

CHARACTERIZATION AND MODIFICATION OF ELECTROCATALYST SURFACES BY ELECTROCHEMICAL METHODS

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SUMMARY

Electrode surfaces modified by monolayers of heavy metals underpotential deposited: Pt/M_{ads} electrodes, electrode surfaces modified by overlayers of their own oxides grown in-situ, i.e. Ir-oxide electrodes, and electrode surfaces with preferred orientations, namely Pt single crystals were the modified electrode surfaces selected for this lecture.

The potentialities and advantages of the electrochemical methods, namely cyclic voltammetry and potential step pulses to produce modified electrode surfaces and simultaneously to monitor changes and to test the stability and the activity of the modified and non-modified electrode surface will be emphasized and illustrated with experimental data.

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1. INTRODUCTION

There are several areas of great scientific and technological importance demanding for more efficient, cheap and stable catalysts. One of this areas is electrochemical energy conversion particularly, fuel cells: good anodes for O_2 evolution and for the oxidation of small organic molecules, like $HCOOH$, CH_3OH , $HCHO$, etc. are required.

Bare or modified noble metals are still the best catalysts in fuel cells technology. Such catalysts can be made by dispersing noble metals in a cheap conducting material, but, they can also be noble metals with superficial or structural modifications induced by various means, namely, by electrodeposition of polymers, by underpotential deposition of heavy metals, by alloying, by covering the electrode surface with thin or thick films of the corresponding oxides or by inducing roughening, facetting or reconstruction on the structure of the bare metal surface. All these modifications can be produced by electrochemical methods, as well as by several other means. It is not our purpose to review the subject, not even to give a broad view covering all types of modified electrode surfaces. There are several and excellent reviews for the various types of modified electrode surfaces and references will be given.

The design of good catalysts requires the understanding of the rôle played by the size, shape and geometric arrangements of active centers. But, first of all, it is of crucial importance to be able to control the state of the electrode surface, before, during and after the electrooxidation processes.

Differences due to the pretreatment of the electrode surface and also on the type of potential profile used for the electrochemical activation of the electrode surface might be the main reason for differences in the activities of the "same" electrode material found by different groups.

Therein, the reason why we will place special emphasis on simple but important aspects, e.g.:

- Control of the state of the electrode surface and of the composition of the medium;
- Reproducibility of the electrochemical response to the same potential perturbation;
- Stability of the bare and of the modified electrode surfaces;

This lecture will rely on our experience with bare Pt electrodes, Pt/M_{ad} and Pt single crystal electrodes, as well as iridium oxide electrodes, which we are planning to test as catalysts for the oxidation of $HCOOH$ and of CH_3OH . It is also the purpose of this lecture to show how electrochemical methods, namely cyclic voltammetry and potential step techniques are a cheap and powerful mean to produce, to control and even to test the activity of the modified electrode surfaces.

2. PLATINUM ELECTRODES MODIFIED BY AD-ATOMS:

Pt/M_{ad} ELECTRODES

Interesting catalytic effects induced by ad-atoms on noble metals have been observed for the oxidation of $HCOOH$, $HCHO$, CH_3OH and other organic molecules, as well as in the reduction of O_2 . But on the other hand, inhibiting effects have also been detected for some redox couples and in the hydrogen evolution reaction.

Thus, ad-atoms seem, to provide a promising method for the modification of the catalytic activity of the various electrode surfaces. As a consequence, the amount of research in this area has been considerable. The subject was reviewed twice by Adzic [1,2] and more recently by Kokkinidis [3].

At the present, some problems remain to be solved, namely the question of the stability of the ad-electrode surfaces, as well as some theoretical aspects.

2.1. THE UNDERPOTENTIAL DEPOSITION OF MONOLAYERS OF HEAVY METALS ON Pt ELECTRODE SURFACES

The modification of the electrode surfaces by ad-atoms is based on the formation of adatoms by the so-called underpotential deposition process (UPD): formation of up to a monolayer of metal adatoms at potentials more positive than the reversible bulk deposition. The process itself, as well as the physical and optical properties of the modified electrode surfaces has been already reviewed by Kolb in 1978 [4]. Since then, many groups working in the field of electrochemistry and also in the field of surface chemistry have undertaken projects with the aim of understanding the UPD process. UPD studies on well defined surfaces, i.e. on single crystals have also been started by Yeager *et al.* [5] with the UPD of Pb on Au single crystals. The process has been undertaken by Bewick *et al.* [6] and by Schultze *et al.* [7], who have concluded about a phase transition in the UPD process, while Lorenz *et al.* [8] were in favour of a cation-adsorption model. From studies with Pt single crystals Bruckenstein and Cadle [9] have concluded that Cu, at low coverages, i.e. at $\theta < 0.5$ deposits preferentially on the Pt (111) crystal face.

Improvements on the existing theories for the UPD process are still demanded. Rigorous data on adatom-adatom interactions, surface electron density and adatom bond energies on various crystal faces are certainly very useful, as well as double-layer data for the non-modified and modified electrode surfaces.

2.2. PREPARATION AND CHARACTERIZATION OF THE Pt/M_{ad} ELECTRODE SURFACES

Pt/M_{ad} ELECTRODES BY LINEAR SWEEP VOLTAMMETRY

Electrochemical methods, namely, linear sweep voltammetry and potential step techniques are simple and suitable means for producing *in situ*, ad-electrodes and, simultaneously a way for measuring the coverage of the modified surfaces.

Fig. 2.1 illustrates the UPD of Bi, Pb, Cd and Cu adatoms on Pt produced by scanning the potential of the Pt electrode between +1.5 and 0.03 V vs. (she), at 0.1 V s^{-1} , in aqueous acidic solutions of the corresponding salts.

The voltammetric responses show particular characteristics of the corresponding underpotential deposition process.

