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Investigations in platinum metal group electrochemistry:
II The Pd(II)–Pd° reduction

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The 'Norbide' boron carbide electrode has been satisfactorily applied to polarographic studies of Pd(II)–Pd° and some other systems involving deposition of metal. By its means the following thermodynamic and kinetic data have been established: standard oxidation–reduction potentials, Pd^{2+}–Pd°, 0·91 V; $Ag^{+}-Ag°$, 0·805 V; stability constants, $PdCl_4^{2-}$, log β_4, 9·38; log K_4, 1·44; $Pd(SO_4)_2^{2-}$, log β_2, 3·16; activation energies, $Pd^{2+}-Pd°$: Q_D, 18·6; $Q°$, 188 kJ $mole^{-1}$. Analytical applications have been briefly examined.

Introduction

Whereas it has been shown that the rotating platinum electrode (RPE) has some application in electrochemical studies of Ir(IV)–Ir(III) systems, the 'Norbide' boron carbide electrode generally offers considerable advantages [1]. In the study of Pd(II)–Pd° couples, the RPE is ineffective due to interference caused by the platinum oxide reduction wave [3]. Studies of the Pd(II) reduction in different media at the 'Norbide' electrode, previously given in summary form [2], are here described in greater detail. All results have been subjected to exhaustive statistical examination for reproducibility and correlation in the manner cited earlier [1].

Experimental

Polarographic equipment including the 'Norbide' electrode, and general procedure have been described previously (1).

Table 1 summarizes preparative and polarographic information on solutions of palladium and other metal compounds examined.

Results and discussion

Palladium(II) perchlorate–palladium° system

Polarography. Reduction waves produced at the 'Norbide' electrode exhibited a sharp rise of current at the decomposition potential, characteristic of a wave for a reduction process involving metal deposition on an inert electrode [4], as would be expected for the likely reaction $Pd^{2+}+2e \rightarrow Pd°$. For such a reversible process [5]

$$E = E_0 + \frac{RT}{nF}\ln f_{Pd^{2+}(x=0)} + \frac{RT}{nF}\ln\frac{C_0}{i_l} + \frac{RT}{nF}\ln(i_l - i) \qquad (1)$$

so that, under given conditions of concentration, C_0, and ionic strength, the slope of the applied

Table 1. Preparative methods and polarographic voltage ranges

Compound	*Supporting electrolytes*	*Solution preparation*	*Voltage range (V v. SCE)*
Pd(II) perchlorate	$HClO_4$ NaCl Li_2SO_4	Repeated evaporation of $Pd(NO_3)_2$ solution to strong fumes with $HClO_4$ until no chloride could be detected	+0·5 to −0·5
$AgClO_4$	$NaClO_4$	Direct dissolution of salt	+0·5 to −0·5
$CuSO_4$	$NaClO_4$ Na_2SO_4	Direct dissolution of salt	+0·4 to −0·5

potential–current curve at its mid-point of $i = 0{\cdot}5 i_l$ is given by

$$-\left(\frac{\mathrm{d}E}{\mathrm{d}i}\right)_{\mathrm{mid}} = \frac{2RT}{nFi_l} \tag{2}$$

from which n can be evaluated.

Similarly, for an irreversible process at the analogous mid-point

$$E_{\mathrm{mid}} = E_0 + \eta_{\mathrm{mid}} + \frac{RT}{\alpha nF}\ln 0{\cdot}5 + \frac{RT}{\alpha nF}\ln f_{\mathrm{Pd}^{2+}(x=0)} + \frac{RT}{\alpha nF}\ln C_0 \tag{3}$$

and

$$-\left(\frac{\mathrm{d}E}{\mathrm{d}i}\right)_{\mathrm{mid}} = \frac{2RT}{\alpha nFi_l}. \tag{4}$$

In practice the majority of potential-current curves did not obey Equation (1) but did obey the normal polarographic equation, $E = E_{1/2} + \frac{RT}{\alpha nF}\ln (i_l - i)/i$, thus suggesting the possible existence of a second diffusion process (of reduced species) comparable in flux with that of the movement of reducible species. This is in distinct contrast to the behaviour of the (reversible) silver system.

