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Publication Date
1978-11-01

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November 1978

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Structure Sensitivity in Electrocatalytic Properties of Pt:
II. Oxygen Reduction on Low Index Single Crystals and the Role of Steps

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ABSTRACT

Single crystal surfaces were used to simulate the different geometric sites that may occur on small ($\sim$ 1 nm) Pt clusters of arbitrary shapes, and to determine the structure sensitivity of oxygen molecule reduction in acid electrolyte. The static electrode configuration for the single crystals restricted the kinetic measurements to the high potential (0.9-1.0V) region where the reaction occurs on an oxygenated Pt surface. In dilute H_2SO_4 or $HClO_4$ there was no measurable difference in the oxygen reduction activity of Pt (111)-(1x1), (100)-(1x1), or stepped surfaces. Post-test analyses of the electrode surfaces by LEED and AES showed that these active surfaces were highly ordered and contained no sublattice or subsurface oxygen (< 0.1 a/o). Triangular sweep potential cycling to anodic limits above 1V, or anodic prepolarization to 2V with potentiostatic reduction of the anodically formed oxide, did not enhance the activity. It was concluded that there are no specifically active sites for oxygen reduction on an oxygenated Pt surface, rather the Pt surface is uniformly active. Cyclic voltammetry did show that at low coverage oxygen reduction intermediates are adsorbed more strongly (irreversibly) at steps than on atomically flat surfaces. At high coverage, repulsive interaction of adsorbed intermediates apparently diminishes the effect of structure on the adsorption energies, so that no structure sensitivity is observed in the potential region under kinetic control.

Structure Sensitivity in the Electrocatalytic Properties of Pt: II.
Oxygen Reduction on Low Index Single Crystals and the Role of Steps

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Introduction

Recent investigations of the oxygen reduction reaction in acid electrolyte with

supported Pt have produced conflicting evidence as to the structure sensitivity of

Pt in this reaction. Bett et. al. [1] concluded that in 1N H_2SO_4 at 70°C there were

no observable differences in the reduction kinetics between Pt black and Pt supported

on graphitized carbon black with crystallite sizes down to 30Å. Blurton et. al. [2]

reported an order of magnitude decrease in rate when the Pt crystallite size was less

than 15Å, i.e., a crystallite size range smaller than that investigated by Bett et.

al. Blurton et. al. reported no crystallite size effect for a supported Pt catalyst

in the same size range used by Bett and co-workers. Kunz and Gruver [3] also

concluded that in hot concentrated H_3PO_4 crystallite size was relatively unimportant

with respect to specific activity for oxygen reduction in the same crystallite size

range studied by Bett et. al. However, Bregoli [4] has claimed that a more thorough

investigation of the performance of fuel cell electrodes using the same catalyst as

in [3] revealed a statistically significant difference in the specific activity of Pt

when dispersed on carbon, a factor of two reduction in activity between 400Å and 30Å

crystallites. The factor of two difference claimed by Bregoli was considered to be

less than experimental accuracy by the previous investigators. The observation

of an effect of crystallite size on catalytic activity does not necessarily mean

that the reaction is structure sensitive. Synergistic support effects or metal-support

interaction can produce an apparent crystallite size effect. In electrocatalysis, one might expect intuitively that the electronic properties of small Pt clusters may be particularly important and if altered would give rise to a true effect of crystallite size. Since the atoms at the edges and corners of metal crystallites have lower coordination numbers than those lying in the crystallographic planes, it has been suggested [5] that in general these sites may have different catalytic activity. As the metal crystallites decrease in size, the fraction of the surface atoms occurring in crystallographic faces will decrease relative to those at the intersection of the planes (edge atoms) so that the specific activity of the catalyst will change with crystallite size when the reaction is structure sensitive. An observable crystallite size effect is, therefore, only evidence that the reaction may be sensitive to the structure of the catalyst surface.

Observations directly related to structure sensitivity can be made using ordered surfaces from single crystals. The present investigation is an extension of the study of Pt single crystal electrodes presented in Part I to the electro-reduction of oxygen. The low index single crystal surfaces (111) and (100) were used to study the catalytic properties of highly coordinated surface atoms, and low index surfaces with well ordered steps were used to study the catalytic properties of atoms in low coordination. The technique for determining the atomic structure of the surface was low energy electron diffraction (LEED), and the procedures used here were identical to those developed in Part I. It will be shown that the low index planes of Pt are equally active for oxygen reduction in acid, and that atoms of low coordination number have equal or possibly lower activity than atoms in low index planes.

Experimental

The apparatus and procedures used to clean and characterize the single crystal surfaces was exactly the same as that described in Part I. As in I, an electrochemical pretreatment was used to clean the surfaces after transfer from the LEED/Auger system through the argon atmosphere. The surfaces were considered clean when the pretreatment cycle produced no change in the voltammogram. For the single crystals and for the polycrystalline foil, the oxygen reduction kinetic measurements were made using a static electrode configuration with oxygen bubbling continuously through the electrolyte. The oxygen gas was Airco Research Grade, used without further purification. A rotating electrode was used to establish the potential region where the kinetics are strongly coupled to oxygen diffusion, and to compare the present results with those of others. The rotating electrode was a 1 mm diameter Pt wire sheathed in a PTFE rod to expose just the unpolished tip. The PTFE rod was driven through a flexible coupling by a Bodine DC motor with a maximum rotation rate of 1700 rpm. The current-potential curves were obtained potentiostatically using a slow (5 mV/s) anodic scan starting at 0.25 V and never exceeding the zero current potential. No other potential excursions or pre-polarizations were used.

The concentrated acids H_2SO_4 (Aristar), $HClO_4$ (Fischer) and H_3PO_4 were purified by refluxing with H_2O_2 (2:1 volume ratio) at $120^{\circ}C$ in a PTFE retorting flask. The acids were diluted to form 1N solutions using purified water as described in Part I. All the experiments were conducted at room temperature and electrode potentials are referred to the reversible (1 atm) hydrogen electrode in the same solution.

