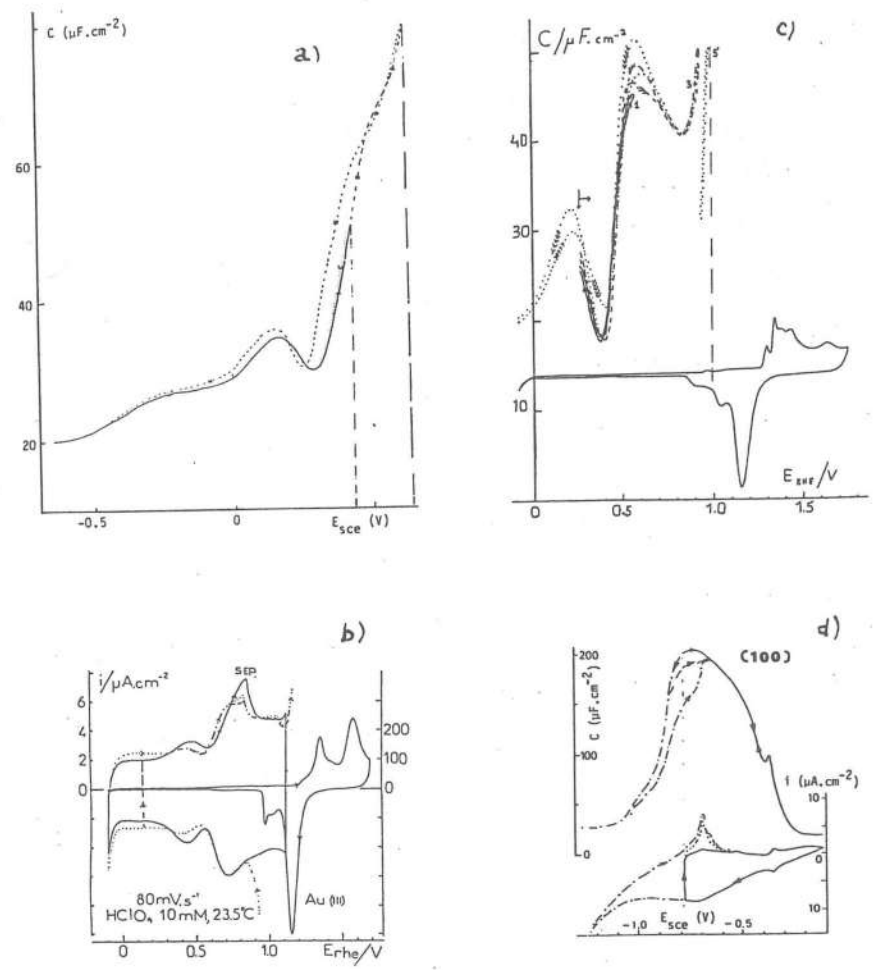


Figure 8. a) Au(111), C(E) ,0.02 M NaBF4 (20 Hz)[5];
b) Au(111), CV in perchloric acid [2];
c) Au(100), C(E) in 0.01 M perchloric acid(20 Hz, 23°C), first, third, fifth, ... cycles are shown for different positive limits. The influence of the negative limit is also shown [6];
d) Au(100), C(E) (20 Hz) in 0.1 M KI, for three negative limits and corresponding CVs for two negative limits and a stop of 30 s at -0.78 V.

It was claimed for Au(100) in dilute perchloric acid, that there is a shift (electrochemically irreversible) of 220 mV of E min [7], for a change of the positive limit of potentials explored from 0.4 to 0.6 V vs SCE between the first and second negative cycles. We have not observed this fact in rigorously clean electrochemical conditions (fig.8 c).

For all faces, if the positive limit, the one we have chosen, is kept constant, and the negative limit shifted negatively of several tenths of a volt, for study of the reduction of the solvated protons, the face is altered. For instance, for Au(100) the profile of the oxidation current is modified after twenty excursions to -0.4 V vs RHE (fig.9); in this case the former curve could not be restored by electrochemical treatment but was restored immediately upon annealing (flame treatment). For Ag(111), exploration in a range of potential in which there is hydrogen evolution alters the C(E) curve (fig.10), a bump corresponding to capacity peaks of high index faces is observed at their potentials.