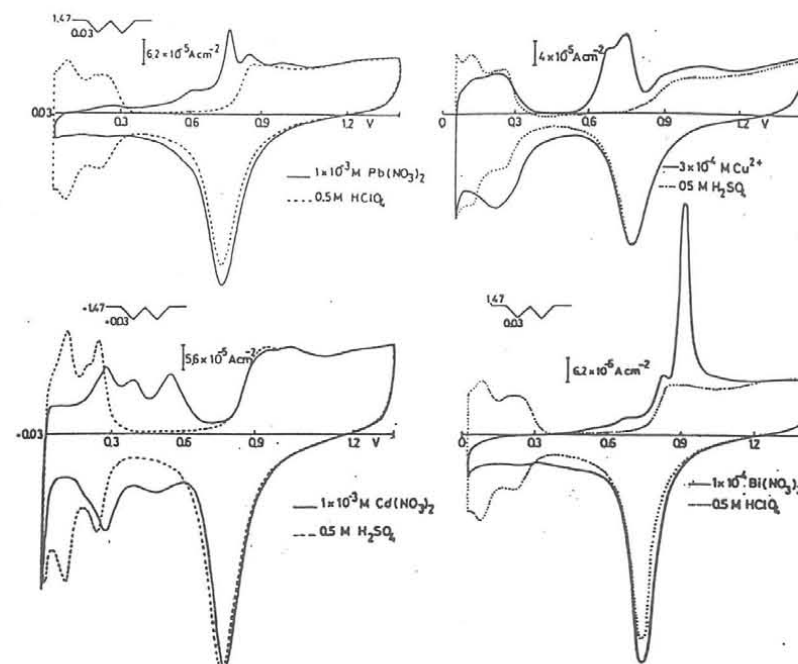


Fig. 2.1. Cyclic voltammograms of the Pt/M_{ad} electrodes. $\nu = 0.1 \text{ V s}^{-1}$ Data from ref. [10-12].

It is clearly shown by the Cyclic Voltammograms (CVs) in Fig. 2.1 that under the same experimental conditions, i.e. concentration of the metallic ions in solution, sweep rate, interval of polarization etc, the complexity of the process varies from metal to metal. For all adatoms the underpotential deposition process takes place after the reduction of the platinum oxide, but starts much earlier in the case of Cd and Cu. The effect of the UPD in the hydrogen adsorption peaks is quite similar for Bi and Pb, but very different for Cd and Cu. Bi and Pb adatoms cause a big suppression on both weakly and strongly bonded hydrogen, while with Cu and Cd under the experimental conditions of Fig. 2.1 bulk deposition starts to occur at 0.6 V, before hydrogen adsorption.

During the anodic sweep the I-E profile of the corresponding voltammetric response shows also to be very much dependent on the adatom chosen. While the removal of Bi and Pb adatoms leads to a similar profile: a well defined and symmetric peak preceded by a pre-peak, in the case of Cu, a broad and complex peak appears between 0.6 and 0.8 V and for Cd two well defined peaks of about the same size are observed at +0.4 and +0.5 V vs. (she) respectively, as well as a peak at ca 0.3 V. This peak at 0.3 V is due to the removal of the bulk deposited cadmium while, the other two are due to the removal of adatoms in two well defined steps.

The complexity of the anodic branches of the voltammetric responses of the various Pt/M_{ad} electrodes can vary greatly: by varying the concentration of the metallic ions in solution, by reversing the potential at less negative values during the cathodic sweep or by holding the electrode for different times, in the UPD region. Results in figures 2.2 to 2.4 illustrate those effects.

The concentration of the metallic ions plays a determinant role in the structure and in the morphology of the Pt/M_{ad} electrode.

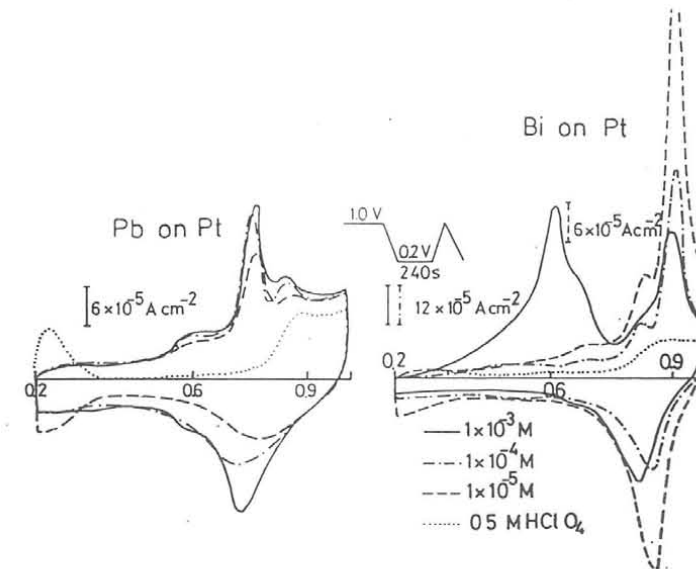


Fig. 2.2. The effect of the concentration of M³⁺ on the UPD process. CVs recorded at 0.1 V s⁻¹.

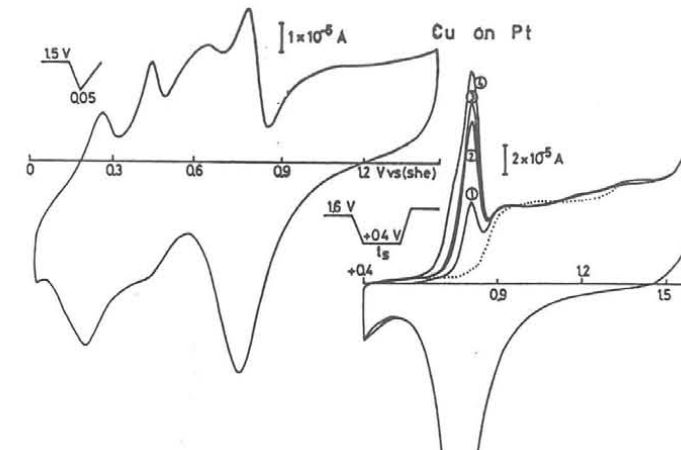


Fig. 2.3. The effect of reversing the potential of the Pt electrode in a solution 1 x 10⁻³ M in Cu²⁺, at two cathodic limits, E_c. v = 0.1 V/s.

According to Fig. 2.3 an homogeneous ad-layer can be obtained by reducing the potential during the negative scan.

