ELECTROCHEMICAL EFFECTS ON THE RESISTANCE MEASUREMENTS OF PD|H ELECTRODE

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ABSTRACT

Additional resistances contributed to that of PdH_x electrode in an electrolyte using the direct current method are calculated. It is found that an electrode with a large ratio of length to radius, an active surface, a surrounding electrolyte with high conductance and high electrolysis current will induce substantial additional resistances.

1. INTRODUCTION

It has long been recognized that the electrical resistance of PdH_x (taken to include PdD_x, as below) is a function of x. This relationship has been used to infer the loading ratio in the electrolysis experiments.[1–8] However, the in-situ resistance measurement (ISRM) has inherent defects, e.g. the non-uniform distribution of H concentration, temperature, electrolyte and applied currents all influence the measured value. In this paper, we will discuss the electrochemical effects on the ISRM in the direct current (dc) situation.

2. MODEL AND RESULTS

The electrochemical factors affect the ISRM in three aspects. First, the solution acts as a resistance in parallel with the electrode and the apparent PdH_x resistance decreases when co-conduction is in progress. Second, the potential drop across the electrode induced by the measuring dc makes it behaves as a concentration-cell, which contributes an additional potential shift to the signal measured. Thirdly, the electrolysis current (ec) contributes another potential drop to the electrode by the current collection into the electrode and the concentration-cell effect. We will theoretically study these problems in turn.

2.1. Co-conduction of electrolyte

Consider a straight rod electrode with length l and radius r, the solution resistance can be seen as the series resistance of two hemispheres with radius r: $R_S = \rho_S l/\pi r$, where ρ_S is the resistivity of solution. The additional resistance contributed to that of PdH_x electrode by the co-conduction of solution, $R_{A,S}$ can be expressed as:

$$\frac{R_{A,S}}{R} = -\frac{R}{R_S} = -\frac{\rho l}{\rho_S r} \tag{1}$$

where R and ρ is the resistance and resistivity of PdH$_x$, respectively.

2.2. Concentration-cell effect of measurement current

Consider a measurement current I_M passing through an electrode, the electromotive force (emf) of the concentration-cell is the potential drop $I_M R$. It can be expressed as $E_C = I_M R(1/2 - z/l)$, where the fraction $1/2$ in the parentheses ensures the average potential to be zero. The overall emf is comprised of the ohm potential drop of external circuit $\Delta E_{\mathrm{PdHx,C}}$, ohm polarization of inner resistance $\Delta E_{\mathrm{S,C}}$ and electrochemical overpotential η_C. The potential drop across the small distance dz at point z in PdH$_x$ electrode is $dE_{\mathrm{PdHx,C}} = -I_C R dz/l$. The electrolyte resistance in the small distance dz can be seen as the resistance of a part of the cylindrical electrode with radius r and surface area $2\pi r dz$ in the solution: $\Delta E_{\mathrm{S,C}} = (\rho/2\pi)\ln[(l/r)dI_C/dz]$. The overpotential of the concentration-cell can be obtained by the differential of electrolysis current density (ecd) j_E with respect to the electrolysis overpotential η: $j_C = f j_{0C} \eta_C$ with the current density of the concentration-cell $j_C = dI_C/2\pi r_0 dz$, $f = F/RT$ and $j_{0C} = \max(j_{0V}, \beta|j_E|)$, where j_{0V} is the exchange current density of the Volmer reaction; β is the stoichiometric number of the hydrogen electrode reaction.[9]

The potential at point z is the sum of above three terms:

$$I_M R(\frac{1}{2} - \frac{z}{l}) = \left(\frac{1}{2\pi r f j_{0C}} + \frac{\rho_S}{2\pi}\ln\frac{l}{r} \right)\frac{dI_C}{dz} + \int_0^z I_C R dz / l \qquad (2)$$

This equation can be simplified to an ordinary differential equation of second order:

$$l^2 \frac{d^2 I_C}{dz^2} + k^2 I_C = -k^2 I_M \qquad (3)$$

with

$$k^2 = \frac{2\rho l^2}{\rho_S r^2}\left(\ln\frac{l}{r} + \frac{1}{r f \rho_S j_{0C}} \right)^{-1} \qquad (4)$$

