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Investigations in Platinum Metal Group Electrochemistry: I Some iridium (IV) - iridium (III) systems

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The 'Norbide', boron carbide, electrode has been shown to be exceptionally good in terms of its chemical inertness, rapid response and high hydrogen overvoltage. It has been applied especially in potentiometric and polarographic studies of the Ir(IV)–Ir(III) system in various media. By its means, supported by evidence from use of other cathodes, certain previous work has been confirmed and standard or formal redox potentials of the following systems have been determined: Ir(IV)–Ir(III)–ClO_4^- (M $HClO_4$), 1·27 V; Ir (IV)–Ir(III)–SO_4^{2-} (0·18M H_2SO_4), 1·08 V; Ir(IV)–Ir(III)–PO_4^{3-} (0·3M H_3PO_4), provisionally 0·99 V; $IrCl_6^{2-}$–$IrCl_6^{3-}$ (0·1M $NaClO_4$ or NaCl), 0·899 V; $IrBr_6^{2-}$–$IrBr_6^{2-}$ (0·1M $NaClO_4$ or NaBr), 0·838 V. The potentials fall in the expected sequence. The possibility of analytical application of the 'Norbide' and rotating platinum electrode has also been examined.

Introduction

Conventional polarography at a mercury cathode is generally unsuitable for the study of platinum metal electrochemistry since the effective potentials may range from values far more positive than the dissolution potential of mercury (>0·45 V *v.* SCE) to values that are negative when certain complexing agents are present. The appearance of catalytic hydrogen waves [1] may also be troublesome. The rotating platinum electrode (RPE) has had restricted application [2–4] but, although it may be used at potentials as positive as +1·0 V, it is limited at the more negative end of the range by the small hydrogen overvoltage on platinum. Mazza and Trassatti [5] have reported the possible use of tungsten, titanium and tantalum carbides and of titanium nitride as electrode materials but reproducible and mechanically-sound electrodes are difficult to prepare.

Voltammetric studies by Mueller *et al* [6, 7] demonstrated that a commercial form of boron carbide, 'Norbide', behaves very suitably as an inert electrode with a working range of +1·1 to ~ −1·0 V in acid solution, mainly due to the high hydrogen overvoltage associated with it. This material is therefore an obvious choice for noble metal electrochemical studies, where it had received very limited application [8].

A more extensive examination of the 'Norbide' electrode, especially applied to certain iridium and palladium systems and supported by other electrochemical evidence, has already been reported in summary form [9], and in this communication the system is described in depth. All results have been subjected to exhaustive statistical examination and reproducibility (standard deviations with at least 9 degrees of freedom) and correlation (usually to 0·001 probability levels) data are quoted.

Experimental

Polarography. A Tinsley, mark 19 instrument, calibrated potentiometrically, was used, normally at an applied voltage rate of 0·15 V/min.

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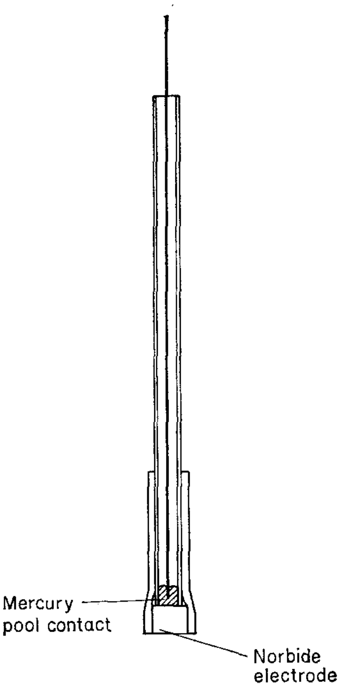

Fig. 1. The 'Norbide' electrode.

Electrodes and general procedure. For rotating platinum electrode (RPE) studies, a standard design [10] was employed. The 'Norbide' electrode was prepared by mounting a cylindrical section, 6 × 7·8 mm diameter of 'Norbide' rod in thick-walled polythene tubing of smaller internal diameter, which had been softened in boiling water. The polythene was cut back flush with the electrode surface, which was then ground and polished with diamond paste (1 μ) on a polishing pad to produce the working surface. The complete electrode (Fig. 1) was fixed and the solution was stirred by a magnetic stirrer running at constant speed. The electrolytic cell was completed with a saturated calomel electrode (SCE) separated by a lithium acetate-agar bridge. To obtain reduction waves in the +1·2 to 0 V potential range, the polarograph was run in 'reverse' with the electrode connections interchanged and the potential dial moving in the direction from −1·2 to 0 V.

The 'Norbide' electrode was repolished and washed successively with alcohol, water and some of the solution before each polarographic run. In general, each fresh surface behaved reproducibly but occasional samples behaved in a more erratic but obvious manner: such cases usually behaved normally after repolishing. Resistances of the cells fell between 3,000–4,000 Ω. The resistances were significant, particularly in the case of the 'Norbide' electrode, which

Table 1. *Preparative methods and polarographic voltage ranges*

Compound	*Supporting electrolytes*	*Solution preparation*	*Voltage range* (*V*)
$(NH_4)_2IrCl_6$	$NaClO_4$ $HClO_4$ $NaNO_3$	Direct dissolution of salt	+1·0 to zero
K_2IrBr_6	$NaClO_4$ $HClO_4$ $NaBr$	Direct dissolution of salt	+1·0 to zero
Ir(IV) perchlorate	$HClO_4$	Evaporation of stock $IrCl_6^{2-}$ solution [23] to fumes with $HClO_4$ followed by dilution with or without N_2 purge	+1·2 to −0·5
Ir(IV) sulphate	H_2SO_4	Evaporation of stock $IrCl_6^{2-}$ solution to fumes with H_2SO_4–$HClO_4$ followed by dilution	+1·0 to zero
$Fe(ClO_4)_3$	$HClO_4$ HCl	Evaporation of $Fe(NO_3)_3$ solution to fumes with $HClO_4$ followed by dilution	+0·8 to −0·5

sustained relatively large currents, and appropriate *iR* corrections were necessary.

Table 1 summarizes preparative and polarographic information on solutions of iridium compounds examined.