Faces may also be altered irreversibly by electrochemical treatment, when the range of potential is extended either to formation of bulk oxide or to stronger hydrogen evolution than considered above. Furthermore even if the range of potential is the one we have shown on our figures, a much faster sweep rate (more than 0.1 V/s) not allowing the metal atoms to remain in their equilibrium situation ,results in a surface modification. For instance, (111) after very fast cycling may display the E min of a polycrystal, then by scanning microscopy little pyramids are seen at the surface. In other words a face is damaged by fast cycling.

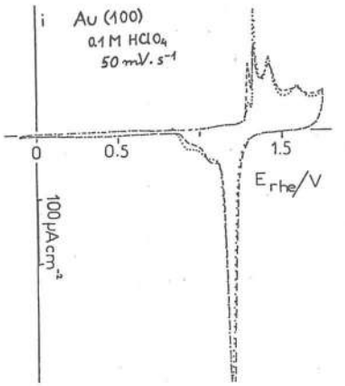


Figure 9. CV for Au(100) in 0.1 M perchloric acid (50 mV/s); (.....)just after flame treatment; (- - -) after 20 extended cycles to -0.4 V at 5 mV/s [8].

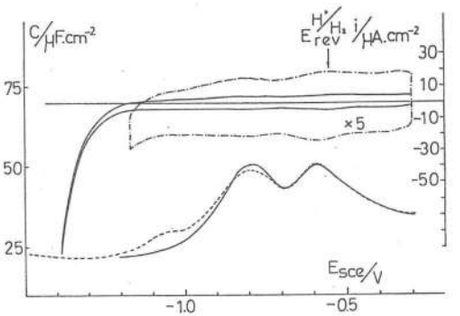


Figure 10. Ag(111) in 0.1 M KPF6, C(E) and CV for different negative limits. Explorations to -1.5 V and further give rise to a bump inbetween -1.15 and -0.95 V corresponding to high values of capacity on defects [9,10].

IV. POTENTIALS OF ZERO CHARGE (pzc).

At an electrochemical interface ,for an imposed potential, a polycrystalline surface is an equipotential but it is not an equicharge. The patchy uncontrolled distribution of charge makes difficult understanding of the results. For single crystal faces, if not perfectly homogeneous, the distribu_ tion of charge is controlled and can be related to the atomic structure. It is the case for pzcs obtained from C(E) (fig.7a,b;8a,c;10). In the case of no adsorption the pzc is related linearly [11] to the electronic work function Φ

$$E_{\sigma=0} = \Phi/e + [\delta\chi^{M}_{o} - g^{S}_{(dip)_o}] + K \qquad (1)$$

Φ , from the atomic description of the faces (see II) is the highest for the most densely close packed face ((111) for the fcc system) and the lowest for the roughest on an atomic scale.The terms in the square brackets are the changes of the metal double layer dipole when put in contact with the solvent and the changes of the solution surface dipoles when put in contact with the metal. K is the absolute potential of the reference electrode. If the term in the square brackets is small, the order of the pzc should be that of the electronic work function: (110) < (100) < (111). It is the case for gold and silver in aqueous solutions.

Irregularities, on an atomic scale, lower the work function and shift the pzc negatively.

Experimentally monoatomic steps on terraces of singular faces shift the pzc negatively. It was observed for 17 different cos of gold. Furthermore these variations parallel the ones of the

calculated surface energy. It is also the case for silver faces [12] (fig.11). Of course all pzcs have to be observed for one concentration of one electrolyte.

Pzcs shift negatively with adsorption of anions.

Comparison of pzcs observed for the three low index faces of gold in the case of slight adsorption is summarized in figure 12. (In no case for gold no shift of the pzc with concentration was observed, except for (111) in KPF6 (fig.13)).

All these pzcs were observed at room temperature. In fact the pzc varies with the temperature of the interface. For Au(111) in 0.01 M perchloric acid, there is a positive shift with temperature (fig.14). A complete study was done for Au(210) in perchloric acid: dEmin/dT varies from +0.020 mV/K in 0.01 M to -0.142 mV/K in 0.1 M. For Au(110) in the same medium, dEmin/dT varies from +0.358 mV/K in 0.0125 M to -0.366 mV/K in 0.1 M. For Au(100) the work is in progress. Each face has a specific beha_ viour. The whole curves are influenced by the temperature (fig.15). For Au(111) the influence of the formation of a monolayer of oxide on C(E) depends on the temperature (fig.16).