Applying the boundary condition: $I_C = 0$ at $z = 0$ and l, we obtain the solution of Eq. (3): $I_C = [(1 - \cos k)\sin(kz/l)/\sin k - (1 - \cos(kz/l))]I_M$. The potential drop contributed to the PdH$_x$ electrode is:

$$\Delta E_{\mathrm{PdHx,C}} = \frac{1}{l}\int_0^l I_C R dz = h(k)I_M R \qquad (5)$$

with

$$h(k) = \frac{2}{k}\tan\frac{k}{2} - 1 \qquad (6)$$

The additional resistance contributed to the original value induced by the measuring dc is:

$$R_{\mathrm{A,M}} = h(k)R \qquad (7)$$

2.3. Effect of electrolysis current.

In the ISRM of electrode during electrolysis process, the ec that is collected in the electrode will contribute a potential drop to the measuring signal because the electrode has a resistance. As a primary approximation, supposing the ec (I_E) uniform distributes on the electrode. From a small distance dz at point z, we obtain the relationship between the increment of current in the electrode and j_E: d$I_E = 2\pi r j_E$dz, where j_E is connected with I_E by $j_E = I_E/2\pi rl$. The potential drop across the small distance dz is d$E_E = -I_E R$dz/l. Combining these two equations and integration dE_E with respect to z, we obtain the potential at a point z caused by the electrolysis current collection is $E_E = I_E R(1/3 - z^2/l^2)$, where the fraction 1/3 in the parentheses ensures the average potential to be zero. The potential drop across the electrode is $\Delta E_E = I_E R/2$. This means that the electrode behaves as that with a half value of the original resistance.

The ec also has a concentration-cell effect. Similar to Eq. (3), we have:

$$l^2 \frac{\mathrm{d}^2 I_C}{\mathrm{d}z^2} + k^2 I_C = -k^2 I_E \frac{z}{l} \tag{8}$$

The solution is $I_C = [\sin(kz/l)/\sin k - z/l]I_E$. The potential shift contributed to the external circuit is $\Delta E_{\mathrm{PdHx,C}} = h(k)I_E R/2$. The corresponding additional resistance contributed to the measurement value is the sum of these caused by the electrolysis current collection and its concentration-cell effect:

$$R_{A,E} = \frac{I_E}{2I_M}\big[1 + h(k)\big]R \tag{9}$$

It must be pointed out that ΔE_E appears instantly while ec is applied; whereas $\Delta E_{\mathrm{PdHx,C}}$ delays by a time interval which depends on the electrode diameter and surface properties.[2]

3. DISCUSSION

Combining Eqs. (1), (7) and (9), we obtain the apparent resistance in the ISRM during electrolysis process:

$$
\begin{aligned}
R_{\mathrm{appa}} &= R + R_{A,S} + R_{A,M} + R_{A,E} \\
&\approx \left\{ \left(1 + \frac{I_E}{2I_M}\right)\left[1 + \frac{\rho l^2}{6\rho_S r^2}\left(\ln\frac{l}{r} + \frac{1}{rf\rho_S j_{0C}}\right)^{-1}\right] - \frac{\rho l}{\rho_S r} \right\}R
\end{aligned}
\tag{10}
$$

From this equation, we find that the three measurement errors with different origins can be incorporated to a more uniform expression. On the whole, four dimensionless quantities, i.e. I_E/I_M, l/r, ρ/ρ_S and $rf\rho_S j_{0C}$ determine R_{appa} as shown in the Figure.

First, it is found that the contribution of electrolysis process to the ISRM depends on the direction and magnitude of ec as shown in Fig. (a). If $I_E/I_M > 0$, it will contribute to the measured resistance a positive shift. Otherwise, it will diminish the magnitude of the measured value while $I_E/I_M < 0$. This is the reason of delta-mode current being used to cannel out the electrolysis contribution in experiments. [3,4]

