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The Automatic Measurement of the Ohmic and Capacitive Components of the Impedance on a Platinum Electrode in Transient States

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A new technique with an electronic circuit is described in which the ohmic and the capacitive components of the impedance of the electrode-solution interface may be registered simultaneously and continuously as a function of the time at a given frequency during polarization with a constant anodic or cathodic current. Impedance measurements were made on a smooth platinum in 2 N perchloric acid, 2 N sodium perchlorate and 2 N sodium hydroxide solutions in the region of oxygen deposition. According to the observed behavior of the impedance of the electrode, the oxide film on the electrode surface may be completed anodically through three stages; first, the adsorption of the hydroxyl radical; second, the formation of oxide (II), and finally, the conversion of this oxide to one of a higher grade. The dependence of the value of the electrode capacity at the first stage on the pH of the solution is discussed on the basis of the ion-exchange adsorption of cations and anions on the electrode surface covered by the hydroxyl radicals.

Much effort has been expended in the past on the study of platinum surface oxidation.[1-26] A chief concern of early investigations was the nature and the extent of surface coverage with oxygen species under a variety of conditions and using a variety of techniques. Early conclusions were based largely on the shape of the charging curve and on the value of the transition time between the onset of surface oxidation and the oxygen evolution.[10-26]

Measurements of the impedance of the electrode-solution interface yield information on the structure of the interface and on the kinetics of electrode reaction.[27-33] Therefore, it is useful in making clear the mechanism of the surface oxidation to measure the impedance change of the electrode during the anodic polarization.

Many methods for the quick measurement of the impedance have been reported.[34-40] All of them, however, appear to suffer from certain disadvantages for the continuous measurement of the impedance, which changes with time. Recently, a new technique has been described by Breiter,[41] in which the impedance of the electrode-solution interface may be obtained as a function of the potential during the anodic and the cathodic sweep of the electrode potential, which changes linearly with time. Baddy and Sundburg[42] and Krischer and Osteryoung[43] have also developed

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methods for measuring the capacity continuously and rapidly.

A technique in which both the ohmic and the capacitive components of the impedance as a function of time during the galvanostatic polarization can be registered immediately and simultaneously on a suitable recorder has been developed and will be reported on this paper.

The technique will be applied to the determination of the impedance of a bright platinum electrode in the region of oxygen deposition in acid, neutral and alkaline solutions.

Principle of the Method

The impedance of the electrode-solution interface may be regarded as equivalent to a resistance, R_s, and a capacitacne, C_s, in series governed by the relation;

$$Z = R_s + 1/jwC_s \tag{1}$$

where Z is the impedance of the circuit. The a. c. current, i, passed through the circuit and the voltage drop, e, across a and b in Fig. 1 are represented as follows:

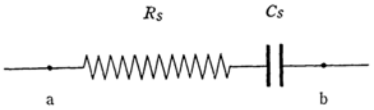


Fig. 1. Equivalent circuit of the electrode.

$$i = I\sin(\omega t+\theta) \tag{2}$$

$$e = E\sin\omega t \tag{3}$$

where I and E are the maximum values of the current and the voltage of the a. c. respectively; ω is the angular frequency, and θ, the phase difference between the current and the voltage. The values of the resistance and the capacitive reactance can be calculated by the following equations:

$$R_s = |Z|\cos\theta = |Z|\sin(\pi/2-\theta) \tag{4}$$

$$1/\omega C_s = |Z|\sin\theta \tag{5}$$

where $|Z|$ is the absolute value of the impedance. If the intensity of the current passed through the circuit is constant, the value of the potential drop, E, is proportional to the magnitude of $|Z|$. Consequently,

$$R_s \sim E\sin(\pi/2-\theta) \tag{6}$$

$$1/\omega C_s \sim E\sin\theta = E\sin(\pi-\theta) \tag{7}$$

The values of R_s and $1/\omega C_s$ are proportional to the instantaneous value of e at the times of $\omega t=\pi/2-\theta$ and $\pi-\theta$ respectively.