Lately gold faces were studied in non-aqueous solvents.

In DMSO the order of the pzcs is the reverse of the order of the electronic work functions: (111) ≤ (100) < (110) < (210) [15].The sum in the square brackets in (1) is obviously very large,i.e.the solvent -metal interactions (gold/DMSO) are strong.

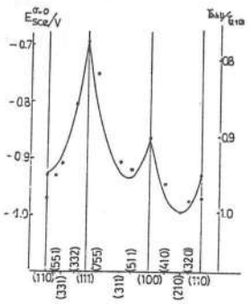


Figure 11. Correlation between the pzcs of Ag faces (o) and the relative surface energy (——) calculated on the basis of the sole nearest neighbour interac_ tions; $\gamma(210)$ =1. The distance of the faces on the x axis is pro_ portionnal to the angle between them. 5 mM KPF6 solution.[12]

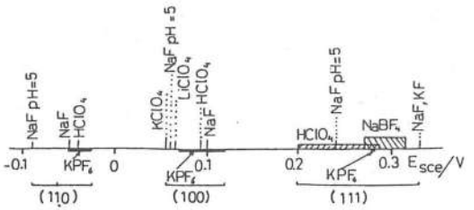


Figure 12. Summary of the different E min published in litterature[13].

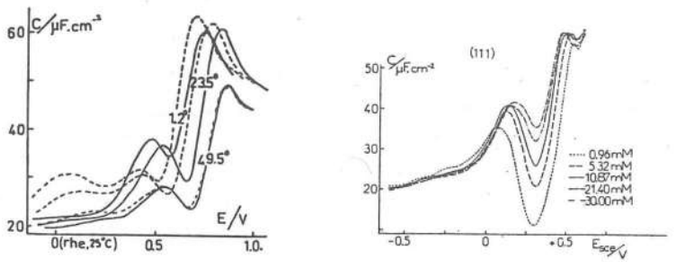


Figure 13. C(E) for Au(111) in 0.01 M perchloric acid (20 Hz) at three different temperatures, for two different potential-time programme: (- - -) after cycles including formation of a monolayer of oxide; (——) for a surface which has never been oxidized [2].

Figure 14. C(E) for different concentrations of KPF6 for Au(111) after two cycles nor including oxidation [13].

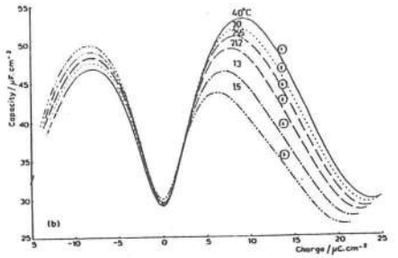


Figure 15. C(σ) curves for Au(210) in 0.03 M perchloric acid under isothermal conditions for different temperatures.The curves are numbered according to experimental sequence observation [14].

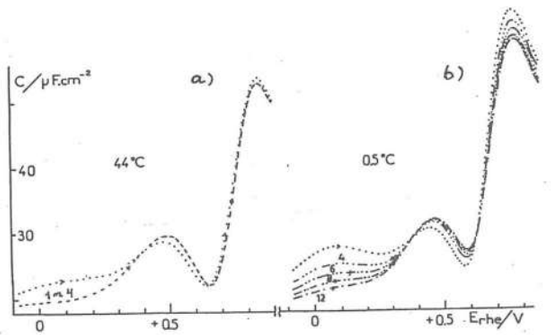


Figure 16. C(E) for Au(111) in 0.006 M perchloric acid (20 Hz). a) At 44°C (.....) after cycles including formation of a monolayer of oxide,(- - - -) after one or more cycles not including formation of oxide; b) at 0.5°C (....) after cycles including formation of a monolayer of oxide, other curves after 4, 6, 8, 12 cycles not including formation of oxide. [2].

V. ION ADSORPTION AND UPD.

The phenomenology of ion adsorption on metal faces is qualitatively what it is for other metal electrodes: with increasing concentration of the ion, the contribution of the diffuse part of the double layer disappears and capacity peaks shift negatively for anion (fig.17) and positively for cations adsorption. For one metal and one electrolyte, the shape of C(E) curves differs significantly for different cos (fig.18). One co gives C(E) curves of the same pattern in all electrolytes (fig.19). Generally three capacity peaks are observed, in some cases one peak can merge with another.