On the other hand, R_{appa} increases with l/r as shown in Fig. (b). It means the length and diameter have

prominent influences on the resistance measurement. This is one of reasons of great value of R_{appa} observed by Carson et al.[2] although they have not predicted it.
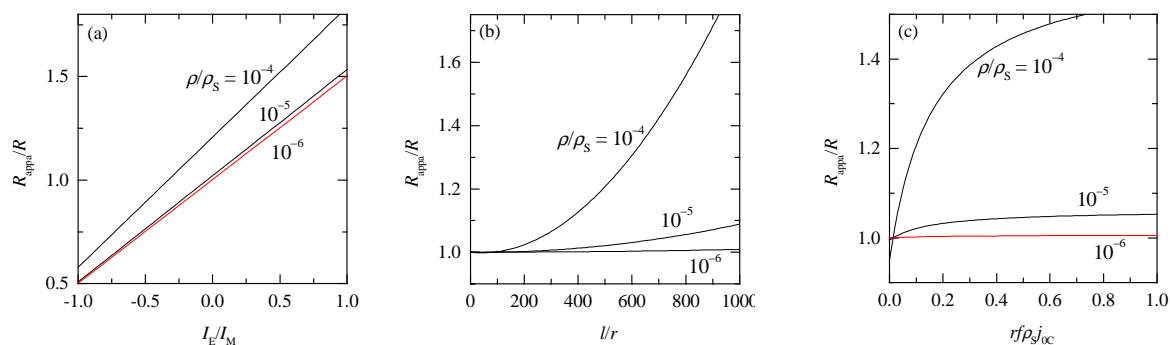

Figure. R_{appa} as functions of (a) I_E/I_M (b) l/r and (c) $rf\rho_S j_{0C}$. The parameters not emphasized are $l/r = 500$, $I_E/I_M = 0$, $rf\rho_S j_{0C} = 0.1$ except cited in each figure.

Figure (c) shows dependences of R_{appa} on $rf\rho_S j_{0C}$. It indicates that the electrode diameter, temperature, electrolyte conductance, electrode roughness and exchange current density of electrode reaction all affect R_{appa}. An electrode with rough surface results in a large value of j_{0V}, hence large values of j_{0C}. At the same time, some additives such as H_2S and thiourea can inhibit the reaction rate of Pd|H electrode, so it is easy to understand that they can diminish R_{appa} as observed experimentally.[2] Another factor is the ecd, a large magnitude of ecd results in great values of j_{0C} and $R_{A,M}$ as the effect of j_{0V}.

Figure also shows that the resistivity ratio ρ/ρ_S has the most important effect. If $\rho/\rho_S < 10^{-6}$, it has only little influence on R_{appa}, otherwise, the additional resistance may not be neglected.

Finally, It must be pointed out that the concentration-cell effect appears only in the single phase PdH_x electrode. In the mixed $\alpha+\beta$ phase, the H chemical potential does not change in PdH_x under the external potential drop[2] and $h(k) = 0$. Even in this case, the electrolysis current collection and electrolyte co-conduction still have contribution to the ISRM, so a low value of I_E/I_M is the necessary condition in the dc method.

Results here are mainly theoretically, their qualitatively aspects are consistent with available experiments.[1,2,4] The quantitative verifications need to be carried out in future experimental works.

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REFERENCES

[1] C.A. Knorr, E. Schwartz, Z. Elektrochem. 39 (1933) 281; 40 (1934) 36.

[2] A.W. Carson et al., Naturwiss 46 (1959) 374; T. Faraday Soc. 56 (1960) 1311; 1324.

[3] D.J. Gillespie, G.N. Kamm, A.C. Ehrlich, P.L. Mart, Fusion Tech. 16 (1989) 526.

[4] T.A. Green, T.I. Quickenden, J. Electroanal. Chem. 368 (1994) 121.

[5] M.C.H. McKubre et al., ib id. 368 (1994) 55; A. Wark et al., ib id. 418 (1996) 199.

[6] A. De Ninno, A. La Barbera, V. Violante, J. Alloy. Compd. 253-254 (1997) 181.

[7] T. Senjuh et al., J. Alloy. Compd. 253-254 (1997) 617.

[8] A.M. Riley et al., J. Electrochem. Soc. 139 (1992) 1342.

[9] W.S. Zhang, X.W. Zhang, H.Q. Li, J. Electroanal. Chem. 434 (1997) 31.