The slopes of E v. $\log(i_l - i)/i$ curves yielded a mean 'αn' value of $1{\cdot}50 \pm 0{\cdot}29$ and in the few cases where $E/\log(i_l - i)$ linearity was observed, 'αn' values, determined via Equation (4), were similar. Since coulometry proved the process to be a two-electron reduction, a quasi-reversible process with a small overpotential term was indicated. Deposition of palladium on the 'Norbide' electrode surface was confirmed both microchemically following prolonged electrolyses and by electron microprobe exploration of the electrode surface. Examination of a section revealed no penetration of palladium into the electrode but the palladium was distributed in small discrete clumps or crystallites over the electrode surface with quite clear areas of boron carbide between them. Thus these facts confirmed that the electrode process involved reduction of Pd(II) to metal without inward diffusion of palladium. The only other possible diffusion process appears to be the migration of ad-atoms along the electrode surface to the ultimate deposition sites revealed by the microprobe. However, it seems unlikely that this would not occur in the case of the reversible silver system, which gave polarographic waves with $E/\log(i_l - i)$ linearity. An electrode upon which silver had been deposited did show clumps of metal, but the intervening electrode surface was covered by a thin film of silver. An alternative explanation may be the effect of irreversibility in distorting the curve of the polarographic wave such that it is no longer reflected in a linear $E/\log(i_l - i)$ relationship but fortuitously approximates instead to E v. $\log (i_l - i)/i$ linearity.

Half-wave potentials became more positive with increasing palladium concentration (Table 2) and E_{mid} was linearly correlated with

Table 2. Polarography in the palladium(II) perchlorate–palladium° system using the 'Norbide' electrode: effect of palladium concentration

Pd concentration (all in 0·2*M* $HClO_4$) (*M*)	i_l (*μA*)	i_l/C (*μA l mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)
1×10^{-5}	4·3	430	
5×10^{-5}	18·5±1·3	370	0·145±0·027
1×10^{-4}	37 ±3	370	0·177±0·016
$1{\cdot}5\times10^{-4}$	55 ±3	367	0·195±0·006
2×10^{-4}	76 ±9	380	0·208±0·005

log [Pd^{2+}], in keeping with Equation (3). Thus, non-conformity with Equations (1)–(4) was found only in the general shape of the polarographic wave, possibly explained by the irreversibility effect. As a consequence, the expression $E_{\frac{1}{2}}$ is used instead of E_{mid} in the calculations below.

The equation of the $E_{1/2}$/log[Pd^{2+}] relationship was calculated as $E_{1/2} = (0{\cdot}58\pm0{\cdot}06)+(0{\cdot}10\pm0{\cdot}01)\log[Pd^{2+}]$. The slope value was high for a two-electron reduction process, corresponding to an 'αn' value of 0·58, in contrast to the 1·5 obtained from E *v.* $\log(i_l-i)/i$ plots. From Equation (3), the intercept value, $0{\cdot}58 = {}$'E_0'$+\dfrac{RT}{\alpha nF}\ln 0{\cdot}5+\dfrac{RT}{\alpha nF}\ln f_{pd^{2+}(x=0)}$ where 'E_0' contains a (small) overpotential term. Using the Debye-Hückel law for evaluation of the activity coefficient $E_0 = 0{\cdot}67$ V *v.* SCE or 0·91±0·06 V *v.* NHE: cf 0·987 V in 4M $HClO_4$ [6] or 0·945 V when corrected to zero ionic strength and 0·915 V [7]. The present result is therefore in fair agreement with these values, although it should include a minor activation overpotential term. It suggests that the latter is indeed small, in keeping with the 'αn' value of 1·5.

Increase of temperature brought about an increase of limiting current and a positive shift in potential. Now it may be shown, by a treatment analogous to that of Vlcek's for a dropping mercury electrode [8], that for a solid inert electrode using the simple Nernst model,

$$\log i_l = \log\frac{nFAC_0D_0}{\delta}-\frac{Q_D}{2{\cdot}303RT} \qquad (5)$$

where Q_D is the activation energy for 'diffusion'. Log i_l was shown to be linearly correlated with $1/T$ and the calculated slope was $-(9{\cdot}74\pm0{\cdot}72)\times10^2$. Hence, from Equation (5) $Q_D = 18{\cdot}6\pm1{\cdot}4$ kJ mole^{-1}. Although not necessarily an activation energy solely for diffusion, as it is likely also to involve convective transfer, this value is within the normal range for mass transfer processes.