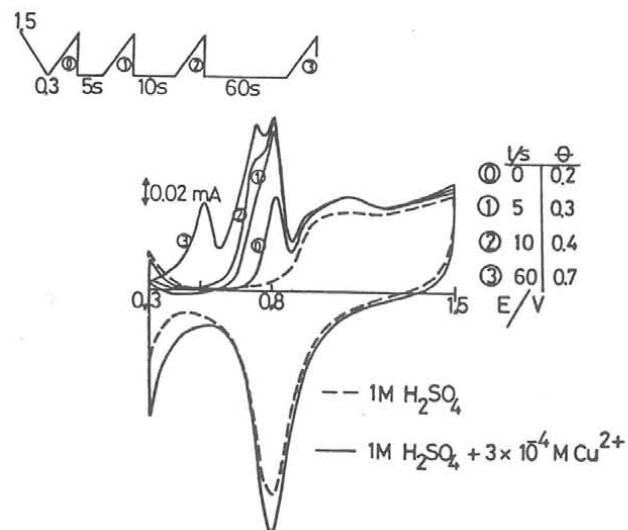


Fig. 2.4. The effect of holding the Pt electrode in the UPD region for various times in a solution $3 \times 10^{-4} \text{ M}$ in Cu^{2+} . $v = 0.2 \text{ V s}^{-1}$

Various degrees of coverage can be obtained by holding the potential for different time intervals at any potential in the adsorption potential region.

Results in Figs. 2.1 to 2.4 show clearly that the simplest and better defined modified Pt/ M_{ad} electrode surfaces can be prepared by reducing the concentration of the metallic ions in solution to levels of the order of 10^{-5} M or by reducing the limits of the potential during the negative sweep.

A great number of heavy metal adatoms can be deposited on the Pt substrate. Thus, Pt electrodes covered by adatoms in a wide potential range between H_2 and O_2 evolution in aqueous solutions or even in a wider range of potential in non-aqueous solutions, can be prepared.

EVALUATION OF COVERAGES, $\theta_{\text{M}}^{\text{Pl}}$

The UPD process is a fast process, therein quantitative data, i.e. coverage, requires the use of fast potential perturbations. Figure 2.5 shows a potential-time sequence used for the evaluation of coverages. The method has been described by Motoo and Furuya [13] and consists mainly in measuring the charge during the anodic sweep after holding the electrode in the adsorption potential region for a certain time. The potential-time sequence consists of a series of scans between +0.05 and +1.6 V vs. (she) for cleaning the electrode surface. Then, the potential is held for 60 s at 1.6 V to ensure the oxidation process. Afterwards, the potential is stepped to +0.3 V and kept there for 600 s to allow the formation of a monolayer of Cu adatoms and finally scanned at 10 V s^{-1} between 0.05 and 1.6 V for the oxidation of the Cu monolayer.

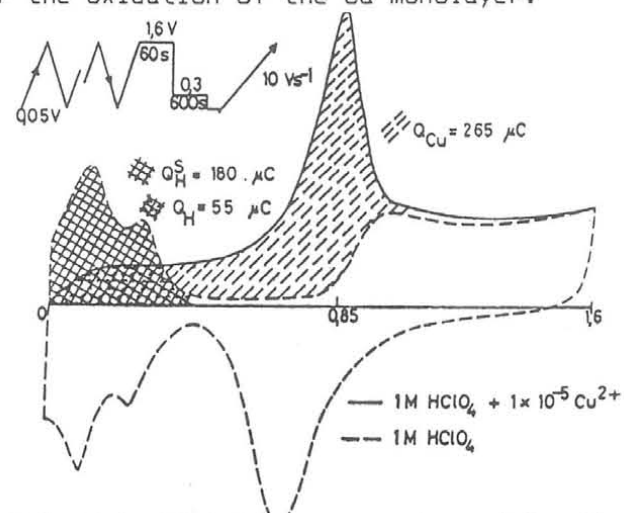


Fig. 2.5. Potential-time sequence used for the evaluation of the coverage, $\theta_{\text{Cu}}^{\text{Pl}}$, and the corresponding voltammetric response recorded at 10 V s^{-1} [11-13].

The Coverages, θ , can be calculated through the measured charges Q_{Cu}^{S} , Q_{H}^{S} and Q_{H} , where Q_{Cu}^{S} represents the charge due to the oxidation of Cu adatoms, Q_{H}^{S} the charge due to the

oxidation of adsorbed hydrogen in a solution free of metallic ions and Q_H the charge due to the oxidation of hydrogen when the modified surface is partially covered by ad-atoms.

The methodology for the calculation of θ assumes that hydrogen does not adsorb on those metals, which are usually underpotential deposited.

ADVANTAGES OF USING CYCLIC VOLTAMMETRY

- (i) Cyclic voltammograms show characteristic features of the UPD process thus, of the corresponding ad-electrode surfaces;
- (ii) Peak potentials and peak currents can be measured with high accuracy, thus accurate thermodynamic and kinetic data of the UPD can be obtained;
- (iii) The coverage of the modified electrode surface, θ , can be calculated by measuring the amount of charge produced during the stripping of the monolayer or submonolayer, previously deposited, assuming $z \times 200 \mu\text{C cm}^{-2}$ as the charge of a monolayer [14];
- (iv) Alloy formation in the UPD region can be distinguished from a monolayer of adatoms through the maximum amount of charge under the I-E curve during the scan of the potential in the positive direction. A limiting value of $z \times 200 \mu\text{C cm}^{-2}$ in the UPD region does not exist for the alloys;
- (v) Kinetic and mechanistic information for the UPD process can be obtained from CVs recorded in a wide range of scan rates;
- (vi) The number of Pt sites occupied by each adatom can be determined through the voltammetric data, i.e. by

using the method described by Furuya and Motoo [13].

- (vii) Surfaces changes can be followed through the recorded CVs.

Some characteristics of the underpotential deposited layers of Bi, Pb, Cu and Cd obtained from electrochemical measurements are given in Table 2.1.

Table 2.1. Characteristics of the Pt/M_{ad} electrodes [15]

Adatom	Solution composition	N ^o of Pt occupied by each adatom	Potential range for adatom removal	E/V $\theta = 0.5$
Bi	$1 \times 10^{-3} \text{M Bi(NO}_3)_3$	3	0.7 — 1.0	0.90
Pb	$1 \times 10^{-3} \text{M Pb(NO}_3)_2$	2	0.5 — 0.75	0.61
Cd	$1 \times 10^{-3} \text{M Cd SO}_4$	2	0.4 — 0.65	0.54
Cu	$1 \times 10^{-5} \text{M CuSO}_4$	1	0.6 — 0.8	0.40

Pt/M_{ad} ELECTRODES BY POTENTIAL STEP PULSES

As stressed by Pletcher *et al.* [11,15] uncertainties associated with the dependence of coverage on potential can disappear if pulse techniques are used instead of linear sweep voltammetry. Potential pulses sequences as those shown in Fig. 2.6, illustrate the application of the pulse techniques for the calculation of the number of Pt sites occupied by each adatom underpotential deposited on Pt. Coverages can be calculated from pulse transients or by a sequence of pulses followed by a ramp of potential (see Fig. 2.6 (b)).

