

Technical Notes

Conditions of Strict Voltammetric Reversibility of the H^+/H_2 Couple at Platinum Electrodes

Aleksander Jaworski, Mikolaj Donten, and Zbigniew Stojek*

Department of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland

Janet G. Osteryoung*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Cyclic voltammetric curves obtained at Pt electrodes for the hydrogen couple, H^+/H_2 , fit very well the Shuman theory, as corrected, for reversible electrode processes of other than 1:1 stoichiometry. Good agreement was obtained for acid concentrations in the millimolar range and for normal scan rates, which minimize the effect of the adsorption peaks. An error in Shuman's equation for potential is corrected. Voltammograms obtained at Pt microelectrodes fit well the theoretical simulated data.

Direct voltammetric reduction of acids at platinum microelectrodes has been examined recently for analytical purposes.^{1–6} It has also been found that the voltammetric waves of weak acids depend in a complex way on the concentration of the supporting electrolyte.² Several mathematical models have been developed to predict this complexity, which involves diffusional and migrational transport and homogeneous equilibrium.^{7–12} Since the electrode process for the reduction of hydrogen ion is also complex and involves adsorption, recombination, and slow electron transfer,¹³ all mathematical models have been limited to predicting steady-state, transport-limited current.

The open questions in the theory prompted us to seek also to explain theoretically voltammetric wave shapes and positions

under those conditions. This in turn prompted a search for practical experimental conditions under which the voltammetric waves obtained at platinum electrodes fulfill the criteria of reversibility. Such reversibility was assumed in the paper of Daniele et al.;⁴ however, it was not documented. Cyclic voltammetric curves for some Brønsted acids and for H_2 have been shown by Sawyer and co-workers.^{14–16} These workers found that half-peak potentials were independent of scan rate and substrate concentration and concluded from this that the process is reversible. However, these dependences cannot be strictly correct for reactions of other than 1:1 stoichiometry. In particular, as discussed below and shown in ref 5, the half-wave potential depends on concentration for a reversible two-electron reduction of 2:1 stoichiometry. Further, they calculated $E_{1/2}$ as the arithmetic mean of the anodic and cathodic peak potentials in various solvents, which is a weak approximation, and determined the diffusion coefficient of H_2 from an equation for i_p valid only for reversible processes of 1:1 stoichiometry.

The reversibility of voltammetric waves of hydrogen ion is particularly interesting, since reversible processes of 2:1 stoichiometry are not common. In this paper, we report conditions for reversible behavior and compare experimental voltammograms with predictions of Shuman's theory for other electrode processes that do not have 1:1 stoichiometry.¹⁷ Shuman's original theory is corrected and extended. The simplicity of conditions and the practical and simple theory, combined with the attractiveness of strong acids as standard substances, make the voltammetric reduction of hydrogen ion a superior experimental test for quality of platinum electrodes.

EXPERIMENTAL SECTION

All reagents were of analytical reagent purity and were used as received. Perchloric acid and lithium perchlorate were purchased from Baker. Ultrapure water (MilliQ, Millipore Corp.) was employed in all solutions and for rinsing. Linear sweep and cyclic

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voltammeteries were performed using a model 273A potentiostat (EG&G PARC) controlled via software on a 486 DX2 66 MHz personal computer (Protech). All measurements were made at 22 °C. Solutions were deoxygenated before voltammetric scans and then blanketed with a stream of argon.

A platinum wire counter electrode and an SCE reference electrode were used. The reference junction was isolated from the solutions without added electrolyte with an auxiliary Vycor-tipped bridge containing only deionized water. Working electrodes were platinum disks of radius 0.8 mm (Bioanalytical Systems), 2.0 mm, (Pine Instrument Co.) and 11 μm (Project Ltd., Warsaw, Poland). The electrodes were initially polished to mirror finish with 1- and 0.05- μm alumina (Buehler) on a polishing cloth. Subsequently, the surface was renewed before voltammetric scans by polishing briefly with 0.05- μm alumina. The electrode was rinsed to remove alumina with a direct stream of water from a wash bottle impinging on the electrode surface. Water was wicked from the surface of the electrode using a dry tissue. The condition of the electrode surface was examined optically using a metal-lurgical microscope PME 3 (Olympus).