In measuring the value of the ohmic component, R_s, the phase of the current, i, was first shifted by $\pi/2$, as is shown in Fig. 2. The a. c. thus shifted is converted to a square-wave current and differentiated in order to make pulses. The sine wave voltage, e, from the cell is sampled with these positive pulses, which are generated at $\omega t=\pi/2-\theta$ in every half cycle. The peak voltage of the pulses thus sampled is proportional to the value of R_s. The value of the capacitive component, $1/\omega C_s$, can be obtained by sampling the value of e with pulses which are generated at $\omega t=\pi-\theta$, as is shown in Fig. 2.

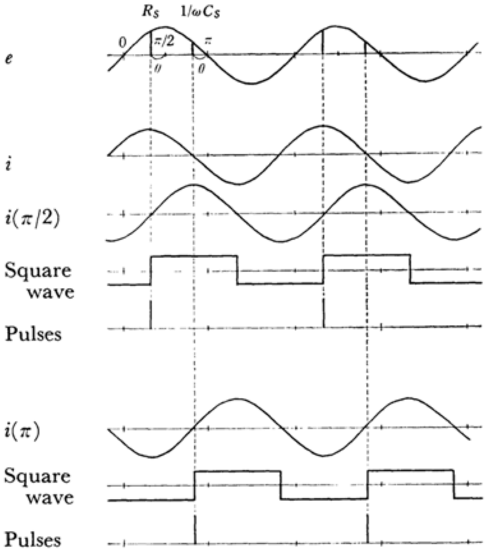


Fig. 2. Principle of the impedance measurement by sampling the signal, e, from the cell with pulses.

Apparatus

The measurements were carried out with an electronic circuit which was designed on the basis of a principle described earlier and constructed in this laboratory. A block diagram of the impedance meter is shown in Fig. 3. For the measurement of R_s, the signal of a given constant frequency from an oscillator is fed through a cathode-follower amplifier to the phase shifter, in which the phase of the signal is shifted by exactly $\pi/2$. The signal from this shifter is then converted with a Schmitt trigger circuit to square-wave a. c. with the same phase and frequency as the input sine wave signal. The rise time in the square wave a. c. was 0.2 μsec. The square wave is differentiated with a resistor and a capacitor in series, and the pulses thus obtained are rectified with a germanium diode. The signal, e, from the cell is sampled with these pulses using a vacuum tube, 6AS6, which has two separate control grids. The signal, e, is fed to one of these grids, while the vacuum tube is gated by the pulses introduced into the other grid. The peak voltage of the pulses from the sampler is proportional to the value of R_s. The

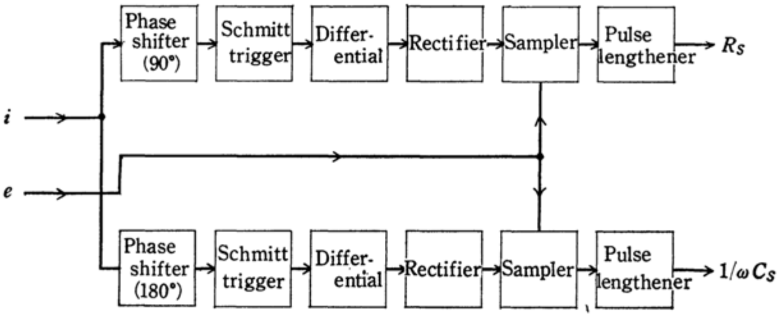


Fig. 3. Block diagram of the impedance measurement.

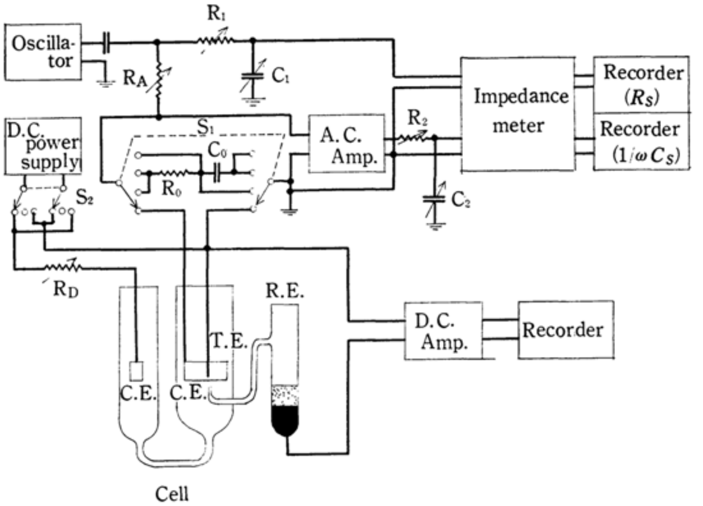


Fig. 4. Circuit diagram.

