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Resistance shifts of a Pd|H electrode in measurement and electrolysis with direct currents

Wu-Shou Zhang *

Institute of Chemistry and Center for Molecular Science, Chinese Academy of Sciences, P.O. Box 2709, Beijing 100080, China

Abstract

Some mistakes in the paper published in the Journal of Electroanalytical Chemistry 528 (2002) 1 are corrected. The resistance changes of a Pd|H electrode caused by the co-conduction of the electrolyte, the concentration-cell effect and collection of electrolysis current in the in situ resistance measurement using direct currents are calculated analytically. Some advice is given for resistance measurements.
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1. Introduction

In an earlier work [1], we discussed some problems on the resistance measurement of palladium hydride to determine the hydrogen content in it in situ. However, we found recently that there are some mistakes in discussions on the electrochemical effects in [1]. The expressions of additional resistance caused by the concentration-cell effect will induce non-physical pictures, and some important factors were omitted. In this paper, we will treat the electrochemical effects in a unified manner. Similarly to the earlier paper, we focus only on the direct current situation; the model and symbols are the same as before [1] except as noted otherwise.

2. Model

The model for measurement of the resistance of a Pd|H electrode during electrolysis is the same as that in Sections 3.5–3.7 and shown in Fig. 9 of [1]. Because most of the mistakes appeared in discussions on the concentration-cell effect of measurement and electrolysis currents, we will discuss these in turn.

2.1. Co-conduction of electrolyte

The co-conduction is the same as in Section 3.5.1 of [1]. In addition, the current in the electrode for a measurement current I_M is

$$I_{M,Pd+H} = \frac{R_S}{R_S + R_{Pd+H}} I_M$$
$$= \left[1 - \frac{R_{Pd+H}}{R_S} + \frac{R_{Pd+H}^2}{R_S^2} + O\left(\frac{R_{Pd+H}}{R_S}\right)^3\right] I_M, \quad (1)$$

where R_{Pd+H} and R_S are the resistances of the Pd|H electrode and electrolytic solution, respectively; values of R_S for different shapes of electrode were shown in Eq. (41) of [1]. The corresponding potential drop across the electrode is

$$\Delta E_M = I_{M,Pd+H} R_{Pd+H}. \quad (2)$$

2.2. Concentration-cell effect of measurement current

This subsection corresponds to Section 3.5.2 in [1]. The potential balance equation for the concentration-cell effect of the measurement current is

* Tel.: +86-10-62554276; fax: +86-10-62559373.
E-mail address: wszhang@iccas.ac.cn (W.-S. Zhang).

$$\frac{1}{l}\int_z^l I_{M,Pd+H}R_{Pd+H}\,\mathrm{d}z = R_C l\frac{\mathrm{d}I_{M,C}}{\mathrm{d}z} + \frac{1}{l}\int_z^l I_{M,C}R_{Pd+H}\,\mathrm{d}z, \tag{3}$$

where $I_{M,C}$ is the concentration-cell current in the electrode, the other symbols are the same as before [1]. The left-hand side of this equation is the electromotive force of the concentration-cell relative to the point $z = l$. The first term in the right-hand side of this equation is the ohmic polarization of the electrolytic solution and the electrochemical overpotential (see Eqs. (49)–(54) in [1]); the second term is the ohmic potential drop of the Pd|H electrode. This equation differs from Eq. (55) of [1] in both sides; on one side, I_M is replaced by $I_{M,Pd+H}$; on the other, the range of integration of the ohmic polarization of the Pd|H electrode, i.e. 0 to z, is replaced by z to l.

Eq. (3) can be simplified to

$$l^2\frac{\mathrm{d}^2 I_{M,C}}{\mathrm{d}z^2} - k^2 I_{M,C} = -k^2 I_{M,Pd+H}. \tag{4}$$

The meaning of k is the same as that defined in Eqs. (57)–(59) of [1].