Similarly, by a treatment parallel to Vlcek's, but for an insoluble reduced species deposited on a solid electrode and when $i = 0{\cdot}5i_l$,

$$\frac{nF\eta_{1/2}}{2{\cdot}303RT} = \log(A^\circ)'-\frac{(Q^\circ-Q_D)}{2{\cdot}303RT} \qquad (6)$$

where Q° is the activation energy for the electrode process at potential E_0 and where, from Equation (3),

$$\eta_{1/2} = E_{1/2}-\left(E_0+\frac{RT}{\alpha nF}\ln 0{\cdot}5+\frac{RT}{\alpha nF}\ln f_{Pd}{}^{2+}+\frac{RT}{\alpha nF}\ln C_{Pd^{2+}}\right). \qquad (7)$$

From equation (6), assuming 'αn' to be constant,

$$\eta_{1/2} = \frac{2{\cdot}303R(A^\circ)'T}{\alpha nF}-\frac{(Q^\circ-Q_D)}{\alpha nF}. \qquad (8)$$

Overpotentials at different temperatures should be calculable via Equation (7) but, although 'αn' values may be determined from E *v.* $\log(i_l-i)/i$ plots and the Debye–Hückel Law employed to derive activity coefficient values, other quantitative information is lacking. Thus, as a two-electron reduction process is involved, charge transfer is likely to occur in more than one step and the overpotential should probably be calculated relative to the standard potential of the rate-determining step with which it is associated. This value is unknown, as is its variation with temperature. Similarly it is probably more correct to use 'αn'/2 (i.e. $n = 1$) values both in overpotential calculations and also in the final evaluation of Q° via Equation (8). Adopting this procedure and assuming a constant E_0 value of 0·915 V [7], a linear relationship of $\eta_{1/2}$ with T was observed: $\eta_{1/2} = 0{\cdot}0075T-(2{\cdot}34\pm0{\cdot}07)$ from which $Q^\circ = 188\pm34$ kJ mole^{-1}. Although the limits of error are appreciable, due mainly to the large standard deviation associated with 'αn', and even considering that this activation energy value should be that associated with the

Table 3. Polarography of the palladium(II)-chloride systems using the 'Norbide' electrode: effect of chloride concentration

Chloride concentration [*all* $10^{-4}M$ *Pd(II) and* 0·2*M* $HClO_4$] (*M*)	i_l (μA)	$E_{1/2}$ (*V v. SCE*)	$\Delta E_{1/2} = (E_{1/2})_s - (E_{1/2})_c$	$\Delta E_{1/2}$ (*second electrode*)
nil	37	$+0{\cdot}179 \pm 0{\cdot}021$	—	—
1×10^{-3}	—	$+0{\cdot}171 \pm 0{\cdot}015$	$0{\cdot}008 \pm 0{\cdot}026$	—
3×10^{-3}	38	$+0{\cdot}163 \pm 0{\cdot}020$	$0{\cdot}016 \pm 0{\cdot}029$	—
1×10^{-2}	35	$+0{\cdot}063 \pm 0{\cdot}031$	$0{\cdot}116 \pm 0{\cdot}037$	$0{\cdot}124 \pm 0{\cdot}017$
3×10^{-2}	36	$-0{\cdot}015 \pm 0{\cdot}014$	$0{\cdot}194 \pm 0{\cdot}025$	—
1×10^{-1}	32	$-0{\cdot}125 \pm 0{\cdot}022$	$0{\cdot}304 \pm 0{\cdot}030$	$0{\cdot}317 \pm 0{\cdot}049$
3×10^{-1}	29	$-0{\cdot}229 \pm 0{\cdot}021$	$0{\cdot}408 \pm 0{\cdot}030$	—
1	—	—	—	$0{\cdot}546 \pm 0{\cdot}054$

charge transfer step having the higher activation energy [9], this calculated value appears unexpectedly high. In the absence of other data for systems such as this, however, it is not possible to go beyond such an opinion and to draw definite conclusions. It may well be that such values are characteristic of almost reversible or 'quasi'-reversible couples at the 'Norbide' electrode: work is continuing on similar systems for classification purposes.