After the polishing procedure, the electrode was cleaned and activated electrochemically in a separate cell containing 0.1 M HClO_4 , while the solution was constantly deoxygenated with a stream of argon. Just for this activation, the platinum electrode was used in a three-electrode system with auxiliary and quasireference electrodes of platinum wires. The potential was cycled from the oxidation peaks of adsorbed hydrogen to the beginning of oxidation of water with a scan rate of 50 mV/s. The scanning was stopped at the potential responding to the most negative reduction peak of adsorbed hydrogen. Usually it was necessary to do about 50 cycles to get well-shaped voltammetric curves.

The reference potential in our case is the potential of the H^+/H_2 system for unit activity of both oxidized and reduced forms dissolved in the solution, $E_{\text{H}^+/\text{H}_2}^{0,c}$. This potential differs from that of the normal hydrogen electrode (NHE), which is a mixed concentration–pressure potential. The difference between these potentials is given by

$$E_{\text{H}^+/\text{H}_2}^{0,c} = E_{\text{H}^+/\text{H}_2}^0 + RT/2F \ln[C_{\text{H}_2} (p_{\text{H}_2} = 1 \text{ bar})] \quad (1)$$

where $C_{\text{H}_2} (p_{\text{H}_2} = 1 \text{ bar})$ is the hydrogen concentration corresponding to the partial hydrogen pressure of 1 bar and the other symbols have their usual meaning.

RESULTS AND DISCUSSION

A typical cyclic voltammetric curve for acid solution obtained at a large platinum electrode with excess supporting electrolyte is shown in Figure 1. Visible are reduction peaks of adsorbed hydrogen ion (C_{ads}) and corresponding oxidation peaks of adsorbed hydrogen (A_{ads}), and the diffusion-controlled reduction peak of hydrogen ion (C_{diff}) and corresponding diffusion-controlled oxidation peak (A_{diff}). The very large increase of the current (C_{OH}) at potentials more negative than -0.65 V is due to the reduction of water. The corresponding peak of oxidation of elemental hydrogen is marked A_{OH} . These peaks are located at more negative potentials, because the reduction of water is considerably less favored energetically than the reduction of solvated hydrogen ion. At potentials more positive than the peak potentials of

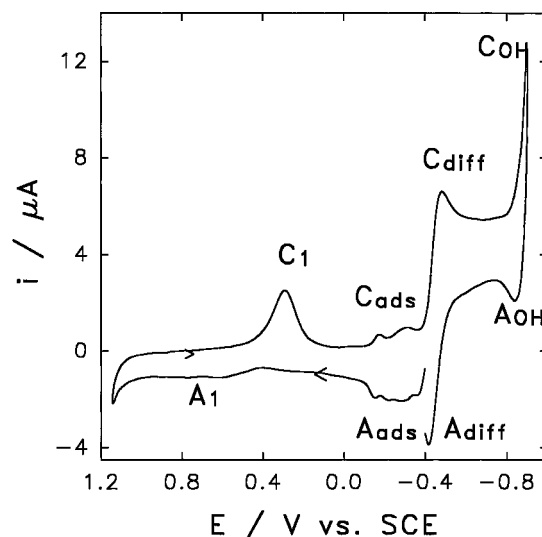


Figure 1. Cyclic voltammetric curve for 0.7 mM HClO_4 at a Pt disk of radius 0.8 mm. Supporting electrolyte 0.1 M LiClO_4 ; $v = 20 \text{ mV/s}$.

adsorbed hydrogen, the surface oxidation waves of platinum (A_1) to the oxides can be seen during the positive-going scan. In the scan to negative potentials, the total surface reduction peak of previously generated platinum oxides to platinum is obtained (C_1). The limit of positive potential arises through the large current increase connected with oxidation of water. The peaks A_1 , C_1 , A_{ads} , and C_{ads} are referred to frequently in the literature and are used as criteria for correct pretreatment and activation of Pt electrodes.¹¹

Here only diffusion-limited peaks C_{diff} and A_{diff} are interesting for us. To test whether the voltammetric peaks are only transport-limited, or whether they depend also on the electron-transfer rate, we have developed a theoretical model based on digital simulation and used Shuman's theory for electrode reactions of non-1:1 stoichiometry. The theoretical model is valid for the reversible electrode reaction of any stoichiometry:



