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Hydrogen absorption and desorption reaction on the platinum electrode

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The processes of adsorption and evolution of hydrogen as well as its absorption onto the surface of platinum in both acidic and alkaline media have been studied by the method of electrochemical impedance spectroscopy. In acidic solutions the Nyquist plots consist of two overlapping semi-circles of variable diameters depending on the extent of the cathodic dc-potential offset. The semicircle at the high frequency side of the spectrum enlarges upon increasing the cathodic shift and is associated to the surface H_{upd}, while the size of the semicircle at the low frequency end decreases in line with the behavior of the charge transfer resistance due to the evolution of hydrogen through surface H_{opd}. Equivalent circuits in perfect agreement with the experimental finding have been proposed and the values of the circuit elements and their correspondence with the electrochemistry of the processes discussed. In alkaline solutions only one semicircle with its diameter decreasing upon the cathodic shift has been observed which is exclusively due to the process of evolution of hydrogen through H_{opd}.

The study of hydrogen evolution and hydrogen absorption reaction on the noble metals by Jerkiwicz *et al.* has shown that the mechanism of proton reduction follows in two steps[1]. If protons reduce at the potential above the thermodynamic potential, H_{upd} (underpotential deposited hydrogen) are formed[1]. Under potential deposited hydrogen is a monolayer[2] or on top of monolayer[1]. Octahedral sites are occupied by H_{upd} which diffuses to subsurface and gets converted to H_{ss}. H_{ss} are inactive at high oxidation potential and leave the surface[3] only by heat treatment.

Over potential deposited hydrogen, H_{opd}, reduces at the potential below the hydrogen reduction potential. H_{opd} are either combined with another atomic hydrogen and evolving over the surface or located on the tetrahedral site on the metallic atom and diffuse through to subsurface layer and gets converted to H_{ss}. H_{opd} prefer to evolve rather than to diffuse.

Two intermediates were recognized in HER (hydrogen evolution reaction) process on the platinum electrode by Raman Scattering Spectroscopy[4]. Volmer Hyrovski mechanism has been theoretically investigated by electrochemical impedance model by Diard *et al.*[5]. According to their studies, one capacitive semicircle followed by an inductive loop and in certain potentials only capacitive behaviors are shown. Each semicircle could be due to free sites or occupied sites depending on symmetrical factor, rate of each step and the resistance of free and occupied sites. Also Bai *et al.* used electrochemical impedance technique to detect the electrochemical double layer capacitance on the bright Pt[6] and porous Pt[7]. The Nyquist diagram showed two semicircles in the alkaline solution. The first semicircle is due to the double layer capacitance and the second one (at more dc offset potentials) is assigned to pseudo capacitance arising from H_{opd} adsorption and it is claimed that H_{opd} can only be adsorbed on the active sites. Dynamic electrochemical impedance measurements were employed to study adsorbed hydrogen on the platinum electrode[8]. Two pronounced peaks were recognized and their intensities reduce at higher frequencies.

The impedance results of hydrogen absorption on the single crystal of platinum showed that, at high frequency, a semicircle was formed with its radius increasing upon reducing the potential to more negative values[2]. This semicircle originated from the H_{upd}. At potential lower than zero point charge potential, another semicircle was recorded, due to anion co-adsorption.

The above impedance results and investigations were performed in the limit of 100 kHz to100 Hz. Only one semicircle followed by a vertical capacitive line was demonstrated in this frequency limit[2]. Conway *et al.* in another set of experiments studied the HER process on different types of platinum crystals and proposed the diffusion of H_2 to the bulk of the electrode[13].

Yang *et al.* studied hydrogen absorption on Pd electrode in alkaline solution. The Nyquist plot of this experiment showed a semicircle at high frequency, due to hydrogen absorption of Volmer reaction. At low frequencies, a Warburg behaviour was observed in the absence of HER and a semicircle due to relaxation of absorbed hydrogen in the domain of HER[9].

In the present work, we wish to gain insight on the behavior of hydrogen absorption and evolution on the platinum electrode by electrochemical impedance technique at low frequencies and at more negative potentials.