Applying the boundary condition $I_{M,C} = 0$ at $z = 0$ and l, we obtain the solution of Eq. (4)

$$I_{M,C} = \left(1 - \frac{\cosh\left[k\left(\frac{z}{l} - \frac{1}{2}\right)\right]}{\cosh\frac{k}{2}}\right) I_{M,Pd+H}. \tag{5}$$

The potential drop across the Pd|H electrode contributed by the concentration-cell effect of the measurement current is

$$\begin{aligned}
\Delta E_{M,C} &= \frac{1}{l}\int_0^l I_{M,C}R_{Pd+H}\,\mathrm{d}z \\
&= \left[1 - \frac{2}{k}\tanh\left(\frac{k}{2}\right)\right]I_{M,Pd+H}R_{Pd+H} \\
&= \left[\frac{k^2}{12} - \frac{k^4}{120} + \mathrm{O}(k)^6\right]I_{M,Pd+H}R_{Pd+H}. \tag{6}
\end{aligned}$$

By comparison with Eqs. (64) and (65) in [1], we find they are different. The divergence of $\Delta E_{M,C}$ at $k = \pi, 2\pi, 3\pi, \ldots$ in Eq. (64) of [1] is avoided, the function $1 - 2\tanh(k/2)/k$ increases with k and approaches 1 when k is large enough as expected; however, its primary approximation, $k^2/12$, is the same as before and the physical pictures of Fig. 10 in [1] are qualitatively correct.

2.3. Collection effect of electrolysis current

This subsection corresponds to Section 3.6.1 in [1]. Provided that the counter electrode is far away from the Pd|H electrode and the electrolysis current is collected at the point $z = l$ as shown in Fig. 9(b) of [1], the potential at a point z is composed of the overpotential, and the ohmic potential drops of solution and electrode resistances. We can obtain a relationship similar to Eq. (3)

$$\text{constant} = R_C l\frac{\mathrm{d}I_{E,Pd+H}}{\mathrm{d}z} + \frac{1}{l}\int_z^l I_{E,Pd+H}R_{Pd+H}\,\mathrm{d}z, \tag{7}$$

where $I_{E,Pd+H}$ is the current collected in the Pd|H electrode during electrolysis with current I_E In this equation, the polarization resistance is the same as that in Eq. (3) because we consider only the shift of overpotential and solution resistance at a point from the average values over the whole electrode, which are included in the left-hand side of Eq. (7). Eq. (7) can be simplified to

$$l^2\frac{\mathrm{d}^2 I_{E,Pd+H}}{\mathrm{d}z^2} - k^2 I_{E,Pd+H} = 0. \tag{8}$$

Applying the boundary condition: $I_{E,Pd+H} = 0$ at $z = 0$ and $I_{E,Pd+H} = I_E$ at $z = l$, we obtain the solution

$$\begin{aligned}
I_{E,Pd+H} &= \frac{\sinh\left(k\frac{z}{l}\right)}{\sinh k}I_E \\
&= \left\{\left[1 - \frac{k^2}{6} + \mathrm{O}(k)^4\right]\frac{z}{l}\right. \\
&\quad \left. + \left[\frac{k^2}{6} - \frac{k^3}{36} + \mathrm{O}(k)^5\right]\frac{z^3}{l^3} + \mathrm{O}\left(\frac{z}{l}\right)^4\right\}I_E. \tag{9}
\end{aligned}$$

In the primary approximation, it is a linear distribution as was supposed before [1]. The electrolysis current density is

$$\begin{aligned}
j_{E,Pd+H} &= \frac{1}{2\pi r_0}\frac{\mathrm{d}I_{E,Pd+H}}{\mathrm{d}z} = \frac{k\cosh\left(k\frac{z}{l}\right)}{\sinh k}\frac{I_E}{2\pi r_0 l} \\
&= \left\{\left[1 - \frac{k^2}{6} + \mathrm{O}(k)^4\right]\right. \\
&\quad \left. + \left[\frac{k^2}{2} - \frac{k^3}{12} + \mathrm{O}(k)^4\right]\frac{z^2}{l^2} + \mathrm{O}\left(\frac{z}{l}\right)^4\right\}\frac{I_E}{2\pi r_0 l}. \tag{10}
\end{aligned}$$

where $j_{E,Pd+H}$ is a constant in the primary approximation as indicated in Eq. (68) of [1]. The potential drop across the Pd|H electrode contributed by the collection of the electrolysis current is

$$\begin{aligned}
\Delta E_E &= \frac{1}{l}\int_0^l I_{E,Pd+H}R_{Pd+H}\,\mathrm{d}z \\
&= \frac{1}{k}\tanh\left(\frac{k}{2}\right)I_E R_{Pd+H} \\
&= \left[\frac{1}{2} - \frac{k^2}{24} + \frac{k^4}{240} + \mathrm{O}(k)^6\right]I_E R_{Pd+H}. \tag{11}
\end{aligned}$$

In the zero order approximation, it is $I_E R_{Pd+H}/2$ as indicated in Eq. (71) of [1].

