

DOUBLE LAYER CAPACITANCE ON PLATINUM

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The determination of the double layer capacitance *vs.* potential relationship at Pt in 1M-H₂SO₄ solution was previously obtained by the use of single, constant, high current density pulses. The present work repeated the measurements using a charge step-decay method. This technique gave the same capacitance *vs.* potential relation determined by the galvanostatic procedure. Use of the charge step-decay method in more dilute solution required the development of a high-speed switching technique to prevent oscilloscope amplifier saturation during addition of the charge increment. This switching circuit allowed observation of the potential decay at times as short as 1 μ s after addition of the charge increment. For all concentrations studied, a plot of the log ΔE *vs.* time yielded the expected straight line for potentials in the range of 0 to 0.2 V *vs.* reversible hydrogen electrode in the same solution (R.H.E.). Following charge injection at more positive potentials, the potential decay was slow and approximated a linear ΔE *vs.* time relationship. A drastic change in the measured capacitance *vs.* potential relationship was found upon decreasing the H₂SO₄ concentration from 1 to $3.6 \cdot 10^{-4}$ M. The "hump" virtually disappeared, and a distinct minimum appeared in the region 0.22–0.33 V *vs.* N.H.E. A less well-defined minimum was also observed in 10^{-3} M solution at the same potential. A comparison with literature values of the p.z.c. on Pt is made.

The measurement of the double layer capacitance on Pt in 1M-H₂SO₄ solution was reported earlier¹. That determination utilized singleshot, high current density galvanostatic pulses and virtually eliminated the effects of fast faradaic reactions, adsorption/desorption, and impurities. However, IR compensation and problems with attainment of precise high voltage constant current pulses limit the use of this galvanostatic technique to concentrated solutions.

The charge-step method is applicable for capacitance measurements in dilute solution^{2,3}, but some method of switching must be devised to prevent saturation

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and resulting slow recovery of the oscilloscope measurement amplifiers caused by the large IR component present while charge is being injected into the working electrode. A fast-acting switch which allows isolation of the reference electrode circuit during high-voltage transients has been described⁴. This switch was used in the present investigation for all measurements reported except for the 1M-H₂SO₄ solution. With this switch and its associated operational amplifier a switching time of less than 1 μ s was realized. The best useable vertical sensitivity for oscilloscope measurement of the voltage increment given to the working electrode by the charge-step was 2.5 mV/cm.

EXPERIMENTAL

The electrochemical cell shown in Fig. 1 is the same as the one used in ref.¹ except that the Teflon tubing for the gas inlet and exit tubes and for the glass electrode connection have been replaced by all-glass fittings. Using standard 1/4" "O"-ring fittings, the cell was coupled into the gas-tight, all-glass system previously described⁵. This cell was much easier to clean and assemble than the earlier ones, and much less difficulty was experienced in maintaining a high degree of solution purity. Small amounts of hydrogen or oxygen were supplied to the cell by the in-line

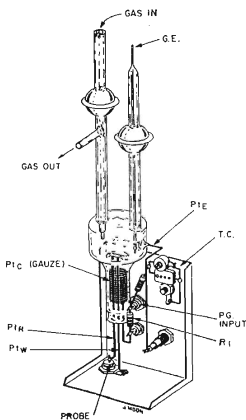


FIG. 1

All-Glass Electrochemical Mini-cell

G.E. Glass electrode; Pt_E electrolytic purification electrode; T.C. trimming circuit; R₁ load resistor; Pt_W, Pt_R, Pt_C — working, reference, and counter electrodes, respectively.

electrolytic generator described in ref.¹. Cell cleaning and solution preparation were the same as those used previously¹. Molarity and pH were determined for each solution. The temperature was maintained at $25 \pm 1^\circ\text{C}$.

Where applicable, tests for solution purity were the same as those described in ref.¹. The test for electrode cleanliness using a high current density anodic charging pulse in solutions more dilute than about $0.1\text{M-H}_2\text{SO}_4$ is not feasible due to IR compensation difficulties. A test that was very sensitive to electrode cleanliness and was useable for all concentrations studied was the rate of decay of potential following the charge-step and was used in the potential range of 0 to 0.2 V. The i_0 value determined for each of the solutions studied was reproducible in a clean system, but in the case of impurities present on the electrode the $\log \Delta E$ -time curves either had smaller slopes or were non-linear. The reproducibility and time-independence of the measured capacitance were also taken as criteria of a clean electrode.