T. E., test electrode. C. E., counter electrode. R. E., reference electrode.

width of the pulses is broadened and made smooth through a pulse lengthener, because the width of the original pulse is so narrow that the direct measurement of its peak voltage is impossible with a usual recorder. The smoothed signal is amplified with a differential amplifier and then introduced to a pen recorder.

In order to measure the capacitive component, $1/\omega C_s$, the signal from the oscillator is fed, after its phase has shifted by π, to the square-wave converter. The subsequent electronical treatment of the signal is quite similar to that for the measurement of the ohmic component described above. The values of R_s and $1/\omega C_s$ as a function of the time are registered continuously and simultaneously on one chart of a two-pen recorder.

Procedure

A simplified schematic diagram of the measurement circuit is shown in Fig. 4. A constant a. c. of a small amplitude which is controlled by a variable resistor, R_A, in series with the cell was superimposed on the constant d. c. The output voltage from the oscillator was 20 V. p-p, while the d. c. voltage from the regulated power supply was 135 V. The intensity of the a. c. passed through the cell was so adjusted that the amplitude of the polarization voltage of the electrode resulting from its a. c. was below 2 mV. The a. c. signal from the cell was amplified with a high-gain a. c. amplifier and then introduced into the impedance meter. The phase of the a. c. signal was shifted through the a. c. amplifier; this is because of the small time constant or the stray inductance of the amplifier. In order to correct this phase shift, the cell in the measuring circuit was replaced with a noninductive standard resistor, and the variable resistor and capacitor, R_1, and C_1, or R_2 and C_2, were so adjusted that the difference in phase between the input signals of i and of e into the impedance meter was eliminated. The elimination of this phase difference was then checked by means of cathode-ray oscilloscopic observation. The impedance meter was calibrated with standard resistors, R_0, and capacitors, C_0, in series. When the applicability of the indicator was checked in the frequency range from 20 to

20000 c. p. s., the accuracy of the indicator was found to be ±2%.

The d. c. potential of the electrode was referred to a 1 N sulfuric acid - mercurous sulfate - mercury electrode for acid electrolytes or to a saturated calomel electrode for neutral and alkaline electrolytes. The values of the potential described in this paper are referred to the standard hydrogen scale. The stop-cock separating the reference electrode from the Luggin capillary was kept close in order to prevent any appreciable diffusion of the electrolyte of the reference electrode to the test electrode. Charging curves with the d. c. were registered by another pen recorder through a d. c. amplifier of a high-input impedance at the same time as the impedance measurement.

Experimental

The conductivity water was prepared by redistilling laboratory-distilled water from an alkaline permanganate solution in a Pyrex still, followed by triple redistillation with a quartz still. The electrolyte solutions used were 2 N perchloric acid, 2 N sodium perchlorate and 2 N sodium hydroxide solutions, all of which were prepared from guaranteed-grade reagents by appropriate dilution with the conductivity water. The electrolyte solutions were freed from dissolved oxygen by passing pure nitrogen gas through.

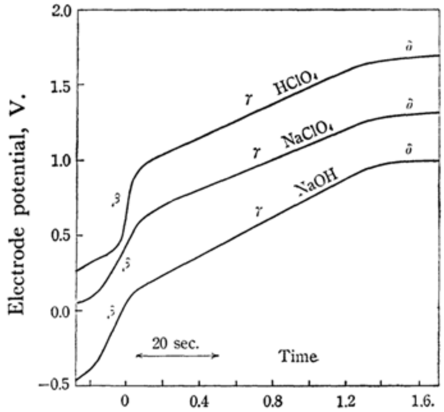
The test electrode was a platinum wire, 0.5 mm. in diameter and 10 mm. long. The counter electrode for the impedance measurement was a platinum gauze in the shape of a cylinder, 20 mm. high and 25 mm. in diameter, which was placed around the test electrode. A platinum plate in the other chamber of the cell served as a counter electrode for the d. c. galvanostatic polarization. The measurement was made in an all-glass vessel described previously[44] at the room temperature of 15±2°C. The test vessel had been in constant use for one year; it was, therefore, well aged. A hot chromic acid was used in order to clean the vessel at the beginning of this series of measurements, and the vessel was soaked in a test electrolytic solution for several days.