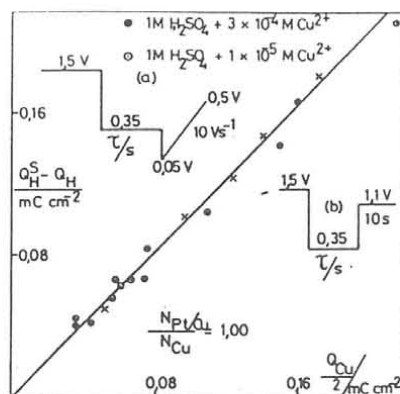


Fig. 2.6. Plots of $(Q_H^S - Q_H)$ vs. $Q_{Cu}/2$. Charges obtained from experiments following sequence (a) \times and sequence (b) \circ [11,12].

Fig. 2.7 gives the coverage of the Pt electrode by Cu adatoms as a function of adsorption and oxidation potentials. Data was obtained from short transients (2s) following the pulse profile (a) for the evaluation of coverage as a function of the adsorption potential and profile (b) for defining the curve θ vs. oxidation potential.

The potential range in which adatom removal occurs, as well as the potential at which a monolayer is completely formed can be deduced from plots, i.e. by those in Fig. 2.7.

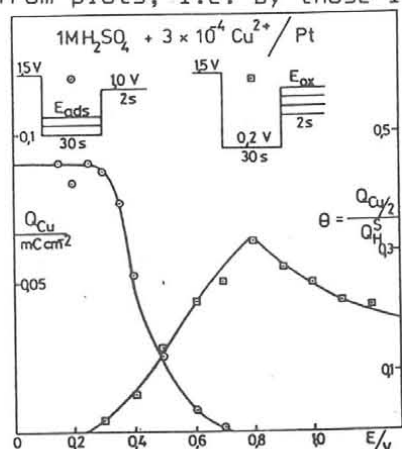


Fig. 2.7. Coverage of the Pt/Cu electrodes as a function of the adsorption θ and of the oxidation potential [11,15].

2.3. STABILITY OF THE Pt/ M_{ad} ELECTRODES

Watanabe *et al.* [16] have recently reported ad-atom electrodes of Pt/Ru and Pt/Sn remaining stable for more than 20 h of polarization at +0.4 V vs. (she) in H_2SO_4 aqueous solutions. Holze and Cattaneo [17] report Pt/ Sn_{ad} electrodes giving essentially the same response in a tin-free and in a tin containing solution. Furuya and Shibata [18] have obtained stable Pt/ Cu_{ad} electrodes acting as catalysts for the reduction of ethylene with a maximum of activity at $\theta \approx 0.1$. Similar results have been obtained by us for the oxidation of HCOOH [19].

3. ELECTRODE SURFACES MODIFIED BY OVERLAYERS OF OXIDES: Ir/OXIDE ELECTRODES

Hydrous oxides on noble and non-noble metals are a topic of increasing interest to electrochemists, as these materials play a central rôle in electrocatalysis, corrosion and passivation of metals, formation of protective and insulating films and in various other branches of material science. There are several evidences of the participation of oxides in various oxidation processes.

Burke and Sullivan [20] report an enhancement in the activity of rhodium for O_2 evolution due to the presence of a thick layer of a hydrous oxide film produced by potential cycling. Arvia and co-workers [21] have also obtained Tafel slopes for O_2 evolution on rhodium strongly dependent on the pretreatment of the electrode by fast potential cycling. Smickler and Schultze [22] in their review on electron-transfer reactions at oxide-covered metal electrodes give a compilation of data illustrative of the influence of the thickness of the oxides on the rate of electron transfer reactions.

The amount of data on the growth of oxides on noble metals,

their physical and optical properties, is considerable (see reviews by Woods [14], by Sullivan and Calvo [23], by Burke and Lyons [24] and by Schultze and Smickler [22], and other more recent publications).

3.1. GROWTH OF HYDROUS OXIDES ON NOBLE METALS

The capability of the electrochemical methods for producing thick oxide films on noble metals was earlier detected in the case of iridium (see review by Woods [14] and references therein). Only more recently, the growth of hydrous oxides on other noble metals like platinum, gold, ruthenium and rhodium electrodes was also achieved (see Burke *et al.* [25-27], Arvia *et al.* [21] and Kötzt *et al.* [28]).

Hydrous oxide films can be produced by repetitive potential cycling between suitable limits or by potential step pulses. Sinusoidal, square or triangular waves of potential can be used; the linear sweep voltammetry, however, is the most popular: the electrochemical spectrum of the growth process is produced. The thickness of the oxide film can be measured and the redox behaviour can be detected.

The upper and lower limits of the potential, as well as the composition of the solution and the sweep-rate play a determinant rôle on the thickness and on the kinetics of the growth process. These and other effects will be illustrated in the next section with examples from our laboratory for the growth of oxides on iridium in acidic medium.

3.2. THE GROWTH OF OXIDES ON IRIIDIUM IN ACID MEDIUM

3.2.1. THE GROWTH OF OXIDES ON IRIIDIUM BY CONTINUOUS POTENTIAL CYCLING

Cycling the potential of the Ir electrode either in H_2SO_4 or in $HClO_4$ aqueous solutions between +0.05 and +1.35 V

vs. (she) leads, after a few runs, to the appearance of highly reversible peaks in the oxide region at $\approx +0.9$ V, their size increasing with the number of cycles (see Fig. 3.1).

Similar behaviour has been reported earlier by Otten and Visscher [29], and later by Burke and Whelam [30] and by Mozota and Conway [31].

A surprising effect not previously reported, is the big difference in the rate of the hydrous oxide growth due to the composition of the solution. This finding has deserved a systematic study of the growth process either in sulphuric and in perchloric medium. Results are summarized in Figs. 3.1. and 3.2 and also on Table 3.1. Q_{ox} is the charge under the anodic branch of the voltammetric curve between +0.3 and +1.35 V vs. (she), after successive cycles of polarization at $0.1 V s^{-1}$.