Results

(i) Oxygen reduction kinetic measurements

(a) Polycrystalline Pt

The oxygen reduction polarization curves for 1N electrolytes at 25°C obtained with the rotating polycrystalline Pt electrode are given in Fig. 1. The true surface area of the rotating electrode was calculated from the area under the hydrogen adsorption peaks of the cyclic voltammogram assuming 210 $\mu C/cm^2$. The points shown represent the average value obtained from three consecutive measurements. The shaded points have been corrected for the effects of diffusion by the equation

$$i_{corr} = i_{obs} \cdot i_{limit}/(i_{limit} - i_{obs})$$

using the values of the observed current (i_{obs}) and the value of the observed limiting diffusion current (i_{limit}). Essentially identical results were obtained with 1N H_2SO_4 and $HClO_4$. The i-V curve for the dilute acids shows a well defined transition in the Tafel slope (defined as the potential change per decade of current, in multiples of $\log_e$) from ~ RT/F to 2 RT/F, occurring in H_2SO_4 or $HClO_4$ at .825-850 V and in H_3PO_4 at .850-875 V. The results appear to be in complete agreement with the theory of Damjanovic and co-workers [6-8] for oxygen reduction and the expectation that the Tafel slope will change from RT/F to 2 RT/F at the potential where O_2 absorption changes from Temkin to Langmuir behavior. The change from Temkin to Langmuir behavior occurs when the coverage of the Pt surface by oxygen species is below $\approx$ 40 $\mu C/cm^2$ [6]. The cyclic voltammetry in Fig. 2 revealed that the potential at which this occurs in 1N H_2SO_4 or $HClO_4$ is .825 V and in 1N H_3PO_4 at .85, just matching the potential at which the transition in Tafel slope was observed. The activity of Pt in 1N H_3PO_4 is about a factor of two lower at every potential (below .95V) than the activity observed in 1N H_2SO_4. The principal reason for the lower

activity in 1N H_3PO_4 relative to H_2SO_4 or $HClO_4$ is the greater coverage of the Pt

surface by anions in the potential region 0.8-1.0 V, e.g. Bagotzky et. al. [9]

indicate coverage by $H_2PO_4^-$ is twice that for $SO_4^=$ in this potential region. The

effect of anion concentration in H_3PO_4 is clearly seen from Fig. 1 by the results

for 85 w/o H_3PO_4 at $25^{\circ}C$. Concentration of the electrolyte lowers the activity level

by roughly an order of magnitude, and extends the $\sim 2\ RT/F$ Tafel slope region to a much

higher potential. This latter observation correlates with the effect of acid concen-

tration on the potential at which oxide formation starts as seen by cyclic voltammetry.

The dependence of the i-V curve on rotation rate is shown in Fig. 3 for 1N H_2SO_4.

It is clear from this plot that purely kinetically controlled currents can be measured

using static electrodes, such as the case for the single crystal electrodes, only in

the very narrow potential region of 0.925-1.000V in 1N acid, and the wider region

0.8-1.00V in 85 w/o H_3PO_4.

(b) Single crystal Pt

The i-V curves for the clean, annealed polycrystalline foil and for the clean

single crystals are shown in Fig. 4 for 1N H_2SO_4 and in Fig. 5 for 85 w/o H_3PO_4

at $25^{\circ}C$. The absolute currents were normalized by the geometric area of the electrode

exposed to the electrolyte to obtain the current densities. The i-V curve for the

annealed polycrystalline foil is in excellent agreement with that for the rotating

wire in the potential region of kinetic control. As in part I, the experiments with

the single crystals were repeated several times with at least two different crystals

of the same orientation. The reproducibility of the kinetically controlled current

density at a fixed potential was ~ 50 percent, i.e., $i \pm 0.5i$. The results of Figs.

4 and 5 show clearly that there were no significant differences in the O_2 reduction

kinetics on ordered (111), (100), (S)[3(111)-(100)] surfaces or on an annealed poly-

crystalline Pt surface. Further, there were no differences between annealed Pt

and Pt subjected to many oxidation-reduction cycles.

(c) Post-test characterization of surfaces by LEED/AES

The foregoing conclusions are, of course, only valid if the ordered or annealed

surfaces are not disturbed by either the pretreatment or the potential excursions

necessary to obtain the O_2 reduction data. All the surfaces were examined after the

electrochemical experiments by transfer into the LEED/AES system. The effect of the

electrochemical pretreatment had been shown as discussed in part I to indicate no

disordering of the ordered surfaces. It was also observed that tens of cycles in

oxygen-free solution between 0-1.0V did cause a disordering of the low index surfaces.

In the present work, the electrodes experienced potentials between 0.250V and 1.000V

in O_2 saturated solution with very slow anodic and cathodic sweep. Post-test LEED

patterns did reveal considerable angular dispersion of the (01) diffraction spot fol-

lowing the kinetic measurements on the (100)-(1x1) surface. The (111) and (S)[3(111)-

(100)] surfaces showed sharper LEED patterns indicating greater stability. Using the

methods discussed in part I for the analysis of angular dispersion of the diffraction

spots, it was concluded that the upper bound on the number of disordered atoms following

the electrochemical testing was ~ 1 in 10. This is a very qualitative statement to

make regarding the structure of what was hoped to be an ordered surface. The LEED pat-

terns do indicate the surfaces investigated were highly ordered on the atomic scale, but

some imperfections did exist, perhaps as many as 1 x 10^{14} per cm^2. Imperfections intro-

duced into the single crystal surfaces due to oxidation-reduction cycling are not, however,

sites of extraordinary activity for O_2 reduction. This was concluded after observing that severe potential cycling of the single crystal electrodes (sufficient to destroy any LEED pattern) did not produce any marked enhancement in the O_2 reduction kinetics.

The Auger electron emission data for oxygen in solids [10] suggests the AES detection limit for oxygen in a metal lattice is ~ 0.1 a/o. AES of the single crystal electrodes removed after the kinetic measurements from the electrolyte while potentiostated at 0.250 V did not reveal any oxygen associated with the Pt lattice. Following the standard kinetic measurements described above, the annealed Pt foil electrode was given numerous anodic prepolarizations used by Appleby [11] to produce "active" Pt. These were potentiostatic holds at 2V for 2 min followed by galvansostatic reduction at 20 $\mu A/cm^2$ until the potential fell to 0.5V (argon purged solution). No increase in the reduction kinetics was observed, although several such prepolarizations did significantly increase the charge for adsorbed hydrogen indicating some surface roughening. AES spectra for the foil after the prepolarization treatment and removed from solution while potentiostated at 0.250V are shown in Fig. 6 . Some oxygen was observed on the foil which was associated with the contamination layer that results from vacuum sublimation of the electrolyte off the surface. Ion sputtering the contamination layer from the Pt surface, as monitored by the carbon peak, completely eliminated any observable oxygen KLL signal. It was concluded that anodization does not cause diffusion of oxygen ions into the Pt lattice such that they become inacessible for reduction. The complete reduction (to < 1 a/o) of the anodic film can be accomplished by potentiostating at 0.25V for several minutes.