To make the theoretical results comparable to experimental data obtained with regular size electrodes and microelectrodes, both linear and spherical coordinates have been applied in the calculations. In the case of linear diffusion, the transport equations and boundary conditions are the following:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3)$$

$$E_{\text{O/R}} = E_{\text{O/R}}^{0,c} + \frac{RT}{nF} \ln \frac{(C_{\text{O}}^0)^m}{(C_{\text{R}}^0)^q} \quad (4)$$

$$q\sqrt{D_{\text{O}}}C_{\text{O}}^0 + m\sqrt{D_{\text{R}}}C_{\text{R}}^0 = q\sqrt{D_{\text{O}}}C_{\text{O}}^* \quad (5)$$

Here subscripts O and R refer to the reactants of eq 2, superscripts 0 and * refer to surface and bulk, respectively, D is the diffusion coefficient, and C is a concentration. In the simulation of the voltammograms for hemispherical microelectrodes, eqs 3

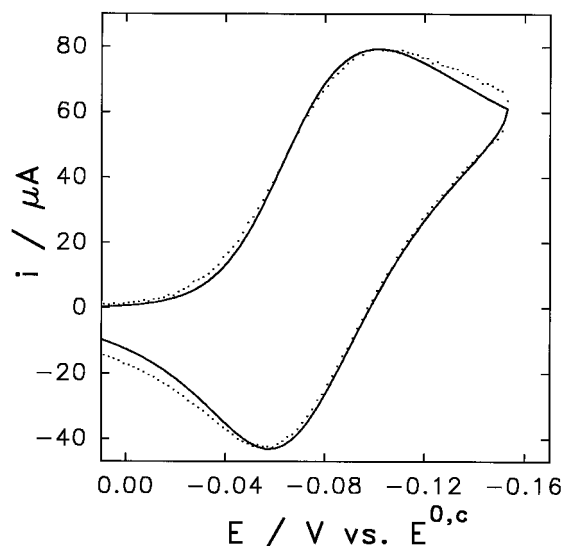


Figure 2. Comparison of theoretical and experimental cyclic voltammograms at 2.0-mm Pt disk electrode for excess supporting electrolyte (0.5 M LiClO₄). HClO₄ 2 mM; dots, experimental points; solid line, Shuman's theory; $\nu = 20$ mV/s.

and 5 were replaced by eqs 6 and 7

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (6)$$

$$qD_O C_O^0 + mD_R C_R^0 = qD_O C_O^* \quad (7)$$

Before the model was applied for the H⁺/H₂ system, it was verified by comparison with Shuman's theory for electrode reactions of 3:1 and 2:1 stoichiometry.¹⁷ Our voltammograms simulated for the parameters used by Shuman agree very well with his tabulated results, provided that the Shuman potential axis is corrected (see next paragraphs).

A comparison between theoretical and experimental cyclic voltammograms obtained at a large disk electrode (radius 2.0 mm) for a strong acid (HClO₄) and for excess supporting electrolyte is shown in Figure 2. This comparison, to be unambiguous, required a sufficiently high acid concentration to minimize the influence of adsorption peaks or, in other words, to decrease effectively the ratio of heights of adsorptive and diffusional peaks. The absolute peak potentials of experimental and theoretical voltammograms usually differed by several millivolts. We attributed this to the problems related to the calculation of the correct H₂/H⁺ potential for excess supporting electrolyte. Therefore, to examine the voltammetric reversibility of the hydrogen couple, we rather moved the experimental curves along the potential axis to make the peaks of the experimental and simulated curves coincide. We then compared the entire shapes of the cyclic experimental and theoretical voltammograms. Good agreement between the experimental curve for a strong acid and the simulated curve indicates that such processes as multistage hydrogen ion reduction and adsorption can be neglected under these experimental conditions. This good agreement was obtained for a scan rate range from 5 to 50 mV/s. The small deviations from the theory, i.e., too large currents seen after both cathodic and anodic peaks, may be related