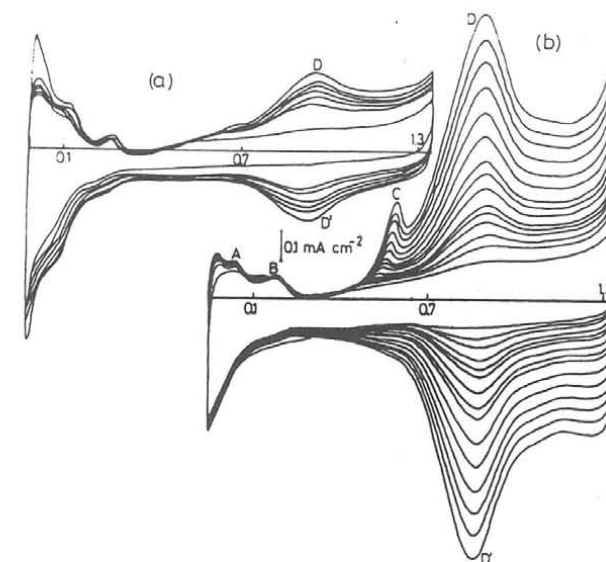


Fig.3.1. The growth of iridium oxide by continuous potential cycling between +0.05 and +1.35 V during 1 h, at $0.1 V s^{-1}$, in: (a) 1M $HClO_4$ aqueous solution; (b) 0.1 M H_2SO_4 aqueous solution.

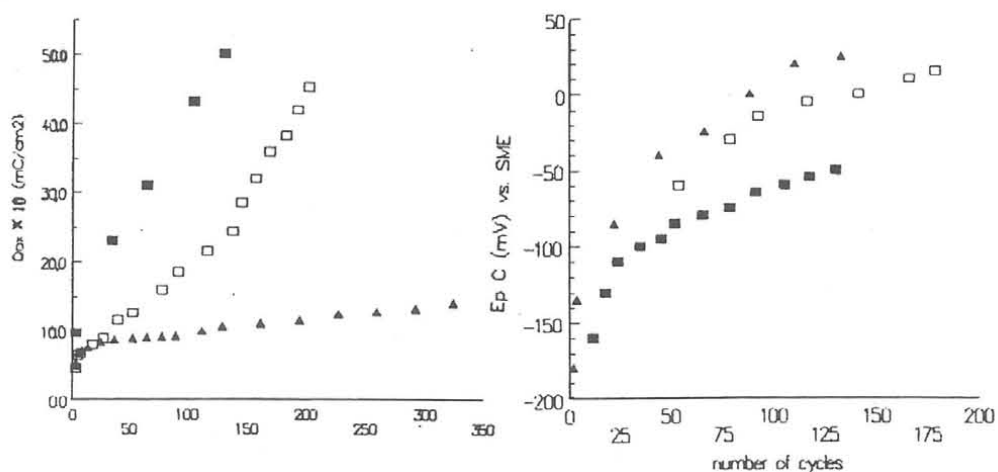


Fig. 3.2. Charges, Q_{ox} , and peak potentials of peak C, E_p^C , as a function of the number of cycles from Ir in: 0.1M H_2SO_4 ■, 0.5 M H_2SO_4 □ and 1M $HClO_4$ ▲ aqueous solutions.

While in $HClO_4$ aqueous medium the increase in charge Q_{ox} tends to a plateau of ca. 1.5 mC cm^{-2} , in H_2SO_4 medium a linear relationship between Q_{ox} and the number of cycles is obtained at least for up to 350 cycles the slopes of the straight lines being dependent on the concentration of H_2SO_4 : higher rates in the oxide growth are obtained with more diluted solutions, i.e. at 0.1 M in comparison with 0.5 M. Another feature resulting from continuous cycling is the displacement of peak C in the positive direction during the anodic scan. The effect is, particularly, noticeable during the first 50 cycles and slows down afterwards (see fig. 3.1 and 3.2).

The process leading to peak D, at $+0.97 \text{ V vs (she)}$ is most probably due to the formation of hydrous iridium oxide, e.g. by:



Differences induced by the composition of the solution may be due to the competition between adsorption of the anions of the base electrolyte and the electrodeposition of OH^- and of O^{2-} species. Effectively, it is well known that SO_4^{2-} and HSO_4^- ions are specifically adsorbed on noble metals. Another possibility resides on the potentialities of SO_4^{2-} as a complexing anion leading to coordination compounds within the film.

In very high acid concentrations, either perchloric or sulphuric, hydrous oxide films do not grow on Ir: after 1 h of cycling at 0.1 V s^{-1} no signs of the reversible peak D was seen and the whole voltammogram is totally reproducible. Therefore, the use of a high concentration of the base electrolyte (i.e. $> 2M$) is a mean to reduce the growth of oxides on iridium to monolayer levels.

3.2.2. THE GROWTH OF OXIDES ON IRIDIUM BY POTENTIAL STEP METHODS

As already mentioned for the Pt/M_{ad} electrodes, potential step methods are very convenient potential perturbations for the preparation of oxide films of known thickness. Potential step profiles, as those reported in Fig. 3.3, were used to grow iridium oxide films on Ir in H_2SO_4 aqueous media.

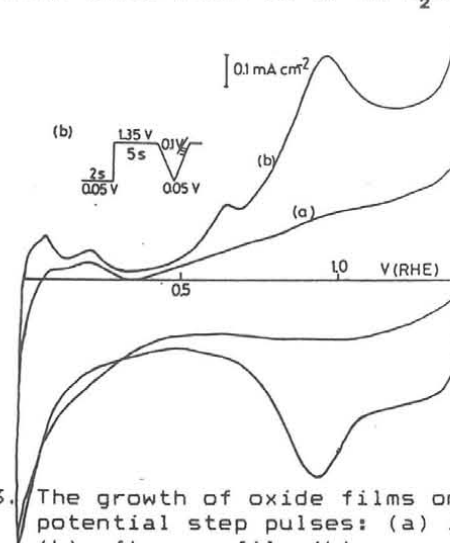
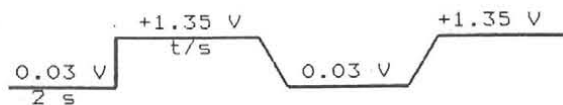


Fig. 3.3. The growth of oxide films on Ir in $0.5 \text{ M } H_2SO_4$ by potential step pulses: (a) initial state; (b) after profile (b).

Table 3.1 summarizes results from potential step pulses.

