Electrochemical reduction of $Pt(CN)_4^{2-}$ ions in molten sodium-potassium cyanide eutectic

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The reduction of $Pt(CN)_4^{2-}$ ions was studied in a NaCN–KCN eutectic melt by means of chronopotentiometry and cyclic voltammetry over the temperature range 510–580° C. The reduction to $Pt(CN)_4^{4-}$ was shown to be a reversible process. The density of the NaCN–KCN eutectic melt was determined as a function of temperature.

1. Introduction

Interest in the electrochemistry of molten cyanides arose from precious-metal extraction work conducted in this laboratory [1, 2]. To the authors' knowledge, the only publications concerned with the electrochemistry of molten cyanides were in connection with precious-metal plating [3–5]. Molten cyanides are excellent solvents for metals of the platinum group because they form stable complexes.

This study is an attempt to elucidate the electrochemistry of molten cyanides containing a small amount of platinum. Platinum was added as potassium chloroplatinite (K_2PtCl_4) pellets. It reacted instantaneously with molten cyanide to form the Pt(II) cyanide complex

$$K_2PtCl_4 + 4CN^- \rightarrow Pt(CN)_4^{2-} + 2K^+ + 4Cl^-. \quad (1)$$
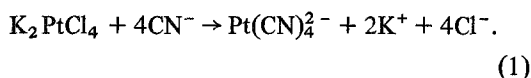
Work by von Winbush [6] showed that cyanide ions act as a reducing agent by forming cyanogen

$$2CN^- \rightarrow (CN)_2 + 2e. \quad (2)$$
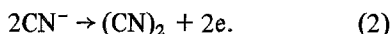
Recently, Lessing and Fouché [7] showed that cyanogen in turn reacts with CN^- ions to form dicyanamide according to the reaction

$$(CN)_2 + CN^- \rightarrow N(CN)_2^- + C. \quad (3)$$
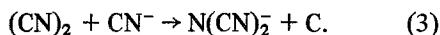
The redox potential of a cyanide melt is then determined by the following equilibrium:

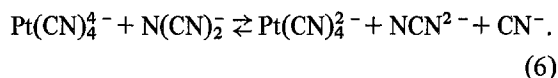$$N(CN)_2^- + 2e \rightleftarrows NCN^{2-} + CN^- \quad (4)$$

i.e. by the dicyanamide/cyanamide ratio. The amount of dicyanamide in the melt is therefore proportional to the amount of platinum added initially [8].

Applying Lessing's findings to a platinum melt would lead to the formation of the Pt(O) complex
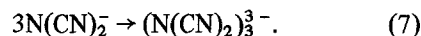
$$Pt(CN)_4^{2-} + 3CN^- \rightarrow Pt(CN)_4^{4-} + N(CN)_2^- + C \quad (5)$$
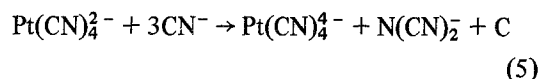
and subsequently to equilibrium between Pt(II) and Pt(O):

$$Pt(CN)_4^{4-} + N(CN)_2^- \rightleftarrows Pt(CN)_4^{2-} + NCN^{2-} + CN^-. \quad (6)$$

The presence of both Pt(II) and Pt(O) in cyanide melts has been confirmed spectroscopically by de Haas and Fouché [8].

Lessing [7] found also that dicyanamide polymerizes continuously:

$$3N(CN)_2^- \rightarrow (N(CN)_2)_3^{3-}. \quad (7)$$

This means that the equilibrium between Pt(O) and Pt(II) in Equation 6 is upset, and that a continuous shift to the left takes place, depending on the rate of trimerization.

The electrochemical reduction of Pt(II) cyanide has been studied by means of chronopotentiometry and linear-scan voltammetry from 510–580° C. In the absence of a standard reference electrode, a titanium quasi reference electrode (QRE) was used.

2. Experimental

2.1. *Density measurements*

Analar KCN and NaCN (Merck) were used to prepare the cyanide eutectic (53 wt.% NaCN). The salts were stored in vacuum desiccators. All preparative work was done inside a glove box with an argon-controlled atmosphere.

The density of the (Na, K) CN eutectic was determined by means of a buoyancy technique described by Janz and Lorenz [9]. Titanium sinkers (99·7% Ti, ICI) were used for the density measurements. Each sinker weighed about 15 g. The density and the expansion coefficient of titanium were taken respectively as $4·507\,g\,cm^{-3}$ and $9·6 \times 10^{-6}\,(^{\circ}C)^{-1}$ at 538° C.

In order to eliminate errors due to the upthrust of the suspension wire by the surface tension forces, short pieces of 0·05 mm diameter platinum wire were used for the KNO_3 melts, and 0·1 mm titanium wire for the cyanide melts. These short pieces were attached to 0·1 mm diameter platinum wire connected to the hook of a precision balance (Mettler, type H20T).