Palladium(II)-chloride systems

For a constant 10^{-4}M palladium concentration, an increase of chloride ion concentration brought about a negative shift of potential (Table 3) and a plot of $\Delta E_{1/2}$ versus log [Cl^-] gave a segmented curve (Fig. 1). This suggested the presence of more than one complex ion, confirmed spectrophotometrically (Fig. 2). In these spectra peaks C and D (279 and 223 nm respectively) are associated with the $PdCl_4^{2-}$ ion [10]. An extract of solid $PdCl_2$ with *iso*-amyl alcohol gave a single peak corresponding to B, suggesting its association with the uncharged $PdCl_2$ species. Since peak A appears at a 1:1 Pd^{2+}/Cl^- concentration ratio, it probably corresponds to the $PdCl^+$ ion but the $PdCl_3^-$ appears to have no associated absorption maximum. Peak C, and therefore the $PdCl_4^{2-}$ ion, became apparent at a chloride concentration of ~0·3M, above which the $\Delta E_{1/2}$/log[Cl^-] plot is linear. The equation of this section of the curve was calculated as: $\Delta E_{1/2} = (0{\cdot}539 \pm 0{\cdot}007) + (0{\cdot}230 \pm 0{\cdot}007) \log[Cl^-]$ based on eighty points, the means of groups of results being shown in Fig. 1.

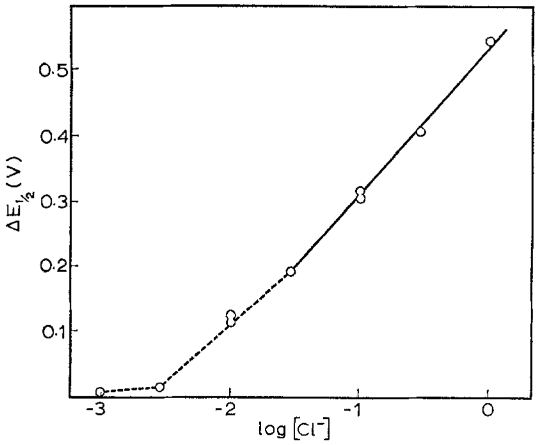

Fig. 1. Palladium-chloride equilibria: plot of $\Delta E_{1/2}$ *v.* log[Cl^-].

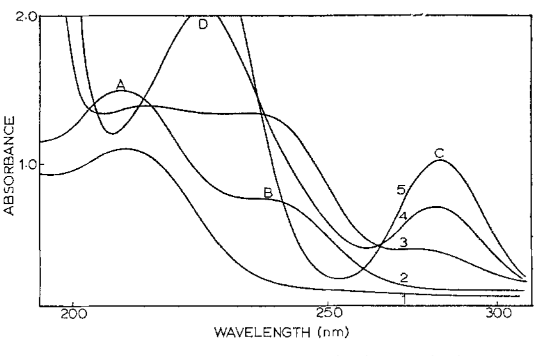

Fig. 2. Absorption spectra of palladium-chloride complexes in solutions all containing 10^{-4}M Pd(II) with

1	2	3	4	5
10^{-4}	10^{-3}	3×10^{-2}	10^{-1}	1M [Cl^-].

It may be shown by a treatment similar to that of Heyrovsky and Kûta [11], but applying Equation (1), that for a reversible process involving reduction of a complex ion, $MX_j^{(n-j)+}$ (having an overall stability constant β_j) with formation of an insoluble deposited reduced species:

$$(E_{1/2})_s-(E_{1/2})_c=\frac{RT}{nF}\ln\beta_j+j\frac{RT}{nF}\ln C_{X^-}+\frac{RT}{nF}\ln\left(\frac{{}_sD_c\delta_s i_{l_s}f_{X^-}}{f_cD_s\delta_c i_{l_c}}\right)$$

where subscripts s and c refer to the 'simple' cation and complex ion respectively.

For an irreversible process:

$$(E_{1/2})_s-(E_{1/2})_c=\frac{RT}{\alpha nF}\ln\beta_j+j\frac{RT}{\alpha nF}\ln C_{X^-}+\Delta\eta_{1/2}+\frac{RT}{\alpha nF}\ln\left(\frac{f_sD_c\delta_s i_{l_s}f_{X^-}}{f_cD_s\delta_c i_{l_c}}\right) \qquad (9)$$

where $\Delta\eta_{1/2}$ is the difference between the polarographic overpotentials for the reduction of the 'simple' and complex ions. Applying the above calculated slope value to Equation (9) and assuming $j = 4$, 'αn' = 1·019±0·030. This result compares well with the mean value of 1·010±0·018 obtained from fifteen E v. $\log(i_l-i)/i$ plots of polarographic waves for 0·1M [Cl^-].