Potentiometry. Due to aquation problems previously encountered with the hexachloroiridate(IV)-hexachloroiridate(III) $(\mathrm{IrCl}_6^{2-}\text{–}\mathrm{IrCl}_6^{3-})$ system [11, 12] the titration procedure, rather than direct potentiometry, was generally adopted. A Pye pH meter/millivoltmeter model 290 was used for measuring potentials indicated by platinum or rhodium electrodes of standard design or by a 'Norbide' electrode, as prepared for polarography, all with respect to SCE via lithium acetate-agar bridge. Solutions of hexachloroiridate(IV) and hexabromoiridate(IV) each dissolved in sodium perchlorate solution, were titrated with a standard hydroquinone solution $(2{\cdot}59 \times 10^{-3}\mathrm{M})$.

Portions of a hexachloroiridate(III) solution were each evaporated with sulphuric acid and perchloric acid, some just to faint fumes (to give the blue-purple coloured complex [13, 14]) and others to a higher temperature ('overheated'). After the solutions had been diluted, potentiometric titrations and ion exchange column tests were carried out and absorption spectra plotted on boiled and unboiled solutions in each batch.

Results and Discussion

Hexachloroiridate(IV)-hexachloroiridate(III) system

Polarography. Reduction waves produced both at the rotating platinum electrode (RPE) and 'Norbide' electrode conformed with the polarographic equation for a reversible process involving a soluble reduced species at a solid electrode [15]: plots of potential against log $(i_l - i)/i$ were linear and gave electron exchange values very close to unity (Table 2), in contrast to the findings of Pshenitsyn *et al.* [2], who had concluded that the process was irreversible.

Linear relationships were observed between limiting current and hexachloroiridate(IV) concentration for both RPE and 'Norbide' electrode (correlation tests indicated significance levels better than 0·001) whilst the half-wave potential remained substantially constant with changing depolarizer concentration at constant ionic strength (Table 2*a*). Reduction half-wave potentials obtained with the 'Norbide' electrode are statistically similar to those obtained with the RPE for the same supporting electrolyte concentration and in general were ~0·05 V more negative than those reported by Pshenitsyn. For the 'Norbide' electrode oxidation waves were 0·074±0·004 V more positive than the corresponding reduction waves (Fig. 2) but this value was virtually the same as the difference exhibited in the case of the reversible $\mathrm{Fe}^{3+} - \mathrm{Fe}^{2+}$ system and seems to be characteristic of the technique rather than the result of any irreversibility of the system. The mean half-wave potential of oxidation and reduction waves was 0·89± 0·01 V (*v.* NHE) for 0·1M sodium perchlorate solution and, in general, an increase of supporting electrolyte concentration resulted in a positive shift of half-wave potential (Table 2*b*).

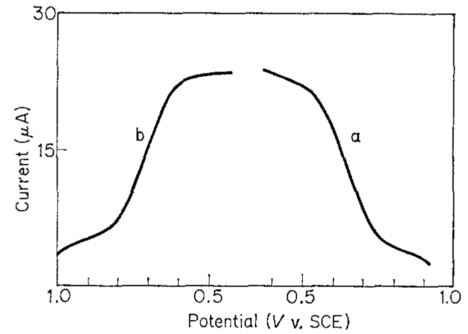

Fig. 2. Polarographic reduction (*a*), and oxidation (*b*), waves of 10^{-4}M $(\mathrm{NH_4})_2\mathrm{IrCl_6}$ in 0·6M $\mathrm{NaClO_4}$ at the 'Norbide' electrode.

Potentiometry. Potentiometric titration curves were virtually identical for rhodium and 'Norbide' indicating electrodes. Steady potentials were rapidly attained in both cases and titrations were stoichiometric for a one-electron reduction process, confirmed by the slope of the *E v.* $\log[\mathrm{IrCl}_6^{2-}]/[\mathrm{IrCl}_6^{3-}]$ plot. The formal redox potential of the hexachloroiridate(IV)-hexachloroiridate(III) system in 0·1M sodium perchlorate at 25°C was found to be 0·899± 0·001 V (*v.* NHE), cf 0·903 V [11]. Thus, assum-

Table 2. Polarography of the hexachloroiridate(IV)–hexachloroiridate(III) system

(a) Effect of $(NH_4)_2IrCl_6$ *concentration—reduction waves*

$(NH_4)_2IrCl_6$ concentration (*M*)	*RPE (all in M* $NaNO_3$*)* i_l (*μA*)	i_l/C (*μA l. mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)	*n*	*'Norbide' electrode (all in 0·1 M* $NaClO_4$*)* i_l (*μA*)	i_l/C (*μA l. mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)	*n*
$2{\cdot}5\times10^{-5}$	0·89±0·02	35·6	0·678±0·006	0·96±0·04				
$5{\cdot}0\times10^{-5}$	1·92±0·10	38·4	0·683±0·005	0·93±0·08	7·6±0·2	152	0·610±0·003	0·90±0·08
$7{\cdot}5\times10^{-5}$	2·96±0·06	39·5	0·684±0·003	0·94±0·02				
$1{\cdot}0\times10^{-4}$	3·95±0·28	39·5	0·673±0·003	1·03±0·05	16·9±1·0	169	0·612±0·006	0·96±0·06
$2{\cdot}0\times10^{-4}$					30·0±0·85	150	0·623±0·004	0·98±0·05
$2{\cdot}5\times10^{-4}$	9·65±0·07	38·6	0·664±0·002	0·99±0·04	37·0±2·5	148	0·629±0·007	0·94±0·06
$4{\cdot}0\times10^{-4}$					64·0±2·0	160	0·622±0·005	1·06±0·04
$5{\cdot}0\times10^{-4}$	18·60±0·86	37·2	0·653±0·004	0·94	78·0±2·0	156	0·626±0·015	0·91±0·06
$1{\cdot}0\times10^{-3}$	38	38	0·664±0·002	0·92±0·02				

(b) Effect of supporting electrolyte on half-wave potential (V v. SCE) and electron exchange value of $10^{-4}M$ $(NH_4)_2IrCl_6$*—reduction waves*

