The Electrodissolution Kinetics of Palladium

A NOTE ON THE EFFECT OF CHLORIDE ION CONCENTRATION

By Joan Genescá
Faculty of Chemistry, U.N.A.M. City University, México

and Lluis Victori
Department of Analytical Chemistry, Instituto Químico de Sarriá, Barcelona, Spain

The anodic dissolution of palladium in deoxygenated acidic chloride solutions has been studied and the reaction order determined. A mechanism which is consistent with the empirical rate expression was developed, and is reported.

On account of its corrosion resistance, palladium is used for a variety of applications. However, fundamental kinetic and mechanistic studies of its electrodissolution in acidic chloride media have not received a great deal of attention. The effect of Cl^- and H^+ concentrations on palladium electrodissolution has been studied previously, and a critical pH value of 5.5 was found (1). Above this value the anodic oxidation process was independent of chloride concentration.

In this report, the electrodissolution kinetics of palladium are considered and a mechanism is proposed to explain the behaviour.

Experimental Method

The detailed preparation and pretreatment procedures for the palladium electrode have been described previously, as have the electrochemical cell, the electrode assembly and the investigative procedure (1). The electrolyte was prepared from analytical grade perchloric acid, sodium perchlorate, sodium chloride and doubly distilled water. Its ionic strength was maintained at 1 M by the use of an inert supporting electrolyte, while the chloride concentration was varied. The perchlorate ion was chosen because it is believed that it does not adsorb strongly on palladium, nor does it have a very strong tendency to act as a ligand in complex formation (2). High purity nitrogen was bubbled through the solutions for an hour to de-aerate them, and magnetic stirring was employed. While measurements were being made stirring was stopped, but nitrogen was slowly bubbled through the solution.

The kinetic parameters for palladium electrodissolution were determined at 25°C from steady-state potentiostatic measurements using a Wenking 70HC3 potentiostat. The time taken to reach a pseudo-steady current at each potential varied from 5 to 10 minutes. The surface areas of the electrodes were estimated approximately using the cyclic voltammetry technique, and the results were used to convert current readings to apparent current density values.

Results of Anodic Polarisation

A typical polarisation curve in 0.5 M $HClO_4$, x $NaClO_4$, y $NaCl$ (x+y=0.5M) solution is shown in Figure 1. The first feature observed is the Tafel region (A) followed by a current peak (B) which corresponds to the formation of a PdO film (1, 3). Then the current decreases as the potential increases until a minimum is reached at (C), after which the current again increases with potential, due to chlorine evolution and to the formation of $[PdCl_6]^{2-}$, until a

second peak (D) is attained with the formation of a PdO_2 film (1, 3). Thereafter it decreases to a second current minimum (E) followed by an increase resulting from oxygen evolution.

Effect of Chloride Concentration on Palladium Electrodissolution

The anodic polarisation behaviour of palladium in the electrolytes used is shown in Figure 2. Within the active region the Tafel lines are straight and parallel with a slope of 110 mV/decade. At 650 mV (S.C.E.) the reaction order for chloride is 2.1, the value for the partial electrochemical reaction order, ν, being calculated from the relationship

$$\nu = \left(\frac{\partial \log j}{\partial \log [Cl^-]} \right)_{T,E,[H^+]} \qquad (i)$$

where j is current density, $[Cl^-]$ is the concentration of chloride ions in mol/dm^3, T is the absolute temperature, E is the electrode potential relative to a standard reference electrode
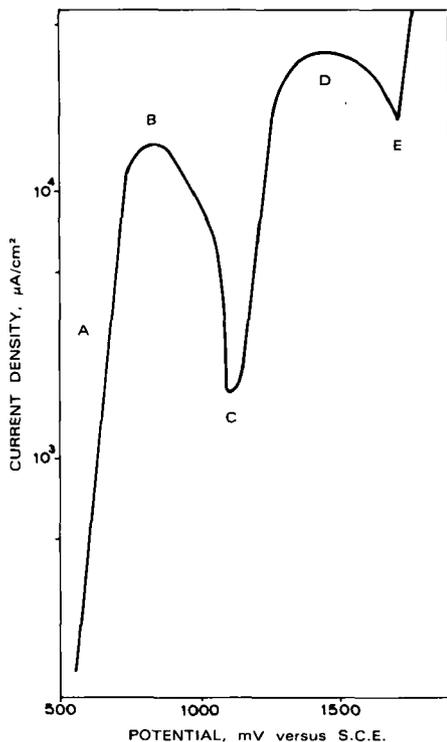