Density measurements were made in molten KNO_3 to test the density apparatus. The measured density of molten KNO_3, as a function of temperature, is given by the equation

$$\rho_{KNO_3} = 2·1202 - 7·437 \times 10^{-4}\,t \pm 0·002\ (S.D.)$$

where t is in $^{\circ}$ C; the density was determined between 351 and 432° C. This result is in good agreement with the density reported by Janz and Lorenz [9].

2.2. *Electrochemical measurements*

Alumina crucibles (Degussit, volume 35 cm^3) were used to contain the cyanide melts. The NaCN–KCN eutectic mixture was mixed with silicon before filtering [10]. Platinum was added to the filtered eutectic in the form of potassium chloroplatinite pellets which instantaneously reacted with the cyanide melt. The loaded crucibles were placed in glass containers which, in turn, were inserted into furnaces attached to the bottom of the glove box. Platinum cyanide concentrations were calculated according to the original amounts of K_2PtCl_4 added. Intervals of about 8 min were allowed

between the recording of successive voltammograms and chronopotentiograms.

Working electrodes were 0·3 mm tungsten wire electrodes (99·9% W, MP), while the reference and counter electrodes were made of titanium foil (0·15 mm, 99·9% Ti, BDH). The working electrodes were immersed to a depth of 1 cm, giving an area of 0·094 cm^2. The immersed areas of the counter and reference electrodes were about 0·40 and 0·55 cm^2 respectively. All electrodes were polished with alumina powder and washed with doubly distilled water. Unless the contrary is stated, new electrodes were used for each corresponding voltammetric and chronopotentiometric measurement. Transition times were measured according to the method of Reinmuth [11] and did not exceed 0·5 s. The potential variation of the titanium QRE before and after a combined chronopotentiometric and voltammetric run was less than 4 mV, measured against a sodium reference electrode [12]. The titanium QRE drifted less than 5 mV against the sodium electrode over a period of four days. Corrections were made for *IR* drop.

Linear-scan voltammograms and chronopotentiograms were recorded on a Hewlett Packard *X–Y* recorder (model 7000A), via a Hi-Tek transient recorder (type AA1). A PAR Universal Programmer (model 175) and a PAR Potentiostat/ Galvanostat (model 173) were used to generate constant-current pulses and voltage scans.

3. Results

3.1. *Density of molten (Na, K)CN Eutectic*

The density of molten (Na, K)CN eutectic in the temperature range of 500–600° C was

$$\rho_{eut} = 1·497 - 4·145 \times 10^{-4}\,t \pm 0·002\ (S.D.)$$

where t is the temperature in $^{\circ}$ C.

3.2. *Chronopotentiometry of Pt(II) cyanide*

Chronopotentiograms in cyanide melts were well-defined. The product of current density and the square root of the transition time ($i\tau^{1/2}$) was constant in the applied current range at each concentration and temperature. Square roots of transition times plotted against reciprocal current densities showed straight lines going through the
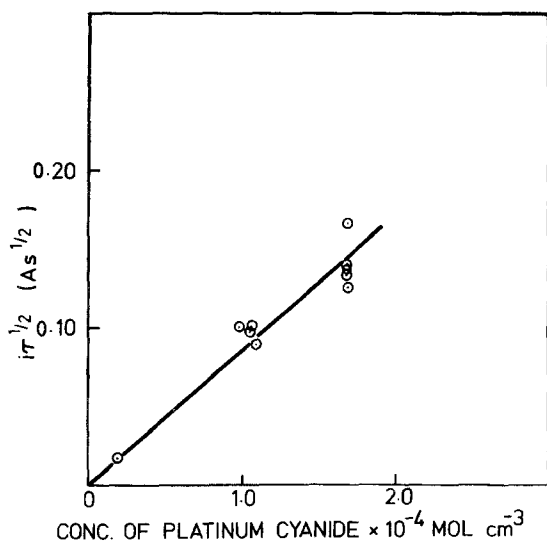
Fig. 1. Plot of $i\tau^{1/2}$ against platinum cyanide concentration.

Fig. 2. (a) Anodic and (b) cathodic cyclic voltammograms of the (Na, K)CN eutectic melt at 539° C. Scan rate: 0·1 V s^{-1}.

3.3. Cyclic voltammetry

3.3.1. Cyclic voltammetry of (Na, K)CN eutectic. Fig. 2 shows an anodic and a cathodic linear-sweep voltammogram (scan rate 0·1 V s^{-1}) at a tungsten working electrode of (Na, K)CN eutectic melt at 539° C. A Ti quasi reference electrode (QRE) was used. An estimate of the stability of NaCN at 800° K derived by theoretical consideration of the free-energy change, $-\Delta G = nFE$, gives a working voltage range of 652 mV [14].