The area of the working electrode was determined by the use of high current density anodic charging curves in H_2 -saturated, $1\text{M-H}_2\text{SO}_4$ solution^{1,5,6}. This area remained constant and was checked after each concentration by the addition of sufficient H_2SO_4 to bring the concentration up to 1M .

The potential of the working electrode as measured vs. the glass electrode was adjusted by several procedures¹. In the first method, potentials between 0 and 0.2 V (vs. reversible hydrogen electrode in the same solution (R.H.E.) were established by adjusting the hydrogen-helium gas ratio. In the second method, potentials between 0 and 1 V (R.H.E.) were established by small amounts of oxygen introduced in the helium line by the electrolytic generator. In the third method, potentials between 0 and 1.2 V (R.H.E.) in helium-saturated solutions were established by the EH 132 A pulse generator after it was internally altered to give a d.c. offset capability for the + pulse output. After the potential was set by one of the described methods, the electrode was allowed to come to a steady-state condition. Normally, the working electrode potential changed very slowly with time. Usually about four to six hours were required to traverse the potential region from 0 V to 0.3 V (R.H.E.), and another four hours or so were required to obtain data up to about 0.8 V. In some cases the electrode was left in He-saturated solution overnight, result-

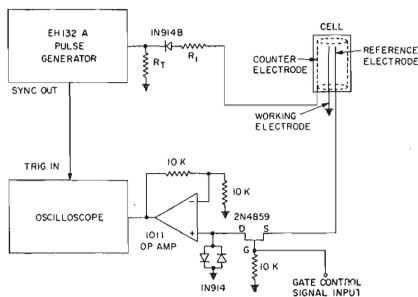


FIG. 2

Block Diagram of Electrical Circuit for Charge Step-Relaxation Measurements

ing in a rest potential of about 0.2 V (R.H.E.). The potential was then changed slowly in a positive or negative direction by one of the described methods. The capacitance determined from controlling the potential by any of these methods was essentially the same.

The circuit used for all measurements except those in the 1M-H₂SO₄ case is shown in Fig. 2. The pulsing and cell circuits are the same as those used in ref.¹. The FET switch used in the reference electrode circuit has been thoroughly discussed⁴. The 2N4859 transistor is an n-channel junction field-effect-transistor (FET). The FET is normally conducting with the gate grounded through the 10 K resistor shown. A signal of -12 V to -15 V applied to the gate from a signal source (in our case, another pulse generator), renders the FET nonconducting. The pair of diodes at the + input of the Philbrick/Nexus Type 1011 operational amplifier serve to limit the transient caused by switching the FET on or off due to the comparative magnitudes of the capacitance of the FET and the operational amplifier. A capacitor also has been used in the place of the diodes, but care must be taken to assure that the size of this capacitor is much less than the capacitance of the working and reference electrodes.

A p-channel, enhancement FET (2N4352) has also been used to hold off positive going reference electrode circuit potentials arising from a cathodic charge-step applied to the working electrode. With this FET, a potential of about -12 V applied to the gate is required to render the FET sufficiently conducting, while grounding the gate renders the FET nonconducting.

The magnitudes of R_T and R_1 were adjusted so that regardless of the solution conductivity, the pulse generator had a total 50 ohm load. For the 1M-H₂SO₄ solutions, R_1 was about 55 ohm and R_T was 500 ohm. For lower solution concentrations, R_1 was held constant at 27 ohm for use as a current monitoring resistor, and R_T was decreased as the solution concentration was lowered.

For the 1M solution, the FET switch and associated operational amplifier was replaced by a Tektronix P6046 differential probe with one input grounded. The small (0.3 V or less) IR present between the reference electrode and ground during the addition of the charge-step was insufficient to cause measurable amplifier saturation. The differential probe sensitivities used to observe the potential decay following charge injection were 2 mV/cm or 5 mV/cm.

The charge introduced during the charge-step was determined by integration of the oscillogram for the differential potential-time response across resistor R_1 or for the current-time response measured with a Tektronix P6020 current probe.