In the last term of Equation (9) it is reasonable to assume that $\frac{f_sD_c\delta_s}{f_cD_s\delta_c}\simeq 1$ and as a logarithm is extremely small. At low chloride concentrations $i_{l_c}\simeq i_{l_s}$ and $f_{Cl^-}\rightarrow 1$; with increasing chloride concentrations i_{l_c} diminishes but so does f_{Cl^-} and $i_{l_s}\cdot f_{Cl^-}/i_{l_c}$ remains substantially constant and equal to unity. Hence the last term of Equation (9) is probably very small and may be neglected. Evaluation of $\Delta\eta_{1/2}$ presents greater difficulties. An approximate $\eta_{1/2}$ may be determined via Equation (7) for the 'simple' cation, but this is not possible for the $PdCl_4^{2-}$–Pd system since no E_0 value at zero ionic strength or $f_{PdCl_4^{2-}}$ for high chloride concentration is available. However, the $E_{1/2}$ temperature coefficients for the two systems were found to be not widely different and consequently $\Delta\eta_{1/2}$ is possibly small. Assuming it to be negligible, then from Equation (9) the intercept value 0·539 = $\Delta E_{1/2} = \frac{RT}{\alpha nF}\ln\beta_4$ and $\log\beta_4$ = 9·38±0·31. It is likely that the approximations assumed in the derivation do not exceed the standard deviation. This result confirms the lower values [12, 13] of numerous previous determinations [6, 12–20] which exhibit considerable scatter and in which the polarographic technique has not been employed.

Linearity of the middle section of the curve (Fig. 1) was also confirmed statistically from sixty-eight points and the equation was established as:

$$\Delta E_{1/2}=(0{\cdot}468\pm0{\cdot}014)+(0{\cdot}178\pm0{\cdot}007)\log[Cl^-].$$

Application of this slope value with the previous 'αn' value of 1·01 to Equation (9) gave $j\simeq 3$, indicating that this section of the curve was related to the $PdCl_3^-$ species. Substitution of the intercept value in Equation (9) gave $\log\beta_3$ = 7·94±0·39 which on subtraction from the $\log\beta_4$ value leads to $\log K_4$ = 1·44±0·50, which is in excellent agreement with previous values [12–14, 20–22].

Palladium(II) sulphate–palladium° system

An increase in sulphate concentration brought about a negative shift of potential (Table 4) and a correlation test confirmed a linear relationship between $\Delta E_{1/2}$ and $\log[SO_4^{2-}]$ and the calculated line equation was:

Table 4. Polarography of the palladium(II) sulphate–palladium° system using the 'Norbide' electrode: effect of sulphate concentration

Sulphate concentration [all $10^{-4}M$ Pd(II) and 0·2M $HClO_4$] (M)	i_l *(μA)*	$E_{1/2}$ *(V v. SCE)*	$\Delta E_{1/2}$
nil	37	0·179±0·021	—
0·1	34	0·146±0·014	0·033±0·025
0·2	29	0·121±0·023	0·058±0·031
0·4	16	0·091±0·015	0·088±0·026
1·0	17	0·078±0·008	0·101±0·022
1·8	9	0·043±0·013	0·136±0·025

$$\Delta E_{1/2} = (0{\cdot}103 \pm 0{\cdot}014) + (0{\cdot}065 \pm 0{\cdot}014)\log[\mathrm{SO}_4^{2-}].$$

Spectra of the solutions revealed only one peak, absent in the palladium perchlorate spectrum, the absorbance of which increased with sulphate concentration (Fig. 3). In ion exchange tests, palladium was taken up from M sulphate solution by a strong base anion exchange resin and was readily eluted by M perchloric acid. These facts suggested the existence of a single anionic species. Application of the above slope value, 0·065, to Equation (9) and substitution of the mean 'αn' value (1·5) obtained from E v. log $(i_1 - i)/i$ plots (all linear) gave $j \simeq 2$, suggesting that the complex was $\mathrm{Pd(SO_4)_2^{2-}}$.

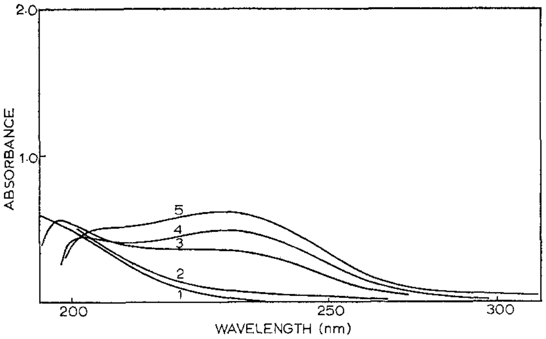

Fig. 3. Absorption spectra of palladium-sulphate complex in solutions all containing 10^{-4}M Pd(II) with

1	2	3	4	5	6
nil	0·01	0·2	0·4	1·0	1·8 M[$\mathrm{SO_4^{2-}}$].

