JOURNAL OF APPLIED ELECTROCHEMISTRY 13 (1983) 383–393

Cyclic voltammetry of group VIII metals in cyanide melts

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Received 24 August 1982

Group VIII metals were studied in a (Na, K)CN eutectic melt by cyclic voltammetry at 550° C. The aim was to obtain an overview of the behaviour of these metals in molten cyanide and possibly determine the oxidation state(s) of the metal complexes. Molten cyanide tends to stabilize low-oxidation-state platinum-group metals. Metal ions (M) were present for iridium and rhodium as M(III) and M(I), while for platinum and palladium as M(II) and M(I) complexes, respectively. The last two elements could also be obtained as M(O) species by electrochemical reduction of M(II) complexes. Cyclic voltammograms of all four elements showed a reversible reaction between two soluble species with a two electron transfer. Other elements studied were ruthenium, osmium, copper and silver which all occurred in one oxidation state only.

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1. Introduction

For several years this laboratory had a molten-salt research programme in which the system molten cyanide/metal was used to separate platinum metals by solvent extraction [1, 2]. This work was in turn supplemented by research in UV-visible absorption spectra of Group VIII elements in molten cyanides [3, 4]. The only electrochemical work done in this laboratory on molten cyanides was a study of chronopotentiometry and cyclic voltammetry on the reduction of $Pt(CN)_4^{2-}$ ions in a molten (Na, K)CN eutectic [5]. Instead of studying one particular reaction, it seemed more illuminating to look at as many Group VIII elements as possible, in this way obtaining an overview of these elements. Cyclic voltammetry seemed the best way of illustrating each element's behaviour. It may shed light on the number of electrons transferred in certain reactions. An acquaintance with oxidation states is not only important for extraction work, but also for plating studies. To our knowledge other work concerning molten cyanides was in connection with precious metal plating [6–8] and work done by Sethi [9] on the electrodeposition of platinum.

Molten cyanide is not an inert medium. It usually reduces high-oxidation-state metal ions added to the melt, to the low-oxidation-state complexes. A reaction product, $(CN)_2$ (cyanogen), which is formed in this process, is stabilized in the melt as dicyanamide, $N(CN)_2^-$. The redox potential of a cyanide melt is determined by the ratio of sodium cyanamide to the sodium dicyanamide present. A preponderance of high-oxidation or low-oxidation species may be obtained by adding sodium dicyanamide (oxidant) or sodium cyanamide (reductant), respectively, to the melt. In this manner, the valencies of the metal complex can be controlled to a large degree, if polyvalent metals are present.

Because of the interaction of the metals with the cyanide melt and the subsequent formation of reaction products such as dicyanamide, it appeared necessary to obtain cyclic voltammograms of melts containing sodium dicyanamide, sodium cyanamide, sodium cyanate and sodium carbonate. Carbonates are present in unpurified melts.

It should be kept in mind that the cyclic voltammograms shown are meant to give an overall impression of each element's behaviour and that the more detailed information in the text or in the tables does not necessarily refer to the particular voltammograms shown. For obvious reasons the number of voltammograms shown had to be reduced to a minimum.

Finally, since only cyclic voltammetry was used to characterize Group VIII metals, confirmative support for conclusions was sought from results

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obtained by spectroscopic means as published by de Haas *et al.* [3, 4].

2. Experimental procedure

Metal cyanide complexes were prepared by either dissolving an appropriate salt or by anodically dissolving a spectroscopically pure metal wire in 30 g of (Na, K)CN eutectic. Two working electrodes could be placed in the melt simultaneously, the wire under investigation and the normal titanium working electrode. The choice of titanium as electrode material was made because it is one of the few metals found to be resistant to chemical attack by molten cyanide. Working electrodes were 1 mm titanium wires (99.9% Ti, Koch-Light) and 1 cm long, while the counter electrodes were made of titanium foil (0.15 mm, 99.9% Ti, BDH). All electrodes were of the 'flag' type, where 0.1 mm tungsten wire was used to weld the electrodes to the supporting titanium rod outside the melt. All electrodes were polished with alumina powder, and washed with doubly distilled water and alcohol.