Table 3.1. Growth of the oxides films on Ir after potential steps e.g.



initial state	$Q_{Ox}^{an} (\mu C)$		initial state
972 μC			532 μC
t (s)	H ₂ SO ₄ (0.5M)	HClO ₄ (1M)	t(s)
90	1290	644	90
180	1350	732	180
300	1410	790	300

Regardless the initial state of the electrode, the successive application of pulses from 0.03 to +1.35 V with different lengths leads to an increase in charge, particularly noticeable for polarization times at 1.35 V smaller than 90 s. Once more, the film grows faster in H₂SO₄ medium (0.5) than in HClO₄ (1M).

Potential step measurements have also shown that thicker oxide films can be produced by potential step pulses in short times (4-300 s), in comparison with those produced by continuous cycling of the potential between the same limits.

3.3. THE REDUCTION OF OXIDE FILMS ON IRIDIUM

The resistance of iridium oxide films to reduction is one of the most important aspects of particular relevance in electrocatalysis. Answers for questions i.e.:

- (i) how stable is the film or (ii) how easy is to reduce

The amount of the iridium-oxide films reduced after submitting the interface to high anodic potentials, i.e., at +1.85 V vs (she), depends strongly on the potential-time perturbation previously used to grow the oxide. This has necessarily to do with the morphology and structure of the grown oxide film.

The iridium electrode cleaned from its oxides by thermal treatment is less sensitive to continuous potential cycling even in H₂SO₄ aqueous medium.

The following conclusions have emerged from our studies:

- Ir oxide films grown by continuous cycling at high sweep rates i.e., at $v > 1$ V/s or by potential steps pulses, between the same potential limits (0.03 — 1.35 V) are harder to reduce than those of identical thickness grown by continuous cycling the potential at low sweep rates (i.e. at 0.1 V/s).
- Polarization at very high anodic potentials, i.e. at +1.85 V, with holding times of the order of 5 minutes depending on the film thickness is an efficient method for the electrochemical reduction of the oxide films grown on iridium electrodes.
- Films of the same thickness grown by continuous cycling in HClO₄ are harder to reduce than those grown in H₂SO₄ medium, the reverse being valid for films grown potentiostatically.
- Thick oxide films on Ir can be reduced to monolayer levels by thermal treatment: heating the electrode for a few seconds in a gas flame (+ \approx 1200 C).
- A reproducible state of the Ir-oxide electrode surface is obtained whenever a cathodic polarization in the hydrogen adsorption/desorption region is applied even during short periods.

the film for recovering the "bare" electrode surface are of crucial importance.

Both states can certainly be achieved depending on the experimental conditions. The establishment of those conditions has been the main purpose of our experiments before testing the electrocatalytic activity of the modified electrode surface. CVs on Figs. 3.4 and 3.5 illustrate the reduction of thick oxide films both by electrochemical means and by thermal treatment

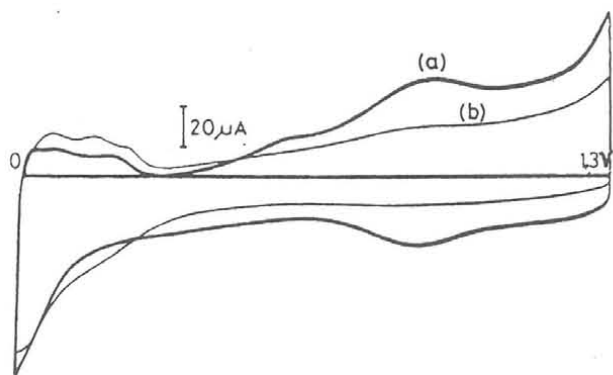


Fig. 3.4. The voltammetric responses of the Ir-Oxide electrode after:
 (a) 70 cycles at 0.1 V/s in 0.5 M H_2SO_4
 (b) 15 minutes at +1.85 V

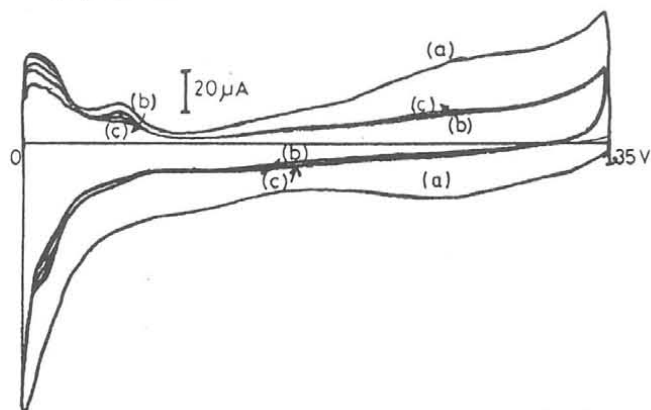


Fig. 3.5. Voltammetric responses of the Ir electrode in 0.5 M H_2SO_4 :
 (a) before and (b) after flame treatment;
 (c) 6 cycles after state (b).

4. ELECTRODE SURFACES WITH PREFERRED ORIENTATIONS: Pt SINGLE CRYSTALS

The importance of the superficial structure of the electrode is well recognized. Not only the kinetics but also the mechanism of several electrooxidation reactions have shown to be strongly dependent on the crystallographic orientation and on the symmetry of the superficial atoms of the electrode surface. Structural effects have been observed for small organic molecules, as well as for larger molecules like the butanol isomers, the D-glucose and the D-sorbitol among others (see the recent review by Parsons and VanderNoot [32] and references therein).

4.1. SINGLE CRYSTAL ELECTRODE SURFACES

The importance of having well defined surfaces has been stressed by several workers.

The most direct approach for the characterization of the single crystal electrode surfaces is Low Energy Electron Diffraction (LEED): each single face gives a definite LEED pattern [33]; the technique, however, is quite expensive, requires high-ultravacuum and is not an *in situ* technique.

Electrochemists have found the possibility of using electrochemical methods, namely cyclic voltammetry for the characterization of the single crystal electrode surfaces. The hydrogen adsorption/desorption region is particularly sensitive to the structure of the electrode. The distribution of the multiple hydrogen adsorption states is quite different from one single crystal orientation to another, thus, leading to peaks at different potentials: the position, the number of peaks, their relative amplitude and size, reflect the structure of the electrode surface. Standard voltammetric responses for the Pt low index single crystals and also for the Au and Ir electrode surfaces either

in acid and in basic medium have been established and reported in the literature [34-47]. Differences reported in the standard voltammetric responses of the low-index crystal planes from the various laboratories might be due to the electrochemical treatment of the electrode surface and its activation by electrochemical means. Structural modifications of the Pt single crystals due to potentiodynamic cycling have been detected by LEED [33]. Differences induced by the electrolyte, particularly for those anions which can be specifically adsorbed have been recently reported by Armand and Clavilier [41] for Pt(100), Pt(111) and Pt(110) single crystals and earlier by Motoo and Furuya [45] for Ir(100), Ir(110) and Ir(111) single crystals.