Materials and Methods

Sulphuric acid and sodium hydroxide used in this work were analar grade of Merck. All solutions were prepared in doubly distilled water and prevented from probable residual chlorine impurity of the electrolyte. Electrochemical studies were carried out in a conventional three electrode cell powered by a fully computerized E G & G and electrochemical system capable of running cyclic voltammetery and impedance spectroscopy. The platinum and silver wire electrodes (polycrystalline) were employed as the working electrodes and their potentials were recorded against home made Ag/AgCl electrode. The auxiliary electrode was a graphite rod. Cyclic voltammetery studies were performed using E G & G model 273A potentiostat/galvanostat, run by an IBM pc/value point computer through 270/250 software, while impedance studies were carried out using a Solartron SI 1255 frequency response analyzer supported by 273A potentiostat/galvanostat or electrochemical interface model SI 1287 and run by the mentioned computer through M398 software or zplot or zview software. Photographs were obtained by camera model SZH10 Olympus.

Results and Discussion

i) *Acidic media*

The cyclic voltammogram of the platinum electrode in 0.5 *N* sulphuric acid solution is shown in Fig. 1, first scan (a). Reduction and evolution of hydrogen are observed at ca −0.50 V/Ag-AgCl and −0.55 V/Ag-AgCl respectively; the peak current for the reduction was decreased upon cycling the potential in the range of 0.0 V to −0.5 V/Ag-AgCl. The reduction peak almost disappeared in the second cycle even though the potential sweep rate was doubled. The results are presented in Fig. 1 and are in agreement with our previous studies[3]. The peak reduction is attributed to the removal of H_{upd} and the presence of impurities[10]. We do not consider such process because in the range of 0.15 to −0.55 V, hydrogen evolution is not observed and H's cannot leave the surface. But H_{upd}'s can diffuse to the bulk of electrode. This mechanism is in accordance with our previous work[3].

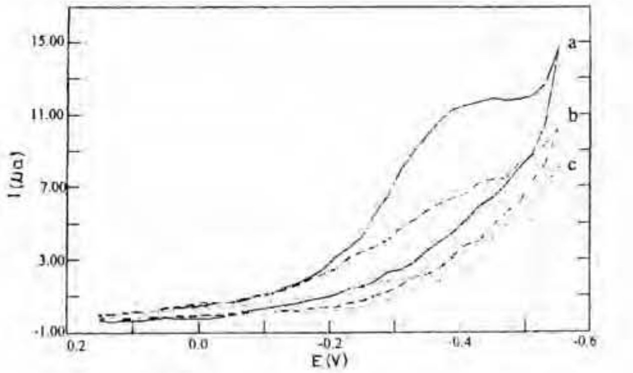

Fig. 1—CV's for Pt electrode in 0.5 *N* H_2SO_4 solution (a) first scan, v=10 mV/s, (b) second scan, v=10 mV/s, (c) third scan, v=20 mV/s

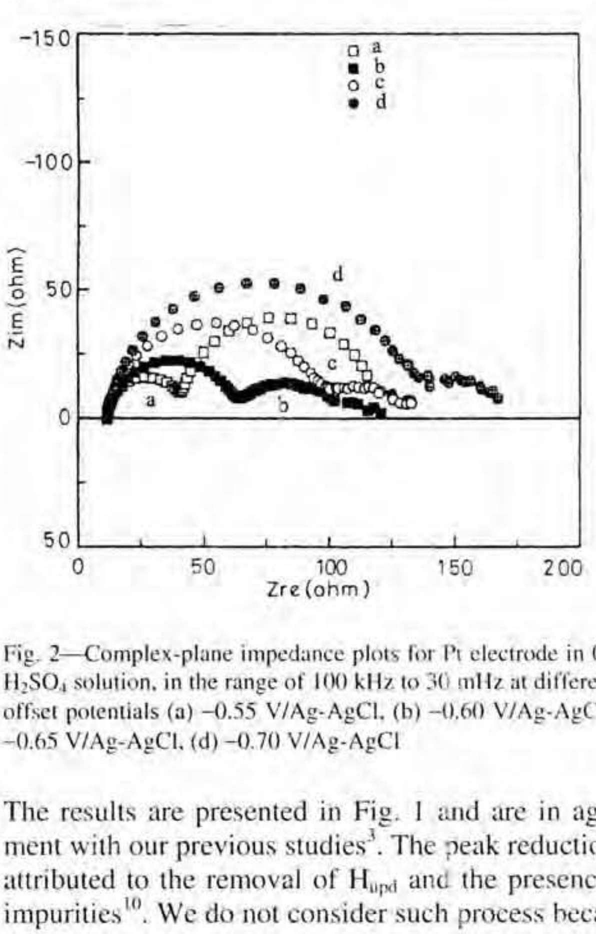

Fig. 2—Complex-plane impedance plots for Pt electrode in 0.5 *N* H_2SO_4 solution, in the range of 100 kHz to 30 mHz at different dc offset potentials (a) −0.55 V/Ag-AgCl, (b) −0.60 V/Ag-AgCl, (c) −0.65 V/Ag-AgCl, (d) −0.70 V/Ag-AgCl