The sodium reference electrode consisted of a Pyrex glass tube (1 mm wall thickness) containing sodium and a tungsten rod (2 mm diameter) as a lead [10]. The pyrex containers were not attacked by molten cyanide, provided the melt was free of water and oxygen. For experimental details regarding cyanide purification see [11]. The argon-purged glove box in which the experiments were conducted contained less than 20 ppm oxygen and 10 ppm water. Cyclic voltammograms were recorded on a Hewlett–Packard *x-y* recorder (Model 7000A). A PAR Universal Programmer (Model 175) and a PAR Potentiostat/Galvanostat (Model 173) were used to generate the voltage scans. Scan rates from 0.05 to 1 V s^{-1} were used. Melt temperatures were held at about 552° C with an accuracy of ± 1° C.

3. Results

3.1. *Non-elemental additions*

When sodium dicyanamide is added to (Na, K) eutectic melt, its cyclic voltammogram shows cathodic peaks at 1.10 and 0.12 V, respectively. It is most likely that the first peak is due to the reduction of dicyanamide to cyanamide

$$N(CN)_2^- + 2e \rightarrow NCN^{2-} + CN^-.$$

When sodium cyanamide is added to a melt containing sodium dicyanamide, its cyclic voltammogram shows the same two peaks as observed in the original melt, but the peak at 0.12 V is considerably enhanced, implying increased cyanamide reduction. Melts containing sodium cyanate also show, one peak at about 0.12 V, as do melts containing sodium carbonate (see Fig. 1 for a cyclic voltammogram of the solvent).

3.2. *Osmium and ruthenium*

Spectroscopic measurements revealed that osmium and ruthenium are present in cyanide melts as $Ru(CN)_6^{4-}$ and $Os(CN)_6^{4-}$ only [12]. The cyclic voltammograms of osmium melts showed only one reduction peak at about 0.2 V, while ruthenium showed a set of ox-red peaks, indicating an irreversible reaction (Figs. 2 and 3). The occurrence of one reduction peak in both cases seems to support the presence of one oxidation state only. Ruthenium and osmium working electrodes were not available.

3.3. *Copper, silver and gold*

Cyclic voltammograms of copper melts showed one reversible deposition of an insoluble product. Only one oxidation state, namely Cu(I) is present in the melt as can easily be confirmed by coulometry [13]. Scan rates of 0.05, 0.1 and 0.2 V s^{-1} gave E_p–$E_{p/2}$ potential differences of 55 to 63 mV, which are of the same order as the 55 mV at 550° C predicted by the equation $E_p - E_{p/2} = 0.77\ RT/nF$ for a reversible deposition of an insoluble product with a transfer of one electron [14]. Silver cyanide was also present as Ag(I) only. Both silver and gold precipitate from cyanide melts and therefore are not of much practical interest. No spectroscopy was done on these elements and no cyclic voltammograms are shown for these elements.

3.4. *Platinum*

A cyclic voltammogram of, for example, 0.2 g K_2PtCl_4 scanned between 1.9 to 0.0 V shows a