By an argument similar to that used for the $\mathrm{PdCl_4^{2-}}$ complex it may be shown that the last term in Equation (9) is again negligible. Similarly, assuming $\eta_{1/2}$ for reduction of the sulphate complex to be similar to that for the uncomplexed ion, the intercept value, 0·103, $= \Delta E_{1/2} = \dfrac{RT}{\alpha nF} \ln \beta_2$. Using the '$\alpha n$' $= 1{\cdot}80 \pm 0{\cdot}08$ value obtained from the calculated $\Delta E_{1/2}$ v. log [$\mathrm{SO_4^{2-}}$] equation, log $\beta_2 = 3{\cdot}16 \pm 0{\cdot}15$. Bearing in mind the uncertainty of $\Delta\eta_{1/2}$, the result is tentative but no previous value appears to have been reported for the complex. However some qualitative support is available in that addition of a chloride to a solution of the palladium sulphate complex readily produces the $\mathrm{PdCl_4^{2-}}$ ion, confirming the lower stability of the $\mathrm{Pd(SO_4)_2^{2-}}$ complex.

Silver(I) perchlorate—silver° system

A comparative investigation of the silver(I) perchlorate–silver° system was made in order to check the performance of the 'Norbide' electrode on a reversible system involving deposition. Satisfactory behaviour was found as the following observations show.

The majority of the polarographic waves, produced at the 'Norbide' electrode has a highly restricted straight section (Fig. 4) and gave linear $E/\log(i_1 - i)$ plots in conformity with Equation (1). Values of "αn" determined via Equation (2) using the slope of the polarographic wave at its mid point and measured by the mirror tangent construction method, had values close to unity ($n_{\mathrm{mean}} = 0{\cdot}92 \pm 0{\cdot}30$).

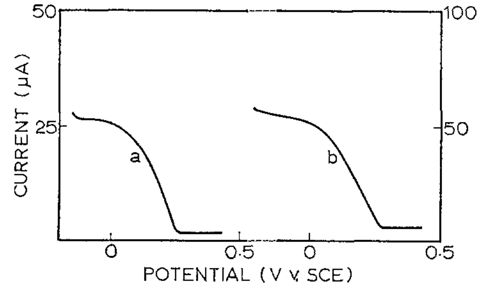

Fig. 4. Typical reduction waves of silver perchlorate at the 'Norbide' boron carbide electrode obeying:
(a) E v. $\log(i_1 - i)$ linearity (10^{-4}M $\mathrm{Ag^+}$ in 0·1M $\mathrm{NaClO_4}$)
(b) E v. $\log(i_1 - i)/i$ linearity (2×10^{-4} M $\mathrm{Ag^+}$ in 0·1M $\mathrm{NaClO_4}$).

Linear relationships were observed at constant ionic strength between limiting current and silver

Table 5. Polarography of the silver(I) perchlorate–silver° system using the 'Norbide' electrode: effect of silver concentration

Silver concentration (all 0·1M $NaClO_4$) (M)	i_l (*μA*)	i_l/C (*μA l mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)
2×10^{-6}	$0{\cdot}58 \pm 0{\cdot}05$	290	$0{\cdot}092 \pm 0{\cdot}011$
1×10^{-5}	$1{\cdot}90 \pm 0{\cdot}11$	190	$0{\cdot}144 \pm 0{\cdot}006$
2×10^{-5}	$4{\cdot}45 \pm 0{\cdot}3$	222	$0{\cdot}172 \pm 0{\cdot}009$
5×10^{-5}	$10{\cdot}4 \pm 0{\cdot}9$	208	$0{\cdot}194 \pm 0{\cdot}010$
1×10^{-4}	$20{\cdot}3 \pm 2{\cdot}1$	203	$0{\cdot}219 \pm 0{\cdot}014$
2×10^{-4}	$47{\cdot}5 \pm 3{\cdot}1$	237	$0{\cdot}242 \pm 0{\cdot}013$
5×10^{-4}	$110{\cdot}0 \pm 4$	220	$0{\cdot}283 \pm 0{\cdot}007$

