

ACTIVATION AND CHARACTERIZATION OF THE Pt/1M H₂SO₄ INTERFACE BY
CYCLIC VOLTAMMETRY

I.T.E. FONSECA and A.C. MARIN

CECUL(INIC) - R. Escola politécnica, 58 - 1294 LISBOA CODEX - PORTUGAL

ABSTRACT

"Major" and "minor" experimental parameters that can influence the catalytic activity of a polycrystalline Pt electrode, in an acid aqueous medium, are emphasized. Typical results, demonstrating such effects are presented.

It is also shown that cyclic voltammetry is a powerful technique, for activation and control of the state of the working Pt surface and also for control of impurities in the base electrolyte solution.

However, the aim of this paper is to give some advices to all those that have to work with Pt, for the purpose of comparing catalytic activity, induced by different means.

1. INTRODUCTION

The applicability of noble metals, namely, **Platinum**, in fundamental and applied electrochemistry has been recognized for a long time.

With the energy crisis of 1973 a number of research teams all over the world have addressed its research programmes into the area of Electrocatalysis, demanding for a more efficient catalyst for, both, fuel oxidation and oxygen reduction. It has been known, for about a

century that Pt, can be rendered more active by cycling its potential between hydrogen and oxygen evolution potentials. By the 69's such increase in activity was attributed to a "cleaning" process of the electrode surface from oxides and traces of adsorbed impurities and also to a "roughening" of the electrode surface¹⁻⁵. However, a better understanding of the process of activation and cleanliness of a Pt electrode was still claimed.

The development of sophisticated optical techniques, i.e., LEED, REED, AES, X-ray, SEM microphotography made possible to follow the structural and other types of changes, induced on a polycrystalline Pt electrode by chemical and/or electrochemical treatments. However, even using LEED analysis, conclusions were not definitive; e.g. Ross⁶ has concluded that electrochemical activation can be either due to structural changes, or to other phenomena, i.e. the oxidation of impurities on the Pt surface.

By 1980 the amount of work produced with Pt single crystals was considerable⁶⁻¹⁷, and in fact, some highlights were introduced in the area of electrocatalysis from such studies.

Standard CV's for the different Pt single crystals have been published in the literature^{7-9,12,15-17}, i.e. for Pt (100), Pt(111), Pt(110), etc. The main differences of the I-E responses due to a particular face were observed in the hydrogen adsorption/desorption region (0.03-0.4 V), particularly, the position of the two peaks associated to the adsorption of weak and strong hydrogen species and its relative size.

Such typical I-E profiles, can be used, e.g. to infer about the

average of certain crystal planes, on a polycrystalline activate Pt surface, as Arvia et al¹⁴ have done.

It has been recognized for some considerable time that electrode kinetics and electroadsorption/electrodesorption studies require ultrapure systems. Quite recently it has been demonstrated by Pletcher et al.^{18,19} and also by Nicol et al.²⁰, that the degree of activation of a Pt electrode can be influenced by the purity and composition of the base electrolyte. Therein, precautions must be taken to minimize interferences from impurities either on the electrode surface or from the electrolyte solutions. In fact, much earlier, Conway et al.²¹ and also Bruckenstein et al.²², have concluded that impurities in the base electrolyte, even at very low levels, can affect the I-E response of a Pt electrode.

As much of the published work on electrocatalysis is based on electrochemical measurements using Pt electrodes of low surface area, so precautions must be taken to avoid poisoning of the electrode.

In a series of papers Arvia et al.^{14,23-26}, have demonstrated how it is possible, to induce preferred single crystallographic faces on a polycrystalline Pt electrode, by applying standard potential perturbations, during the electrochemical treatment of the electrode, e.g., by sweeping continuously the potential between O₂ and H₂ evolution regions, at very fast sweep-rates, i.e. $v > 10^4 \text{ V s}^{-1}$. But, on the other hand, they have also verified that the development of preferred orientations on the polycrystalline Pt electrode, depends on its history, including the chemical and mechanical treatments and

also composition and purity of the electrolyte solution.¹⁴

According to Arvia et al.¹⁴, the type of effect obtained on the Pt surface, by sweeping the potential, is critically dependent on the range of sweep-rates, i.e.: $1 \text{ mV/s}^{-1} < v < 0.1 \text{ V s}^{-1}$ produces small changes in the electrode active area; $0.1 \text{ V s}^{-1} < v < 1000 \text{ V s}^{-1}$ produces considerable increase in the real surface area; fast sweep-rates i.e. $v > 10^4 \text{ V s}^{-1}$ produces preferred orientation on the polycrystalline Pt surface.