Discussion

Surfaces well-ordered on the atomic scale with geometries (111)-(1x1) and (100)-(1x1) are equally active for oxygen reduction at room temperature in 1N acids or in concentration H_3PO_4. A surface with ordered atomic steps, (S) [3(111)-(100)], such that 33 a/o of the atoms have an edge atom coordination (coordination number 7) is not more active than the atomically flat densely packed surfaces (111)-(1x1) and (100)-(1x1), indicating that low coordination sites are not extraordinarily active. This conclusion was also reached by Bett et. al. [1] based on their work with dispersed Pt. No evidence was found to support the hypothesis made by Appleby [11] that a disordered surface containing dissolved oxygen is catalytically more active than an atomically flat oxygen-free surface. It is suggested that the prepolarization treatments used by Appleby were necessary in order to obtain a clean Pt surface, e.g. AES of "degreased" Pt foils indicate significant coverage by sulfur and carbon. It should be noted that the current densities reported here for annealed polycrystalline Pt and for the single crystal electrodes are even _higher_ (factor of 3) than Appleby's results for "active" Pt produced by anodic prepolarization. Damjanovic and Brusic [6] have also reported that anodic-cathodic pulsing did not improve the activity of a thermally annealed electrode, although they did use a lower anodic potential (1.7 V for a few seconds rather than 2 V for 2 minutes) for pretreatment.

The foregoing conclusions must, however, be restricted just to the acids studied here at room temperature and to the potential regions where kinetic control was observed. In the 1N acids, this potential region was > 0.9V. Measurements of the coverage of Pt by oxygenated species have been made by numerous investigators [12-14] and all clearly indicate that for potentials > 0.9V in 1N acid that the coverage

by 2e⁻ species is at least 0.2 monolayers. The high coverages by reaction inter-mediates suggests that with repulsive interactions between like species the adsorption of intermediates can be described by a Temkin isotherm. Damjanovic and Brusic [6] proposed a mechanism for the reduction of oxygen on Pt in the same potential region as investigated here in which the reaction step

$$O_2 + H^+ + e^- \rightarrow (O_2H)_{ads}$$
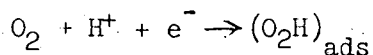
is rate-determining under Temkin conditions of adsorption of reaction intermediates. They give the rate equation as

$$i = k\, p_{O_2}\, a_{H+}\, \exp\left[(-\Delta G^+ + \alpha r\theta + \beta FV)/RT\right] \tag{1}$$

where ΔG^+ is the chemical part of the activation energy, $r\theta$ represents the change of adsorption energy of reaction intermediate with total coverage θ of all intermediates, α is the Bronsted coefficient and β is the symmetry factor. Assuming that the oxidation products of H_2O (-O and -OH) are in equilibrium on the electrode, and that the value of $r\theta$ is the same for these species as for any intermediate, it is easily shown [15] that

$$r\theta = FV + RT \ln a_{H+} + const \tag{2}$$

and with $\alpha \approx \beta \approx 1/2$

$$i = k\, p_{O_2}\, a_{H+}^{3/2}\, \exp\left(-FV/RT\right) \tag{3}$$

so that the expected Tafel slope under Temkin conditions of adsorption is RT/F. In this investigation, the activity level and Tafel slope were observed to be independent of the Pt surface geometry on an oxygenated Pt surface. To extend these conditions to the lower potential region, 0.6-0.8V, where the transition to Langmuir adsorption occurs would require a rotating single crystal electrode in order to obtain

kinetically controlled current densities. Such electrodes are not inconceivable

but were beyond the scope of the present apparatus.

The rotating polycrystalline wire electrode results of Fig. 1 indicated that

a kinetically controlled Tafel slope of 110 mV was observed in 85 w/o H_3PO_4. The

cyclic voltammetry in 85 w/o H_3PO_4 also indicated that Temkin conditions of adsorption

occur only at potentials higher than $\approx$ 0.925, so that at potentials < .925 one might

expect Langmuir conditions for the adsorption of oxygenated species. When r = 0,

equation (1) predicts a Tafel slope of 2 RT/F, in reasonable agreement with the

experimental Tafel slope. Although the kinetic results suggest that the heat of

adsorption of reaction intermediates is not changing with electrode potential (for

potentials below .925V), it is likely that the heat of adsorption of intermediates

is lower on Pt surfaces in 85 w/o H_3PO_4 than in the 1N acids. The dramatic decrease

in activity with increasing anion concentration is probably due to specific adsorption

of anions that not only reduces the number of available Pt sites but also reduces

the heat of adsorption of intermediates, the latter having the more profound effect

on activity. It is possible that differences in the heat of adsorption of the rate

determining intermediate (postulated as $-O_2H$) due to surface morphology are masked

by the larger effect due to adsorbed anions. In the case of hydrogen on Pt, nearest

neighbor repulsion reduces the heat of adsorption to such an extent that for high

coverages the difference in Pt-H bond energy with site geometry is unobservable [16].

Such an effect may be present in the single crystal experiments in 85 w/o H_3PO_4.