For all concentrations studied the amount of charge added to the working electrode during the charge-step was in the range 10^{-8} to 10^{-7} C/cm². The length of the charge-step, which was in most cases a true square pulse, varied from 80 to 150 ns for the 1M solution and was about 1 to 2 μ s for the $3.6 \cdot 10^{-4}$ M-H₂SO₄ solution. Depending on the solution concentration, the oscilloscope sweep rate varied from 0.1 μ s/cm to 5 μ s/cm. A Tektronix 535 with a Model 1A5 plug-in and a Tektronix 454 oscilloscope were used interchangeably. As shown in Fig. 2, when the FET switch was used a $\times 2$, operational amplifier gain in the reference electrode circuit was employed. Since the noise level of the FET switch and operational amplifier was about 0.7 mV, the best useable vertical sensitivity was 2.5 mV/cm.

RESULTS

The determination of the differential double layer capacitance, C , by the charge-step method requires only a measurement of the net charge, Δq , added to the working electrode, and the potential change resulting from this charge increment²,

$$C = \Delta q / \Delta E_{t=0} \quad (1)$$

where $\Delta E_{t=0}$ is the potential increment given the working electrode at the end of an idealized instantaneous charge-step. The determination of the value of $\Delta E_{t=0}$ and the correction for any possible faradaic process occurring during the charging period may become quite involved for some applications. In the present investigation, near 0 V (R.H.E.), we have assumed a simple electron transfer process controlling the return of the potential to equilibrium following a charge-step. The potential increment was normally kept below 10 mV, so that a linear current-potential response should apply. Thus the equation (ref.²), which describes the relaxation of the double layer after charge injection:

$$\frac{\eta}{\eta_{t=0}} = \exp \left[- \left(\frac{i_0}{C} \right) \left(\frac{nF}{RT} \right) t \right] \quad (2)$$

should be applicable in this case, where i_0 is the equilibrium exchange current density, η is the overvoltage at decay time t , and n , F , R , and T have the usual meaning. The i_0 value was determined from the slope of the linear $\log \eta$ vs. t relation. The value of $\eta_{t=0}$ was determined from the intercept. From the i_0 values for each concentration studied, the charge lost to the faradaic process during the charging period was calculated in order to determine the need for correction of the capacitance. This effect was calculated to be less than 3% for the worst case, and no correction was made to any of the data shown here. At potentials more positive than 0.15–0.20 V (R.H.E.), the potential decay is very slow compared to the value near 0 V. At these more positive potentials, simple linear extrapolation of the potential-time response was used to determine the $\Delta E_{t=0}$ value. This technique appeared to be valid since variation of the sweep rate by a factor of at least five did not measurably change the $\Delta E_{t=0}$ value.

The apparent exchange current, i_0 , was determined for each concentration studied from the slope of the $\log \eta$ -time plots (2). These determinations were made for each system at 0 V (R.H.E.), *i.e.*, for the equilibrium electrode in the solution of given molar concentration and a constant 1 atm H_2 . The dependence of the apparent exchange current on the molar concentration of H_2SO_4 was found to obey the theoretical equation²

$$i_0 = i_{01}(C_M)^{1-\alpha}, \quad 1 - \alpha = 0.51 \pm 0.05, \quad (3)$$

where i_{01} is the i_0 value measured for the 1M solution, 0.44 A/cm², and C_M is the molar concentration of H_2SO_4 present. This equation held for the entire range of concentrations studied, for both cathodic and anodic charge-step relaxations. This relationship gives the $\alpha = 0.5$ for the hydrogen discharge step which is the value considered to be correct by most electrochemists.

For solutions which were less than $10^{-2}M$, the imposition of a charge-step to the working electrode resulted in a potential overshoot that was short-lived and quickly decayed. In the case

of the $9.5 \cdot 10^{-3} \text{ M}$ solution this overshoot was apparent for about $1 \mu\text{s}$, increasing only slightly with an increase in the total charge added to the working electrode. For the most dilute solution studied, $3.6 \cdot 10^{-4} \text{ M}$, the overshoot was apparent for about $5 \mu\text{s}$ following the charge-step. It is felt that this overshoot is due to an uneven current distribution at the electrode-glass point of contact. Regardless of the cause of this small overshoot, its effect disappeared in a period of time which was short compared to the measurement time of interest. After this short-lived potential overshoot, the expected straight line was found at 0 V (R.H.E.) for the $\log \eta$ vs. time plot for each concentration studied. This effect should not be due to the creation of a significant non-equilibrium diffuse double layer⁷ since the effect was not strongly dependent on the amount of charge added. The amount of charge injected was very small so that there was always a sufficient number of ions within 10^{-6} cm of the electrode.