Although some knowledge has been achieved about the parameters that can influence the activity of substrates, little agreement exists about the most appropriate "recipe" for an initially clean and active electrode surface. From our own experience and from so much already published, we would like to emphasize, that for the purpose of comparison of the catalytic activity induced in a working surface, by other means, i.e. by underpotential deposited monolayers, the essential thing is to begin with a standard and reproducible surface, stable at least, during the measurements.

The aim of this paper is (i) firstly to point out some "major" and "minor" parameters that can influence the behaviour of a Pt working surface (ii) secondly to emphasize the advantages of cyclic voltammetry i.e.:

- a) activation of the working surface "in situ";
- b) determination of the real area through the recorded CV;
- c) control of the degree of activation and stabilization of the initial surface;
- d) detection of impurities on the working surface or from the solution;

and

- e) information about the % of certain crystal faces on the polycrystalline Pt surface, by comparison of the recorded CV with standard CV's published for single crystals.

2. EXPERIMENTAL

Base Electrolyte Solutions

Special care was taken in preparing clean solutions. Hence, glassware was carefully cleaned, first with an ethanol/potassium hydroxide solution, then with 1:2 $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture and finally washed in boiling triply distilled water.

Triply distilled water obtained from two different methods was tested, namely:

(A) 3-D Water obtained from a Quartz destilator and (B) 3-D Water redistilled from alkaline permanganate, under an inert atmosphere of pure N_2 , for the oxidation of organic impurities.

Base electrolyte solutions were made up from water 3-D (A) or (B) and H_2SO_4 , "Analar" from BDH or "Aristar R".

Since solutions made up with water (B) have demonstrated the introduction of some uncertainties related to contamination by traces of organics, we have decided to carry on these studies, mostly with fresh distilled water (A).

3-D water and solutions were kept always in glass material, carefully cleaned. Contacts with rubber or plastic material were avoid.

Solutions were deoxygenated with N_2 of high purity, for about 30 m, before each set of experiments. Also here, rubber tubes were avoided, whenever possible.

Cells and Electrodes

Typical 3 electrode, three compartment cells were used.

The working electrode was a smooth platinum wire, 1.15 cm long, with a geometric area of 0.201 cm^2 , carefully made by the glassblower of Southampton University, with Pt from Goodfellow's (99.99% of purity). The counter electrode was a 10 cm long platinum spiral.

The reference electrode was a laboratory constructed H_2 electrode separated from the working electrode, by a Luggin capillary. Before each set of experiments, the potential of the RE was checked against a commercial saturated calomel electrode (SCE). A good reproducibility in potential was maintained, during the life-time of the reference electrode.

Cleaning and activation of the working Pt electrodes

Working Pt electrodes after being chemically cleaned and carefully washed with 3-D water were introduced in the base electrolyte and submitted to different potential perturbations, for the electrochemical activation, till a standard CV as described by Conway²¹ was obtained. After some preliminary experiments we have established a standard procedure for the electrochemical treatment. However, a "recipe" cannot be given, because each electrode, has its own history.

Our standard procedure consists mainly in sweeping continuously between H_2 and O_2 evolution potentials using sweep-rates ranging from

($0.2 - 10 \text{ V s}^{-1}$) and then in the reverse way ($10 \text{ V s}^{-1} - 0.2 \text{ V s}^{-1}$) according to the potential profile indicated in fig. 1. Immediately, afterwards, the correspondent CV at 0.1 V s^{-1} was recorded continuously. If reproducibility was obtained then the correspondent CV was recorded at 0.1 V s^{-1} . The tests suggested by Conway²¹ for a clean activate Pt surface were then applied to the recorded CV and since they were verified the electrochemical treatment was stopped, by holding the potential at the positive limit of 1.5 V. Afterwards, the electrode was carefully and quickly transferred to the cell containing the solution under study.

When not in use the electrode was kept in contact with 3-D water

During experiments, at least, two cells in parallel were always used one for checking the state of the electrode surface and the other containing the solution for the electrochemical studies.