The anodic current is due to the formation of cyanogen. This gas is stabilized in the melt by reaction with CN$^-$ ions to form dicyanamide. The cathodic current at increasing cathodic potentials is most likely due to alkali–metal deposition.

3.3.2. Cyclic voltammetry of Pt(II) cyanide. Only one wave was observed after scanning a Pt(II) cyanide melt between 0·4 and $-0\cdot4$ V with respect to a titanium QRE. Cyanide eutectic melt to which dicyanamide was added did not show a peak within the above-mentioned limits. Voltage scan rates (ν) were varied from 0·1 to 10 V s^{-1}. At scan rates greater than 1·0 V s^{-1}, the cathodic and anodic peak potentials shifted cathodically and anodically respectively. Results in Table 2 concern only scan rates of 0·1 to 1·0 V s^{-1} at W working electrodes. The cathodic peak potentials remained constant between scan rates of 0·1 and 1·0 V s^{-1} in a particular melt. However, marked differences effected by changes in temperature, scan rate and concentration, were observed during the anodic

origin, implying a diffusion process without adsorption of the electroactive species.

Table 1 summarizes the chronopotentiometric results. The use of different melts probably gives rise to the relatively large scatter of quarter-time potentials. Repeated use of the same electrodes stabilized the quarter-time potential, but gave larger $i\tau^{1/2}$ values, as can be seen from Fig. 1 and the last concentration in Table 1. The transition time constant $i\tau^{1/2}/C$ showed a large scatter, mainly due to high values at temperatures exceeding 550° C (Table 1).

For a reversible process with a soluble product, a plot of potential versus $\log (\tau^{1/2} - t^{1/2})/t^{1/2}$ should give a straight line with a slope of $2\cdot3 RT/nF$ [13], where R, T, n and F have their conventional values. This expected slope is given in brackets in Table 1. The n values were calculated from the average slope obtained from all current densities at each particular temperature and concentration. The reduction of the Pt(II) cyanide appears to be a reversible process with a soluble product and a transfer of two electrons. At temperatures exceeding about 540° C, slopes close to $2\cdot3 RT/nF$ were limited to the upper half of the applied current range of 20–70 mA, indicating complications in the mechanism at the lower currents. Diffusion coefficients of the platinum cyanide complex were calculated from the slopes of the $\tau^{1/2}$ versus $1/i$ plots, assuming a two-electron transfer.
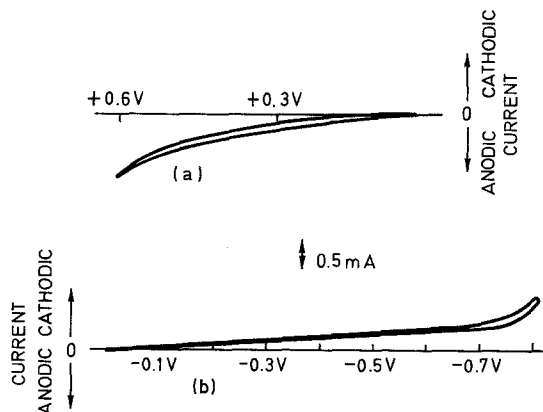
Table 1. Results of chronopotentiometry of platinum cyanide melts

Concentration × 10^4 (mol cm^{-3})	Temperature (°C)	$i\tau^{1/2}$ ± S.D. (A s$^{1/2}$ cm^{-2})	$i\tau^{1/2}/C$ (A s$^{1/2}$ cm mol^{-1})	$E_{\tau/4}$ (mV)	$D \times 10^5$ (cm^2 s^{-1})	Slope of potential versus $\log [(\tau^{1/2} - t^{1/2})/t^{1/2}]$	n
0·20	510	0·0169 ± 0·0002	845	−114 ± 1	2·45	0·087 ± 0·004 (0·078)	1·8 ± 0·1
0·20	544	0·0173 ± 0·0003	866	−104 ± 3	2·57	0·082 ± 0·002 (0·081)	2·0 ± 0·1
1·10	540	0·089 ± 0·002	809	−154 ± 2	2·27	0·089 ± 0·005	1·8 ± 0·1
1·69	538	0·135 ± 0·003	799	−118 ± 3	2·16	0·082 ± 0·001 (0·080)	2·0 ± 0·1
1·07*	560	0·101 ± 0·004	944	−123 ± 2	3·02	0·088 ± 0·006 (0·083)	1·9 ± 0·1
1·07*	580	0·099 ± 0·003	925	−133 ± 3	2·96	0·082 ± 0·006 (0·085)	2·1 ± 0·1
1·68†	527	0·125 ± 0·002	744	−103 ± 3	2·01	0·074 ± 0·008 (0·079)	2·1 ± 0·1
1·68‡	526	0·139 ± 0·002	827	−117 ± 2	2·23	0·087 ± 0·003	1·9 ± 0·1
1·68‡	562	0·137 ± 0·003	815	−116 ± 2	2·32	0·080 ± 0·002	2·1 ± 0·1
0·99	560	0·100 ± 0·002	1010	−152 ± 2	3·52	0·083 ± 0·009	2·0 ± 0·2
1·69§	555	0·166 ± 0·007	982	−155 ± 3	3·30	0·082 ± 0·006	2·0 ± 0·1