Electrolyte	*Molarity*	0·1	0·2	0·4	0·6	1·0
'Norbide' electrode						
$NaClO_4$	$E_{1/2}$	0·612±0·006	0·627±0·004		0·656±0·008	0·665±0·004
	n	0·96±0·06	0·97±0·07		0·97±0·07	1·02±0·06
$HClO_4$	$E_{1/2}$	0·578±0·008	—	0·595±0·003	—	0·607±0·003
	n	1·04±0·08	—	1·14±0·05	—	1·08±0·04
$NaNO_3$	$E_{1/2}$	0·627±0·002	—	—	—	—
	n	0·91±0·05	—	—	—	—
RPE						
$NaNO_3$	$E_{1/2}$	0·625±0·004	—	—	—	0·673±0·003
	n	0·98±0·04	—	—	—	1·03±0·05

ing the diffusion coefficients' contribution to the half-wave potential to be negligible, the polarographic value compares favourably with the potentiometric formal redox potential for this ionic strength. There was similar agreement at higher ionic strengths and all the tests suggest that the electrode process is a reversible one, in contrast to previous conclusions [2]. The results verify the work of George *et al.* [11] and confirm that other, more positive, electrode potential values [16–19] were in error.

Hexabromoiridate(IV)-hexabromoiridate(III) system

Polarography. As in the case of the analogous hexachloroiridate(IV)–hexachloroiridate(III) system, reduction and oxidation waves gave linear *E v.* log $(i_l - i)/i$ graphs with slopes corresponding to electron exchange values close to unity: n_{mean} = 0·96±0·11 (reduction waves), 1·02±0·14 (oxidation waves). For reduction waves, a linear relationship was observed between limiting current and hexabromoiridate(IV) concentration (significance level better than 0·001) (Table 3*a*). The mean half-wave potential of oxidation and reduction waves was 0·845±0·010 V (*v.* NHE) for 0·1M sodium perchlorate and in general an increase of supporting electrolyte concentration resulted in a positive shift (Table 3*b*).

Potentiometry. Titres in all cases were stoichiometric for a one-electron reduction. *E v.* log$[\mathrm{IrBr}_6^{2-}]/[\mathrm{IrBr}_6^{3-}]$ slopes were close to unity in the cases where a 'Norbide' electrode was used, but appreciably greater (1·3–1·4) in the case of a rhodium electrode which, however, responded less rapidly to potential changes. This suggested that results from the 'Norbide' electrode were more reliable.

Application of the Debye Hückel Law to the Nernst expression for the potential of the hexabromoiridate(IV)–hexabromoiridate(III) system at 25°C shows that

$$(E_0' - E_0)^{-1} = 6{\cdot}65\, I^{-1/2} + 2{\cdot}19 \times 10^8 a \qquad (1)$$

where E_0' is the formal redox potential at any given ionic strength *I*, and *a* is the 'distance of closest approach'. The best values of E_0 were obtained from the fortuitous linear relationship between E_0' and $I^{1/3}$, thence confirmed in Equation (1). Resulting values of E_0 are: 0·815±0·001 V and 0·805±0·001 V (both *v.* NHE) at the rhodium and 'Norbide' electrodes respectively. Of the two, the latter is considered to be the better and is in agreement with polarographic results. The distance of closest approach

Table 3. Polarography of the hexabromoiridate(IV)–hexabromoiridate(III) system using the 'Norbide' electrode

(a) Effect of K_2IrBr_6 concentration—reduction waves

K_2IrBr_6 concentration(M) (all in 0·1M $NaClO_4$)	*i_l (μA)*	*i_l/C (μA l. mmole^{-1})*	*$E_1/_2$ (V v. SCE)*
5×10^{-5}	4·95±0·45	99	0·548±0·011
1×10^{-4}	10·0±0·4	100	0·567±0·004
2×10^{-4}	21·2±1·3	106	0·574±0·011
4×10^{-4}	40·0±1·0	100	0·572±0·001
5×10^{-4}	50·0±2·0	100	0·581±0·008

(b) Effect of supporting electrolyte on half-wave potential (V v. SCE) of 10^{-4}M K_2IrBr_6—reduction waves

Molarity	0·1	0·4	0·7	1·0
$NaClO_4$	0·559±0·004	0·594±0·006	0·608±0·016	0·601±0·005
$HClO_4$	0·529±0·007	0·552±0·004	0·545±0·004	0·550±0·004
NaBr	0·554±0·004	0·577±0·008	0·580±0·006	—

and coefficient of $I^{-1/2}$ derived from pooled results applied to Equation (1) are respectively $4{\cdot}4\pm0{\cdot}5\times10^{-7}$ mm and $6{\cdot}6\pm0{\cdot}2$.

The value of E_0, some 0·17 V more negative than a previous result [20], reverses the order with respect to the hexachloroiridate(IV)–hexachloroiridate(III) system, making it less positive than that of the latter. As the behaviour of iridium towards halide ions is similar to that of platinum, this reversed order is that expected by analogy with the Pt(IV)–Pt(II)–halogen system sequence, where redox potentials increase in the ligand series $I<Br<Cl<F<H_2O$ [21]. There is little doubt that errors in previous values resulted from the presence of appreciable concentrations of the aquated iridium(III) bromo-complex in the system.

Iridium(IV)-iodide mixtures.

Attempts to prepare iodoiridic acid, by dissolution of iridium(IV) hydroxide in hydriodic acid, were abortive: oxidation of iodide occurred with the formation of iodine, as observed by Malatesta [22].

Similarly, addition of hexachloroiridate(IV) to an iodide solution produced a pale yellow solution, the potential of which corresponded to that of the I_2–I^- system. All the evidence indicated that the hexaiodoiridate(IV)–hexaiodoiridate(III) system [19] is a fictitious one.

Iridium(IV)–irdium(III)–perchlorate system

Polarography. With the 'Norbide' electrode, and solutions that had or had not been purged with nitrogen, a double wave was produced (Fig. 3). The RPE gave a single wave that proved to be identical with the more positive ('first') wave of those at the 'Norbide' electrode.