Equipment

The equipment used was mainly a PAR potentiostat/galvanostat, mod. 173 and a PAR wave-form generator mod. 175 and a Philips X-Y recorder mod. 8143.

3. RESULTS

Activation of the Pt electrode by cycling at fast sweep-rates

After having chemically cleaned the Pt electrode following the procedure described in section 2, the electrode was immersed in the base electrolyte - an aqueous solution 1M in H_2SO_4 . Then, a potential perturbation consisting in cycling continuously the potential between

0.03 and 1.5 V vs. NHE at 0.1 V s^{-1} , was applied to the Pt electrode, during about 5 minutes. CV's corresponding to the 1st, 2nd and 10th cycles of sweeping at a 0.1 V s^{-1} are shown in fig. 1.

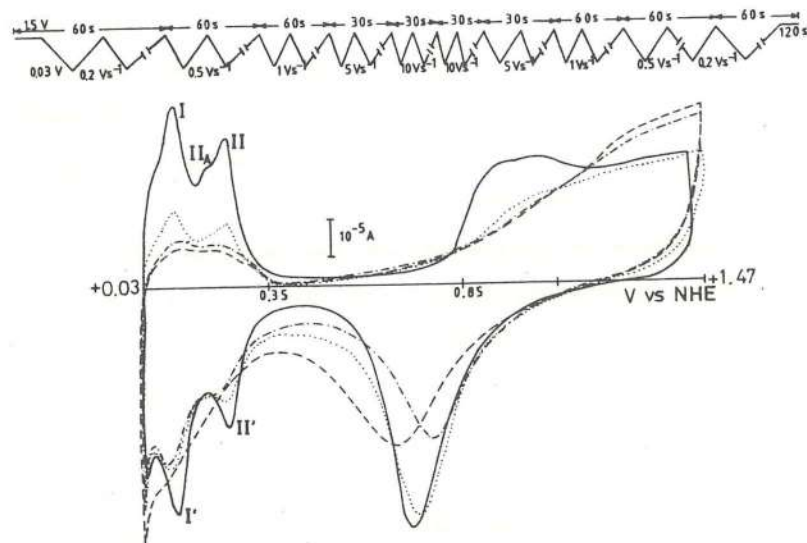


Fig. 1. CV's from Pt/1M H_2SO_4 aqueous solution, recorded at 0.1 V s^{-1} . Geometric area of the Pt electrode = 0.201 cm^2 . (---) 1st cycle at 0.1 V s^{-1} ; (-.-.-) 2nd cycle at 0.1 V s^{-1} ; (...) after 10 cycles at 0.1 V s^{-1} ; (—) immediately after the application of the potential profile indicated.

From CV's in fig. 1, it can be seen that some improvement was obtained after 10 cycles of sweeping, at 0.1 V s^{-1} . However, only after sweeping at fast sweep-rates, e.g. from $0.2 - 10 \text{ V s}^{-1}$ and then from $10 \text{ V s}^{-1} - 0.2 \text{ V s}^{-1}$ according to the profile shown, the typical voltammetric response was obtained (full line in fig. 1.). Such response was then submitted, to the diagnostic proposed by Conway et al.²¹ for a cleaned and activated Pt/1M H_2SO_4 interface.

In fact, the I-E response (—) in fig. 1., reveals the following features:

- two cathodic peaks I' and II', and the correspondent anodic peaks I and II, respectively at 0.11 ± 0.005 and $0.24 \pm 0.005 \text{ V}$ vs NHE. Peak II is preceded by a pre-peak (II_A);
- peak currents and peak potentials follow the relationships:

$$I_p \propto v \quad \text{and} \quad \Delta E_p = 0$$

- the ratio between anodic and cathodic charges, under the region 0.03 to 0.35 V approaches unity, in the final CV (—);
- in the double-layer region (0.35 — 0.75), no faradaic or adsorption currents are observed;
- for $E \geq 0.80 \text{ V}$ the anodic current increases steeply and a broad peak is observed, correspondent to the PtO formation;
- the ratio between anodic and cathodic charges correspondent to the oxide region (0.8 to 1.5 V and 1.2 to 0.5 V), changes from 3.0 to 1.5, from the 1st recorded CV (---) till the final (—).