Electrochemical impedance technique was employed to shed further light on the details of the surface processes. The Nyquist plots of the hydrogen reduction in the potential range of −0.55 V to −0.7V/Ag-AgCl are shown in Fig. 2. Two partially overlapping semicircles have been observed where the radius of the first one increases with increase in the cathodic potential, while the radius of the second one decreases. Similar results have been reported by Conway[13].

In a comparable study Conway *et al.*[2] associated the first semicircle to hydrogen adsorption on the surface in the form of H_{upd}. The second semicircle is attributed to the process of hydrogen evolution from the surface, where its charge transfer resistance reduces upon increasing the cathodic potential.

Formation of mono or multi layers of H_{upd} on the surface of platinum is reported by several researchers[1,2]. Accordingly, H_{upd}'s have to leave surface before any hydrogen reduction. Solubility of hydrogen onto the platinum is reported to be low[11]. So, H_{upd} diffuses through the bulk of platinum. The diffusion coefficient of hydrogen to the bulk of the electrode is much smaller than the diffusion coefficient of proton inside the solution, consequently the rate of reduction of H_{opd} depends on the diffusion coefficient for the migration of hydrogens from surface through the bulk which is actually the rate determining step for hydrogen reduction. Referring to impedance data, the first semicircle is small and the second one is large at high frequency and at dc offset potential of −0.55 V. At more negative potential the first semicircle gets larger and the second one gets smaller (Table 1). This trend is contrary to the theoretical results calculated by Diard[5]. In our opinion the first semicircle is due to hydrogen absorption. The increase in radius of the first semicircle is contributed to the increase in R_{abs}. At more negative potential the radius of the second semicircle decreases. At this potential density of adsorbed hydrogen on the surface is very high[10]. So a high-adsorbed capacitance is expected. On the other hand, as the potential moves through more negative values, the current density increases and resistance diminishes, as observed on the polarization curves. The equivalent circuit, Fig. 3(a), is actually a part of general hydrogen evolution equivalent circuit. The first semicircle could not be due to the electrical double layer, since the capacitance of the electrical double layer is independent of the dc offset potential in the alkaline media[6]. The Bode plots show that the capacitance of the first semicircle is formed at medium frequency (1000 Hz) (Fig. 4). Careful observation of the Bode plot shows a phase angle of 70 degree at low frequency and dc offset potential of 0.0 V, which are due to absorption of anions[2,12]. When the dc offset potential approaches to more negative values, the intensity of the adsorption decreases. At medium frequency a new bending appears and the phase angle increases upon increasing the cathodic potential. The new time constant is due to diffusion of hydrogen through platinum forming a low capacitance. The simulated pattern is shown in Fig. 5.

Table 1—Values of the equivalent circuit, calculated by data fitting

Edc/ Volt	R_{sol}/Ω	R_1/Ω	R_2/Ω	$C_1/\mu F$	C_2/F
−0.55	11.47	32.54	76	6.25	2.1e-3
−0.60	11.38	54.44	36	6.3	2.23e-3
−0.65	11.36	88.65	35	6.61	2.53e-3
−0.70	11.37	128.5	31	7.21	2.6e-3