Fig. 1 This characteristic diagram of the polarisation curve of a palladium electrode in 0.5 M $HClO_4$, 0.3 M NaCl, 0.2 M $NaClO_4$ solution at 25°C shows the five main features observed.
    A—Tafel region,
    B—first peak,
    C—current minimum,
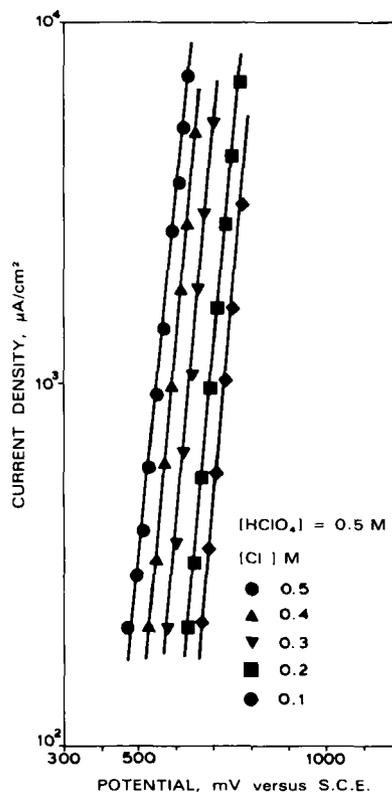   D—second peak,
    E—second current minimum

Fig. 2 The effect of chloride concentration in the Tafel region, showing the electrodissolution rate versus potential at various chloride concentrations for palladium in 0.5 M $HClO_4$, x $NaClO_4$, y NaCl where x + y = 0.5 M
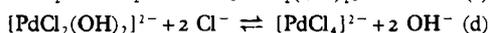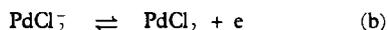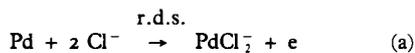
(not the overpotential), and $[H^+]$ the hydrogen ion concentration in mol/dm^3, the last three terms being constant when the measurements are made. Studies of the chloride effect were performed at constant $[H^+] = 0.5$ M.

Discussion

The results reported in (1) correspond to those obtained with different solutions containing the same Cl$^-$ ion concentration, but with varying HClO$_4$ concentrations. There is no dependence of pure palladium electrodissolution on $[H^+]$, in accordance with previous results reported by Heumann and Schurmann (4). The Tafel slopes in the apparent Tafel region are 110 mV/decade, compared to anodic slopes of 120 mV/decade reported for pure palladium in chloride solutions (5, 6). In agreement with the findings of Kratsov and Zelenskii for palladium (5, 6) the reaction order with respect to Cl$^-$ in the apparent Tafel region (A) is 2.1. This suggests the dominant reaction is

$$Pd + 2\,Cl^- = PdCl_2^- + e \qquad (ii)$$

The fact that for a given potential the current density depends on $[Cl^-]^2$ in the active branch indicates that PdCl$_2$ is formed in the primary process of anodic dissolution and subsequently reacts with water to form the complex $[PdCl_2(OH)_2]^{2-}$ (7). This in turn equilibrates with Cl$^-$ ions to form $[PdCl_4]^{2-}$, although the equilibrium point is displaced more towards the former complex. The proposed mechanism is

$$
\begin{aligned}
\text{r.d.s.} \qquad\qquad\qquad & \\
Pd + 2\,Cl^- \;\;\xrightarrow{}\;\; PdCl_2^- + e & \qquad (a) \\
PdCl_2^- \;\;\rightleftharpoons\;\; PdCl_2 + e & \qquad (b) \\
PdCl_2 + 2\,H_2O \;\;\rightleftharpoons\;\; [PdCl_2(OH)_2]^{2-} + 2H^+ & \qquad (c) \\
[PdCl_2(OH)_2]^{2-} + 2\,Cl^- \;\;\rightleftharpoons\;\; [PdCl_4]^{2-} + 2\,OH^- & \qquad (d)
\end{aligned}
$$

The formation of $[PdCl_4]^{2-}$ has been demonstrated by colorimetric analysis (1) and this complex is approximately 10^{11} times more stable than $[Pd(H_2O)_4]^{2+}$ (2).
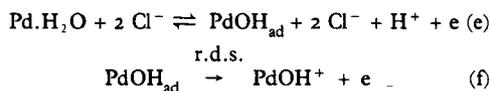
When (a) is the rate determining step, the kinetic parameters predicted by this are

$$j_a = k_a \cdot [Cl^-]^2 \cdot \exp\,(\beta\,FE/RT) \qquad (iii)$$

where j_a is current density, k_a is a constant,

[Cl$^-$] is the concentration of chloride ion in mol/dm^3, β is the transfer constant, F is the Faraday constant, E is the applied electrode potential (that is the equilibrium electrode potential E_e plus the overpotential η) relative to a standard hydrogen electrode, R is the molar gas constant and T the absolute temperature.