The correctness of the elimination of the ohmic potential drop which is caused by the electrolytic resistance between the test and the counter electrode in the a. c. measurement was checked with an R_s curve at 10000 c. p. s., according to the method described by Breiter.[45]

Results and Discussion

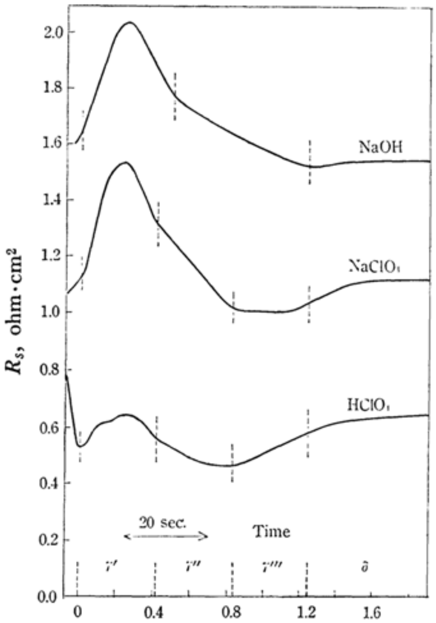
Figure 5 represents typical charging curves for each solution; the regions of β, γ and δ are attributed to the charging of the double layer, to the formation of oxygen layer, and to the evolution of oxygen respectively. The shapes of these curves have been discussed extensively. The quantities of electricity consumed in the γ regions of the solutions are nearly equal to one another. Figure 6 shows the curves of the corresponding ohmic component, R_s, while Fig. 7 shows those of the capacitive component, $1/\omega C_s$, of the impedance at 540 c. p. s. The three characteristic regions, i. e., γ', γ'' and γ''', are marked for these impedance curves corresponding to the γ region of the charging curves. The quantity of electricity consumed for each of those three regions is nearly the same, about 0.43 millicoulombs/cm².

In a previous paper,[45] it was suggested that the first step of the surface oxidation in acid solutions



Quantity of electricity passed through the electrode in the region of γ, millicoulombs/cm²

Fig. 5. Anodic charging curves. $i_a=22$ μamp./cm²



Quantity of electricity passed through the electrode in the region of γ, millicoulombs/cm²

Fig. 6. Ohmic component of the interfacial impedance at 540 c. p. s. as a function of time during the constant current anodic polarization. $i_a=22$ μamp./cm²

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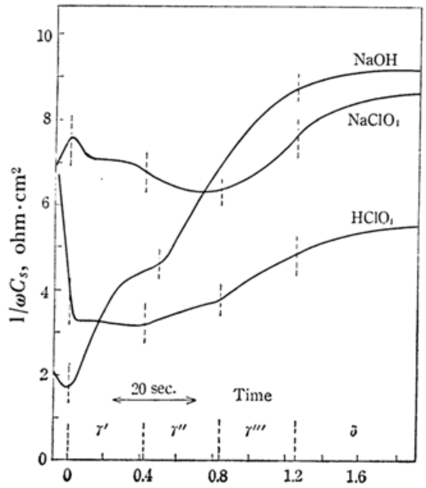


Quantity of electricity passed through the electrode in the region of γ, millicoulombs/cm²

Fig. 7. Capacitive component of the interfacial impedance at 540 c. p. s. as a function of time during the constant current anodic polarization. $i_a = 22$ μamp./cm²

is the formation of a layer of hydroxyl radicals adsorbed on the surface; this reaction takes place in the region from the initial potential of the region, γ, to 1.15 V. in the charging curve, which corresponds to the γ' region described here. If was also suggested that in the region above 1.15 V. definite oxide films are formed. If this suggestion is correct, the mechanism of the surface oxidation in acid solutions may be proposed as being by the following three stages in terms of the equal amount of electricity required in each of three regions.

The first stage, γ', is the adsorption of hydroxyl radicals on the platinum surface:

$$\mathrm{Pt+H_2O \rightarrow Pt\text{–}OH+H^+ + e} \qquad (8)$$

The formation of Pt–OH species is reasonable, since it requires the transfer of only one electron.