In Fig. 3, a pair of typical ΔE vs. time curves are shown for the potential decay following charge-step in the case of $10^{-3} \text{ M-H}_2\text{SO}_4$. The upper curve is the potential response to a charge-step for an equilibrium electrode at 0 V (R.H.E.). The lower curve is the response of an electrode in He-saturated solution at a rest potential of 0.474 V (R.H.E.). The sensitivity for both pictures is 2.5 mV/cm and the sweep rate is $2 \mu\text{s/cm}$.

A sequence of operations were used to obtain the data in Fig. 3*. At the lower left of each picture the working electrode rest potential is shown as the sweep begins. This trace was terminated after about $0.3 \mu\text{s}$ when the trace was driven slightly off screen by the gate control signal, which turns off the FET and thereby holds off the reference electrode signal from the oscilloscope. A very short time later, usually after about $0.1 \mu\text{s}$, the EH132A charge-step pulse generator shown in Fig. 2 was then turned on for approximately $0.2 \mu\text{s}$. After waiting about $0.8 \mu\text{s}$ to allow the potential overshoot to decay, the FET gate control signal was removed, so that the reference electrode signal was again passed to the oscilloscope.

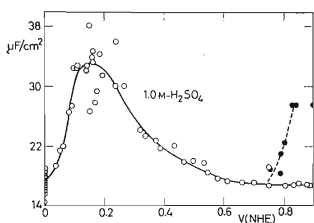


FIG. 4

Double Layer Capacitance vs. Open-circuit Potential at Pt in $1 \text{ M-H}_2\text{SO}_4$. Determined by the Charge-step Method

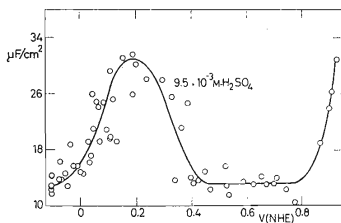


FIG. 5

Double Layer Capacitance vs. Open-circuit Potential at Pt in $9.5 \cdot 10^{-3} \text{ M-H}_2\text{SO}_4$ solution

* See insert facing p. 368.

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Double Layer Capacitance on Platinum

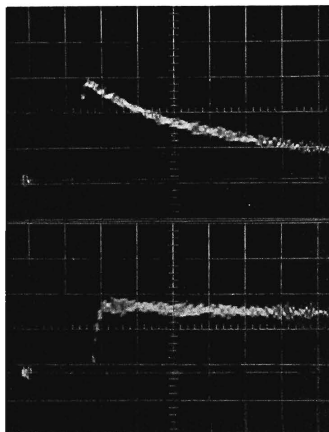


FIG. 3

Potential-Time Response Following a Charge-step for a Pt Electrode in $10^{-3}\text{M-H}_2\text{SO}_4$.
 $\Delta q = 5.5 \cdot 10^{-8} \text{ C/cm}^2$. Upper trace, rest potential 0 V (R.H.E.). Lower trace, rest potential 0.474 V (R.H.E.). Oscilloscope sweep rate $2 \mu\text{s/cm}$, vertical sensitivity 2.5 mV/cm .

The double layer capacitance *vs.* potential relation of Pt in 1M-H₂SO₄ as determined by the charge-step method is shown in Fig. 4. The results over the potential range studied are virtually identical with the earlier reported¹ high current density galvanostatic determination. The scatter of data near the capacitance maximum for a series of measurements for a single experimental setup was very large. Our earlier work¹ showed that impurities caused a uniform decrease in the capacitance maximum rather than a random scatter. Since the scatter in the present work was completely random, we believe that impurities were not the primary cause. No similar effect was seen on either side of the maximum.

The filled circle shown at 0.9 V is the capacitance measured at an electrode in He-saturated solution after polarization at 1.8 V for a few hours, followed by leaving the electrode at open circuit for 2 1/2 days. The two filled circles shown near 0.80 V were measured at 20 min intervals about 20 min after the 0.90 V measurement, but after the application of several cathodic pulses, the total charge of these cathodic pulses being equivalent to about 10⁻³ C/cm². These cathodic pulses lowered the potential from 0.90 V to near 0.8 V, yet had no effect on the measured capacitance. As more cathodic pulses were applied, the capacitance fell quickly to the normal steady-state values. The lower filled circles show that as the oxygen is removed from the electrode, the capacitance is lowered until it finally falls to the normal steady-state value. Although these high capacitance values are not steady-state values, they point out the long-time effect of the presence of oxygen on the measured capacitance.