The most negative peak is possibly due to reorientation of the solvent dipoles in the inner layer, the middle peak occurs for about half coverage (inflexion point of the isotherm), the third peak could be connected to reorganisation of the adsorbate or charge transfer.

For silver C(E) curves are similar for positive and negative sweeps, it is not the case for gold (fig.8d,20). The origin of this hysteresis of the curves is in changes of the interface, possibly of the structure of the face. It is electrochemically reversible.

Understanding of ionic adsorption was improved by consideration of the influence of the co in a general way: to systematic changes of co of faces (on one zone of Unit Projected Stereographic Triangle, see figure 2) correspond systematic changes of the C(E) curves (fig. 21). The TLK model of the surfaces explains these systematic changes : adsorption of one anion requires less energy on steps than on terraces. The peak due to adsorption on steps increases with the density of steps at the surface, the peak corresponding to adsorption on terraces increases with the width of terraces.

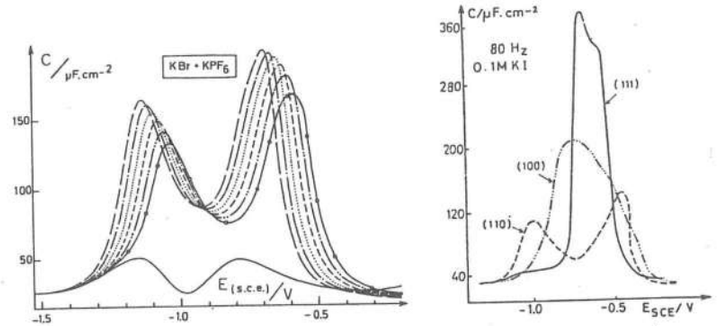


Figure 17. C(E) for Ag(110) in x M KBr + (0.02 - x) M KPF6. x=0 (———); 0.00062 (- o - o); 0.00125 (-..-..);0.0025(- - -); 0.005 (.....); 0.01 (-.-.); 0.02 (-- -- --)[4].

Figure 18. C(E) for low index faces of gold in 0.1 M KI.

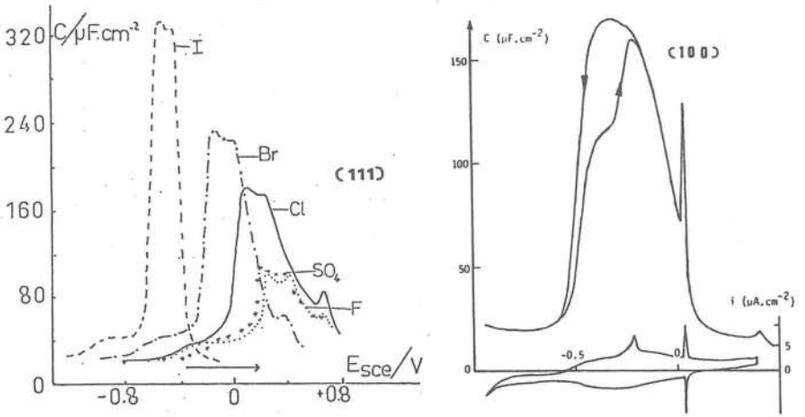


Figure 19. C(E) for Au(111) in 0.1 M KI, KBr, KCl, K2SO4, NaF (80 Hz).

Figure 20. Au(100) in 0.002 M KBr. C(E) (20 Hz) and corresponding CV (20 mV/s)

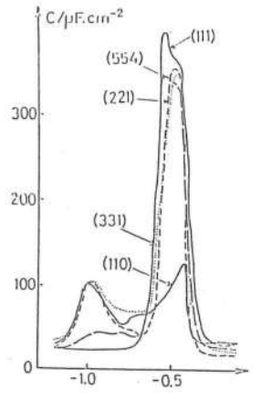


Figure 21. C(E) for gold faces of the (111)-(110) zone in 0.1 M KI (see text).