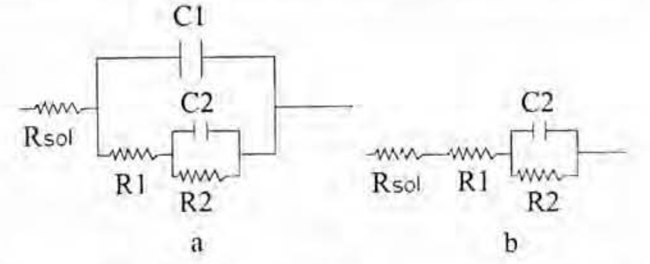

Fig. 3—Equivalent circuit, (a) for acidic solution, (b) for alkaline solution

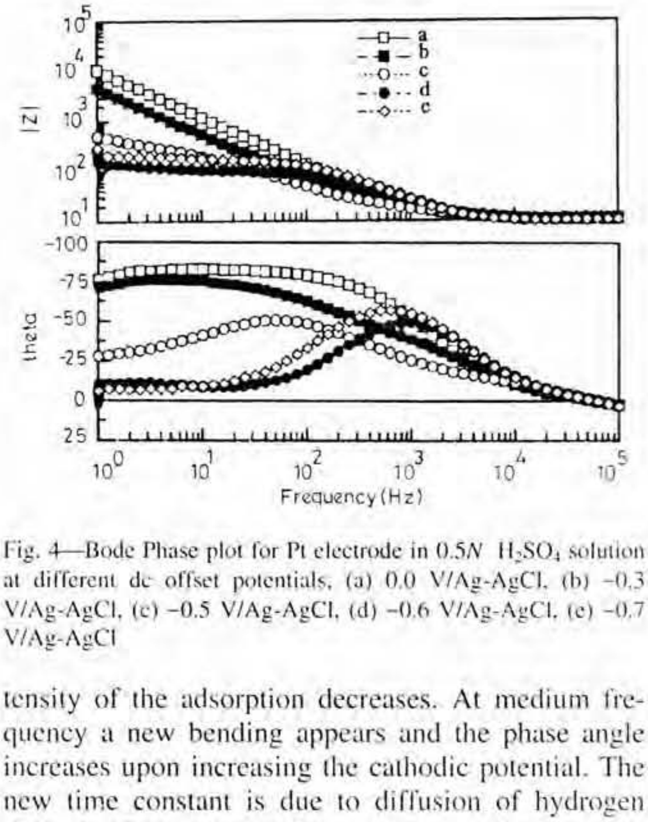

Fig. 4—Bode Phase plot for Pt electrode in 0.5*N* H_2SO_4 solution at different dc offset potentials, (a) 0.0 V/Ag-AgCl, (b) −0.3 V/Ag-AgCl, (c) −0.5 V/Ag-AgCl, (d) −0.6 V/Ag-AgCl, (e) −0.7 V/Ag-AgCl

In order to differentiate between the behavior of surface metals having H_{upd} and surface metals lacking H_{upd} such as silver[2], similar experiments were performed on the Ag electrode. The results are presented in Fig. 6. Only one rather squashed semicircle has

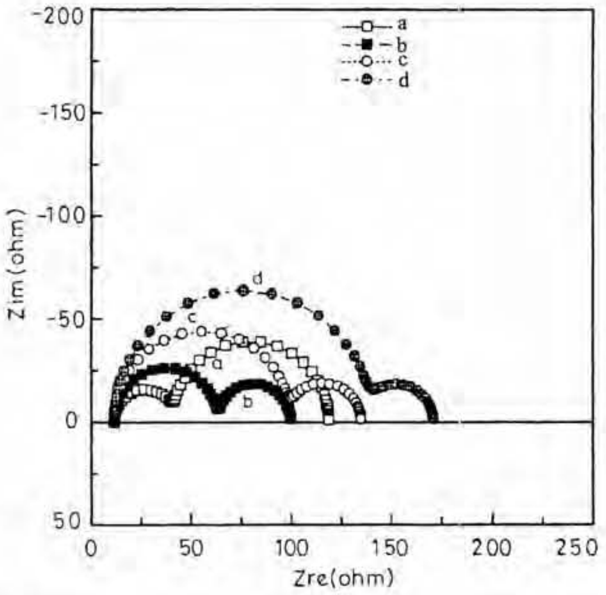

Fig. 5—Simulated complex-plane impedance plots for Pt electrode according to the data presented in Table 1, at different dc potentials (a) −0.55 V/Ag-AgCl, (b) −0.60 V/Ag-AgCl, (c) −0.65 V/Ag-AgCl, (d) −0.70 V/Ag-AgCl

appeared on the Nyquist plot, with its radius decreasing upon increasing the cathodic potential. The impedance spectra were obtained at the dc offset potential of −0.6 V/Ag-AgCl after cycling the potential of the platinum electrode once in the direction of −0.55 to −0.7 V/Ag-AgCl and again in the reverse direction. The Nyquist plots of the two experiments are not superimposable. This attributes to the formation of H_{upd} during the first set of the potential cycling and low removal of hydrogens from the bulk in the course of impedance measurement. Obviously, the second impedance measurement at the potential of −0.6 V/Ag-AgCl "sees" the precovered Hupd surface which would obviously perform differently. Oxidizing the electrode at the oxidation potential of hydrogen and at even higher potential (not so high as to change the surface property, 0.0 V/Ag-AgCl), no superposition of the Nyquist plots was observed (Fig. 7). Interestingly, the fitting was only made after heat treatment of the surface (Fig. 8), due to merging of free states again.