* Same melt but different electrodes.
† 1 cm long tungsten working electrode sealed in Pyrex tubing; counter and QR Ti flag electrodes.
‡ A sodium reference electrode was used instead of Ti QRE.
§ Same melt and electrodes as previous concentration, but K$_2$PtCl$_4$ added to increase Pt concentration.
Values in brackets indicate expected slope ($2 \cdot 3\, RT/nF$) for a reversible process.

Table 2. Results of cyclic voltammetry of platinum cyanide melts

Concentration × 10^4 (mol cm^{-3})	Temperature (°C)	E_p (mV)	$E_{1/2}$ (mV)	$\Delta E = E_p - E_{p/2}$ (mV)	n	$D \times 10^5$ (cm^2 s^{-1})	i_a/i_c	Slope of potential versus $\log [(i_p - i)/i]$	n
0·20	510	−167	−117	97 (74, 26)	1·6	1·38	0·8 → 1·0	0·072 (0·078)	2·2
0·20	544	−152	−106	90 (77, 27)	1·7	2·15	0·9 → 1·0	0·076 (0·081)	2·2
1·10	510	−173	−130	88	1·7	1·59	1·2 → 0·8	0·075	2·1
1·10	540	−176	−143	74	2·1	1·76	1·7 → 1·1	0·074	2·1
1·69	538	−147	−113	69	2·3	1·72	1·1 → 1·0	—	—
1·68*	527	−139	−100	80	1·7	1·55	1·3 → 1·2	—	—
0·20	560	−197	−150	95 (79, 28)	1·7	1·88	0·8 → 1·0	0·075 (0·083)	2·2
9·99§	560	−198	−163	82	1·9	1·90	2·6 → 1·3	0·079	2·1
1·69§	555	−202	−167	81 (78, 27)	1·9	1·90	1·8 → 1·3	0·082	2·0
1·69‖	555	−200	−168	66	2·4	2·40	2·1 → 1·5	—	—

† and § See footnotes to Table 1.
‖ Same melt as previous one, different set of electrodes.
Values in brackets indicate ΔE for a reversible process yielding a soluble and insoluble product respectively.
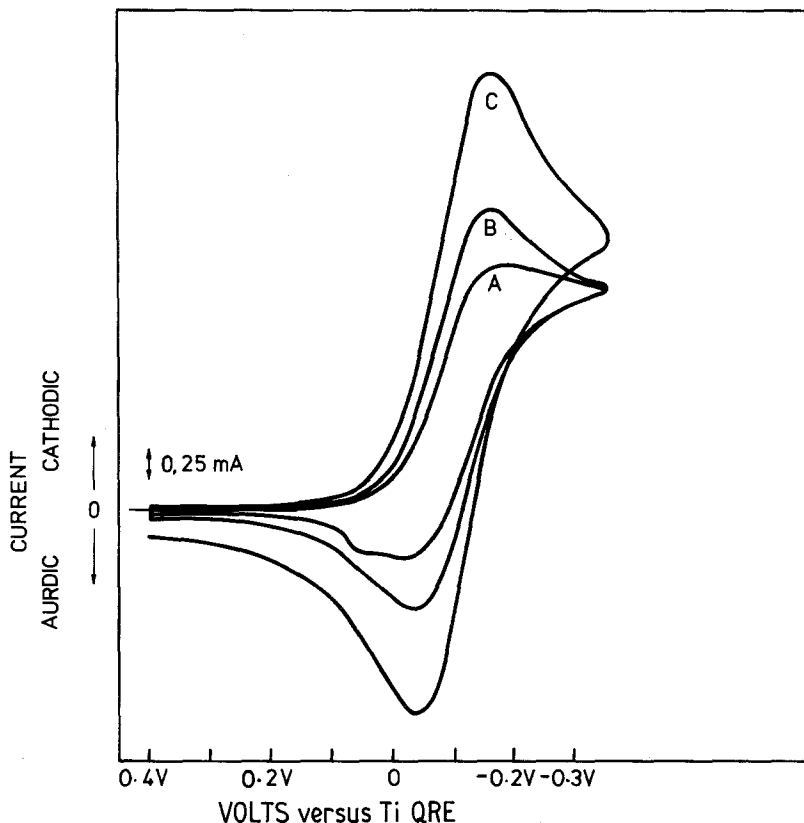Values in brackets under heading 'Slope of . . .' are $2 \cdot 3\, RT/nF$ values.