UPD, Under Potential Deposition of a submonolayer (or monolayer) of a foreign metal (lead) on gold faces is a case of adsorption with complete charge transfer at each imposed potential. For faces distributed on the three main zones of the Unit Stereographic Projected Triangle, the current-potential curves for stripping are given figure 22. These results are easily understood if we accept the convenient notation for stepped faces given in section II. Obviously the more negative peak is due to adsorption on steps, its amplitude increases with the step density at the surface (from (111) to (110) for instance), and the other current peak is due to stripping from terraces. (311) and (210) appear as turning points on their respective zones, so they are in the stepped face notation. To systematic changes of the surface of the electrode correspond systematic changes of the electrochemical results. Definitely the atomic structure of the electrode is reflected by the adsorption phenomena.

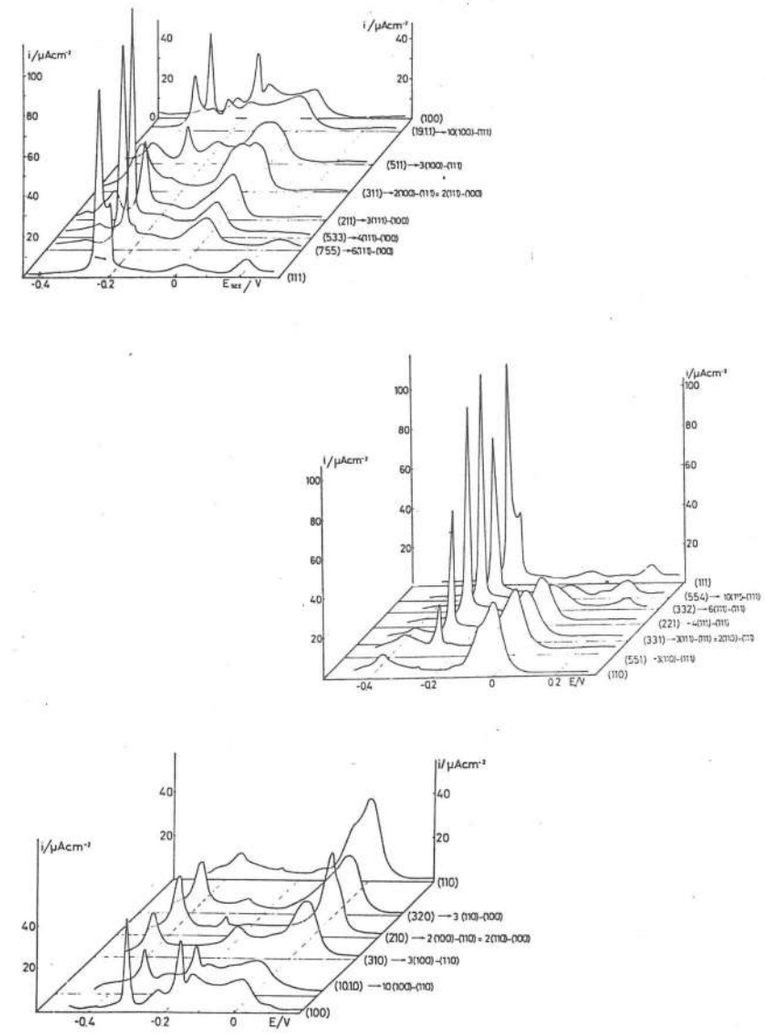


Figure 22. Current-potential curves for stripping of a monolayer of lead from different gold faces distributed on the three main zones of the Unit Projected Stereographic Triangle (see fig.2).

VI. REDUCTION OF SOLVATED PROTONS AT GOLD FACES.

On CVs of gold faces at potentials more negative than the RHE potential, a current can be observed which corresponds to the reduction of the solvated protons (fig.7 a,b, 8 b, 9). By extending the excursion of potential to -0.4 V vs RHE, this reaction can be studied by linear sweep voltammetry. Not only the three faces of simple indices of gold, but also (332) which is on the (111)-(110) zone, (311) and (210) which have shown extreme electrochemical behaviours and (531) which is inside the unit projected stereographic triangle, were studied (fig.2). Furthermore a polycrystalline electrode was prepared and studied in the same manner as the faces.

This study was first conducted in 1 M perchloric acid, the reaction was found slower on the densely packed faces and faster when there are kinks and steps on the surface of the electrode. For the polycrystal the rate constant has an intermediate value (fig.23 a).