According to our previous work[3] in acidic solution, absorbed bulk hydrogens have low activity at the oxidation potential. In the cyclic voltammetry experiments, first, the electrode was pumped by hydrogen at the cathodic scan, then the reverse scan potential was imposed on it. The Nyquist plot of this electrode was recorded demonstrating a high charge transfer resis-

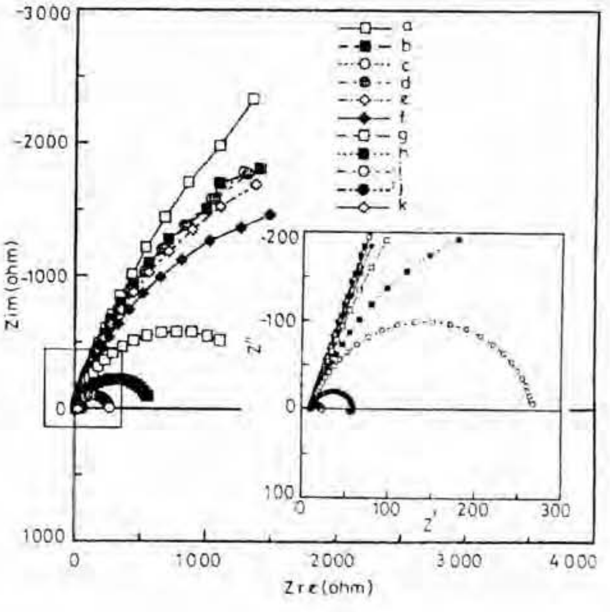

Fig. 6—Complex-plane impedance plots for Ag electrode in 0.5 *N* H_2SO_4 solution in the range of 100 kHz to 1 Hz at different dc potentials (a) −0.30 V, (b) −0.40 V, (c) −0.50 V, (d) −0.55 V, (e) −0.60 V, (f) −0.65 V, (g) −0.70 V, (h) −0.75 V, (i) −0.80 V, (j) −0.90 V, (k) −1.0 V. The inset is shown in the corner on the plot

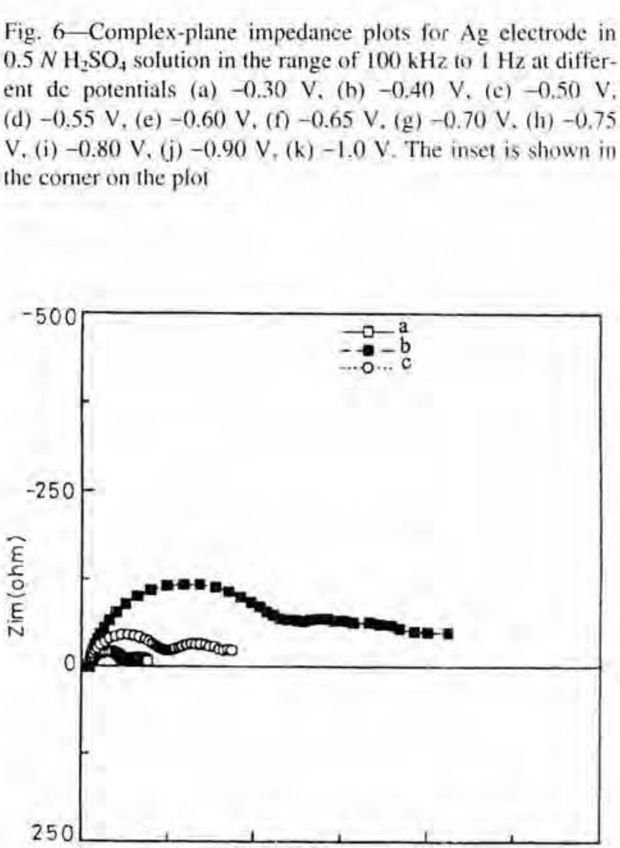

Fig. 7—Complex-plane impedance plots in the range of 100 kHz to 30 mHz for (a) forward scan, (b) reverse scan, (c) after oxidation; at dc offset potential 0.0 V, in 0.5 *N* H_2SO_4 solution at dc potential −0.6 V/Ag-AgCl