concentration (Table 5) and between E_{mid} and $\log[Ag^+]$. The latter was in accordance with Equation (3) and a correlation test indicated a significance level better than 0·001 with the equation of the line: $E_{\text{mid}} = (0{\cdot}532 \pm 0{\cdot}009) + (0{\cdot}0776 \pm 0{\cdot}0020) \log [Ag^+]$. The slope value is high for a reversible one-electron reduction process, corresponding to a value of 0·77. However, applying this to Equation (3) and introducing the Debye–Hückel Law for evaluation of the activity coefficient, then $E_0 = 0{\cdot}564$ V *v.* SCE or $0{\cdot}805 \pm 0{\cdot}009$ V *v.* NHE. Although based only on reduction waves, i.e. it is likely to have a negative bias, this value is comparable with the standard electrode potential value of 0·799 V *v.* NHE [23]. The general conformity of these results to the polarographic wave equations (1) and (2) for reduction involving deposition of an insoluble reduced species on a solid inert electrode confirms the validity of derivation based on the simple Nernst concentration gradient model and lends support to the arguments used in the case of palladium systems. However, a small proportion of the waves had a more extensive straight section (Fig. 4) and tended to linear E *v.* $\log(i_1 - i)/i$ plots with n values greater than unity ($n_{\text{mean}} = 1{\cdot}6$). No difference could be discerned between the conditions producing the two types of waves.

Copper(II)–Copper° system

A brief investigation of the copper(II)–copper° system was made to evaluate its possible interference in analysis of the platinum metals.

Polarographic waves at the 'Norbide' electrode exhibited a linear E *v.* $\log(i_1 - i)/i$ relationship over much of the curve and had no resemblance to a wave involving deposition. However, the mean electron exchange value was $1{\cdot}95 \pm 0{\cdot}50$, confirming the $Cu^{2+} \rightarrow Cu^{\circ}$ reduction. Half-wave potentials for 10^{-4}M $CuSO_4$ were −0·13 V and −0·15 V *v.* SCE in 0·1M $NaClO_4$ and Na_2SO_4 respectively.

Analytical applications

With the 'Norbide' electrode, consecutive determinations of iridium and palladium become possible in chloride and sulphate solutions.

Table 6. Reduction half-wave potentials (V v. SCE) of 10^{-4}*M metal ions using the 'Norbide' and rotating platinum electrodes*

	Supporting electrolyte—Molarity														
	$HClO_4$		*$NaClO_4$*		*$NaNO_3$*		*HCl*		*NaCl*		*NaBr*		*H_2SO_4*	*Li_2SO_4 or Na_2SO_4*	
Metal system	0·1	1·0	0·1	1·0	0·1	1·0	0·1	1·0	0·01	0·1	0·1	0·7	0·36	0·1	1·0
Iridium															
$IrCl_6^{2-}$–$IrCl_6^{3-}$	0·58	0·61	0·61	0·66	0·63 (0·63)	(0·67)									
$IrBr_6^{2-}$–$IrBr_6^{3-}$	0·53	0·55	0·56	0·60							0·55	0·58			
Ir(IV)–Ir(III)perchlorate	0·85 (0·86)	0·93 (0·92)*													
Ir(IV)–Ir(III)sulphate													0·73 (0·74)		
Palladium															
Pd(II)–Pd°	0·18	0·17							0·06	−0·13				0·15	0·08
Silver															
Ag(I) perchlorate–Ag°			0·22	0·23											
Ag(I) sulphate–Ag°														0·18	
Iron															
Fe(III)–Fe(II)	0·41	0·28					0·39	0·20							
Copper															
Cu(II)–Cu°			−0·13											−0·15	

* Values in parentheses are for the rotating platinum electrode.

However, the presence of silver interferes with palladium waves in sulphate and perchlorate solutions and, although the copper wave is too negative to cause interference in sulphate and perchlorate solutions, the negative shift of the palladium wave in 0·1M NaCl makes it almost coincident with that of copper. As a consequence, consecutive determinations of iridium, palladium and silver are not feasible and silver cannot be determined in the presence of palladium in any of these solutions. This becomes clear from the half-wave potentials given in Table 6.

Reproducibility of the 'Norbide' electrode

In this and the previous paper of the series [1] note was made of slight irreproducibility of the electrode during metal deposition. For example, palladium usually deposited with a linear E *v.* $\log(i_1 - i)/i$ relationship but occasionally with E linearly related to $\log(i_1 - i)$ while silver acted in the reverse manner. Attempts were made to discover the reasons for this behaviour by examination of the electrode surfaces and by testing other 'Norbide' samples. No obvious correlation could be found between surface properties and performances and, indeed, in the course of this work it was found that electrodes made from 'Norbide' rods purchased after 1967 often displayed more marked irreproducibility. This took the form of large residual currents in acid solutions thus rendering the electrode useless for investigating iridium(IV) and palladium(II) reduction processes. Those electrodes in such batches that gave small residual currents could also give distorted, seemingly highly irreversible, iridium(IV)–iridium(III) reduction waves in perchlorate media contrary to the results from earlier supplies.