In the second stage, γ'', the definite oxide layer is formed by the further oxidation of Pt–OH:

$$\mathrm{Pt\text{–}OH \rightarrow PtO+H^+ + e} \qquad (9)$$

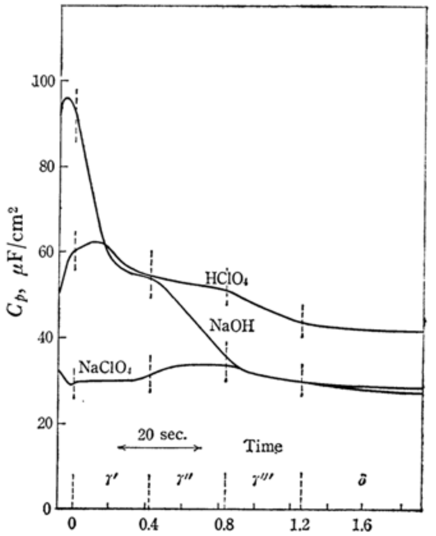
where the symbol PtO is used for the oxygen film instead of Pt–O, because it seems to be a monolayer of true oxide rather than an adsorbed layer of oxygen atoms.

The oxide layer thus formed is converted to a higher oxidized state in the final stage, γ''':

$$\mathrm{PtO+H_2O \rightarrow PtO_2H+H^+ + e} \qquad (10)$$

Reactions in the neutral and the alkaline solutions may be similar to the reaction in the acid solution, except that not water molecules but hydroxyl ions are discharged.

Figure 8 shows the capacity, C_p, of the interfacial impedance in a parallel circuit as a function of the time for 4000 c. p. s. during the anodic polarization of each solution. The value of C_p was computed in the usual way from the measured values of R_s and $1/\omega C_s$. The values of C_p measured with such a high frequency may represent mainly the differential capacity of the ionic double layer, because these C_p curves resemble in shape the capacity curve[45] which was measured by the short pulse technique. In the acid solution the capacity exhibits a maximum value in the first region, γ'. The appearance of such a maximum is frequently explained in terms of an additional capacity in the inner double layer,[46-48] and it is assumed that the change in the double-layer capacity is brought about by the presence of an additional charge or dipolar species in the inner double layer.[48]



Quantity of electricity passed through the electrode in the region of γ, millicoulombs/cm²

Fig. 8. Capacity of the electrode at 4000 c. p. s. as a function of time during the constant current anodic polarization. $i_a = 22$ μamp./cm²

Various metal oxides with a hydrated surface generally have an ion-exchange property. The hydroxyl group which exists on a metal surface in aqueous solutions usually dissociates in one of two ways, depending on the pH of the solution[49]:

$$\mathrm{MOH \rightleftarrows M^+ + OH^-} \text{ (in acid solutions)} \qquad (11)$$

$$\mathrm{MOH \rightleftarrows MO^- + H^+} \text{ (in alkaline solutions)} \qquad (12)$$

where M represents a metal atom on the surface. These $\mathrm{OH^-}$ or $\mathrm{H^+}$ ions are held near the $\mathrm{M^+}$ or $\mathrm{OM^-}$ ions respectively.

In order to understand the marked dependence of the capacity value of the platinum electrode in

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the γ' region on the pH of the solution, the anion adsorption in acid solutions and the cation adsorption in alkaline solutions due to the ion exchange are assumed in the inner double layer:

$$Pt^+OH^- + ClO_4^- \rightleftarrows Pt^+ClO_4^- + OH^- \qquad (13)$$

$$PtO^-H^+ + Na^+ \rightleftarrows PtO^-Na^+ + H^+ \qquad (14)$$

The lower value of the capacity in the γ' region for the neutral solution is explained in terms of a small dissociation of Pt–OH on the surface. The large capacity value which appears in the first half of the γ' region in the alkaline solution is not fully understood, but it is not probably caused by the ion-exchange but by a specific adsorption of sodium ions. The capacity behavior resulting from the ion-exchange outlined above can be expected to hold for the formation of a Pt–OH surface, but it will not hold for surface oxidation to PtO and PtO_2H.