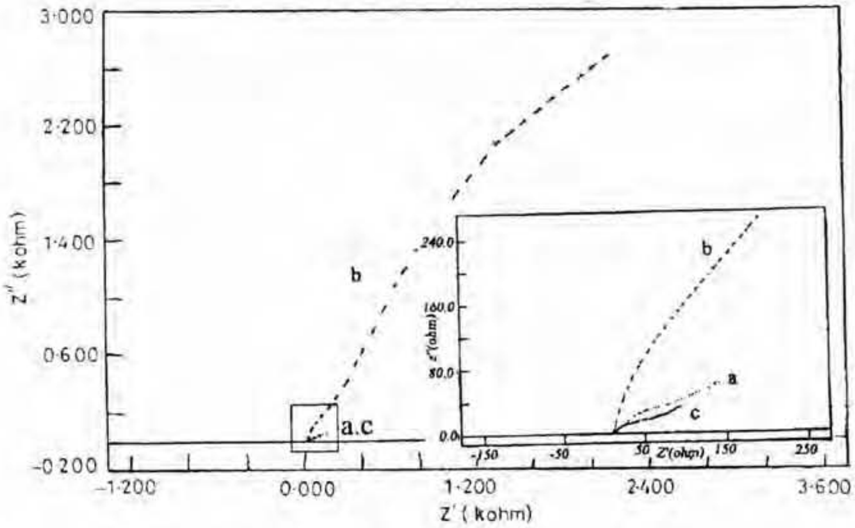

Fig. 8—Complex-plane impedance plots for (a) forward scan, (b) reverse scan, (c) after heat treatment in 0.5 *N* H_2SO_4 solution at dc potential 0.0 V/Ag-AgCl

Fig. 9—Photographic pictures of Pt electrode (a) normal, 30 enlarged, (b) after heat treatment, 30 enlarged, (c) after heat treatment 60 enlarged

ance arising from deep hydrogens which have low activity towards oxidizing. So the radius of the first semicircle is increased and cannot be fitted on the semicircle belonging to the impedance obtained after forward scan potential. When the electrode with deep hydrogens are preoxidized, the Nyquist plot showed an intermediate pattern, in comparison with one obtained after the forward and the reverse scan potentials (Fig. 6). The octahedral (Oh), and tetrahedral (Td) sites are occupied by H_{upd} and H_{opd} respectively. The EAM (embedded atomic method) has shown that Oh sites are more stable than Td sites. Therefore some H_{opd}'s are expelled during the oxidation process, while H_{upd}'s are preserved .The surface of the electrode was destroyed upon heat treatment due to the loss of hydrogens originating from the subsurface layers. This drastic effect can be easily observed by naked eyes and ordinary photographing (Fig. 9). Lack of fitting of the Nyquist plots obtained for the fresh surface and after heat treatment, is due to the damage to the surface signified as decrease in all the resistances.

ii) *Alkaline media*

The impedance plots of platinum and silver electrodes in the 0.05 *N* NaOH solution, present generally the same behavior in which the size of the entire pattern decreases upon increasing the cathodic potential (Figs 10 and 11). Similar trend was observed at higher concentration of NaOH up to 0.5 *N*, but the resistance of the solution was decreased. The impedance plot of the silver electrode (hydrogen nonabsorbing) is as