The real surface area of the polycrystalline Pt electrode was calculated by integration of the charge due to the adsorption of H, in the

potential region from 0.03 to 0.35 V, in the final CV ((—) in fig.1), following the procedure indicated by Gilman²⁷. The real surface area was obtained by assuming a charge of 210 $\mu\text{C cm}^{-2}$ for a monolayer of adsorbed hydrogen²⁸. A roughness factor ranging from 1.7 to 2.0 was obtained.

During the electrochemical treatment it was also observed that when the electrode is completely deactivated, if the anodic limit of the potential perturbation, for the electrochemical cleaning does not reach the oxide region, the standard CV response with well developed hydrogen peaks is not obtained, even after submitting the electrode to fast sweepings. The electrode can only be activated, after the oxidation of impurities and its removal from the electrode surface. However, once the electrode is cleaned and activated, the anodic limit of potential can be reduced to 0.75 V, and successive runs between 0.03 and 0.75 V would give reproducible I-E curves - such a feature has actually been indicated as a test for the cleanliness and activation of the Pt surface.

Fig. 2 is an example of the observed behaviour.

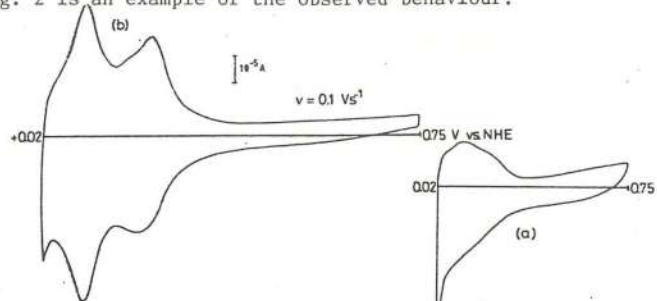


Fig. 2. Voltammetric responses from a Pt/1M H₂SO₄ interface, after being submitted to a potential profile of the type indicated in fig. 1.

(a) When the anodic limit of the potential perturbation has not overcome 0.75 V.

(b) When the anodic limit of potential has been previously extended to 1.5 V.

O₂ in the solution detected by Cyclic Voltammetry

After being cleaned and activated the Pt electrode was carefully and quickly transferred to another cell containing the same base electrolyte 1M H₂SO₄, previously deoxygenated, but only during 10 minutes. The correspondent voltammetric response, at 0.1 V s⁻¹ is shown in fig. 3 (—).

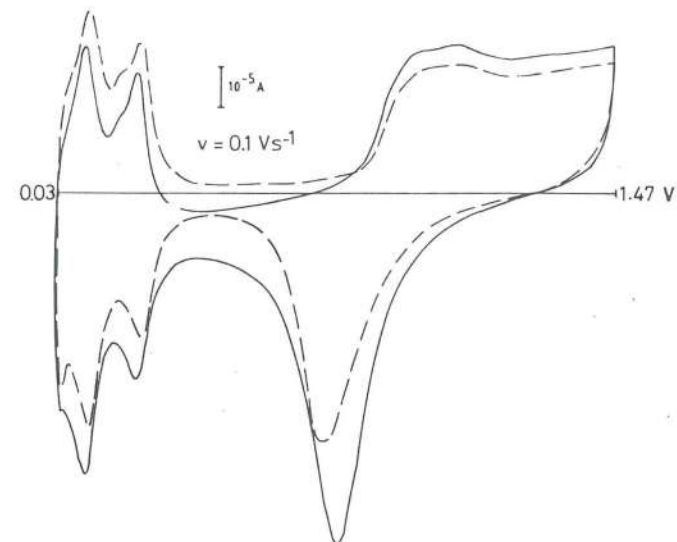


Fig. 3. Effect of some residual O₂ on the CV response of the Pt/1M H₂SO₄ interface. $v = 0.1 \text{ V s}^{-1}$. Pt = 0.201 cm².
 (—) 1M H₂SO₄ aqueous solution with some remaining O₂.
 (---) 1M H₂SO₄ aqueous solution free of O₂.

The correspondent curve shows the typical shape of a standard CV for a Pt/1M H₂SO₄ interface, apart from the displacement of current in the cathodic direction.

Stability of the activated Pt surface

Some tests were performed, in order to verify for how long the electrode can keep its state of activation. Fig. 4 demonstrates some of the conclusions.