2.4. Concentration-cell effect of electrolysis current

This subsection corresponds to Section 3.6.2 in [1]. Similarly to Eq. (3), we have

$$\frac{1}{l}\int_z^l I_{E,Pd+H}R_{Pd+H}\,\mathrm{d}z = R_C l\frac{\mathrm{d}I_{E,C}}{\mathrm{d}z} + \frac{1}{l}\int_z^l I_{E,C}R_{Pd+H}\,\mathrm{d}z. \tag{12}$$

Utilizing Eq. (9), we can simplify Eq. (12) to

$$l^2 \frac{\mathrm{d}^2 I_{\mathrm{E,C}}}{\mathrm{d}z^2} - k^2 I_{\mathrm{E,C}} = -k^2 \frac{\sinh\left(k\frac{z}{l}\right)}{\sinh k} I_{\mathrm{E}}. \tag{13}$$

Applying the boundary condition $I_{\mathrm{E,C}} = 0$ at $z = 0$ and l, we obtain the solution of Eq. (13)

$$I_{\mathrm{E,C}} = \frac{k\left[\sinh\left(k\frac{z}{l}\right)\cosh k - \frac{z}{l}\cosh\left(k\frac{z}{l}\right)\sinh k\right]}{2\sinh^2 k} I_{\mathrm{E}}. \tag{14}$$

The potential drop across the Pd|H electrode caused by the concentration-cell effect of the electrolysis current is

$$\Delta E_{\mathrm{E,C}} = \frac{\sinh k - k}{4k\cosh^2\left(\frac{k}{2}\right)} I_{\mathrm{E}} R_{\mathrm{Pd+H}}$$
$$= \left[\frac{k^2}{24} - \frac{k^4}{120} + \mathrm{O}(k)^6\right] I_{\mathrm{E}} R_{\mathrm{Pd+H}}. \tag{15}$$

This equation differs from Eq. (77) in [1]; however, their primary approximations are the same and Fig. 11 in [1] is appropriate when k is small.

3. Results and discussion

Combining Eqs. (2), (6), (11) and (15), we obtain the overall potential drop across the Pd|H electrode while the measurement current I_{M} is applied during electrolysis with current I_{E}

$$\Delta E = \Delta E_{\mathrm{M}} + \Delta E_{\mathrm{M,C}} + \Delta E_{\mathrm{E}} + \Delta E_{\mathrm{E,C}}$$
$$= 2\left[1 - \frac{1}{k}\tanh\left(\frac{k}{2}\right)\right] I_{\mathrm{M,Pd+H}} R_{\mathrm{Pd+H}}$$
$$+ \frac{3\sinh k - k}{4k\cosh^2\left(\frac{k}{2}\right)} I_{\mathrm{E}} R_{\mathrm{Pd+H}}. \tag{16}$$

The apparent resistance can be expressed as

$$\frac{R_{\mathrm{appa}}}{R_{\mathrm{Pd+H}}} = \frac{\Delta E}{I_{\mathrm{M}} R_{\mathrm{Pd+H}}}$$
$$= 2\left[1 - \frac{1}{k}\tanh\left(\frac{k}{2}\right)\right] \frac{I_{\mathrm{M,Pd+H}}}{I_{\mathrm{M}}}$$
$$+ \frac{3\sinh k - k}{4k\cosh^2\left(\frac{k}{2}\right)} \frac{I_{\mathrm{E}}}{I_{\mathrm{M}}}. \tag{17}$$

Applying Eq. (1), we obtain the series expansion of Eq. (17)

$$\frac{R_{\mathrm{appa}}}{R_{\mathrm{Pd+H}}} = \left(1 + \frac{1}{12}\frac{R_{\mathrm{Pd+H}}}{R_{\mathrm{C}}} - \frac{1}{120}\frac{R_{\mathrm{Pd+H}}^2}{R_{\mathrm{C}}^2} + \mathrm{O}\left(\frac{R_{\mathrm{Pd+H}}}{R_{\mathrm{C}}}\right)^3\right)$$
$$\times \left(1 - \frac{R_{\mathrm{Pd+H}}}{R_{\mathrm{S}}} + \frac{R_{\mathrm{Pd+H}}^2}{R_{\mathrm{S}}^2} + \mathrm{O}\left(\frac{R_{\mathrm{Pd+H}}}{R_{\mathrm{S}}}\right)^3\right)$$
$$+ \left(\frac{1}{2} - \frac{1}{240}\frac{R_{\mathrm{Pd+H}}^2}{R_{\mathrm{C}}^2} + \mathrm{O}\left(\frac{R_{\mathrm{Pd+H}}}{R_{\mathrm{C}}}\right)^3\right) \frac{I_{\mathrm{E}}}{I_{\mathrm{M}}}. \tag{18}$$