The double layer capacitance of Pt as a function of potential in 9.5 · 10⁻³, 10⁻³, and 3.6 · 10⁻⁴ M-H₂SO₄ are shown in Figs 5–7, respectively. The filled circles in Fig. 6 are for a Pt electrode that had been taken above 0.6 V (N.H.E.) in a solution containing a small amount of oxygen. A small amount of H₂ was then added to the He flow and capacitance measurements were then made as the potential slowly moved in a more negative direction. The effect of oxygen disappeared quickly at about 0.10 V, so that upon addition of a small amount of oxygen to the He flow, the lower curve was followed as the potential again became more positive.

DISCUSSION

The scatter in the data for all the lower concentrations is undoubtedly the result of several effects. It is difficult to precisely measure the charge added and, as discussed earlier, the back extrapolation of the voltage increment to determine $\Delta E_{t=0}$ is subject to some error. The reproducibility of the electrode surface at a given potential may also be a factor here. The scatter of points is small around the capacitance minimum for the 3.6 · 10⁻⁴ M concentration. As will be discussed below, it is felt that this minimum represents the potential of zero charge for Pt in this solution. The good reproducibility around this capacitance minimum can then be explained on the basis

that the diffuse double layer is controlling the measured capacitance, so that small compact double layer changes on the electrode surface do not have such a strong effect.

A comparison of the capacitance *vs.* potential relationships of Pt for three concentrations of H_2SO_4 is shown in Fig. 8. The capacitance *vs.* potential relationship for the $9.5 \cdot 10^{-3}\text{M}$ solution is very similar to that found for the 1M case. The capacitance of the former at 0 V (N.H.E.) is almost equal to that of the latter at 0 V (N.H.E.). The capacitance continues to decrease uniformly at more negative potentials. The capacitance maximum near 0.20 V is only slightly less than the one in the 1M solution and the maxima occur at very nearly the same potential. Only at potentials more positive than about 0.30 V does the capacitance measured in the $9.5 \cdot 10^{-3}\text{M}$ solution fall below that of the 1M solution.

The rise in capacitance due to the presence of oxygen occurs at a lower potential as the H_2SO_4 concentration is reduced. This effect is due to the shift in potential at which oxygen is produced as the pH is lowered. The portion of the 1M curve positive to 0.90 V is the capacitance-potential relationship found from the earlier reported work in ref.¹ and is shown for comparison purposes only.

The most striking point observable in Fig. 8 is the capacitance minimum apparent at about 0.23 V (N.H.E.). The maximum which develops for the $3.6 \cdot 10^{-4}\text{M-H}_2\text{SO}_4$ appears to be interrupted by this sharp minimum on the anodic side of the maximum so that it never reaches the high capacitance values found for more concentrated solutions. This finding is similar to the behavior of the double layer capacitance on mercury in ionic aqueous solutions⁸, except that in the case of Hg the maximum occurs on the anodic side of the p.z.c.

At 0.41 V, the capacitance for the $3.6 \cdot 10^{-4}\text{M}$ concentration rises above that of the $9.5 \cdot 10^{-3}\text{M}$ solution. This increase in the capacitance above that found for the more concentrated solution may be due to the presence of a small amount of oxygen

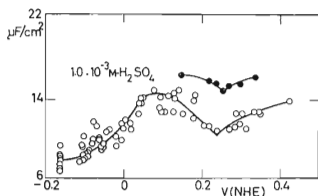


FIG. 6

Double Layer Capacitance *vs.* Open-circuit Potential at Pt in $10^{-3}\text{M-H}_2\text{SO}_4$ Solution

See text for meaning of filled circles.

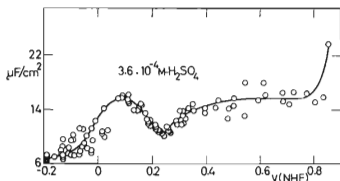


FIG. 7

Double Layer Capacitance *vs.* Open-circuit Potential at Pt in $3.6 \cdot 10^{-4}\text{M-H}_2\text{SO}_4$ Solution

on the electrode in this potential region. Although it is unlikely, the possibility of the capacitance of the Pt in the more concentrated solution being lowered by the presence of extremely small amounts of impurity can not be totally discounted. However, the earlier¹ galvanostatic data in 1M solution showed the magnitude of the capacitance maximum to be very dependent upon surface impurities, so that the level of impurities in the $9.5 \cdot 10^{-3} \text{M}$ solution must be negligibly low.