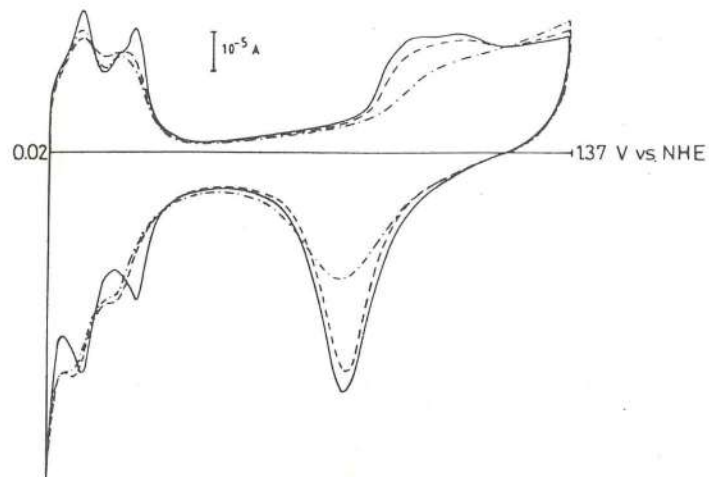


Fig. 4. CV's from a Pt/LM H_2SO_4 aqueous interface. $v = 0.1 V s^{-1}$
 $Pt = 0.201 cm^2$.

(—) standard CV response; (---) after having the electrode at open circuit for about 30s. After having the electrode in contact with the atmosphere: (—) 30s; (---) 150s; (-.-.-) 180s.

The full line represents the standard CV response of our electrode previously cleaned and activated. It can be seen that after being in contact with the atmosphere for about 30s the response of the surface coincides with the 1st one. But, for time intervals longer than 150s the CV response deviates from the standard CV, as shown by

the dashed lines in fig. 4. Such time intervals are necessarily dependent on the aggressivity of the atmosphere of the laboratory where the experiments are being performed.

If the electrode is left in high purity base electrolyte, then it can keep its state of activation for at least 24h, even at open circuit. Nevertheless, if some activity is lost meanwhile, then a few cycles of sweeping would be enough to restore it. Therein, between experiments the electrode was carefully kept, either in the base electrolyte solution, or in pure 3-D water. Contacts with the atmosphere of the laboratory were always avoided.

In any case, the electrode was kept in open circuit only when its potential was at the anodic limit (in the oxide region).

Interferences from a S.C.E. used as reference electrode

Most workers, in the area of Electrocatalysis, use the hydrogen electrode (NHE) as reference electrode even though it is less convenient when compared with a commercial saturated calomel electrode.

In our first experiments we used a SCE as reference electrode, during the electrochemical treatment of the electrode. After a certain number of cycles, at relatively fast sweep-rates, a CV at $0.1 V s^{-1}$ was recorded and anomalous features, which were not originally observed, were detected as shown by CV's in fig. 5.

In fact, curve -1- in fig. 5. shows that the oxide formation has been inhibited and at the anodic limit of 1.5 V the current rises suddenly showing that a new process is occurring. According to the potential, the process can be attributed either to O_2 or Cl_2 evolution.

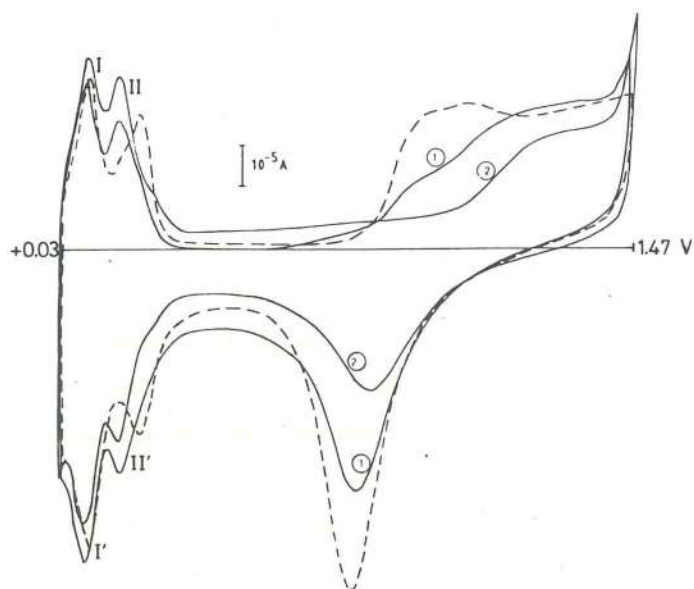


Fig. 5. CV's from a Pt/1M H₂SO₄ + xM Cl⁻ interface. $v = 0.1V s^{-1}$.
Pt = 0.201 cm² (---) x = 0; (—○) - traces of Cl⁻ coming from the R.E.; (—○) - 1 x 10⁻³M Cl⁻ added to the solution.