(*i*) *First wave.* The difference between the oxidation and reduction half-wave potentials was $0{\cdot}076\pm0{\cdot}013$ V, and applied potential *v.* log $(i_l-i)/i$ plots were linear with slopes corresponding to $n = 1{\cdot}07\pm0{\cdot}12$ (reduction) and $1{\cdot}08\pm0{\cdot}07$ (oxidation waves). Results in Table 4 show that at both electrodes, half-wave potentials became similarly less positive with decreasing ionic strength (especially at $I<0{\cdot}1$M) and, although current and concentration followed a good linear relationship with no significant change of half-wave potential at a given ionic strength, the ratio $i_l/[\mathrm{Ir(IV)}]$ fell at low concentrations of supporting electrolyte. The positive slope of the $E_{1/2}$ versus $\sqrt{I}$ plot resembles that from potentiometric work and is characteristic of an anionic iridium species.

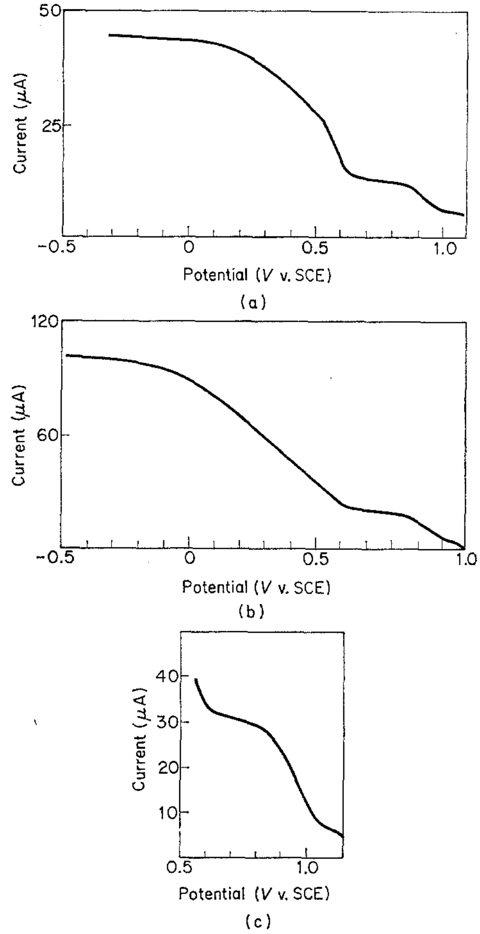

Fig. 3. Polarographic ('Norbide' electrode) reduction waves of iridium solutions, diluted to M $HClO_4$ after oxidation in fuming perchloric acid:

(*a*) 2×10^{-4}M Ir(IV) (*b*) 5×10^{-4}M Ir(IV) (*c*) as *b*, first wave only.

The evidence suggests that the species undergoing reduction in a nitrogen-purged solution is a hydroxy-cation of the type $Ir(H_2O)_{6-n}(OH)_n{}^{(4-n)+}$ in which *n* increases with decreasing ionic strength (especially of hydronium ion). This may even apply in M perchloric acid where the formal redox potential proposed is $1{\cdot}27\pm0{\cdot}02$ V (*v.* NHE) although the sensitivity

Table 4. *Polarography of the iridium(IV)–iridium(III)-perchlorate system*

(*a*) *Effect of iridium concentration—reduction waves, without nitrogen treatment*

Iridium concentration (M)	*RPE (all in* 0·18*M HClO$_4$)* i_l (μA)	i_l/C (μA *l. mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)	*'Norbide' electrode (all in M HClO$_4$)* *First wave* i_l (μA)	i_l/C (μA *l. mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)	*Second wave* i_l (μA)	i_l/C (μA *l. mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)
5×10^{-5}	0·23±0·02	4·6	0·905±0·007	1·82±0·22	36·4	0·931±0·012	4·78±0·15	95·6	0·587±0·003
1×10^{-4}	0·43±0·03	4·3	0·912±0·004	3·39±0·30	33·9	0·930±0·005	12·36±0·45	123·6	0·543±0·018
2×10^{-4}	—	—	—	6·40±0·4	32·0	0·936±0·007	28·9±0·4	144·6	0·520±0·006
$2·5\times10^{-4}$	1·13±0·07	4·5	0·907±0·003	—	—	—	—	—	—
$3·5\times10^{-4}$	—	—	—	11·3±0·2	32·2	0·940±0·011	51·0±0·5	146	0·400±0·008
5×10^{-4}	2·08±0·06	4·2	0·887±0·002	17±1·6	33·4	0·956±0·019	75±1·0	150	0·430±0·017

(*b*) *Effect of nitrogen treatment ('Norbide' electrode only)—reduction waves*

	First wave i_l (μA)	i_l/C	$E_{1/2}$	Second wave i_l (μA)	i_l/C	$E_{1/2}$
5×10^{-4} *M* Ir (in *M* HClO$_4$)	16±2·1	—	0·992±0·011	71±6·9	—	0·475±0·045

(*c*) *Effect of supporting electrolyte concentration on* 5×10^{-4}*M Ir solutions—reduction waves*

HClO$_4$ (M)	*RPE* $E_{1/2}$ (*V v. SCE*)	*'Norbide' electrode* *First wave* i_l (μA)	$E_{1/2}$ (*V v. SCE*)	*Second wave* i_l (μA)	$E_{1/2}$ (*V v. SCE*)
0·05	—	14·0±0·3	0·814±0·004	no wave	
0·1	0·861±0·005	14·1±0·6	0·854±0·006	8±2	0·115±0·011
0·2	—	15·6±0·9	0·905±0·010	37±7	0·199±0·023
0·25	0·895±0·006	—	—	—	—
0·5	0·918±0·003	16·1±0·5	0·923±0·008	56±7	0·283±0·027
0·1+ 1·0M Mg(ClO$_4$)$_2$	—	15·0±0·4	0·941±0·005	61±0	0·430±0·017
1·0	0·918±0·002	16·7±1·6	0·956±0·019	75±1	0·456±0·029
1·0+ 1·0M NaClO$_4$	0·933±0·005	—	—	—	—

of $E_{1/2}$ to changes of hydrogen ion concentration is decreasing at such high acid concentrations. The quoted potential is more positive than that of the hexachloroiridate(IV)–hexachloroiridate(III) system, fitting with the expected sequence [21].