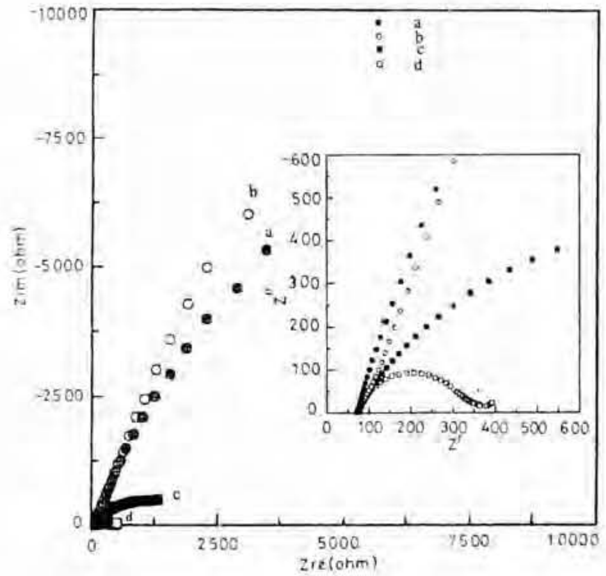

Fig. 10—Complex-plane impedance plots for Pt electrode in 0.05 *N* NaOH solution in the range of 100 kHz to 50 mHz at different dc potentials (a) −0.9 V/Ag-AgCl, (b) −1.0 V/Ag-AgCl, (c) −1.1 V/Ag-AgCl, (d) −1.2 V/Ag-AgCl. The inset is shown in the corner on the plot

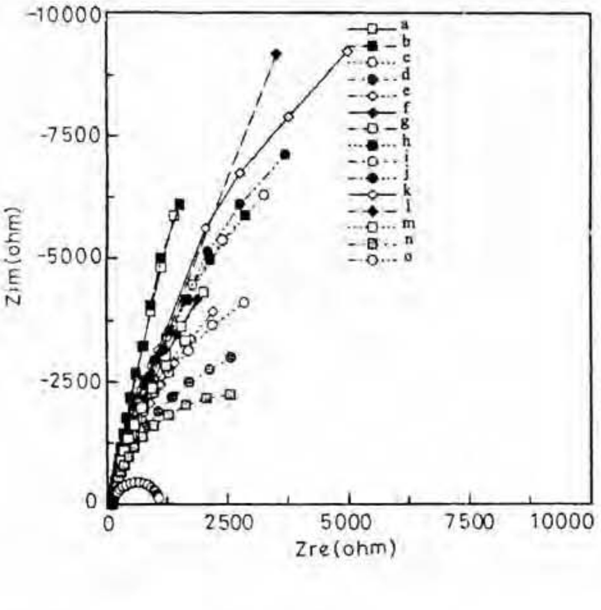

Fig. 11—Complex-plane impedance plots for Ag electrode in 0.05 *N* NaOH solution in the range of 100 kHz to 1 Hz at different dc potentials (a) −0.2 V, (b) −0.3 V, (c) −0.4 V, (d) −0.5 V, (e) −6 V, (f) −0.7 V, (g) −0.8 V, (h) −0.9 V, (i) −1.0 V, (j) −1.1 V, (k) −1.2 V, (l) −1.3 V, (m) −1.4 V, (n) −1.5 V, (o) −1.6 V

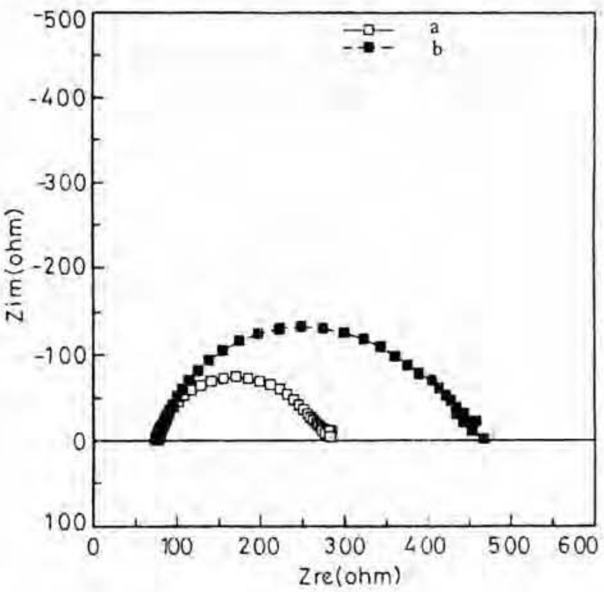

Fig. 12—Complex-plane impedance plots for Pt electrode in 0.05 *N* NaOH solution in the range of 100 kHz to 50 mHz at dc offset potential −1.3 V/Ag-AgCl (a) forward scan, (b) reverse scan

expected, comprising one semicircle at the potential of hydrogen evolution. The Nyquist pattern of platinum-solution interface consists of a semicircle terminating to a segment of a straight line. We believe that due to the very low concentration of protons in basic solutions there would be no contribution from the Hupd species on the surface, but their presence are only recognized in the impedance plot which was recorded after the reverse scan potential (Fig. 12), and therefore only the second semicircle is observed. The terminating segment signifies the mass transfer restriction imposed due to the negligibly low concentration of proton in alkaline solutions.