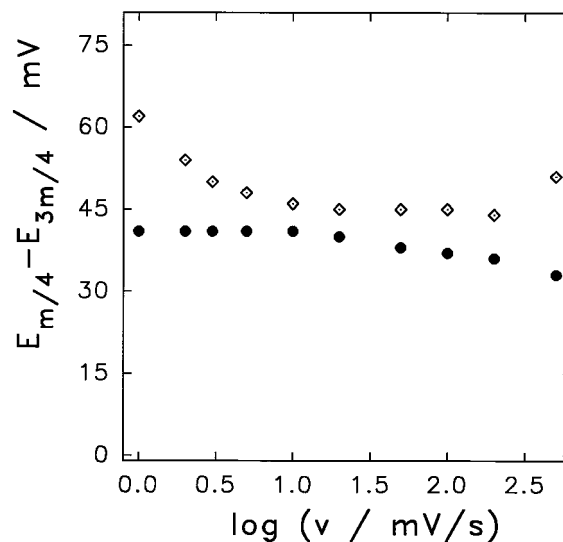


Figure 3. Comparison of theoretical (filled circles) and experimental (dotted diamonds) data for $E_{m/4} - E_{3m/4}$ vs logarithm of scan rate obtained for a 11- μ m Pt microelectrode for 1 mM HClO₄ in excess supporting electrolyte (0.1 M LiClO₄).

to the convection generated by partial evolution of gaseous hydrogen and to some dissolution of hydrogen in platinum, respectively. The existence of adsorptive peaks should also have a small contribution to the increase of current after the anodic peak. The theoretical curve in Figure 2 was simulated for $m = 2$, $n = -2$, and $q = 1$. Linear coordinates were used in this calculation.

Having developed the simulation scheme for hemispherical microelectrodes, we also carried out experiments with platinum disk microelectrodes (a factor of $2\pi/4$ was used to adjust the microdisk current to that of a microhemisphere) and found that the scan-rate range of reversibility is even larger (3–200 mV/s) than that for the 2-mm electrode. The quantitative conclusions regarding reversibility of the voltammograms obtained for the reduction of strong HClO₄ acid at Pt disk microelectrodes were based on the comparison of experimental and theoretical $E_{m/4} - E_{3m/4}$ values, where $E_{m/4}$ and $E_{3m/4}$ are the potentials corresponding to $1/4$ and $3/4$ of the maximal current, respectively (see Figure 3). It is worth noting that $E_{m/4}$ and $E_{3m/4}$ are placed neither symmetrically vs Shuman's $E_{1/2}$ nor at constant potentials. They depend on acid concentration. We believe that the larger scan-rate range of reversibility for microelectrodes can be explained by the fact that the transport of H₂ from the microelectrode surface is much more effective than the transport at regular electrodes. Also, the capacitive current for the 2-mm disk starts to be substantial at scan rates higher than 50 mV/s, which leads to an extra separation of the peaks. Prolonged hydrogen evolution also leads to increased separation of the peaks; therefore, before each scan, the electrodes were kept at a potential positive to that of the hydrogen couple to oxidize completely any hydrogen produced in the previous cycle.

Shuman presented a general integral equation for cyclic voltammetry for the reaction described by eq 2. He provided detailed computational results for the current function for the

cases $m = 2, 3$; $n = -2$; and $q = 1$. The tabulated values given by Shuman are correct. However, the potentials in the table are given vs the polarographic half-wave potential, $E_{1/2}$, the expression for which contains an error. The correct equation for the relation of the half-wave potential to the formal potential (eq 1) is

$$E_{1/2} = E^{0,c} - \frac{RT}{nF} \left[q \ln \left(\frac{\gamma q}{m} \right) + (q - m) \ln C_O^* + (m - q) \ln 2 \right] \quad (8)$$

where γ equals $(D_O/D_R)^{1/2}$ or D_O/D_R for linear or spherical diffusion, respectively. The last term in brackets is omitted in Shuman's paper. Equation 8 can be derived by substituting concentrations of O and R at the electrode surface at the half-wave potential calculated from eqs 5 or 7 for linear or spherical diffusion, respectively, into the Nernst equation (eq 4). The

quantity $E_{1/2}$ was used by Shuman as the reference point, since the difference between peak potential and half-wave potential does not depend on concentration. We have used simulation to calculate voltammetric curves for a wide range of values of m , n , and q , which could not be done by Shuman due to limitations of the analytical method he used and the less powerful computers available at that time. Half-wave potentials obtained from these curves agreed with those predicted by eq 8.

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