Fig. 3. Cyclic voltammogram for the reduction of platinum cyanide at 510° C, concentration: $0 \cdot 20 \times 10^{-4}$ mol cm^{-3}; (A) $0 \cdot 1$; (B) $0 \cdot 2$; (C) $0 \cdot 5$ V s^{-1}.

scanning. The melts with the lowest platinum concentration often showed flat or composite anodic peaks at the $0 \cdot 1$ V s^{-1} scan rate, but conventional peaks at higher scan rates ($0 \cdot 2$ to $1 \cdot 0$ V s^{-1}). Figs. 3–5 show cyclic voltammograms at different concentrations, scan rates and temperatures.

Table 2 lists, at various temperatures and concentrations, the main voltammetric parameters: the peak potential E_p, the potential at 85% of the peak current, $E_{1/2}$ (half-wave potential), the difference between half-peak and peak potential ΔE, the n value calculated from ΔE, the diffusion coefficient, i_a/i_c ratio, slope of plot of potential versus $\log (i_p - i)/i$ and the n value derived from this slope. The half-wave potential and the n values were calculated on the assumption that the reduction of platinum cyanide is a reversible charge transfer with a soluble product. The half-peak to peak potential difference in this case is given by $\Delta E = E_p - E_{p/2} = 2 \cdot 2 RT/nF$ [15]. In the case of

a reversible deposition of an insoluble product, $\Delta E = 0 \cdot 77 RT/nF$ [16]. Both expected ΔE's are listed in brackets in Table 2 after the observed ΔE's. Standard deviations of the observed potentials in Table 2 averaged ± 5 mV. The last three melts in Table 2 were prepared by progressively adding K$_2$PtCl$_4$ to the last $0 \cdot 2$ melt. In all other melts the initial platinum concentration remained unchanged and only temperatures were varied.

The n values calculated according to

$$\frac{i_p/v^{1/2}}{i\tau^{1/2}} = 54 \cdot 86 \, (n/T)^{1/2}$$

[17] appeared to depend on scan rate and temperature. They were found to be $2 \pm 0 \cdot 2$ at scan rates of $0 \cdot 2 - 0 \cdot 5$ V s^{-1} at $510°$ C, and at the higher temperatures at scan rates of $0 \cdot 5$ to $2 \cdot 0$ V s^{-1}.

Plots of peak-current densities against the square root of the scan rate gave straight lines intercepting the ordinate. Fig. 6 shows such a plot for the same concentration at two different temperatures. The
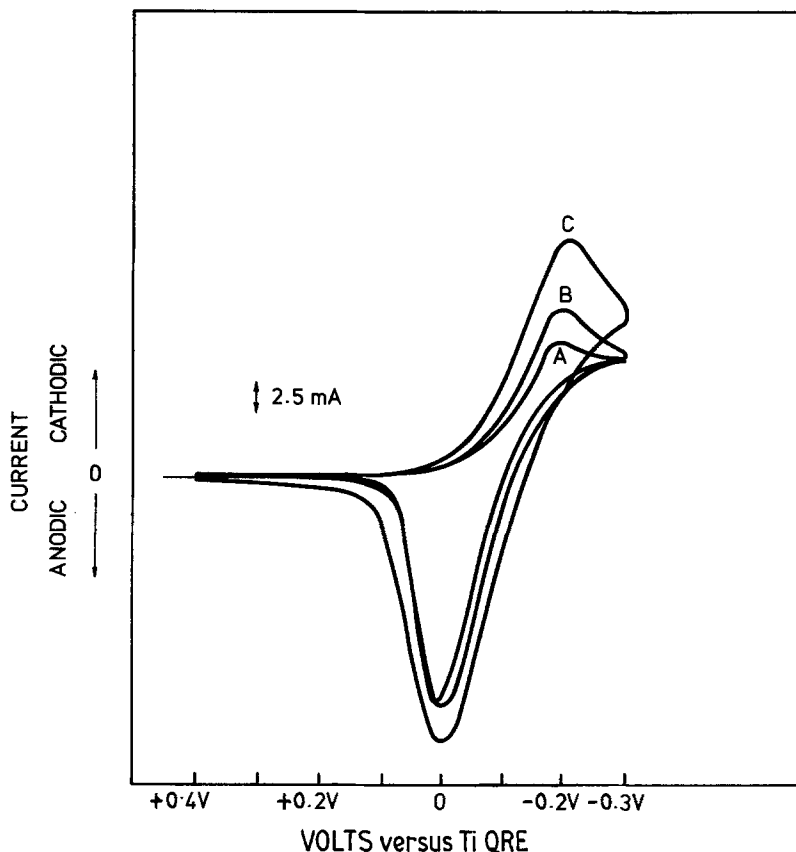
Fig. 4. Cyclic voltammogram for the reduction of platinum cyanide at 560° C; concentration: 1.07×10^{-4} mol cm^{-3}; (A) 0.1; (B) 0.2; (C) 0.5 V s^{-1}.

function $i_p/\nu^{1/2}$ decreased with increasing scan rate, especially at increasing platinum concentrations (Fig. 7). This sort of behaviour is usually attributed to a catalytic regeneration or a disproportionation of the reactant. In this case it is more likely due to convective mass transfer, because at scan rates less than 0.1 V s^{-1} no peaks, but only reduction waves, were observed [18].