The cause of the capacitance maximum near 0.17 V in the more concentrated solutions is unknown. It does not appear to be a faradaic pseudocapacitance peak because the $\log \Delta E$ vs. time plots are well behaved in this region, with a uniform decrease in the rate of potential decay following the charge-step as the rest potential becomes more positive. Also, this maximum was virtually unaffected by a 100-fold decrease in solution bulk concentration, even though the time required for addition of the charge-step was longer in the $9.5 \cdot 10^{-3} \text{M}$ solution than in the 1M solution, and the oscilloscope sweep rates for the recording of the ΔE vs. time curves differed by a factor of twenty.

The p.z.c. observed at 0.23 V (N.H.E.) compares well with the values determined by several other investigators. Balashova and Kazarinov⁹, using an adsorption method, found the p.z.c. for Pt in a dilute mixture of Na_2SO_4 and H_2SO_4 to be at 0.18 V (N.H.E.). Using a.c. methods, Burshtein, Pshenichnikov and Shevchenko¹⁰ found a capacitance minimum in dilute H_2SO_4 solution at 0.23 V (N.H.E.). Also, a capacitance minimum on Pt in dilute HClO_4 was found at about 0.10 V (N.H.E.)¹¹.

The determination of the p.z.c. of Pt by *impedance methods* seems to be facilitated by a number of fortunate circumstances. The p.z.c. is sufficiently positive to 0 V (R.H.E.) for each solution concentration so that the faradaic pseudocapacitance apparent on the reported curves^{10,11} near 0 V does not strongly interfere with the measurement, but not so positive that the presence of oxygen on the electrode will interfere. However, since in dilute solution these effects are apparently not widely separated in potential (see ref.¹¹), Fig. 1, for example, it is conceivable that the true p.z.c. may not coincide exactly with the position of the capacitance minimum.

At potentials removed from the p.z.c. our capacitance-potential curves differ from those determined by a.c. impedance methods. Near 0 V (R.H.E.) for each

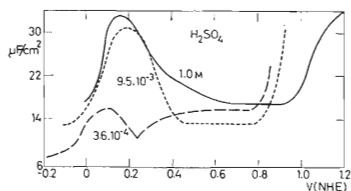


FIG. 8
Comparison of the Double Layer Capacitance vs. Open-Circuit Potential for Pt in Three Concentrations of H_2SO_4

solution concentration, the contribution of the reaction $H = H^+ + e$ to the measured capacitance has been eliminated. Also, each capacitance point in the present investigation was taken after the electrode was essentially at steady-state. No potential cycling of the electrode was performed, so that no residue of oxygen remained in the electrode during the low potential measurements. For the $10^{-3}M$ and the $3.6 \cdot 10^{-4}M$ solutions, the effect of residual oxygen was significant and long-lived. Pre-electrolysis of the working electrode was normally carried out at between 1.5 V and 1.8 V (R.H.E.) in these solutions saturated with hydrogen. For thirty minutes or more after the electrolysis was terminated, even though the working electrode returned quickly to within a few mV of 0 V (R.H.E.), a charge-step measurement resulted in slow, non-linear $\log \eta$ vs. time curves. Apparently the oxygen contained in and on the electrode is removed much more slowly from Pt electrodes immersed in dilute H_2 -saturated solutions than in more concentrated solutions.

Bockris, Argade and Gileadi^{12,13} determined the p.z.c. on Pt by several different methods, finding a value of (0.56–0.067 pH) V vs. N.H.E. Although they attributed their p.z.c. value to an H-free electrode, this work has been strongly criticized^{14,15} since the technique to eliminate hydrogen from the electrode most likely had little effect on removing oxygen from within the electrode.

Although most of our measurements began at 0 V vs. R.H.E., the potential was changed very slowly to more positive values as measurements were made. For instance, in the case of the $3.6 \cdot 10^{-4}M$ solution many hours, sometimes even overnight, were required to reach the p.z.c. potential region. At the p.z.c. potential, which is more positive than 0.4 V (R.H.E.) for this solution, essentially no hydrogen should be associated with the electrode.

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