Various cleaning treatments designed to change the nature of the surface were tried: these included boiling with hydrochloric and nitric acids separately and mixed, boiling with dilute sodium hydroxide or hydrofluoric acid, heating in an atmosphere of chlorine at 500–700°C and 900°C, and both anodic and cathodic electrolytic treatment in hydrochloric acid. Of these, only those involving nitric acid effected any substantial improvement to the residual current curves and to the reduction waves. Work is continuing to discover the cause of and a cure for the anomalies of later supplies of 'Norbide', and boron carbide from other sources is undergoing test.

In the meantime the present results must still be regarded as reliable in view of the stringent electrochemical and statistical tests applied, but caution should be exercised in accepting results from an untested boron carbide electrode.

Conclusions

In general, results obtained by the use of selected 'Norbide' boron carbide electrodes (Table 7) were found, where comparisons were possible, to conform with values established by other workers.

In the case of the reversible Ag^+–Ag° system, the waves conformed to the appropriate polarographic equation. This was also generally true in the case of the Pd(II)–Pd° systems but certain anomalies were found, such as the unexpected E *v.* $\log(i_1 - i)/i$ linearity. Results also confirm

Table 7. Summary of results

System or compound		*E_0 (V v. NHE)*	*log β_2*	*log β_4*	*log K_4*	*Q_D kJ mole^{-1}*	*Q^0 kJ mole^{-1}*
Pd^{2+}–Pd°	Determined	0·91 ±0·06				18·6±1·4	188±34
	Published	0·915 [7]				—	—
$PdCl_4^{2-}$	Determined	0·64 ±0·01		9·38 ±0·31	1·44±0·50		
	Published	0·61 [12]		10·42 [12]	1·43 [21, 22]		
$Pd(SO_4)_2^{2-}$	Determined	0·82 ±0·01	3·16±0·15				
Ag^+—Ag°	Determined	0·805±0·009					
	Published	0·799 [23]					

and extend the analytical possibilities of the boron carbide electrode in polarography. Extension of its application to other platinum metals and gold is being made.

List of symbols

A	Area of the working electrode
$(A^\circ)'$	Apparent frequency factor of the Arrhenius relationship
'αn'	Nominally the product of the transfer coefficient, α, and the number of electrons, n, involved in an electrochemical process. In practice it is the value obtained from the slope $\frac{RT}{\alpha nF}$ of the line E $v.$ $\ln(i_l - i)/i$ or $v.$ $\ln(i_l - i)$
β_j	Product of dissociation constants of successive complexes: $K_1 \times K_2 \times \ldots \times K_j$
C_0	Bulk concentration in the aqueous phase of species undergoing electrochemical reduction or oxidation
D_0	Diffusivity of that species in the aqueous phase immediately adjacent to the electrode surface
δ	Thickness of a diffusion layer
$E_{1/2}$	Half-wave potential, at which $i = i_l/2$ in a polarographic wave of the form $E = E_{1/2} + \frac{RT}{\alpha nF} \ln(i_l - i)/i$
E_{mid}	Potential at which $i = i_l/2$ in a wave of the form $E = E_{\text{mid}} + \frac{RT}{\alpha nF} \ln(i_l - i)$
$\Delta E_{1/2}$	Displacement of half-wave potential caused by complexing of reducing species
$\eta_{1/2}$	Overpotential at the half-wave potential, $E_{1/2}$
η_{mid}	Overpotential at E_{mid}
f	Activity coefficient, e.g. $f_{\text{Pd}^{2+}(x=0)}$ the activity coefficient of Pd^{2+} species in the aqueous phase at the electrode surface
i_l	Limiting current
i	Current at any stage of the electrochemical processes governed by E $v.$ $\ln(i_l - i)$ or $\ln(i_l - i)/i$ relationships
j	Number of complexing ligands associated with a cation—e.g. for PdCl_3^-, $j = 3$
Q°	Arrhenius activation energy of the electrochemical process of a reduction at a working electrode [8]
Q_{D}	Arrhenius activation energy of the diffusion stage of an electrochmical reduction [8]

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