The ratios of anodic to cathodic peak heights (i_a/i_c) were calculated for each sweep by means of an expression developed by Nicholson [19]. This expression assumes an uncomplicated reversible electron transfer. Table 2 shows the variation in i_a/i_c ratio from 0.1 to 1.0 V s^{-1}.

Plots of potential versus log $(i_p - i)/i$ showed straight lines in the range of $0.35-0.70\, i_p$. The slopes of these lines were best predicted by the Heyrovsky–Ilkovic equation

$$E = E_{1/2} + \frac{2.3\,RT}{nF} \log (i_p - i)/i$$

which assumes that the reduced metal forms a soluble product in the melt or a surface alloy with the metal electrode [20]. Expected slopes are given in brackets behind the observed slopes, and there is fair agreement between the observed and expected slopes. In the 1.69×10^{-4} mol cm^{-3} platinum cyanide melts, slopes usually increased rapidly as a function of scan rate, or showed large scatter.

4. Discussion

The results obtained from chronopotentiometry indicate that the reduction of Pt(II) cyanide is a reversible reaction yielding a soluble product and involving two electrons in the charge transfer. Results from cyclic voltammetry appear more confusing. Cathodic peak potentials remained constant in a particular melt when scan rates were varied from 0.1 to 1.0 V s^{-1}. They shifted cathodically at scan rates exceeding 1 V s^{-1}, indicating a certain degree of irreversibility at these
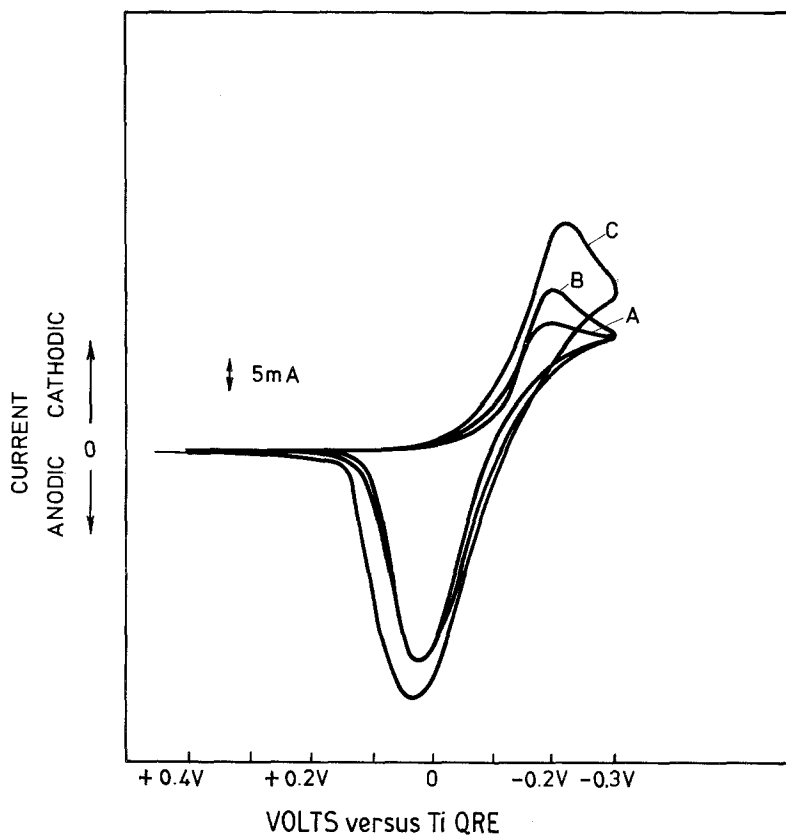
Fig. 5. Cyclic voltammogram for the reduction of platinum cyanide at 555° C; concentration: $1 \cdot 69 \times 10^{-4}$ mol cm^{-3}; (A) $0 \cdot 1$; (B) $0 \cdot 2$; (C) $0 \cdot 5$ V s^{-1}.
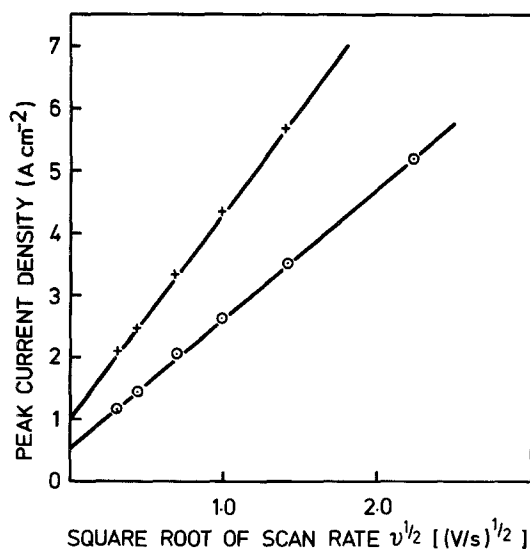

