

Impedance analysis of hydrogen adsorption on palladium in 0.1 M NaOH solution

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(Received March 21, 1991)

Abstract

The behaviour of hydrogen adsorption on palladium has been investigated by a.c. impedance measurements in 0.1 M NaOH solution of pH 13 at 298 K. The electrode impedance has been measured by superimposing an a.c. voltage of 5 mV amplitude ranging between 10^{-1} and 10^4 Hz on a d.c. potential range from -0.76 to 0.44 V (standard hydrogen electrode (SHE)). The equivalent circuit representing the hydrogen adsorption reaction is proposed from the analysis of the frequency dependence of electrode admittance. The capacitance, arising from the adsorbed hydrogen, has been determined as a function of applied potential by complex non-linear least-squares curve fitting method based on the proposed equivalent circuit. As the cathodic applied potential increased from -0.36 to -0.76 V (SHE), the adsorption capacitance considerably increased owing to the enhanced coverage of hydrogen adsorbed on the palladium surface. In the applied potential range from -0.36 to 0.24 V (SHE), the adsorption capacitance exhibited a minimum value, characterizing a double-layer region.

1. Introduction

For the measurements of hydrogen permeation through metals such as iron, steel and copper, palladium is usually electroplated on the metal surface to minimize surface contamination and to eliminate surface impediments to hydrogen entry [1]. Hydrogen injection into the palladium layer is largely influenced by the hydrogen adsorbed on the palladium electrode surface. Although much research [2, 3] has been conducted as to the transfer of hydrogen in the bulk of palladium, the behaviour of hydrogen adsorbed on the palladium surface has still not been fully understood.

The present paper is concerned with the hydrogen adsorption on a palladium electrode surface by using a.c. impedance measurements. For this purpose this work first suggests an equivalent circuit for the hydrogen adsorption, particularly in the cathodic applied potential ranges.

2. Experimental details

A palladium film on pure copper substrates was prepared by electro-deposition. The copper substrate, 3 cm × 3 cm in area and 0.1 cm in thickness, was degreased in acetone, chemically polished in a mixture of 200 ml nitric acid and 200 ml distilled water, and then activated in 20% sulphuric acid solution for 30 s at room temperature. For palladium plating a bath containing 1 g PdCl₂, 111 g Na₃PO₄ · 3H₂O, 0.7 g C₆H₅COOH and 133 g distilled water was worked for 5 min at a d.c. current density of 2 mA cm⁻², at pH 11 and at a temperature of 338 K.

The impedance measurements of the palladium-plated electrode were conducted in 0.1 M NaOH solution by superimposing an a.c. voltage of 5 mV amplitude ranging from 10⁻¹ to 10⁴ Hz supplied from a lock-in amplifier (EG&G, model 5208) on a d.c. potential applied with a potentiostat (EG&G, model 273). The electrolytic solution was deaerated by bubbling with nitrogen for 24 h before the impedance measurements. The exposed surface area of the palladium-deposited electrode was 1.37 cm². A platinum wire and a saturated calomel electrode were used as a counterelectrode and a reference electrode respectively.

3. Results and discussion

In the cathodic applied potential ranges, hydrogen is adsorbed on the surface of a palladium electrode in alkaline solutions according to the following reaction:



The adsorbed hydrogen mainly affects the electrode impedance.

It is convenient to represent generally the equivalent circuit of an electrochemical cell in a parallel combination of capacitance C_p and resistance R_p . The admittance of the parallel circuit of C_p and R_p can be given as follows:

$$Y = Z^{-1} = Y' + jY'' = R_p^{-1} + j\omega C_p \quad (2)$$

We first assumed an equivalent circuit for the hydrogen adsorption on the palladium electrode in alkaline solution is the circuit as shown in Fig. 1(a),



Fig. 1. Equivalent circuits for hydrogen adsorption on a palladium electrode in 0.1 M NaOH solution: (a) simplified circuit; (b) the circuit accommodated to the experimental data.