From this equation, we find that there are three parameters, $R_{\mathrm{Pd+H}}/R_{\mathrm{C}}$, $R_{\mathrm{Pd+H}}/R_{\mathrm{S}}$ and $I_{\mathrm{E}}/I_{\mathrm{M}}$, influencing the measured value of the electrode resistance. For conve-

nience, we illustrate their effects for a straight rod electrode (shape I in Fig. 9(a) of [1]); the dimensionless parameters $R_{\mathrm{Pd+H}}/R_{\mathrm{C}}$ and $R_{\mathrm{Pd+H}}/R_{\mathrm{S}}$ are

$$\frac{R_{\mathrm{Pd+H}}}{R_{\mathrm{C}}} = 2\frac{\rho_{\mathrm{Pd+H}}}{\rho_{\mathrm{S}}}\left(\frac{l}{r_0}\right)^2\left(\ln\frac{l}{r_0} + \frac{1}{r_0 f \rho_{\mathrm{S}} j_{0\mathrm{C}}}\right)^{-1} \tag{19}$$

and

$$\frac{R_{\mathrm{Pd+H}}}{R_{\mathrm{S}}} = \frac{\rho_{\mathrm{Pd+H}}}{\rho_{\mathrm{S}}}\frac{l}{r_0}, \tag{20}$$

respectively. On the whole, the above measurement errors with different origins can be expressed by four dimensionless quantities, $I_{\mathrm{E}}/I_{\mathrm{M}}$, l/r_0, $\rho_{\mathrm{Pd+H}}/\rho_{\mathrm{S}}$ and $r_0 f \rho_{\mathrm{S}} j_{0\mathrm{C}}$:

$$\frac{R_{\mathrm{appa}}}{R_{\mathrm{Pd+H}}} = f\left(\frac{I_{\mathrm{E}}}{I_{\mathrm{M}}}, \frac{l}{r_0}, \frac{\rho_{\mathrm{Pd+H}}}{\rho_{\mathrm{S}}}, r_0 f \rho_{\mathrm{S}} j_{0\mathrm{C}}\right). \tag{21}$$

The corresponding numerical results are shown in Fig. 1.

First of all, it is found that the contribution of the electrolysis process to resistance measurements depends on the direction and magnitude of the electrolysis current as shown in Fig. 1(a). If $I_{\mathrm{E}}/I_{\mathrm{M}} > 0$, it will contribute a positive shift to the measured resistance. Otherwise, it will diminish the magnitude of the measured value while $I_{\mathrm{E}}/I_{\mathrm{M}} < 0$. This is the reason for the delta-mode current being utilized to cancel out the electrolysis contribution in the experiments given in [2,3] and discussed previously [1]. However, the period of the delta current must be much less than the diffusion time of hydrogen along the radial direction; otherwise, concentration-cell effects of the measurement current also exist.

Fig. 1(b) illustrates the effects of l/r_0 When l/r_0 is small, R_{appa} increases with l/r_0 because the concentration-cell effect increases with increasing l/r_0 as indicated by Eqs. (17) and (19). However, the co-conduction of electrolyte will dominate the resistance measurement while l/r_0 is enough large as indicated by Eqs. (17), (19) and (20). For an electrolyte with large conductance, the co-conduction effect is prominent and its concentration-cell effect is relatively small.