Differences are also observed in the hydrogen adsorption/desorption peaks. Peak II and II' are displaced cathodically and a slight increase in charge is also observed.

After comparing these results with published work namely with Breiter's results²⁹ we suspected that the anomalous effects observed could be due to the diffusion of Cl⁻ through the Luggin reaching the working electrode surface after a certain time.

To confirm our idea we have added some Cl⁻ to the base electrolyte. The correspondent CV also shown in fig. 5 confirms diffusion of Cl⁻.

It might happen that one can use the SCE without interfering with the state of the working surface, but our advise is do not use it.

In a previous paper¹⁹ we have demonstrated the deleterious effects of Cl⁻ in the oxidation process of HCOOH, at Pt in acidic medium.

Detection of impurities in the solution

The tolerable level of impurities in electrode kinetics studies is very low. A concentration of 2 x 10⁻⁹M of impurities will block 10% of the surface of an electrode with a surface to volume ratio of 1:100. The importance of a rigorous control of impurities even, at very low levels, should be stressed.

In fact, it was observed that, if for some reason, the triple-distilled water or the H₂SO₄ was not of high purity, some additional peaks were observed in the recorded CV's, as shown, in fig. 6.

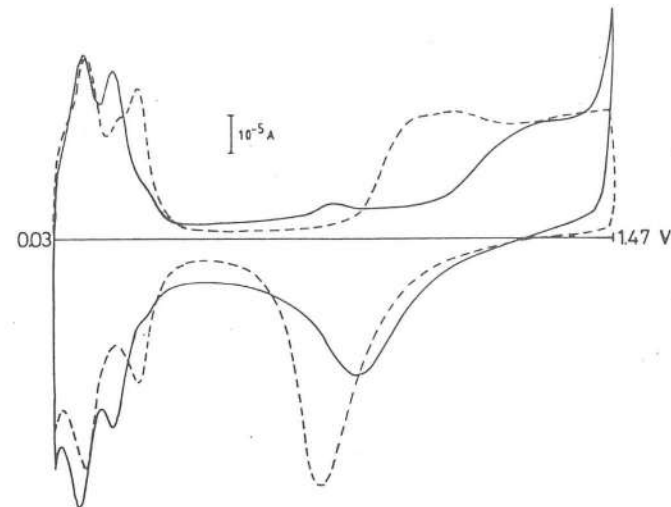


Fig. 6. CV's from a Pt/1M H₂SO₄ aqueous solution, with traces of impurities (—) and without impurities (---). $v=0.1Vs^{-1}$.

Concluding remarks

From our experience and also from vast published work we know that the conclusions about the electrocatalytic activity of a Pt working electrode can be adversely affected by the state of the surface. Therein the reason for the following advices:

- Establish "your standard methodology" for preparing a cleaned, activated and reproducible Pt surface.
- Keep your Pt electrode in the base electrolyte solution or in 3- \bar{I} distilled water. Do not touch it when transferring it from one to another cell. If possible keep it with a drop of water or solution.
- Use always the hydrogen electrode as reference electrode.
- Use high purity water and chemicals. Avoid contact with plastic or rubber.
- Use always, at least, two cells in paralell, one with the solution containing the species under study and the other, with the base electrolyte for checking the state of the electrode, whenever you find it necessary.

Finally,

- Record a CV of your cleaned and activated Pt electrode. Keep it as a picture for the present and for the future.

Acknowledgements

A.C. Marin is grateful to INIC for her scholarship.

I. Fonseca thanks INIC for financial support.

We are both grateful to Dr. D. Pletcher for fruitful advices and to the glassblower of Southampton University, Mr. C. Godden, for his kindness and skill in making our Pt working electrodes.