The resistance of the solution in the alkaline medium was apparently much higher than that in the acidic solution. In the alkaline solution coverage of H on platinum is much smaller than such coverages in acidic media[10]. Due to very low concentration of Hupd's, the capacitance of C1 is so low that we can ignore this capacitance. The result is the equivalent circuit presented in Fig. 3(b). As can be easily noticed, the resistance of solution is added to the resistance of the process of migration of the surface hydrogen to the underlying sites and only one high resistance is detected at high frequency. This resistance increases upon increasing the cathodic potential, which can be contributed to the covering of the surface with more atomic hydrogen. Actually, we are

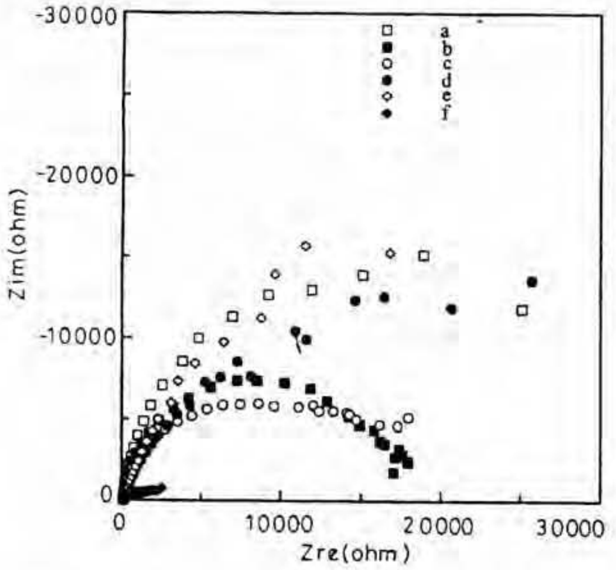

Fig. 13–Complex-plane impedance plots for Pt electrode in 0.05 *N* NaOH solution in the range of 100 kHz to 50 mHz at different dc potentials (a) –0.6 V/Ag-AgCl, (b) –0.7 V/Ag-AgCl, (c) –0.8 V/Ag-AgCl, (d) –0.9 V/Ag-AgCl, (e) –1.0 V/Ag-AgCl, (f) –1.1 V/Ag-AgCl. Note, emergence of semicircle and appearance of Warburg element and regeneration of semicircle again

confronting with a "hydrogen surface" rather than a bare platinum electrode. On the other hand, the semicircles convert to straight line at dc offset cathodic potentials at this step. At this step bubbles of hydrogen are observed on the electrode, and when the next impedance was performed the semicircle was emerged again (Fig. 13). Since a blanket of hydrogen was covering the electrode, protons must diffuse through this region to reach the platinum and be reduced. Consequently a Warburg behavior is observed.

After hydrogen evolution, the hydrogen blanket is removed, and normal behavior is observed again.

Conclusions

On the basis of this study the following conclusions could be made:

(i) Hydrogen adsorption and evolution on the platinum electrode follows two different routes giving rise to H_{upd} and H_{opd}; (ii) the formation of subsurface absorbed hydrogen atoms have been clearly and conclusively demonstrated; (iii) in low alkali concentrations the real resistance at the initial high frequency side is partly due to the high resistance of the solution but largely associated with the accumulation of hydrogen atoms on the surface; and (iv) 4-H_{ss} species cannot be removed from the surface by oxidizing at 0.0 V/Ag-AgCl, but can be partly removed upon extensively heating of the surface, where the ensued damage to the surface is visible to the naked eye.

Appendix

The equations employed for obtaining the quantities in Table 1 are as follows[15]:

$$Z(p) = R_1/(1+ R_1 C_1 p) + 1/C_2 p$$
$$= (1+ R_1 (C_1 + C_2)p) / (C_2 p (1+ R_1 C_1 p))$$
$$Z(p) = K(1+\tau N p) / [p(1+\tau D p)] = K[1+P/\omega CN)] / [p(1+ P/\omega CD)]$$
$$K = 1/C_2 \quad \tau N = R_1 (C_1 + C_2) \quad \tau D = R_1 C_1$$
$$\omega CN = 1/\tau N \quad \omega CD = 1/\tau D$$

Theoretical data obtained according to above equations are similar to the data obtained by simulation using Zplot software.

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