Therefore, although no effect of surface geometry on oxygen reduction kinetics was

observed in 85 w/o H_3PO_4 at 25°C, no conclusions could reasonably be made about

structure sensitivity under truly Langmuirian conditions of adsorption, i.e.
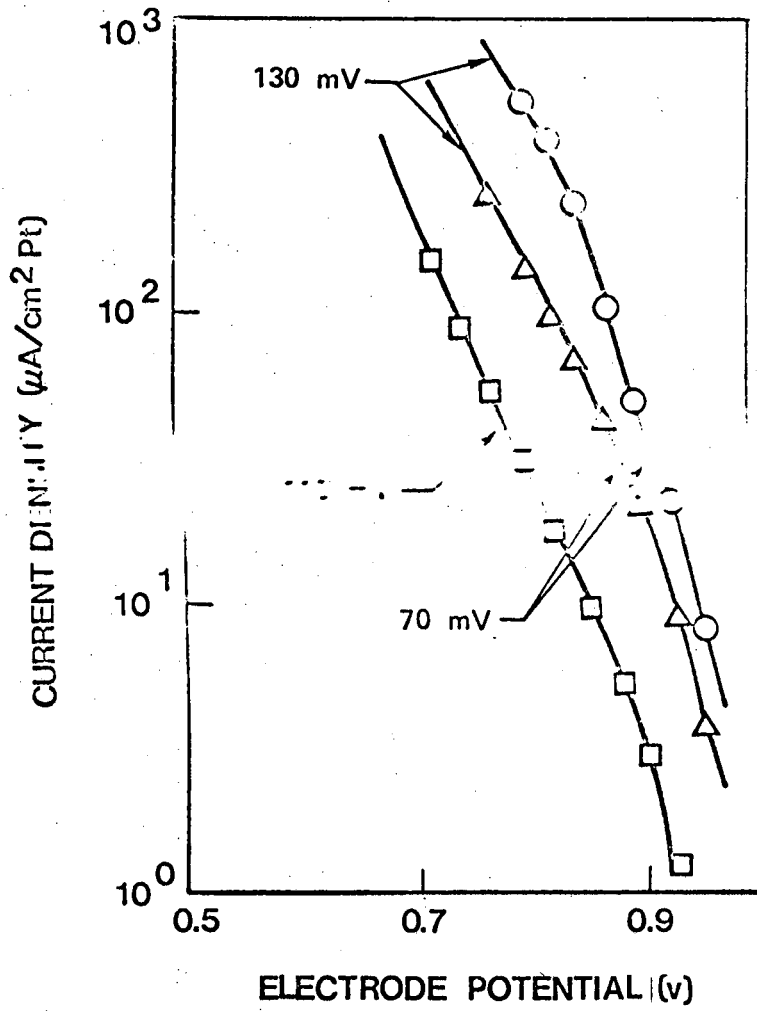
on a truly metallic Pt surface.

Recent results from a study of oxide formation on Pt single crystals [17] indicated that the bond energies of water oxidation products are structure sensitive in non-absorbing electrolytes. The voltammogram of the stepped surface (S) [3(111)-(100)] in 0.1M $HClO_4$ reproduced in Fig. 7, indicated an oxide reduction peak shifted cathodically to the peak formed on either the (111) or (100) atomically flat surface with the potentiodynamic characteristics of an irreversible oxide. A similar cathodic shift in the oxide reduction peak potential was observed by Lundquist and Stonehart [18] with highly dispersed Pt on carbon. It is tempting to associate the irreversibility of oxide reduction to the nature of the oxide formed at low coordination surface atoms such as those along the steps of the [3(111)-(100)] surface and at the surface of small (20Å) Pt clusters. If the oxide formed at steps is kinetically different from the oxide formed at atomically flat surfaces, then it seems likely that the heats of adsorption of oxide precursors such as $-O_{ads}$, $-OH_{ads}$, $-O_2H_{ads}$ are different. The oxygen reduction kinetics would be directly affected by these differences in adsorption energy in non-adsorbing electrolyte as discussed above, or more generally could be affected indirectly due to a change in the state of the surface at higher temperatures. A more exothermic heat of adsorption at steps would result in selective oxidation of atoms at steps as the temperature is raised from room temperature. The present work on single crystals suggests a promising direction for future studies relating to structure sensitivity in the electrocatalytic properties of Pt would be this nature of the oxide formed at low coordination number atoms, particularly at fuel cell operating temperatures.
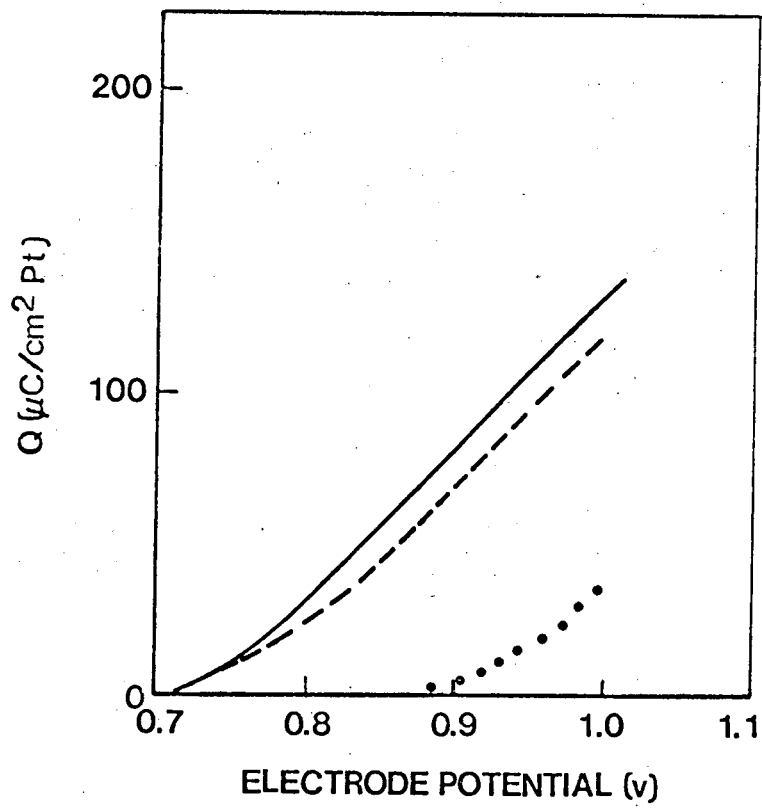
References

1. J. Bett, J. Lundquist, E. Washington and P. Stonehart, Electrochim. Acta, 18, 343 (1973).

2. K. Blurton, P. Greenberg, H. Oswim, D. Rutt, J. Electrochem. Soc., 119, 559 (1972).

3. H. Kunz and G. Gruver, J. Electrochem. Soc., 122, 1279 (1975).

4. L. Bregoli, to be published in Electrochimica Acta, 1978.

5. G. Somorjai, J. Electrochem. Soc., 124, 205C (1977).

6. A. Damjanovic and V. Brusic, Electrochim. Acta, 12, 615 (1967).

7. M. Pancirova, D. Drazic and A. Damjanovic, Electrochim. Acta, 18, 945 (1973).

8. A. Jamjanovic and M. Genshaw, Electrochim. Acta, 15, 1281 (1970).

9. V. Bagotzky, Y. Vassileyev, J. Weber and J. Pirtakhalawa, J. Electroanal. Chem., 27, 31 (1970).

10. P. Palmberg, G. Reach, R. Weber and N. MacDonald (eds), Handbook of Auger Electron Spectroscopy, Physical Electronics Ind., Edina MN, 1972.