Fig. 6. Plot of cathodic peak-current density against square root of scan rate at 560° C; platinum cyanide concentration: (o) $0 \cdot 99$ and (+) $1 \cdot 69 \times 10^{-4}$ mol cm^{-3}.
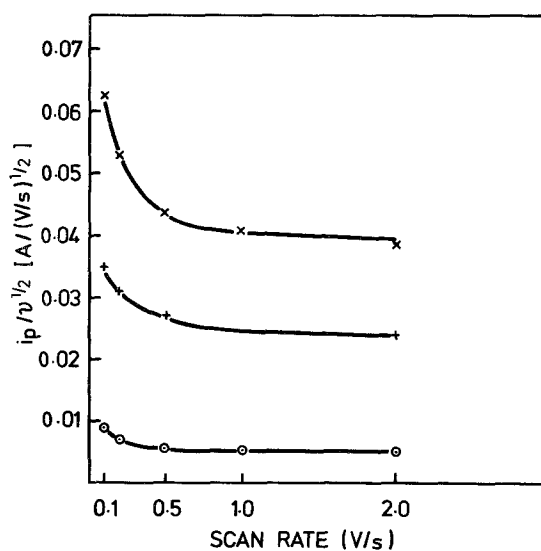
Fig. 7. Variation of $i_p/\nu^{1/2}$ with scan rate at 560° C; platinum cyanide concentration: (o) $0 \cdot 20$; (+) $0 \cdot 99$; (X) $1 \cdot 69 \times 10^{-4}$ mol cm^{-3}.
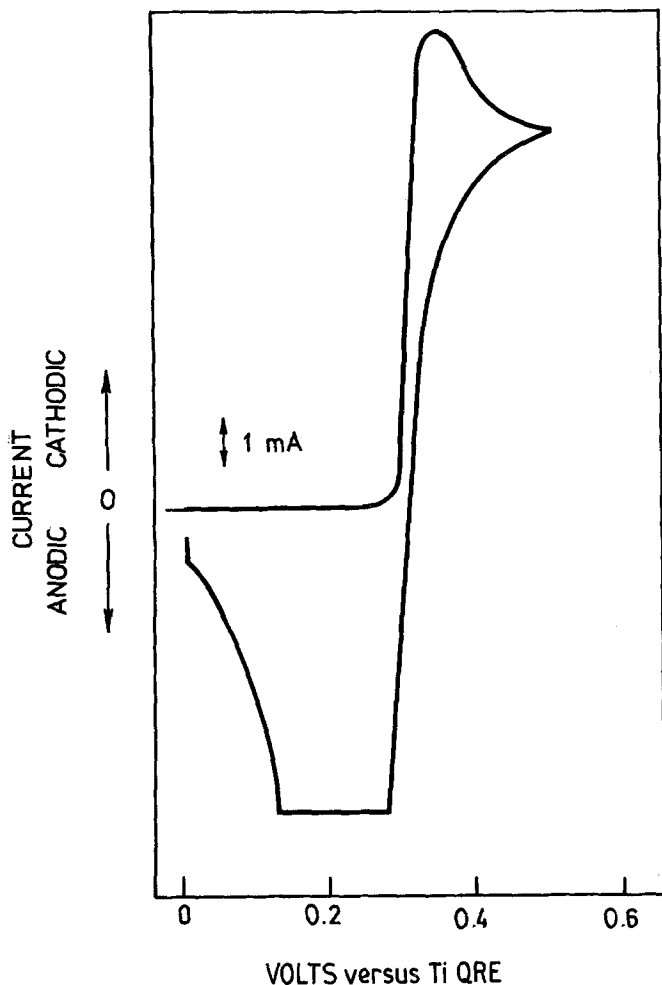
Fig. 8. Cyclic voltammogram for the reduction of zinc cyanide at $510°$ C; concentration: $0.77 \, mol \, cm^{-3}$; $0.1 \, V \, s^{-1}$.

higher scan rates. Larger than expected cathodic–anodic ($>115 \, mV$) and half-peak to peak potential differences characterized all cyclic voltammograms.