consisting of a parasitic electrolyte resistance R_E in series combination with the circuit proposed by Dolin and Ershler [4] for hydrogen adsorption on a platinum electrode surface in acidic solution. The cell admittance for this equivalent circuit is given by

$$Y = (R_E + [j\omega C_D + \{r + (j\omega C_A)^{-1}\}^{-1}]^{-1})^{-1} \quad (3)$$

$$Y' = R_p^{-1} = \frac{\omega^2(\omega^2 R_E L^2 + K^2 R_E + K C_A r - L)}{(1 - \omega^2 R_E L)^2 + \omega^2 (C_A r + K R_E)^2} \quad (4a)$$

$$Y'' = \omega C_p = \frac{\omega \{K - R_E K \omega^2 L + \omega^2 L (C_A r + K R_E)\}}{(1 - \omega^2 R_E L)^2 + \omega^2 (C_A r + K R_E)^2} \quad (4b)$$

where C_D is the double-layer capacitance, C_A is the adsorption capacitance due to the storage of hydrogen on the surface of the palladium electrode, r is the charge transfer resistance associated with reaction (1), $K = C_A + C_D$, and $L = C_A C_D r$. From eqns. (4a) and (4b), we obtain the relations $R_p^{-1} \rightarrow 0$, $C_p \rightarrow C_A + C_D$ for $\omega \rightarrow 0$, and $R_p^{-1} \rightarrow R_E^{-1}$, $C_p \rightarrow 0$ for $\omega \rightarrow \infty$.

Figure 2 shows the frequency dependence of R_p^{-1} obtained at various cathodic potentials. The value of R_p^{-1} approaches zero as $\omega \rightarrow 0$ and approaches to value of the inverse parasitic electrolyte resistance R_E^{-1} as $\omega \rightarrow \infty$. These experimental findings can be readily accounted for by eqn. (4a). The frequency dependence of C_p is shown in Fig. 3. The value of C_p approaches to zero as $\omega \rightarrow \infty$ and increases as $\omega \rightarrow 0$. The circuit presented in Fig. 1(a) indicated that the theoretical value of C_p converges to the constant value of $C_A + C_D$ as $\omega \rightarrow 0$. This means that the equivalent circuit presented in Fig. 1(a) should include the circuit elements which can accommodate the deviation in the low frequency ranges. For the correction of this deviation, we considered

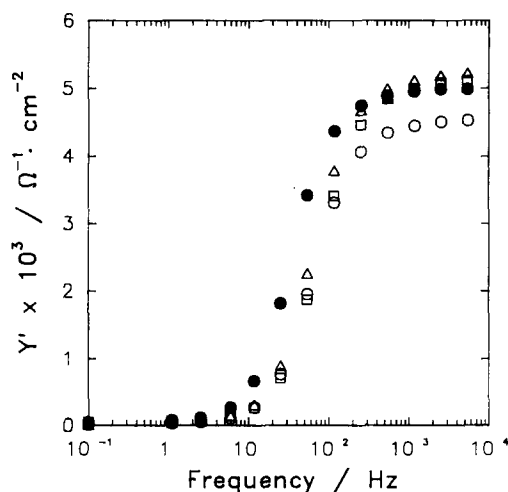


Fig. 2. Frequency dependence of the parallel conductance R_p for hydrogen adsorption on a palladium electrode in 0.1 M NaOH solution, measured at various applied potentials: \circ , 0.04 V (SHE); \square , -0.16 V (SHE); \triangle , -0.36 V (SHE); \bullet , -0.56 V (SHE).

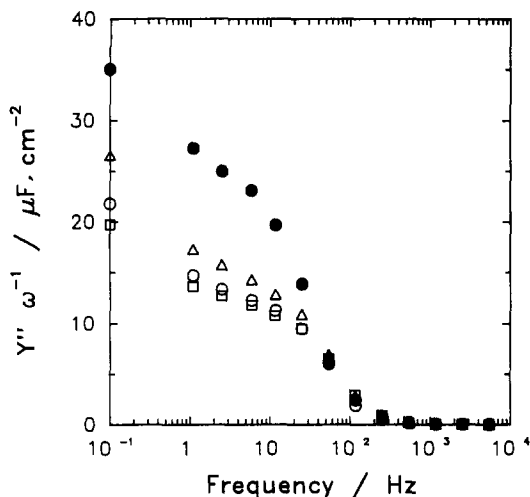


Fig. 3. Frequency dependence of the parallel capacitance C_p for hydrogen adsorption on a palladium electrode in 0.1 M NaOH solution, measured at various applied potentials: ○, 0.04 V (SHE); □, -0.16 V (SHE); △, -0.36 V (SHE); ●, -0.56 V (SHE).

next the equivalent circuit shown in Fig. 1(b) which is identical to the circuit proposed by Llopis *et al.* [5] for ferrous–ferric and halide–halogen redox reactions on the platinum electrode. The cell admittance resulting from the circuit presented in Fig. 1(b) is expressed as

$$Y = [R_E + \{j\omega C_D + (r_A + [j\omega C_A + \{(r_A + \sigma\omega^{-1/2})^{-1} - j\sigma\omega^{-1/2}\}^{-1}]^{-1})^{-1}\}^{-1}]^{-1} \quad (5)$$

where r_A is the resistance that is related to the adsorption rate and σ is the Warburg impedance coefficient representing the diffusion process of adsorbed hydrogen.