11. A. Appleby, J. Electrochem. Soc. 117, 641 (1970).

12. W. Boeld and M. Breiter, Electrocheim. Acta, 5, 145 (1961).

13. H. Wroblowa, M. Rao, A. Damjanovic and J. O'M. Bockris, J. Electroanal. Chem. 15, 139 (1967).

14. H. Angerstein-Kozlowska, B. Conway and W. Sharp, J. Electroanal. Chem., 43, 9 (1973).

15. Equations (29)-(31) in Ref. 6

16. K. Christmann and G. Ertl, Surf. Sci., 60, 365 (1976).

17. P. N. Ross, Jr., to be presented at 154th Meeting of the Electrochemical Society (Pittsburgh), 1978.

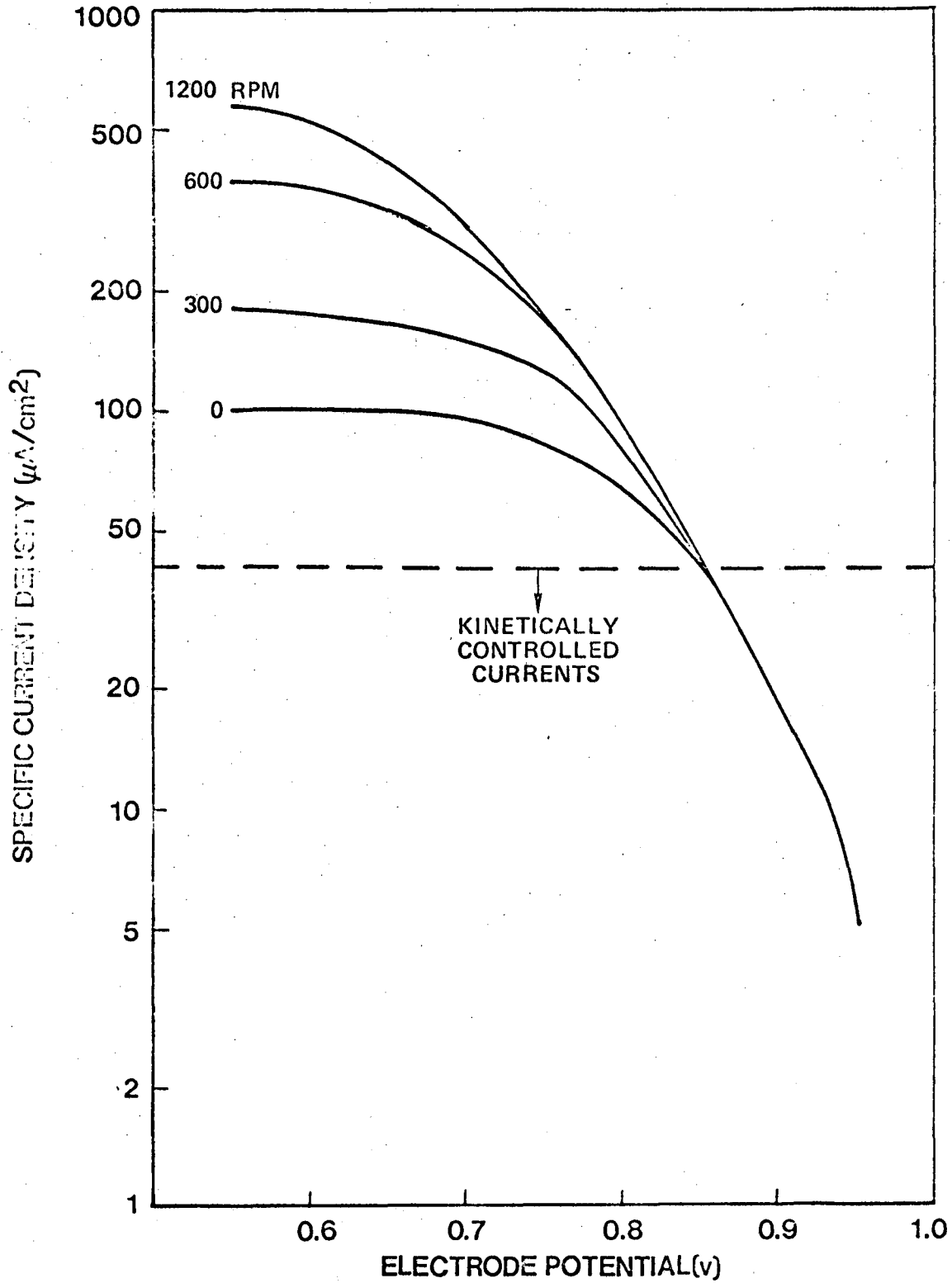18. J. Lundquist and P. Stonehart, Electrochim. Acta, 18, 349 (1973).
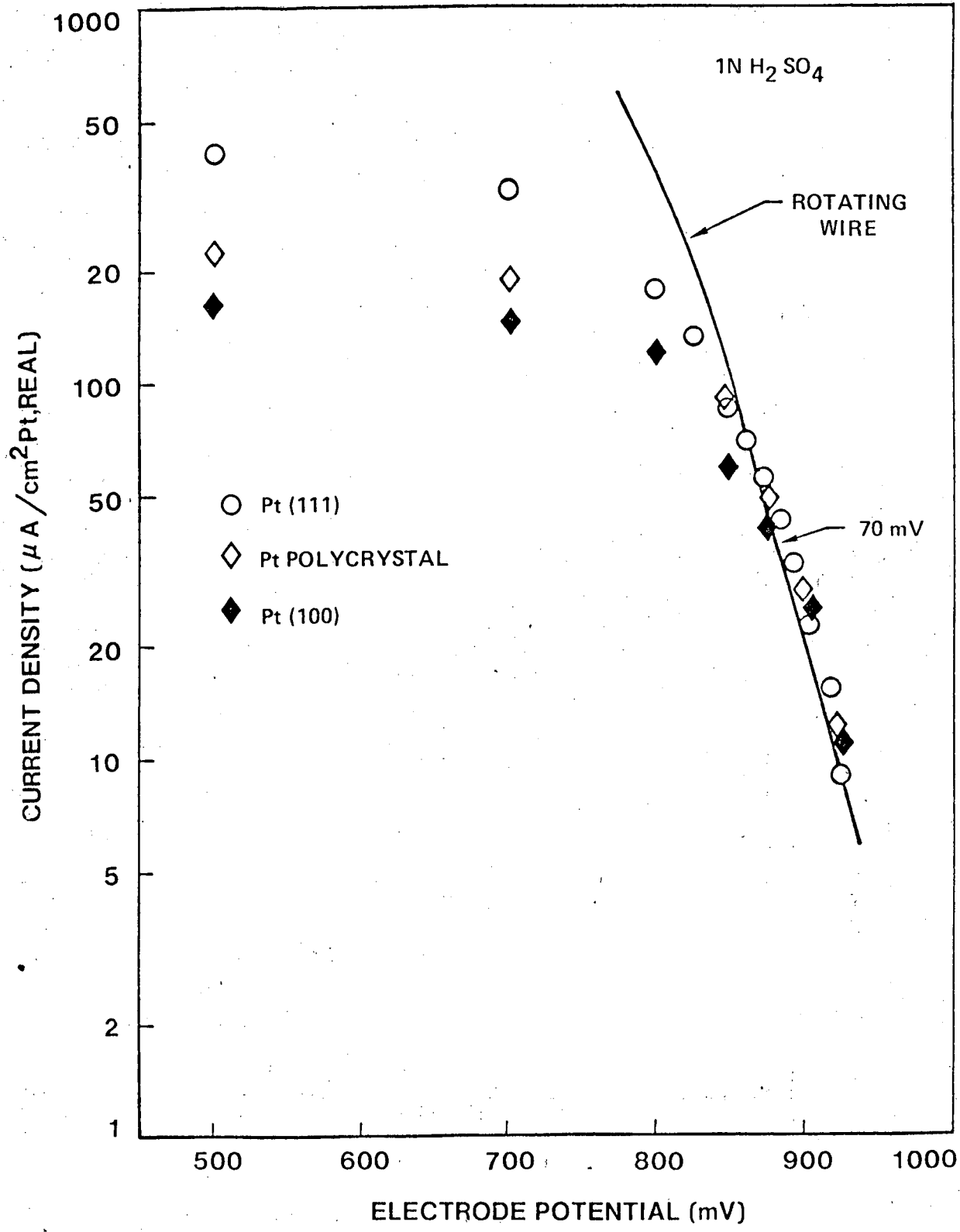
Figure Captions