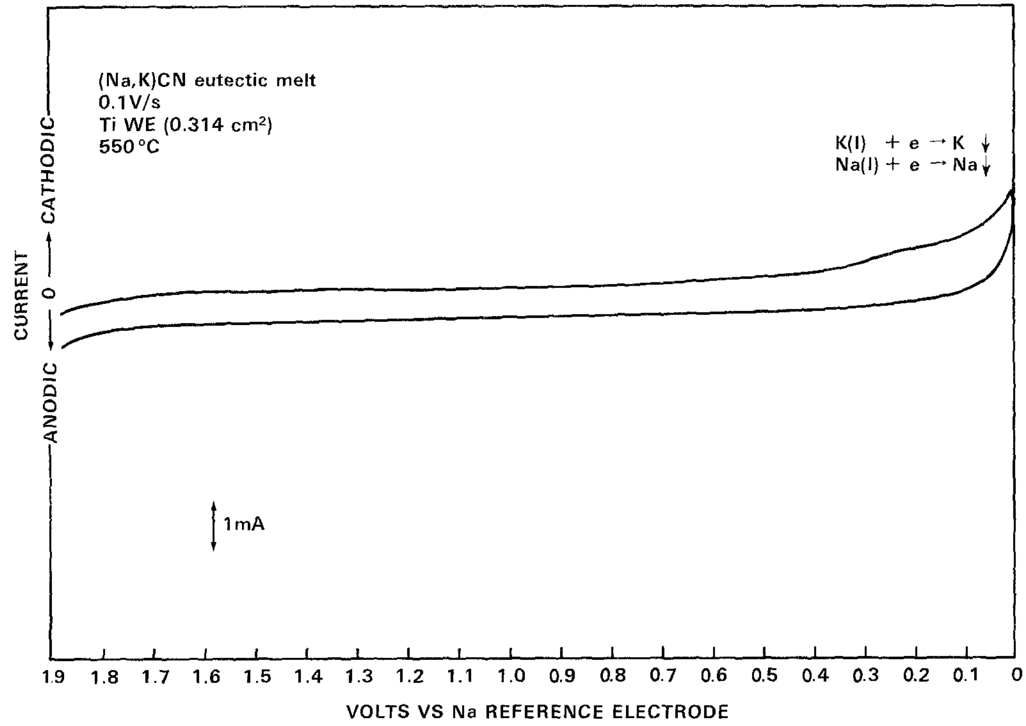

Fig. 1. Cyclic voltammogram of (Na, K)CN eutectic melt. ↓ indicates metal deposition.

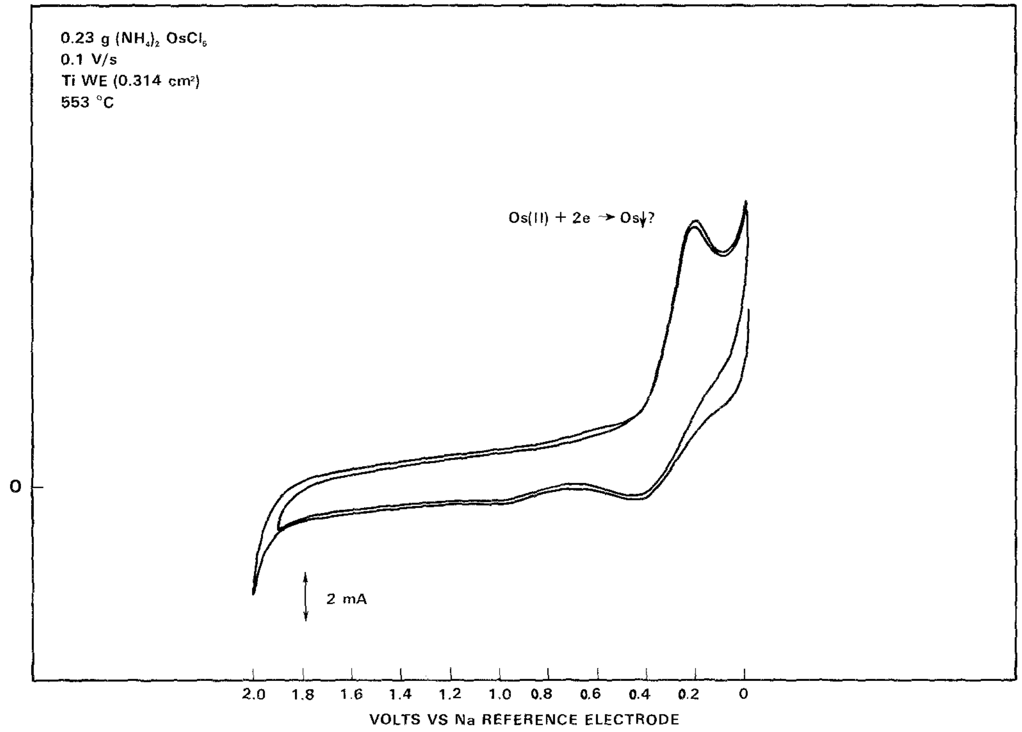

Fig. 2. Cyclic voltammogram of a cyanide melt containing osmium.