The parallel capacitance C_p is shown in Fig. 4 as a function of applied potential, measured at various frequencies. If the contribution of the Warburg impedance term is ignored, the parallel capacitance C_p approximately equals the sum of the double-layer capacitance and the adsorption capacitance $C_D + C_A$ at low frequencies [6]. Figure 4 shows that the value of C_p becomes almost constant in the applied potential range from -0.36 to 0.24 V (standard hydrogen electrode (SHE)), characterizing the double-layer region. For more detailed analysis, the double-layer capacitance C_D is obtained at 0.04 V (SHE), within the double-layer region, by extrapolating to high frequency in the graphical representation of Y''/ω vs. frequency after the subtraction of the parasitic electrolyte resistance R_E [7]. The double-layer capacitance of the palladium electrode in 0.1 M NaOH solution is obtained to be about $7 \mu\text{F cm}^{-2}$.

In the present work, the complex capacitance representation (Y'/ω vs. Y''/ω plot) is used for the analysis of hydrogen adsorption on the palladium electrode. Figure 5 shows the plot of complex capacitance (Y''/ω vs. Y'/ω) obtained at 0.04 V (SHE). The plot of the complex capacitance based on the circuit of Fig. 1(a) is usually characterized by the occurrence of a

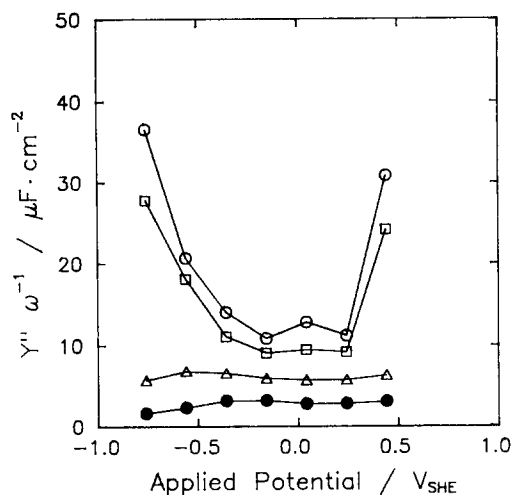


Fig. 4. Applied potential dependence of the parallel capacitance C_p for hydrogen adsorption on a palladium electrode in 0.1 M NaOH solution, measured at various frequencies: \circ , 0.5 Hz; \square , 4.7 Hz; \triangle , 40 Hz; \bullet , 100 Hz.

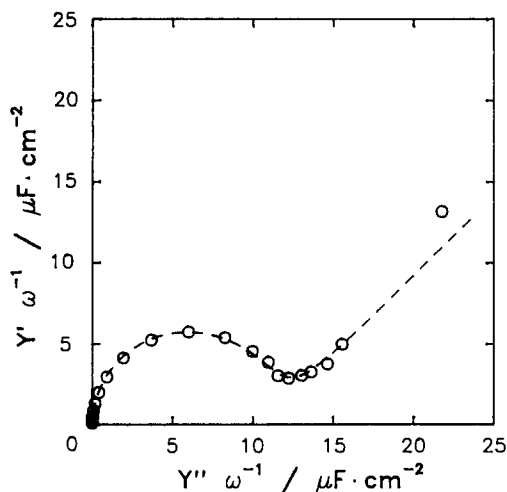


Fig. 5. Complex capacitance representation (Y''/ω vs. Y'/ω plot). \circ , measured experimentally in 0.1 M NaOH solution, at an applied potential of 0.04 V (SHE) and in the frequency range from 10^{-1} to 10^4 Hz; ---, theoretical curve based on the circuit of Fig. 1(b), where $R_E = 200 \Omega \text{ cm}^2$, $C_D = 7 \mu\text{F cm}^{-2}$, $r = 50 \Omega \text{ cm}^2$, $C_A = 4 \mu\text{F cm}^{-2}$, $r_A = 0 \Omega \text{ cm}^2$, $\sigma = 50\,000 \Omega \text{ cm}^2 \text{ s}^{-1}$.

semicircle. However, the plot shown in Fig. 5 actually deviates from the semicircle in the low frequency ranges. The broken line in Fig. 5 represents a theoretical curve which was obtained from the complex non-linear least-squares curve fitting method [8] based on eqn. (5). Figure 5 indicated that the plot of complex capacitance obtained experimentally is best fitted to the circuit of Fig. 1(b).