Figure 1   Oxygen reduction on a rotating (1700 rpm) Pt wire electrode in (o)
1N $HClO_4$ and 1N H_2SO_4, (Δ) 1N H_3PO_4 and ($\square$) 85 w/o H_3PO_4 at 25°C, 1 atm
O_2.

Figure 2   Coverage of polycrystalline Pt by oxygenated species as a function of
potential as measured by cyclic voltammetry: (——) 1N $HClO_4$, (---) 1N
H_3PO_4, ($\cdots$) 85 w/o H_3PO_4. 25°C.

Figure 3   Rotation rate dependence of oxygen reduction in 85 w/o H_3PO_4 at 25°C
on a rotating Pt wire electrode, 25°C, 1 atm O_2.

Figure 4   Oxygen reduction on static Pt single crystal electrodes in 1N $HClO_4$
or H_2SO_4 as a function of orientation: (o) (111), ($\Diamond$) (100) and
(S) [3(111)-(100)], ($\blacklozenge$) clean, annealed polycrystalline foil. 25°C,
1 atm O_2.

Figure 5   Oxygen reduction on static Pt single crystal electrodes in 85 w/o H_3PO_4
as a function of orientation: (Δ) (111), (o) (100) and (S)[3(111)-(100)],
25°C, 1 atm. O_2.

Figure 6.   Auger electron spectra of Pt(111) crystal after anodic polarization
treatment (see text) and removed from solution while potentiostated
at 0.25V.   All the transitions are those for Pt except those identified
otherwise.