(*ii*) *Second wave*. The slope of the second wave changed with iridium concentration: at higher concentrations it obeyed an E *v*. $\log(i_l - i)/i$ relationship but this passed into the resemblance of an E *v*. $\log(i_l - i)$ line at lower values (Fig. 3). However, even after prolonged electrolysis, an electron-probe microanalysis revealed no trace of deposited iridium, in contrast to the result of equivalent tests with palladium. Irreversibility of the wave was demonstrated by the difference between anodic and cathodic waves ($0{\cdot}101 \pm 0{\cdot}012$ V) and the value of 'αn' ($0{\cdot}28 \pm 0{\cdot}01$) obtained at higher iridium concentrations. There was correlation between i_l and [Ir(IV)] but distinctly non-linear, the limiting current falling sharply both with decreasing iridium concentration and ionic strength. Half-wave potentials became markedly more positive with decreasing iridium concentration. Since this wave disappeared at perchloric acid concentrations below 0·05M but was restored with magnesium perchlorate it was considered that the wave was a function of perchlorate ion and certainly not of iridium or even hydrogen ion: it probably indicates reduction of perchlorate, possibly catalysed by the iridium species in solution. Evidently this process had little effect on the reduction Ir(IV)→Ir(III) demonstrated at the first wave.

Potentiometry. Potentiometric titrations of Ir(IV)–perchloric acid mixtures have already been discussed [23]. Further evidence to support the conclusions that reasonably volatile but associated oxidizing species, removed by lengthy nitrogen purging, are produced during fuming of iridium compounds with perchloric acid is provided from the polarographic investigations, especially on the first wave. In these, no significant change of limiting current occurs with the nitrogen treatment but the small positive shift of half-wave potential can be explained by the dissociation and volatilization of the oxidizing species from the iridium(IV) in the solution. Presumably, the oxidants (say, chlorine or its oxides) have half-wave potentials too positive to be revealed under the oxygen evolution reaction.

Iridium(IV)-iridium(III) sulphate systems

Polarography. For iridium taken to the blue-purple oxidation stage and diluted without boiling, reduction waves exhibited linearity of limiting current with iridium concentration at constant ionic strength, using both RPE and 'Norbide' electrodes. However, half-wave potentials became less positive and 'αn' values decreased with increasing iridium concentration, the potentials for the two electrodes overlapping one another (Table 5). Correlation tests established a linear relationship between half-wave potential and log[Ir(IV)] with significance level better than 0·001 for the results of each electrode. But gradients of the $E_{1/2}$ *v*. log[Ir(IV)] plots differed and half-wave potentials were significantly dissimilar for common concentrations of iridium. Nevertheless, correlation tests on combined results for the two electrodes at constant ionic strength revealed a linear relationship between $E_{1/2}$ and 'αn' with significance level much better than 0·001. A possible explanation of these phenomena is that the product of electrode reduction is adsorbed and influences the rate of the electrode process [24]. Higher concentrations of depolarizer would give increased adsorption and lower rates of reaction. The different surface properties of the two electrodes, with the 'Norbide' (a sintered product) probably having fewer active sites than the platinum, may

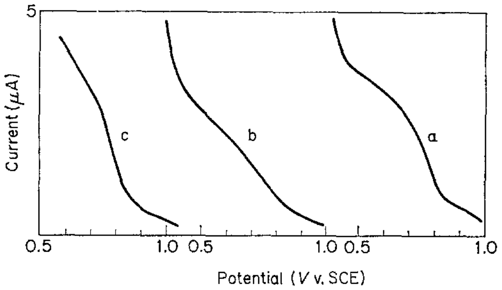

Fig. 4. Polarographic (RPE) reduction waves of iridium previously oxidized in sulphuric acid solution to:
(*a*) blue stage and diluted only (*b*) blue stage, diluted and boiled (*c*) overheated pink stage and diluted only.

Table 5. Polarography of the iridium(IV)–iridium(III)–sulphate systems

(a) Effect of iridium concentration in solutions taken to blue-purple stage, diluted to 0·36*M* H_2SO_4 *but not boiled—reduction waves*

Iridium concentration (M)	*RPE*				*'Norbide' electrode*			
	i_l (*µA*)	i_l/C (*µA l. mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)	*'αn'*	i_l (*µA*)	i_l/C (*µA l. mmole*$^{-1}$)	$E_{1/2}$ (*V v. SCE*)	*'αn'*
$2{\cdot}5\times10^{-5}$	0·46±0·03	18·4	0·770±0·010	1·09±0·08	—	—	—	—
$5{\cdot}0\times10^{-5}$	0·96±0·03	18·3	0·749±0·0	0·92±0·09	—	—	—	—
$7{\cdot}5\times10^{-5}$	1·56±0·06	20·8	0·751±0·005	0·91±0·06	—	—	—	—
$1{\cdot}0\times10^{-4}$	1·98±0·10	19·8	0·744±0·015	0·93±0·07	7·2±0·3	72	0·726±0·002	0·77±0·04
$2{\cdot}5\times10^{-4}$	—	—	—	—	20·8±1·8	83·2	0·690±0·008	0·67±0·04
$5{\cdot}0\times10^{-4}$	10·7±0·2	20·4	0·704±0·002	0·73±0·04	40·5±2·7	81·0	0·669±0·012	0·61±0·07
$7{\cdot}5\times10^{-4}$	—	—	—	—	61·2±4·5	81·6	0·653±0·007	0·52±0·05

(b) Effect of supporting electrolyte concentrations on $2{\cdot}5\times10^{-4}$ *M Ir solutions*

H_2SO_4 *Concentration (M)*	*'Norbide' electrode*		
	i_l (*µA*)	$E_{1/2}$ (*V v. SCE*)	*'αn'*
0·18	18·8±0·6	0·697±0·003	0·63±0·04
0·54	18·0±0·7	0·716±0·003	0·66±0·04
1·08	18·2±0·3	0·717±0·004	0·60±0·03
1·62	8·7±0·3	0·729±0·004	0·57±0·04