References

1. S. Gilman, *J. Electroanal. Chem.*, **9** (1965) 276.
2. M.W. Breiter, *Electrochim. Acta*, **11** (1966) 905.
3. S.D. James, *J. Electrochem. Soc.*, **114** (1967) 1113.
4. T. Biegler, *J. Electrochem. Soc.*, **116** (1969) 1131.
5. D.F. Untereker and S. Bruckenstein, *J. Electrochem. Soc.*, **121** (1974) 360.
6. F.T. Wagner and P.N. Ross, *J. Electroanal. Chem.*, **150** (1983) 141.
7. F.G. Will, *J. Electrochem. Soc.*, **112** (1965) 451.
8. P.N. Ross Jr., *J. Electroanal. Chem.*, **76** (1977) 139.
Ibid, *Surf. Sci.*, **102** (1981) 463.
9. A. Hubbard, R.M. Ishikawa, J. Katekaru, *J. Electroanal. Chem.*, **86** (1978) 271.
10. R.R. Adzic, A.V. Tripkovic and W.O'Grady, *Nature*, **296** (1982) 137.
11. J. Clavilier, R. Parsons, R. Durand, C. Lamy and J.M. Leger, *J. Electroanal. Chem.*, **124** (1981) 321.
12. F.E. Woodard, C.L. Scottichini and C.N. Reilley, *J. Electroanal. Chem.*, **151** (1983) 109.
13. S. Shibata and M.P. Sumino, *Electrochim. Acta*, **17** (1972) 395.
14. R.M. Cervino, W.E. Triaca, A.J. Arvia, *J. Electroanal. Chem.*, **182** (1985) 51.
15. E. Yeager, W.E. O'Grady, M.Y.C. Woo and P. Hagus, *J. Electrochem. Soc.*, **125** (1978) 125.
16. K. Yamamoto, D.M. Kolb, R. Kotz and G. Lehmpuhl, *J. Electroanal. Chem.*, **96** (1979) 233.
17. R.M. Cervino, A.J. Arvia and W. Vielstich, *Surf. Sci.*, **154** (1985) 623.
18. D. Pletcher and V. Solis, *Electrochim. Acta*, **27** (1982) 775.
19. I.T.E. Fonseca and D. Pletcher, *Port. Electrochim. Acta*, **1** (1983) 219.

20. B.D. Nicol, R. Miles and R.T. Short, *Electrochim. Acta*, **28** (1983) 1285.
21. B.E. Conway, H. Angerstein-Kozłowska, W.B.A. Sharp and E.E. Cridle, *Anal. Chem.*, **45** (1973) 1331.
22. M.Z. Hassan and S. Bruckenstein, *Anal. Chem.*, **46** (1974) 1962.
23. R.M. Cervino, W.E. Triaca and J.A. Arvia, *J. Electrochem. Soc.*, **132** (1985) 267.
24. E. Custidiano, A.C. Chialvo and A.J. Arvia, *J. Electroanal. Chem.*, **196** (1985) 423.
25. J.C. Canullo, W.E. Triaca and A.J. Arvia, *J. Electroanal. Chem.*, **175** (1984) 337.
26. A.J. Arvia, J.C. Canullo, E. Custidiano, C.L. Perdriel and W.E. Triaca, *Electrochim. Acta*, **31** (1986) 1359.
27. S. Gilman, *J. Electroanal. Chem.*, **7** (1964) 382.
28. R. Woods, *Electroanal. Chem.*, in A. Bard **9** (1976) 1.
29. M.W. Breiter, *Electrochim. Acta*, **8** (1963) 925.

(Received 18 December 1986)

ADSORPTION OF UREA FROM AQUEOUS SODIUM CHLORIDE SOLUTIONS

BY

FERNANDO SILVA* e M. ROSA BARBOSA

Departamento de Química

Faculdade de Ciências

Pr. Gomes Teixeira

4000 PORTO, PORTUGAL.

ABSTRACT

Measurements of the differential capacity of a Hg electrode in contact with six aqueous solutions of urea were made using a computer controlled system which sampled 75 times during the drop life. The parameters of the adsorption isotherm are determined under appropriate thermodynamic conditions. The results indicate that urea adsorbs much less strongly than thiourea.

I - INTRODUCTION

The electrochemical adsorption of urea has received considerably less attention than the similar compound, thiourea, in contact with the many physical chemistry studies of its biological influence^{1,2,3,4}. Parsons and Peat⁵ studied the electrochemical adsorption of urea from aqueous 1.0 M KNO₃ and found that urea was adsorbed on a Hg electrode