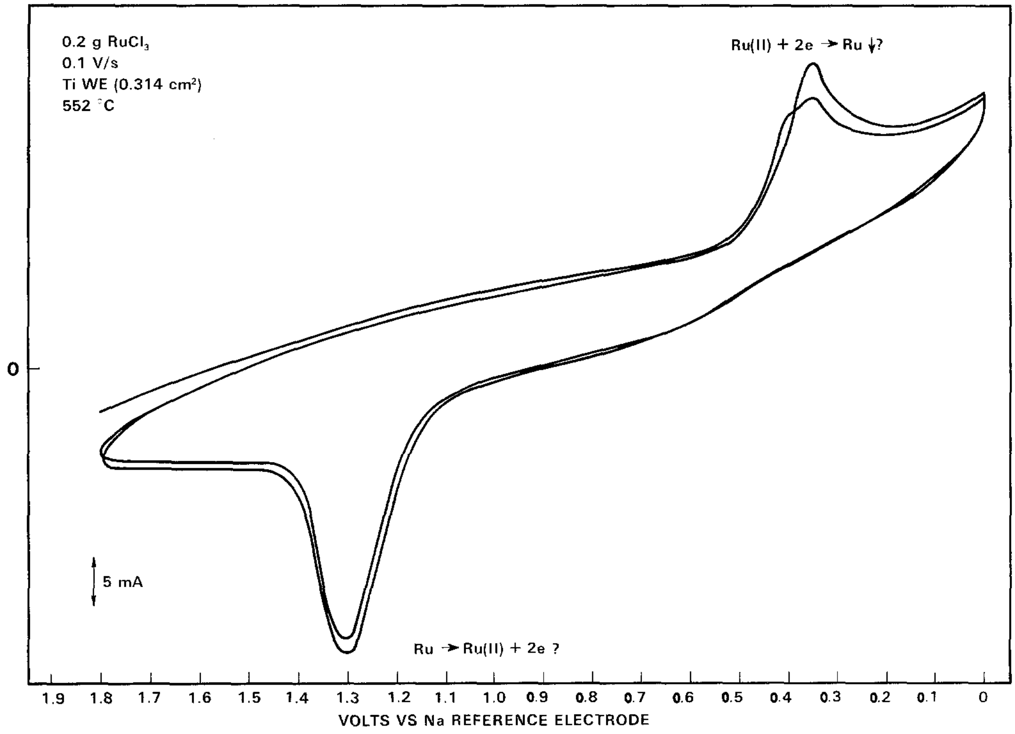

Fig. 3. Cyclic voltammogram of a cyanide melt containing ruthenium.

reversible reaction between two soluble species, followed by a deposition-stripping reaction. The two reactions are separated by about 400 mV. Details of the reversible reaction are given in Table 1. They were obtained from scanning the melt between 1.9 and 0.9 V, at scan rates ranging from 0.05 to 0.2 V s^{-1}. This reaction has also been studied in a previous publication [5], indicating a two-electron transfer. The second reduction wave showed a half-peak to peak potential difference of about 80 mV. For a reversible deposition of an insoluble product this potential difference should be 55 and 27 mV for a one and a two electron transfer, respectively, (see Section 3.3). It follows that the second reaction is not a completely reversible deposition reaction.

Two other experiments were made on platinum melts. The first one was to anodize a platinum wire and the second one was to try out multiple scanning.