Figure 7   Cathodic shift (ΔE_c) of the "oxide" reduction peak for the "oxide" formed
on (S)[3(111)-(100)] relative to the reduction peak for annealed poly-
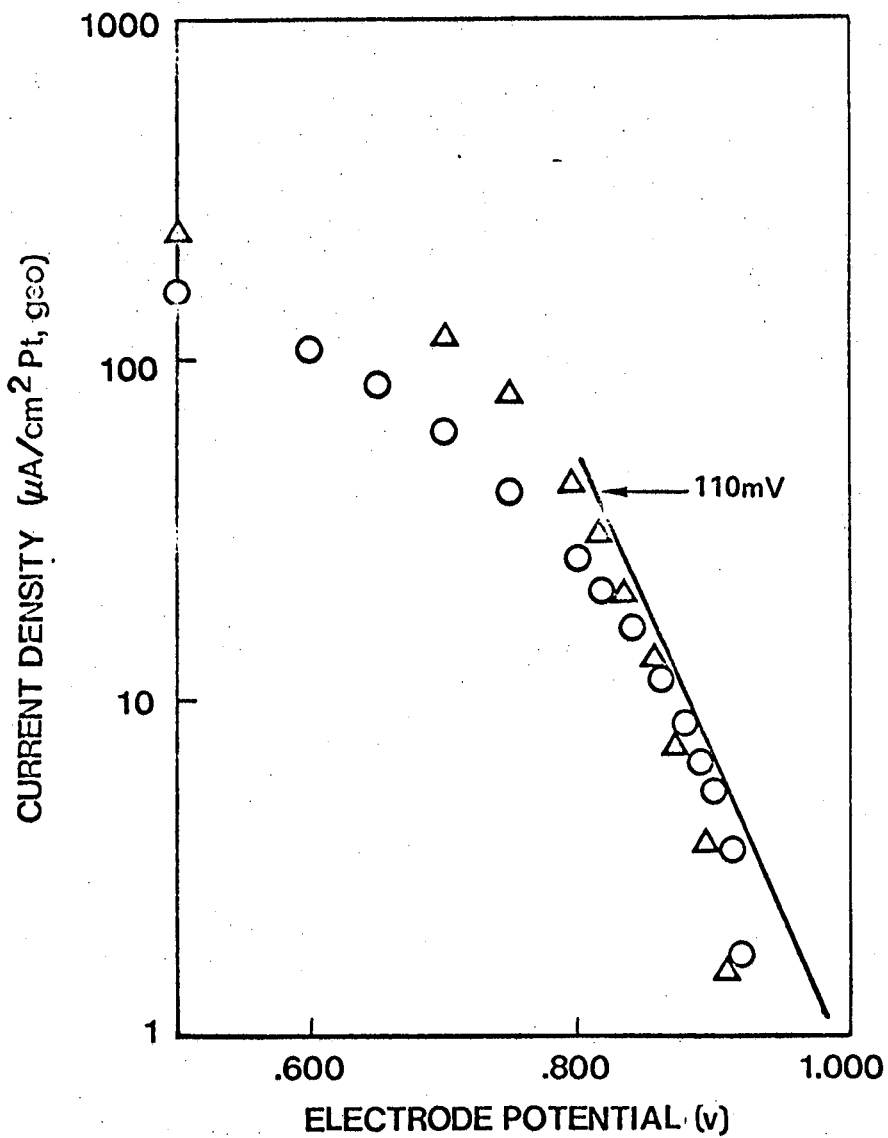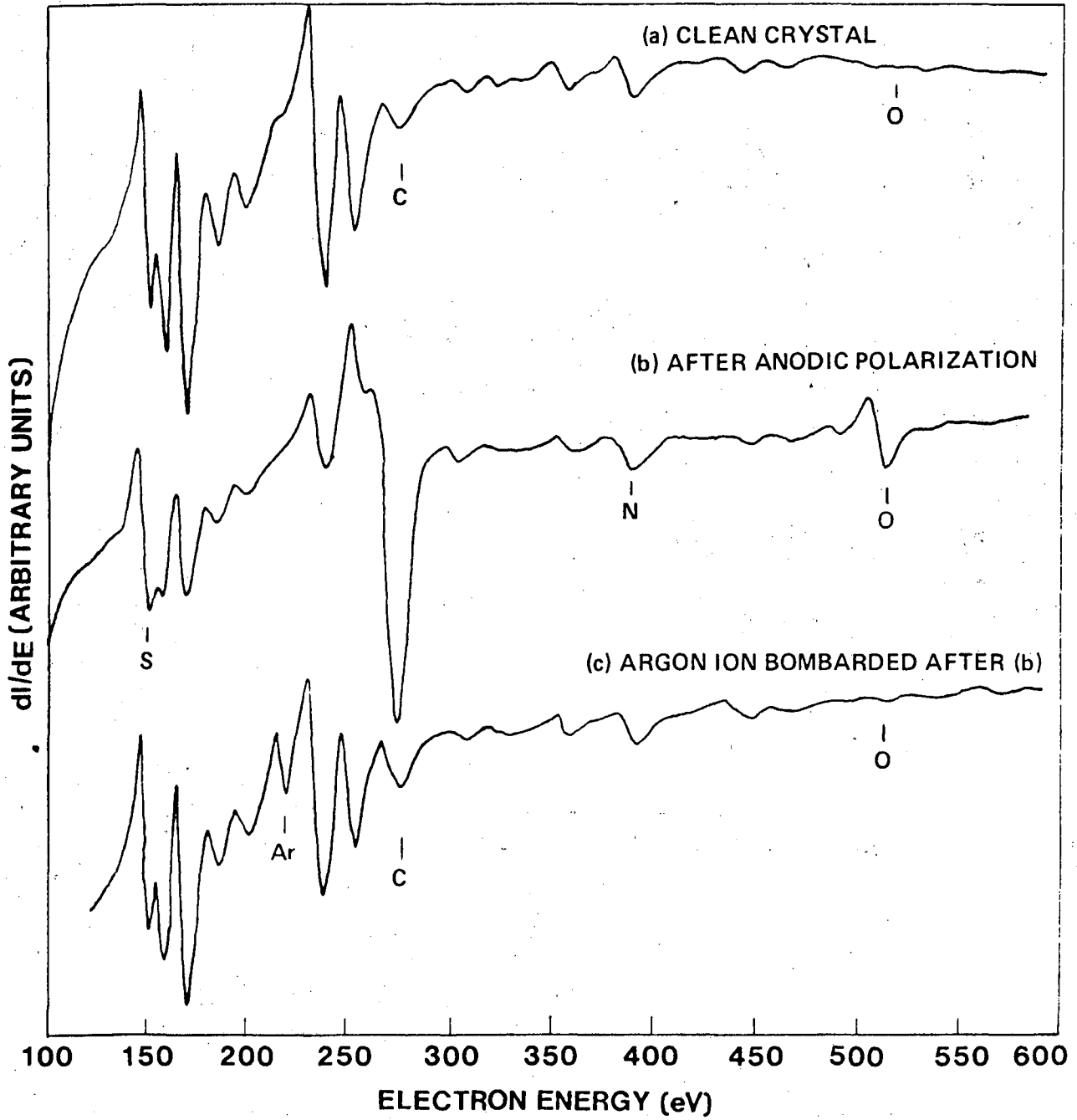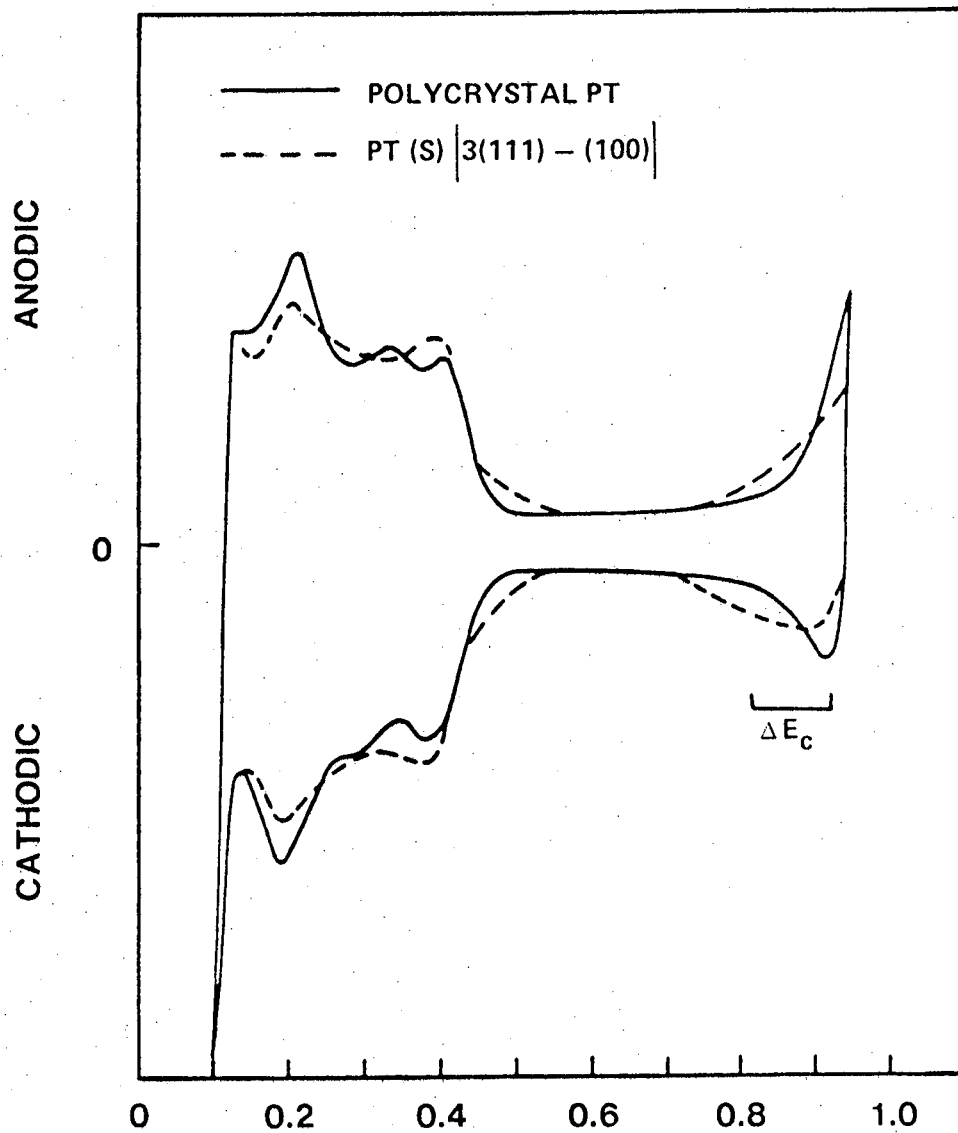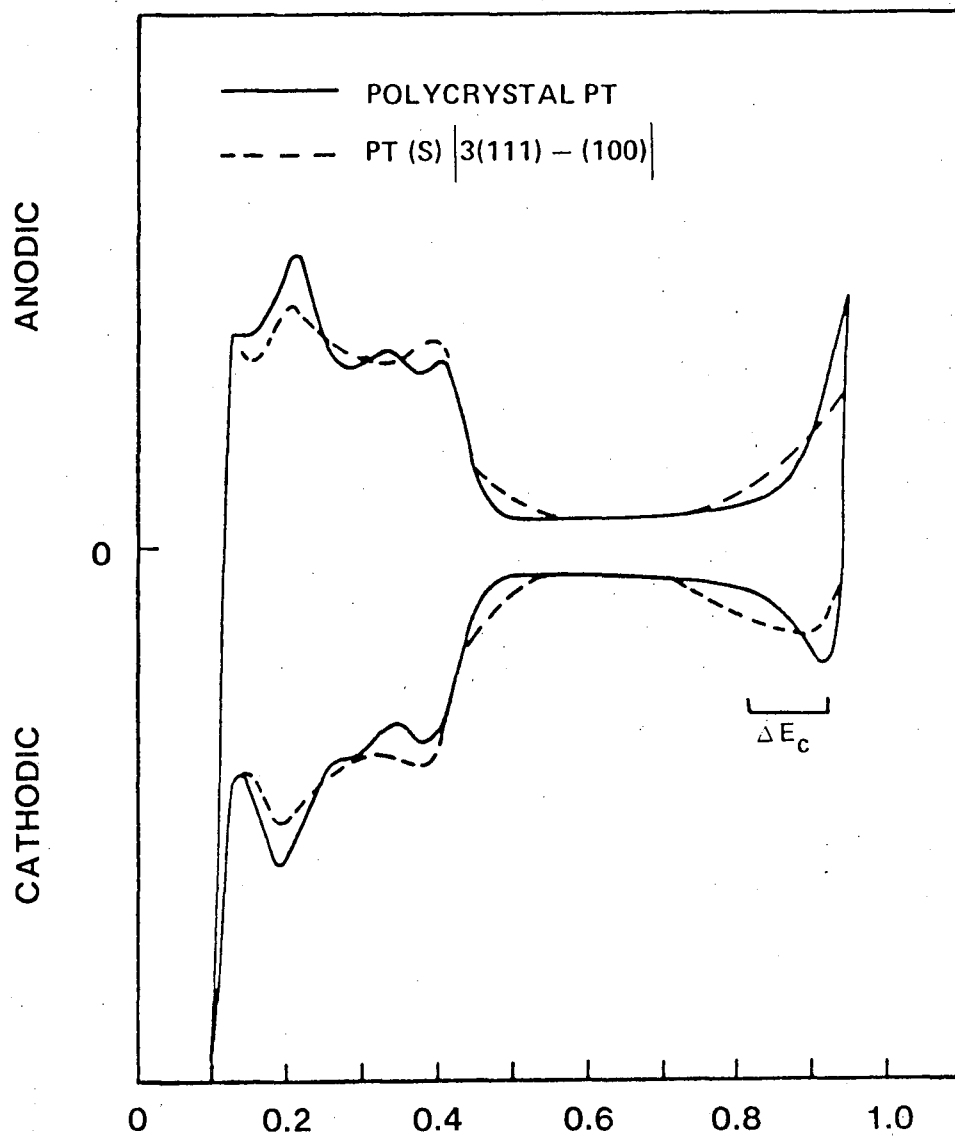crystalline Pt.   100 mV/s sweep rate, 0.1N $HClO_4$, 25°C.

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Figure with y-axis "CURRENT DENSITY (µA/cm² Pt)" ranging from 10⁰ to 10³, x-axis "ELECTRODE POTENTIAL (v)" from 0.5 to 0.9. Labels "130 mV" and "70 mV".

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(4)

77-11-222-3

19

77−12−166−1