Fig. 1(c) shows dependences of R_{appa} on $r_0 f \rho_{\mathrm{S}} j_{0\mathrm{C}}$ This indicates that the electrode diameter, temperature, electrolyte conductance, electrode roughness and exchange current density of the electrode reaction all affect R_{appa}. An electrode with a rough surface results in a large value of $j_{0\mathrm{V}}$ hence large values of $j_{0\mathrm{C}}$. At the same time, some additives such as H_2S and thiourea can inhibit the reaction rate of the Pd|H electrode, so it is easy to understand that they can diminish R_{appa} as was observed experimentally [4–6]. Another factor is the electrolysis current density; a large magnitude of electrolysis current density results in high values of $j_{0\mathrm{C}}$ and R_{appa} as the effect of $j_{0\mathrm{V}}$. When $r_0 f_S j_{0\mathrm{C}}$ is small enough, the concentration-cell effect can be neglected, but the co-conduction effect is prominent especially while the solution conductance is large.
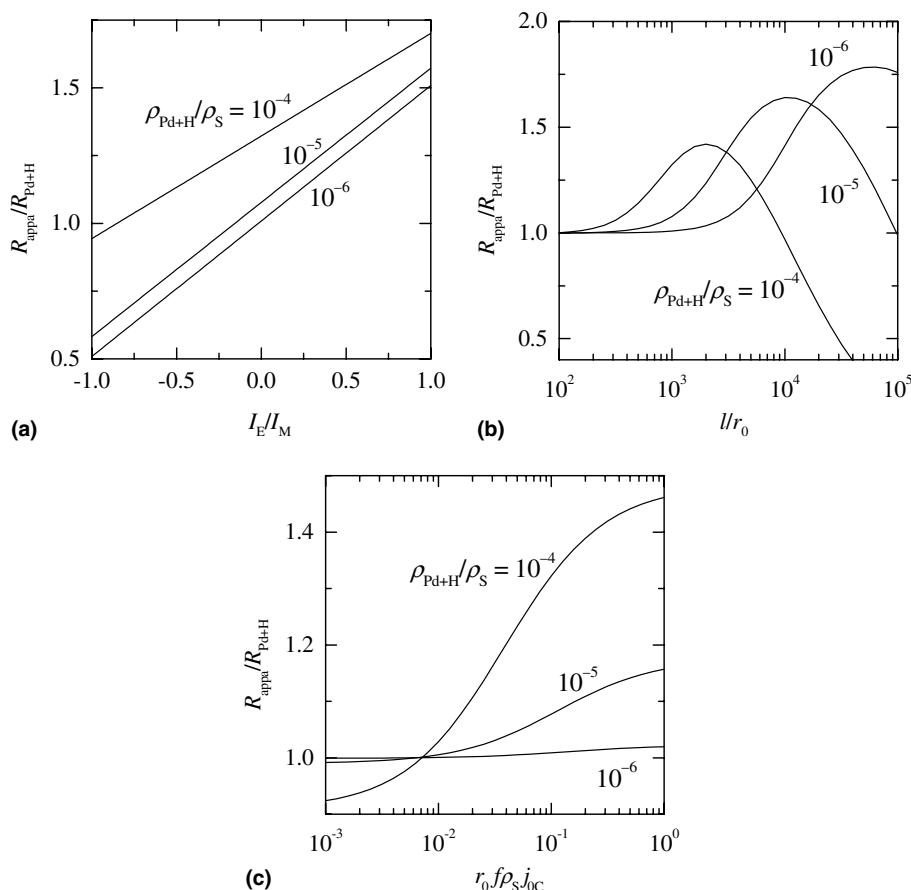
Fig. 1. R_{appa} as functions of (a) I_E/I_M (b) l/r_0 and (c) $r_0 f \rho_S j_{0C}$ for a straight rod Pd|H electrode. The parameters not emphasized are $l/r_0 = 10^3$, $I_E/I_M = 0$, $r_0 f \rho_S j_{0C} = 0.1$ except for the independent variable and that cited in each figure.

Fig. 1 also shows that the resistivity ratio ρ_{Pd+H}/ρ_S has the most important effect. If $\rho_{Pd+H}/\rho_S < 10^{-6}$, it has only a slight influence on R_{appa} with other parameters being fixed; otherwise, the additional resistance may not be neglected.

For the electrodes with shapes of W and U in Fig. 9(a) of [1], R_{appa}/R_{Pd+H} depends d_W/r_0 and d_U/r_0 respectively, besides the four dimensionless parameters indicated in Eq. (21). Their apparent resistances differ from that of shape I mainly by the co-conduction effect because R_{Pd+H}/R_S depends more strongly on the shape of the electrode than R_{Pd+H}/R_C with the same length and radius as indicated by Eqs. (41), (50), (57)–(59) in [1]. This means the apparent resistance has the maximum value for shape I.

Although our treatments are focused on the Pd|H electrode, the main conclusions can be extended to other metal (and/or alloy) hydride electrodes with some parameters modified. On the other hand, the actual samples may be spheres, plates and other shapes but not cylinders, as here, the apparent resistance must be calculated specifically. However, the qualitative aspects are the same as here. Finally, the present results are mainly theoretical; the qualitative aspects are consistent with available experiments [4–6]. The quantitative verifications need to be carried out in future experimental work.

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