(c) Effect of overheating—solution taken to pink-purple stage

	RPE			*'Norbide' electrode*		
	i_l (*µA*)	$E_{1/2}$ (*V v. SCE*)	*'αn'*	i_l (*µA*)	$E_{1/2}$ (*V v. SCE*)	*'αn'*
1×10^{-4}M Ir in 0·36M H_2SO_4	1·91±0·06	0·779±0·005	1·23±0·05	—	—	—
$2{\cdot}5\times10^{-4}$M Ir in 0·36M H_2SO_4	—	—	—	19·5±0·9	0·707±0·009	0·53±0·03

result in different adsorption characteristics. Thus, reaction sites on the 'Norbide' surface would tend to be blocked sooner, inducing lower reaction rates than in the case of the platinum, where alternative sites would remain available longer. For the 'Norbide' waves, this would result in greater apparent irreversibility with a more negative half-wave potential for the same iridium concentration, as was observed. For constant iridium concentration there was a trend to more positive half-wave potentials with increasing ionic strength, consistent with the shift for an anionic system.

When iridium solutions, taken to the blue oxidation stage, were diluted and boiled, the polarographic waves were modified. They assumed a rather indefinite shape and probably consisted of more than one wave (Fig. 4*b*).

Overheated solutions of iridium, cooled and diluted without boiling, gave reduction waves with diffusion currents similar to those for unboiled blue-oxidation-stage solutions of the same iridium concentration (Fig. 4*a*, *c*) but the half-wave potentials were rather more positive.

Potentiometry. A summary of the results of

Table 6. Summary of potentiometric results from Ir(IV)-sulphate systems

Trials	*Oxidation stage*	*Number of inflexions*	*Titration curve*	*Ion exchange tests —species present*
Batch 1	blue-purple (*a*) unboiled	1	non-stoichiometric	completely anionic
	(*b*) boiled	2	stoichiometric	cationic *and* anionic
Batch 2	pink-purple (*a*) unboiled	?	non-stoichiometric	completely anionic
	(*b*) boiled	2	non-stoichiometric	cationic *and* anionic

potentiometric titrations and ion-exchange tests of variously-prepared sulphate solutions are given in Table 6. In all cases boiling of the diluted solutions produced partial transformation to a cationic form. For the batch 1 trials, absorption spectra (Fig. 5) exhibited maxima at 580 and 555 nm for the unboiled and boiled solutions respectively. During titration of the unboiled solution, the absorption maxima remained stationary with respect to wavelength but, in the case of the boiled solution, it gradually changed to ~530 nm. Ion-exchange tests on the reduced, unboiled solution after titration indicated the presence of only anionic Ir(III) species. In the case of the boiled solution after reduction, both anionic and cationic iridium(III) species were present, indicating that reduction proceeds in two stages as follow:

$$\mathrm{Ir_a^{IV}} + \mathrm{Ir_c^{IV}} \xrightarrow[\text{stage 1}]{} \mathrm{Ir_a^{III}} + \mathrm{Ir_c^{IV}} \xrightarrow[\text{stage 2}]{} \mathrm{Ir_a^{III}} + \mathrm{Ir_c^{III}}$$

(where a = anionic c = cationic).

Only these blue-purple boiled solutions gave titres which were stoichiometric for a one-electron reduction, as observed by Pollard [25]. The blue-purple iridium solutions evidently contain decomposition products of perchloric acid which are readily removed by boiling. Analysis of the titration curves for these boiled blue-purple solutions yielded a formal redox potential of +0·86 V (*v*. SCE) and $n > 1$ for the anionic section, whereas for unboiled solutions $E_0' = 0{\cdot}80$ with $n < 1$. The mainly irreversible polarographic waves had given reduction half-wave potentials ranging from 0·65 to 0·78 V, the latter value corresponding to waves with *n* very close to unity, indicating the formal redox potential to be more positive than 0·80 V. Amendment of the slopes of the titration curves to give some E_0' value between 0·80 and 0·86 V would cause both *n* values to move nearer to unity. Thus, on this basis and assuming similar anionic species in the boiled and unboiled solutions, an approximate formal redox potential of 0·84 V (*v*. SCE) or 1·08±0·03 V (*v*. NHE) in 0·18M sulphuric acid is proposed. The iridium(IV) sulphate anionic complex has low stability as evidenced by its ready conversion to the cationic state on boiling and the difficulty of isolation [13, 14]. As it is consequently less stable than the hexachloroiridate(IV) ion, the potential for the Ir(IV)–Ir(III) sulphate system should fall between that for the chloro system and that for the aquo cationic system. That the observed sequence of potentials

$$\mathrm{Ir^{IV}\text{–}Ir^{III}}\ \text{cationic} > \mathrm{Ir^{IV}\text{–}Ir^{III}}\ \text{sulphate} > \mathrm{IrCl_6^{2-}\text{–}IrCl_6^{3-}} > \mathrm{IrBr_6^{2-}\text{–}IrBr_6^{3-}}$$

is completely in keeping with that anticipated

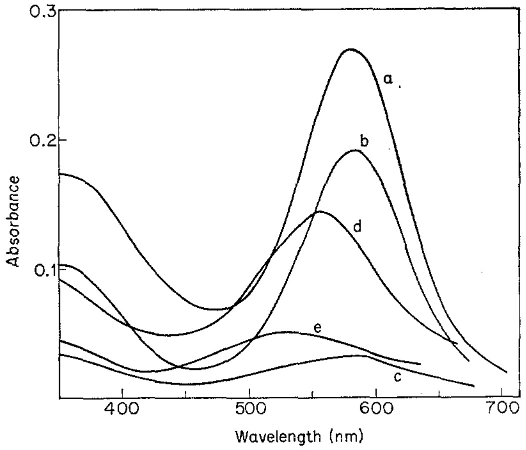

Fig. 5. Absorption spectra of blue iridium-sulphate complexes. Unboiled solution: (*a*) before titration (*b*) and (*c*) during titration; boiled solution: (*d*) before titration (*e*) during titration.

gives further confirmation of the newly-determined values for the iridium systems.