The least-squares procedure is to determine a set of circuit parameters that minimize the sum of squares function S given by

$$S = \sum_{i=1}^k f_i \left[\left\{ \frac{Y_i}{\omega_i} - \frac{Y'(\omega_i)}{\omega_i} \right\}^2 + \left\{ \frac{Y''_i}{\omega_i} - \frac{Y''(\omega_i)}{\omega_i} \right\}^2 \right] \quad (6)$$

where i is the sequential number of the data point associated with ω_i , ω_i is the frequency experimented with, f_i is the weight factor associated with the i th data point, Y_i and Y''_i are the conductance and susceptance experimentally obtained at ω_i , and $Y'(\omega_i)$ and $Y''(\omega_i)$ are the conductance and susceptance theoretically calculated at ω_i . The weight factor is given by

$$f_i = \frac{1}{|Y_i/\omega_i|^2} \quad (7)$$

so that all data sets contribute equally to the sum of the squares function S in eqn. (6).

Figure 6 shows the change with applied potential in the adsorption capacitance C_A which was determined by applying the curve-fitting method to the plot of complex capacitance obtained for the applied potential range from -0.76 to 0.44 V (SHE). As the cathodic potential increased from -0.36 to -0.76 V (SHE), the adsorption capacitance considerably increased owing to the raised coverage of hydrogen adsorbed on the surface of the palladium electrode. The adsorption capacitance of the order of $10 \mu\text{F cm}^{-2}$, measured on the palladium electrode, is much smaller than that of the order of $10^3 \mu\text{F cm}^{-2}$ usually observed from a platinum electrode [6] in the absence of specifically adsorbed ions. The diminished adsorption capacitance is presumably attributable to the high solubility of hydrogen in the palladium electrode. In the applied potential range from -0.36 to 0.24 V (SHE), the

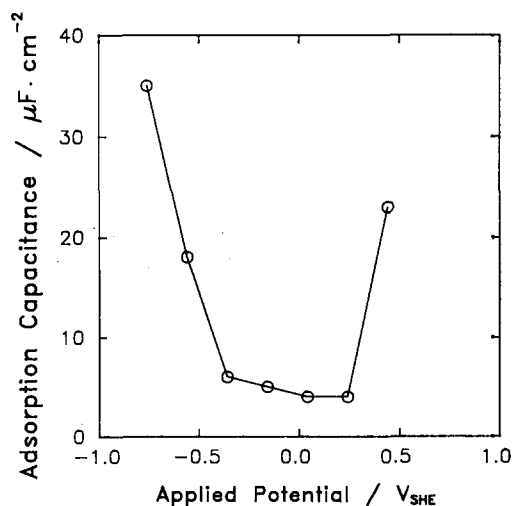


Fig. 6. The adsorption capacitance C_A as a function of applied potential for hydrogen adsorption on a palladium electrode in 0.1 M NaOH solution.

adsorption capacitance exhibited a minimum value, indicating the presence of the double-layer region.

4. Conclusions

(1) The circuit elements of faradaic impedance describing hydrogen adsorption on palladium were determined from the analysis of the frequency dependence of the electrode admittance. The faradaic impedance proved to consist of an adsorption capacitance C_A in parallel combination with an adsorption resistance r_A and a Warburg impedance Z_w .

(2) As the cathodic applied potential increased from -0.36 to -0.76 V (SHE), the adsorption capacitance considerably increased owing to the increase in hydrogen coverage.

(3) In the applied potential range from -0.36 to 0.24 V (SHE), the adsorption capacitance was determined to have an almost constant value of $4 \mu\text{F cm}^{-2}$, indicating the presence of the double-layer region.

Acknowledgment

The receipt of a research grant 1988/89 from the Ministry of Science and Technology, Korea, is gratefully acknowledged.

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