In acidified lithium or sodium perchlorate solutions the sequence of rate constants is the same. It is not within the scope of this lecture to discuss the effect of the different cations, we just intend to show the influence of the surface structure.

In sodium perchlorate solution the reaction is 3.5 faster on (210) than on (111) (fig.23 b). To ascertain this point correction for the double layer effect was done. The magnitude of this correction is the largest for (111) and the smallest for (210), it accentuates the influence of the co (fig.23 b). The reaction rate dependency is outside the estimated range of experimental precision.

For all faces the proton discharge seems rate determining as the corrected transfer coefficient is 0.50 to 0.55 and n=1.

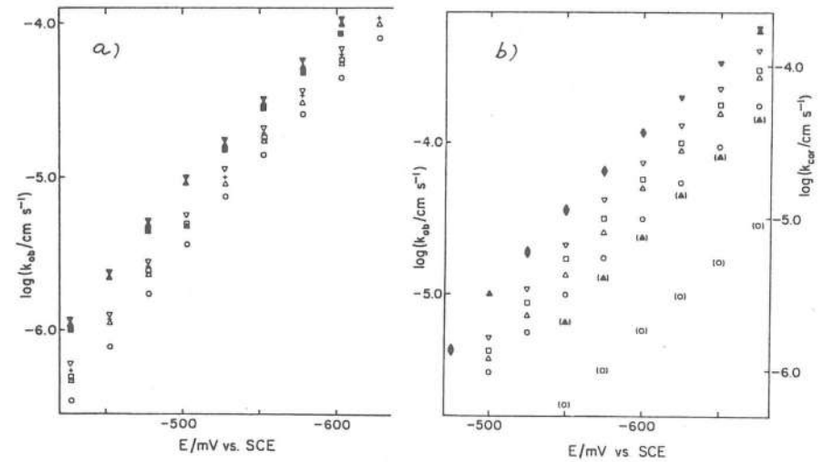


Figure 23. Logarithm of observed rate constant on gold faces plotted against electrode potential. (o)(111); (Δ)(100); (∇)(110); (□)(332); (■)(331); (▲)(210); (▼)(531); (+)polycrystal.
a) in 0.1 M perchloric acid;
b) in 0.09 M sodium perchlorate + 0.01 M perchloric acid. Points in parentheses are double layer corrected values using density of charge on the metal and potential drop in double layer (extracted from pzcs and C(E) curves using the Gouy-Chapman model) [8].

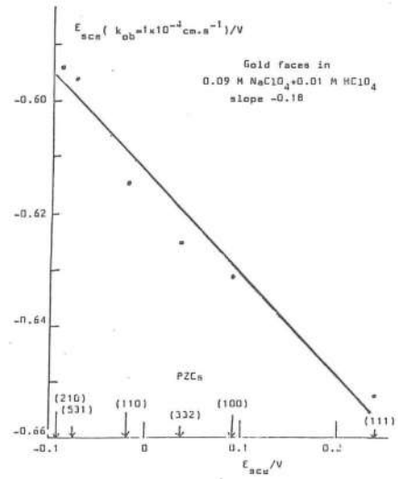


Figure 24. Variations of the electrode potential for an observed rate constant of 1x10^{-4} cm/s, at various gold faces as a function of their pzcs. Electrolyte: 0.09 sodium perchlorate + 0.01 M perchloric acid [8].

The potential, at constant observed reaction rate , versus the pzc is roughly linear with a slope of -0.18 (fig.24). Equivalently this crystal face dependence can be expressed in terms of rate changes at a fixed potential as a function of the pzcs: then the slope (Δ log k ob/Δ E pzc) is -1.1 to -1.6 / V.

The dependence of the proton reduction rate upon the nature of the metal has been shown by Trasatti [16] for a wide range of polycrys_ talline metals: the proton reduction uniformly increases with the electronic work function (or the pzc), the slope is +7 / V. This trend for our faces is opposite and smaller. It can be understood: for different metals the chemical potential of the electrons varies, while for different faces the chemical potential of the electrons is, of course, the same, but the surface dipole component (see II) varies.

To conclude this section , less positive pzc is observed (in aqueous solvent) for the higher index faces and the most positive for the most densely packed faces. Faster reaction at high index faces shows that low coordination sites exert a catalytic influence, probably involving a greater stabilization of the hydrogen intermediates [8].

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