For the batch 2, overheated, pink-purple solutions, whether boiled or unboiled, the titres were excessive. This was in agreement with Pshenitsyn [13] who considered that the decomposition products of perchloric acid accumulate at these excessive temperatures. Since boiling the diluted solution did not reduce the titre appreciably, whereas prolonged nitrogen treatment did, and since the polarographic diffusion current was similar to that of the blue-purple solution, it is probable that the situation is similar to that for the iridium perchlorate system. Thus, at higher oxidation temperatures, perchloric acid decomposition product(s) probably forms some association with the iridium species, which is not broken down by simple boiling.

Iridium(IV)–iridium(III)–phosphate system

A preliminary investigation was made using the RPE on phosphate solutions, prepared by evaporating hexachloroiridate(III) with excess orthophosphoric acid containing a trace of perchloric acid and diluting. The dilutions, followed by warming to hydrolyse polyphosphoric acids, provided various concentrations of iridium(IV) in 0·3M orthophosphoric acid as orange solutions (λ_{max} = 333 nm) containing anionic species only. Plots of E *v.* $\log(i_l - i)/i$ were excellently linear, 'αn' values and half-wave potentials remained constant over a wide range of iridium concentrations ('αn' = 0·85±0·04 and $E_{1/2}$ = 0·695±0·004 V *v.* SCE) and the Ilkovic equation was obeyed well (i_l/C = 30·2 μAl.mmole^{-1}). Overheating during the evaporation led to blue-purple solutions, presumably similar to those of Pshenitsyn [13, 14] containing only anionic iridium. Polarographic reproducibility of these solutions was poor but 'best' results were: 'αn' = 0·74±0·04, $E_{1/2}$ = 0·748±0·004 V *v.* SCE.

The reduction processes are evidently reasonably reversible with respective formal reduction potentials (*v.* NHE) likely to be slightly more positive than the 0·94 (orange form) and 0·99 (blue-purple form) obtained from the half-wave potentials.

Table 7. Polarography of iron(III)–iron(II) system using the 'Norbide' electrode (a) Effect of ferric iron concentration—reduction waves in 0·1M $HClO_4$

Fe(III) concentration (M)	i_l *(μA)*	i_l/C *(μA 1. mmole^{-1})*	$E_{1/2}$ *(V v. SCE)*
5×10^{-5}	5·6±0·1	112	0·430±0·003
1×10^{-4}	11·7±0·2	117	0·429±0·005
2×10^{-4}	20·9±0·6	105	0·411±0·003
3×10^{-4}	35·4±0·2	118	0·413±0·005
4×10^{-4}	41·5±2·0	104	0·412±0·011
6×10^{-4}	64·0±0·5	106	0·411±0·002

(b) Effect of supporting electrolyte on half-wave potential (V v. SCE) of 2×10^{-4}*M Fe(III)*

Electrolyte	*Parameter*	*Molarity*			
		0·05	0·1	0·5	1·0
$HClO_4$	$E_{1/2}$ (V *v.* SCE)	—	0·411±0·003	0·355±0·007	0·277±0·009
	'αn'		0·96±0·03	0·43±0·0	0·30±0·03
HCl	$E_{1/2}$ (V *v.* SCE)	0·416±0·004	0·394±0·003	0·296±0·004	0·200±0·004
	'αn'	0·87±0·01	0·70±0·02	0·33±0·03	0·30±0·03

Iron(III)-Iron(II)systems

A comparative investigation of the ferric-ferrous couple in acid media was made in order to check the performance of the 'Norbide' electrode on a reversible system and to evaluate iron's possible interference in any iridium analysis. In practice, the electrode behaved reasonably well, as the following observations show.

For 10^{-4}M ferric solutions in 0·1M perchloric acid, oxidation half-wave potentials were more positive than the corresponding reduction values with a mean difference of $0{\cdot}047 \pm 0{\cdot}009$ V. Applied potential *v.* $\log(i_l - i)/i$ plots were linear and gave electron exchange values close to unity: $n_{\text{mean}} 1{\cdot}05 \pm 0{\cdot}05$ (reduction) and $0{\cdot}84 \pm 0{\cdot}06$ (oxidation). For higher perchloric acid concentrations, the 'αn' values decreased considerably and the waves became apparently irreversible. It was a feature of the waves that the decomposition potentials remained substantially constant while the half-wave potentials became more negative by the virtue of the decreasing slope. The effect was slightly more pronounced in the case of hydrochloric acid as supporting electrolyte.

Application of the Debye-Hückel Law to the relationship $E_{1/2} = E_0 + \frac{RT}{nf} \ln D_R\delta_0 f_o/D_0\delta_R f_R$ gives, when no complexing occurs and the product aB is unity for both oxidized and reduced forms,

$$\Delta E = E_o - E_{1/2} = 0{\cdot}149\sqrt{I}/n\alpha\,(1+\sqrt{I}).$$

Assuming E_o (*v.* SCE) = 0·429 V, plots of the difference, ΔE, *v.* $\sqrt{I}/n\alpha(1+\sqrt{I})$ derived from data given in Table 7 were shown to be linear with intercepts of zero within experimental error. Slopes were $0{\cdot}10 \pm 0{\cdot}01$ and $0{\cdot}14 \pm 0{\cdot}01$ in perchloric and hydrochloric acids respectively. It should be noted that the data in Table 7 obey remarkably linear relationships between ΔE and ionic strength, I, but this is due to the perhaps fortuitous experimental relationship between 'αn' and $I^{-1/2}$.

Despite the spreading of the waves associated with decreasing values of 'αn', the values of $E_{1/2}$ show that little interference should be encountered in examination of iridium solutions unless the concentrations of iron(III) are relatively high, as demonstrated in Fig. 6.

Analytical applications

In the polarographic work, linearity of limiting current with concentration was observed in almost all cases for both the RPE and 'Norbide' electrode, suggesting the possibility of analytical applications.

With the RPE, reduction polarograms were obtained for iridium(IV) in chloride, perchlorate and sulphate solutions without interference from platinum(IV), rhodium(III) and palladium(II).