PRETREATMENT AND ACTIVATION OF THE SINGLE CRYSTAL ELECTRODE SURFACES

Work with single crystals is very delicate. Single crystals are very expensive and they can easily suffer structural modifications during electrochemical polarization. They are also very sensitive to impurities in the solution. As it has been detected by Wagner and Ross [33] and, by several others that the upper limit of the potential during the positive scan is critical. Wagner and Ross report stability of the Pt low index surface, in acid medium, only when the value of 0.82 V vs (she) is not exceeded.

The procedure developed by Clavilier [34] and by Adzic *et al.* [37] for the pretreatment of the single crystal electrode surfaces is quite different. The methodology of Clavilier has been most widely used and consists of thermal treatment in a gas oxygen flame followed by rising with ultrapure water, the electrodes being protected by a droplet of water during their transfer to the electrochemical cell.

ELECTROCHEMICAL ACTIVATION

The state of the electrode surface as well as the purity of the system can be checked through the cyclic voltammograms recorded from the electrode in the base electrolyte. The upper limit of the potential shall be carefully chosen and polarization should preferably start in the negative direction (see Figs. 4.1 to 4.3).

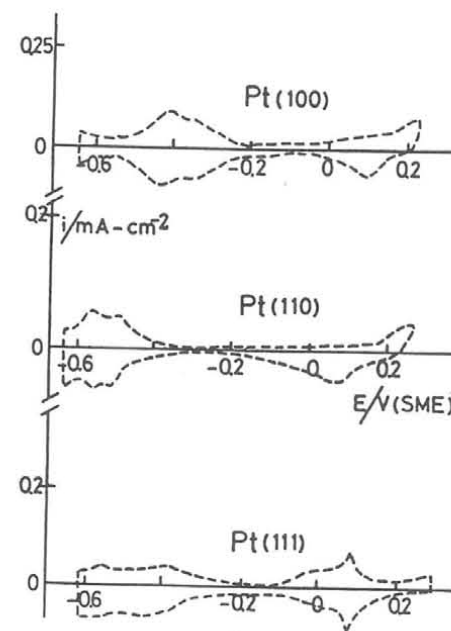


Fig. 4.1. Voltammetric responses of the Pt (hkl) low-index planes in 1 M HClO₄. $v = 50 \text{ mV s}^{-1}$ [42].

Extending the upper limit of potential into the oxide region leads to different voltammetric profiles, both in the hydrogen adsorption/desorption region and in the oxide region. In basic medium Pt(110) and Pt(111) undergo reconstruction after repetitive adsorption-desorption of oxygen at high coverages. The effect is even more drastic in acid medium.

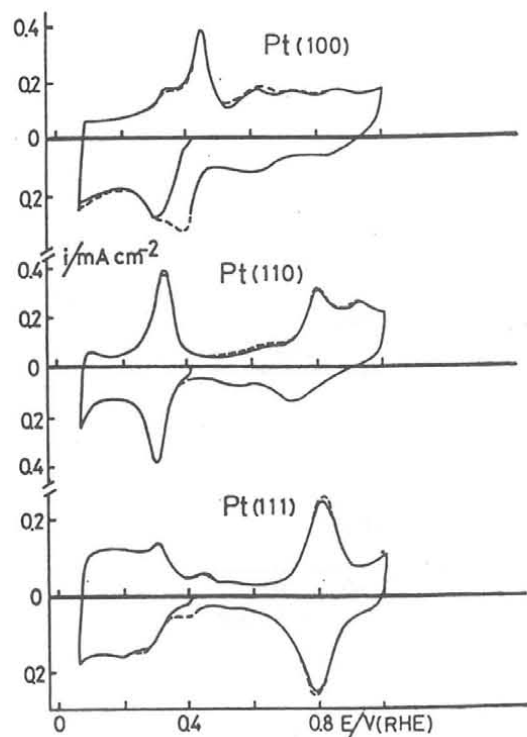


Fig. 4.2. Voltammetric responses for the Pt(hkl) low-index planes in 0.1 M NaOH. $\nu = 0.2 \text{ V s}^{-1}$ [46].

The electrocatalytic activity of the single crystal electrode surfaces decreases rapidly with continuous cycling in the presence of the electroactive species, but the lost of activity depends on the structure of the electrode surface. It has been observed recently [48] that after five cycles the electroactivity of the Pt(hkl) low-index planes, for the oxidation of the D-sorbitol in perchloric medium decreases 57%, 74%, 68% and 52% for the Pt(100), Pt(110), Pt(111) and Pt(poly), respectively (see Table 3.1).

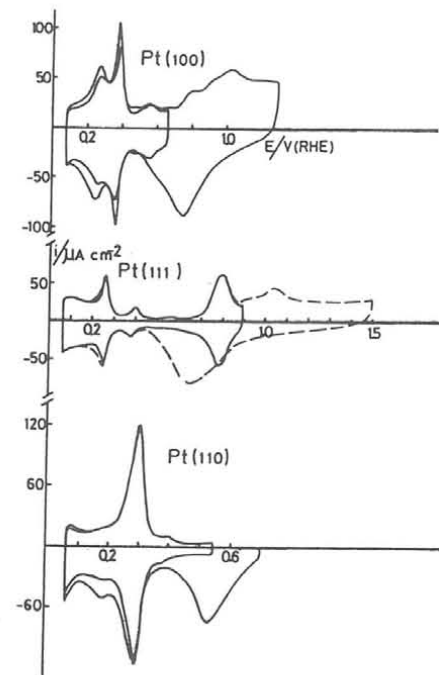


Fig. 4.3. Voltammetric profiles from the Pt(hkl) low-index planes in 0.1 M NaOH after extending the upper limit of the potential [47].

TABLE 3.1.

Maximum peak current densities and peak potentials for the oxidation of 0.1 M D-sorbitol at $\nu = 100 \text{ mV s}^{-1}$, on Pt electrodes of different structures [48].