Unusually large cathodic–anodic peak potentials have been reported by Clayton et al. [21, 22]. This was attributed to alloy formation between the reduced metal and the working electrode. Large peak to half-peak potentials were also reported by Chessmore and Laitinen [23] who in turn referred to White and Lawson [24, 25]. The last two authors attributed broadening of the cathodic peak to sub-monolayer deposition. However, no satisfactory explanation for the peak broadening in cyanide melts can be given, although W–Pt alloys are known to exist [26].

It is interesting to compare the cyclic voltammograms obtained for Pt(II) cyanide with those of Zn(II) cyanide. Fig. 8 gives an example of the

latter. It shows the steep rise in current as the peak potential is approached, which is characteristic of the deposition of an insoluble product [27]. In the case of Zn(II) cyanide, only one oxidation state is present in the melt, and the reduction to the metal takes place without intermediate steps

$$Zn(CN)_4^{2-} + 2e \rightarrow Zn + 4CN^-. \quad (8)$$
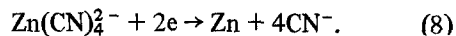
In cyanide melts two stable platinum complexes may be present simultaneously, as already mentioned in the introduction. Since chronopotentiometry and cyclic voltammetry indicate a soluble product for the reduction reaction, it is most likely to be the Pt(0) complex. Soluble reduction products were also found in other cyanide melts where Pd(II), Rh(III), and Ni(II) were reduced to Pd(0), Rh(I) and Ni(I) respectively [28]. The following reaction scheme is therefore proposed:
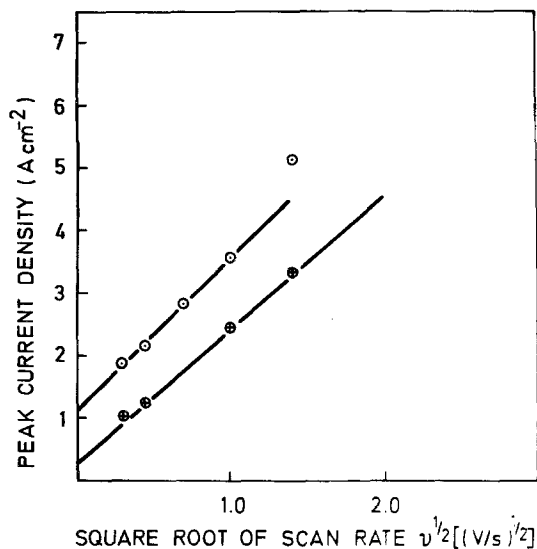
$$Pt(CN)_4^{2-} + 2e \rightleftarrows Pt(CN)_4^{4-} \rightarrow Pt + 4CN^- \quad (9)$$

Fig. 9. Plot of cathodic peak—current density against square root of scan rate for a melt without (+) and with (o) excess sodium dicyanamide; temperature 540° C; initial concentration: $1 \cdot 10 \times 10^{-4}$ mol cm^{-3} platinum cyanide.

of which only the first step is observed under present conditions. Vlček proposed a similar mechanism for the reduction of Ni(II) complexes in cyanide solutions [29].

There is reasonable agreement between the diffusion coefficients obtained from chronopotentiometry and linear-scan voltammetry (Tables 1 and 2). They are of the same order as that usually quoted for ions in molten salts.

The QRE maintained a constant potential ($\pm$ 2 mV) in one particular melt over a period of 4 days, as measured against a sodium electrode. Quarter-time potentials derived from chronopotentiometry, and half-wave potentials from cyclic voltammetry, agreed reasonably well for results obtained within the same melt. The quarter-time potential derived from chronopotentiometry, and the half-wave potential derived from cyclic voltammetry, should be identical for a reversible reaction with soluble reactants and products [18]. However, both potentials varied from melt to melt. It is known that the QRE is extremely sensitive to small impurities present in the melt. Different cyanide melts inevitably contain small but varying amounts of oxygen, leading to slightly different potentials of the QRE's. The independence of the reduction peak (E_p) as a function of

platinum concentration within the same melt was especially examined. The results are given in the last four concentrations in Table 2.

Excess sodium dicyanamide (oxidizing agent) was added to a melt to test the possible presence of Pt(0) complex. If the peak current increases after addition, it means that an extra amount of Pt(II) has been produced. Fig. 9 shows the peak currents at several scan rates before and after the addition. Although increased peak currents were found, the cathodic peak potentials shifted cathodically about 320 mV with respect to the Ti QRE.

The reduction became irreversible, which is presumably due to reoxidation of the reduced metal by dicyanamide. The cathodic shift might be due to the different environment the QRE is 'seeing'. Assuming the peak current to be proportional to the Pt(II) concentration, the Pt(II) concentration before addition of dicyanamide must have been 54% to 70% of the final Pt(II) concentration.

Acknowledgement

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