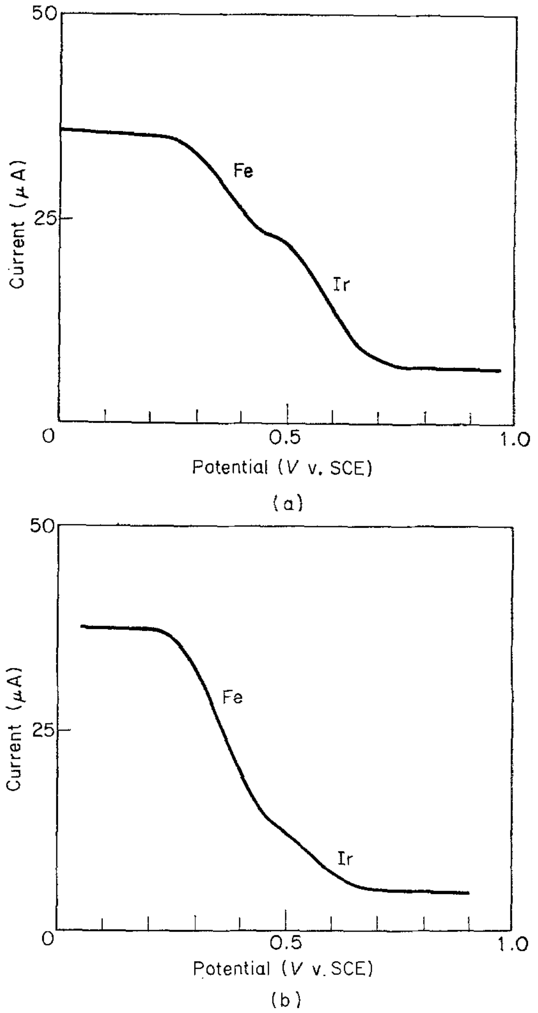

Fig. 6. Polarograms ('Norbide' electrode) of solutions containing (*a*) 10^{-4}M IrI_6^{2-} and 10^{-4}M Fe(III) in 10^{-1}M HCl (*b*) 5×10^{-5}M $IrCl_6^{2-}$ and 2×10^{-4}M Fe(III) in 10^{-1}M HCl.

This group of metals gave no reduction waves prior to the appearance of the hydrogen wave and produced no modification of the iridium reduction waves. Thus this electrode appears to offer a means of determining iridium at low concentrations in a variety of solutions with a minimum of interference. Using the sample d.c. technique a satisfactory working range appears to be $10^{-5}\rightarrow10^{-3}$M.

With the 'Norbide' electrode, satisfactory polarographic waves were produced for iridium(IV) without interference from palladium(II), silver(I), copper(II) or iron(III) in dilute perchlorate solution. However, in 0·1M chloride solution, although iridium(IV) and iron(III) waves could be resolved at low concentrations of the latter, at higher concentrations of iron(III) differentiation of the two individual waves became more difficult (Fig. 6).

This appears to set the working limits at $10^{-5}\rightarrow2\times10^{-4}$M of iridium provided that a concentration of 10^{-4}M iron(III) is not exceeded.

As examples of analytical procedures at the RPE, iridium can be determined in 100 mg samples of platinum–iridium alloy or rhodium sponge by taking the metals into solution by standard methods (respectively, dissolution in aqua regia and evaporation with 33% hydrochloric acid, and fusion with 10 g of zinc metal under ammonium chloride followed by removal of zinc in dilute sulphuric acid and then dissolution of the residue in 5 ml of hot 98% sulphuric acid containing 2·66% w/v of lithium sulphate). After taking up in 50 ml of 0·1M hydrochloric acid or after fuming with 1 ml of perchloric acid, and cooling and diluting to 50 ml, polarograms can be obtained in the range 1 to 0 V. The method of standard additions is satisfactory for both determinations.

Conclusions

It has been established that the 'Norbide', boron carbide, electrode can be effectively employed in the potentiometry and polarography of the platinum metals (as represented by iridium and palladium [26]). Used as an indicating electrode in potentiometry, it has been found generally superior to platinum and rhodium in its speed of response and its stability.

In polarography it was more extensively applicable than the rotating platinum electrode in its greater potential range afforded by the appreciable hydrogen overpotential. Residual current curves were flat and reasonably smooth, in contrast to the findings of Hartley and Axelrod for boron carbide from an alternative source [27]. The waves produced by the 'Norbide' electrode in general conformed to the appropriate polarographic equations and, where comparison was made, they were similar to those obtained using the rotating platinum electrode. However, a few of the results were anomalous, such as those for the iridium(IV)–iridium(III) sulphate system. These anomalies may be due to the peculiarities of the electrode process, which is perhaps different from that at a metallic electrode. The 'Norbide' electrode appears to be a sintered product with a discontinuous surface, which possibly modifies some stage in the normal process.

Besides providing apparently reliable thermodynamic and possibly kinetic information as in Table 8, the 'Norbide' electrode offers a useful

Table 8. Summary of formal electrode potentials

	E°_{formal} (*V v. NHE*)			
	Published	*Potentiometry*	*Polarography*	*'nα'*
Ir(IV)–Ir(III)–ClO_4^- (M $HClO_4$)	—	0·82[23]	1·27	1
Ir(IV)–Ir(III)–SO_4^{2-} (0·18M H_2SO_4)	—	1·08	—	—
(0·36M H_2SO_4)	—	—	1·01	0·6–1·0
Ir(IV)–Ir(III)–PO_4^{3-} orange form	—	—	0·94 0·3M	0·85
blue form	(1·08) [26]	—	0·99 H_3PO_4	0·75
$IrCl_6^{2-}$–$IrCl_6^{3-}$(0·1M $NaClO_4$ or NaCl)	0·903 [11]	0·899	0·89	1
$IrBr_6^{2-}$–$IrBr_6^{3-}$ (0·1M $NaClO_4$ or NaBr)	1·023 [20]	0·838	0·84	1
(zero ionic strength)	0·99 [20]	0·805	—	—

analytical tool. Extension of its application to other platinum metals and gold is being made.

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