Electrode surface	$i_p / \text{mA cm}^{-2}$	$E_p / \text{V (vs. RHE)}$	Peak decrease (%)	
			1 st → 2 nd cycle	1 st → 5 th cycle
Pt(100)	3.8	0.72	30	57
Pt(110)	2.9	0.63	64	74
Pt(111)	2.4	0.68	40	68
Pt(poly)	2.2	0.65	44	52
	1.4	0.75	36	67

4.2. ELECTROCHEMICAL FACETED ELECTRODE SURFACES

Arvia *et al.* [49] have noticed that fast electrochemical perturbations can induce morphological and structural modifications on polycrystalline metal electrodes. From those observations new electrochemical methodologies for producing electrodes with well-defined surface structures were established. The methodologies are well described by Arvia *et al.* [49] and consist mainly in the application of fast repetitive potential perturbations of preselected characteristics.

The characteristics of the potential perturbations such as the limits of potential, range of sweep rate, range of frequencies, symmetry of the ramp, etc. have been well established by Arvia *et al.* for the platinum, gold, rhodium and palladium polycrystalline electrode surfaces [50-52].

The development of the preferred crystallographic orientations on the polycrystalline metal electrodes have been identified through their voltammetric responses and also confirmed by the corresponding X-ray diffractograms.

In general, faceted metal surfaces without appreciable changes in roughness can be obtained by fast repetitive potential perturbations such as, repetitive square wave potential scanning, repetitive triangular potential sweeps, or repetitive sinusoidal potential perturbations, applied to the polycrystalline electrode surfaces.

Arvia *et al.* [50] have tested the stability of those electrode surfaces with preferred crystallographic orientations and have concluded that such modified electrodes remain stable for long times, either in contact with pure water and pure electrolyte solutions or even in the presence of a clean nitrogen atmosphere.

Electrode surfaces of noble metals can also be roughened by electrochemical methods. Nearly two decades ago Biegler and Woods [53] have reported enhancement of roughness and smoothing of electrode surfaces due to low frequency anodic-cathodic polarization of the corresponding electrode surfaces in the supporting electrolyte.

Recent results on polycrystalline platinum electrodes have demonstrated the ability of the anodic-cathodic treatments to produce changes in surface topography depending on frequency, symmetry and limits of the periodic perturbations [49,50].

These and other results obtained by Arvia and collaborators show that data obtained with different relaxation techniques must be handled with special care because of the possible modifications induced on the electrode surface.

The electrochemical procedure for the activation of the polycrystalline Pt electrodes in acid medium established in our laboratory and reported in a previous paper [54] have caused differences in the corresponding voltammetric responses that might be due mainly to the roughening of the electrode surface. Peaks in the hydrogen adsorption-desorption region become better defined, as well as those in the oxide region; the position and the relative size of the peaks in the hydrogen region, however, do not show significant changes, as it is clearly shown by the CVs in Fig. 4.4.

Enhancements in the degree of roughness of smooth electrode surfaces can be produced by electrochemical polarization of the Pt electrodes over a wide range of potential. Electrochemical activation, however, can produce apart from roughness, also structural modifications, depending on the limits of the scanning potential, rate of scanning, etc.

own electrodes depending on the type of potential perturbation used for the electrochemical activation.

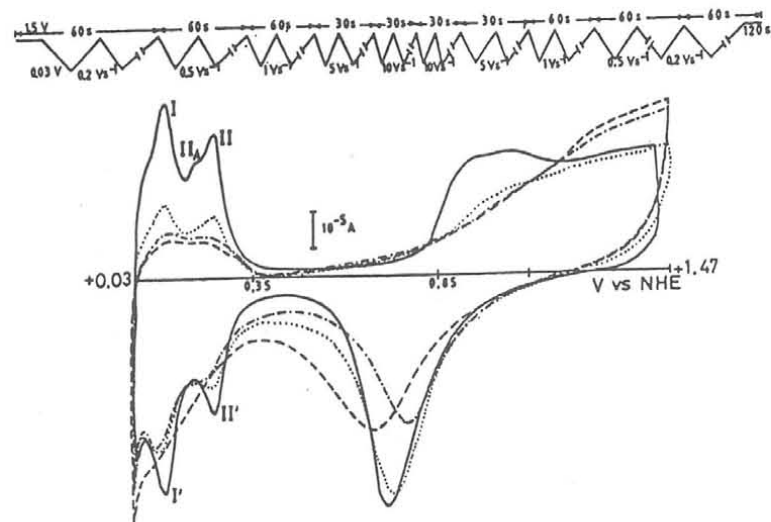


Fig. 4.4. CV's from Pt/1 M H₂SO₄ interface at 0.1 V s⁻¹. (---) 1st cycle; (-.-.-) 2nd cycle; (...) after ten cycles at 0.1 V s⁻¹; (—) immediately after the application of the potential profile given inside [54].

FINAL REMARKS

The potentialities of the electrochemical methods as a cheap means to produce modified electrode surfaces and to control their state, before, during and after their utilization as electrocatalysts have been demonstrated.

We would not like to conclude this lecture, however, without mentioning two particular aspects:

(i) The relevant and increasing importance of the spectroelectrochemical methods, namely of EMIRS, PMRS and SNIFTIRS, in the identification of the poisoning species

responsible for the loss of activity of the modified and non-modified electrode surfaces and

(ii) The importance of several other types of modified electrode surfaces, namely of electrode surfaces modified by polymers, by complexes species chemically attached, by electrodeposited redox centers, by ion implantation, etc.

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POROUS CARBON ELECTRODES FOR NON-MERCURY
CHLOR-ALKALI CELLS

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SUMMARY

Porous carbon electrodes were prepared using carbon powders of different types using various catalysts. Physical properties of the prepared electrodes were evaluated using scanning electron microscopy (SEM), surface area analyser etc. Performance characteristics of these electrodes were evaluated by galvanostatic polarisation at various temperatures in 6M potassium and sodium hydroxide solutions.

INTRODUCTION

Chlorine and caustic are almost entirely produced by electrochemical means. Caught between high energy cost and low product prices, chlor-alkali producers world-wide are now turning towards membrane cell technology for survival. Membrane based technologies have improved so much in recent years. One development is the oxygen depolarizing cathode process. In this process, an alternate cathodic reaction, that is, the reduction of oxygen rather than the conventional decomposition of water, is used for producing caustic [1].

Electrochemical power sources such as metal/air batteries and fuel cells contain carbon electrodes for oxygen

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