It has been assumed that the surface coverage of the intermediate $[PdCl_2^-]_{ad}$ is low and that the Langmuir isotherm is valid. By assuming values of $\beta = 1/2$, the Tafel slope corresponding to equation (iii) is in reasonable agreement with the experimental kinetic parameters obtained for palladium electrodissolution in 1 M HClO$_4$–NaClO$_4$–NaCl solutions. Thus, the proposed mechanism predicts values of 120 mV and 2 for the anodic Tafel slope and the reaction order with respect to the chloride ion concentration, respectively. These calculated values are in reasonable agreement with the experimental data. At the critical pH region, the lack of influence of chloride ion on the electrodissolution of palladium (1) can be interpreted by a OH$^-$ accelerated mechanism proposed by Bockris for iron (8):

$$
\begin{aligned}
Pd.H_2O + 2\,Cl^- \;\rightleftharpoons\; PdOH_{ad} + 2\,Cl^- + H^+ + e & \qquad (e) \\
\text{r.d.s.} \qquad\qquad\qquad\qquad & \\
PdOH_{ad} \;\rightarrow\; PdOH^+ + e & \qquad (f)
\end{aligned}
$$

This mechanism proceeds in competition with mechanisms (a–d). By assuming that step (f) is rate determining, the above mechanism predicts a Tafel slope of $2.3 \times 2/3$ RT/F and seems to be consistent with the experimental anodic Tafel slope obtained, that is 44 mV/decade for chloride solutions (0.5 to 1.0 M) at pH = 5.

There is, however, no experimental evidence for the reaction order with respect to the hydrogen ion concentration of -1 which is predicted by this mechanism.

This last mechanism seems to explain why the electrodissolution rate of palladium in acidic chloride media changes with the increase of pH.

The adsorption of OH$^-$ at a critical pH value allows the passivation process to occur

first. The proposed mechanism implies a competitive adsorption between OH^- and Cl^- with respect to the free sites of the metal surface prior to the discharge reactions. In other words, the formation of $[PdCl_7^-]_{ad}$ is inhibited by the presence on the metal surface of $PdOH_{ad}$, the first step in the anodic passivation of palladium.

Conclusions

Two reaction mechanisms of anodic dissolution of palladium in acidic chloride solutions are proposed, as functions of the pH value. At lower pH, the effect of chloride ion on electrodissolution kinetics increases as the hydrogen ion concentration increases. In a critical pH region, the adsorption of OH^- competes with Cl^-, resulting in the formation of $PdOH_{ad}$ which then inhibits the corrosion process.

References

1 F. Domenech, J. Genescá and L. Victori, *Rev. Metal.*, CENIM, 1978, **14**, (6), 321

2 L. Victori, J. Tomás and F. Malgosa, *Afinidad*, 1975, **32**, 867

3 J. Genescá and L. Victori, *Rev. Coat. Corros.*, 1981, **4**, (4), 325

4 Th. Heumann and R. Schurmann, *Z. Elektrochem.*, 1963, **67**, 601

5 V. I. Kratsov and M. I. Zelenskii, *Elektrokhimiya*, 1966, **2**, 1138

6 V. I. Kratsov and M. I. Zelenskii, *Vestn. Leningr. Univ., Fiz. Khim.*, 1966, **21**, (4), 128

7 J. Llopis, *Catal. Rev.*, 1968, **2**, (2), 161

8 J. O'M. Bockris, D. Drazic and R. Despic, *Electrochim. Acta*, 1961, **4**, 325

A New Generation of Platinum Metals Catalysts

Supported Metal Complexes, Catalysis by Metal Complexes

BY F. R. HARTLEY, Reidel, Dordrecht, 1985, 318 pages, Dfl.165,00/£45.75

Since 1970 a new area of catalysis has emerged in which the catalyst is supported on a polymer or reactive inorganic support. This book reviews the progress that has resulted from this fresh approach, which has been inspired by the desire to keep the advantages of homogeneous catalysis systems by using every metal atom in the catalysed reaction and yet facilitate recovery of the catalyst, especially from liquid phase reaction systems.

Stoichiometric attachment of platinum metals catalysts to reactive sites on supports via covalent bonding, and their cost effective removal after use, could be important factors in their economic viability. For example, the corrosion and plating out problems experienced in the oxidative acetylation of ethylene to vinyl acetate process could in principle be circumvented using this approach. Potential advantages could also accrue from increased selectivity caused either by promoting preferred orientations for the substrate or by controlling the stereochemistry of the catalytic site.

An illustration of the problems experienced with this approach is seen in the rhodium/methyl iodide catalysed carbonylation of methanol. The homogeneous reaction is very clean giving acetic acid, with 99 per cent selectivity. A supported catalyst having both rhodium and a pseudo alkyl halide bonded to a polymer is active, but much less so than its homogeneous counterpart. On continuous use its activity drops due to loss of both rhodium and cocatalyst. An alternative anionic rhodium(I) system supported on polystyrene-poly(4-vinylpyridine) quaternised with methyl iodide has high initial activity but also suffers from rhodium leaching.

Large sections of this book are concerned with the preparation of supported catalyst systems. Further chapters are then devoted to each important type of reaction investigated. For platinum metals catalysts these include hydrogenation, hydrosilylation, carbonylation, hydroformylation and oxidation reactions. The most important commercial applications for this type of catalyst are likely to be where the support is used both to heterogenise the catalyst and to contribute to the total environment of the active site, in a similar manner to that already established in nature for enzyme catalysts. Thus the metal complex and the support would combine to provide a uniquely active and selective catalyst site.

This book consists of a useful review of the present state of the art, but more innovation is required if these techniques are to realise their full potential.   D.T.T.