Table 1. Peak potential, half-peak to peak potential difference, anodic–cathodic peak potential difference for melts containing 0.482, 0.120 *and* 0.955 × 10^{-3} mol Pt, Pd *and* Rh *dissolved as* K_2PtCl_4, $PdCl_2$, $RhCl_3$, *respectively. The iridium melt was obtained by anodizing iridium wire. Values in parentheses are the predicted theoretical values for a two-electron transfer at* 550° C [17]. *Scan rates were varied from* 0.05 *to* 0.2 V s^{-1}. *Types of working electrodes and standard deviations are also indicated*

Metal present in melt	E_p (V)	E_p–$E_{p/2}$ (mV)	E_{ap}–E_{cp} (mV)	*Working electrode*
Pt	1.058 ± 0.005	88 ± 2 (78)	100 ± 7 (79)	Ti
Rh	1.468 ± 0.005	85 ± 5	98 ± 8	Ti
Pd	1.378 ± 0.005	90 ± 5	110 ± 8	Ti
Ir	1.066 ± 0.005	86 ± 6	105 ± 14	Ir

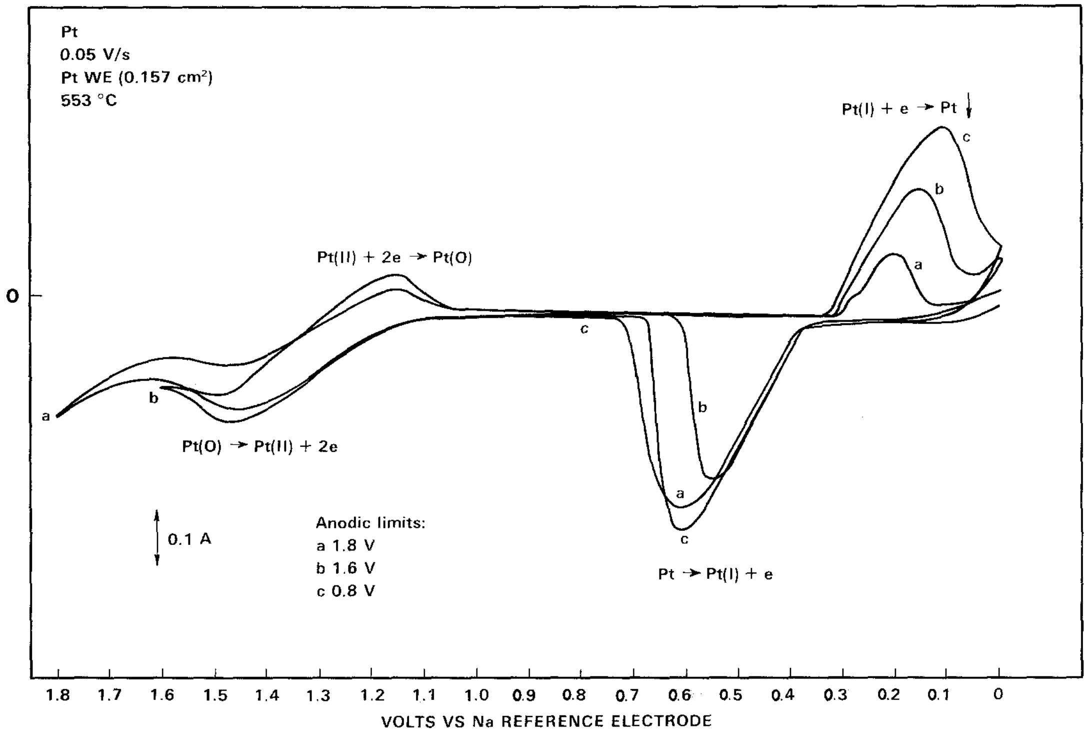

Fig. 4. Cyclic voltammogram of a cyanide melt showing anodic dissolution of a platinum working electrode leading to Pt(I)-complex formation (scan c); at 1.8 V Pt(II)-complex formation occurs (scan a).

When a platinum working electrode was anodized, two distinct anodic stripping peaks were observed: one at 1.9 and the other at 0.6 V suggesting the formation of two different platinum oxidation states. Since additions of both Pt(IV) and Pt(II) salts gave identical cyclic voltammograms, the highest oxidation state for platinum appears to be two. Similar voltammograms were obtained by dissolution of platinum wire at 1.9 V, indicating Pt(II) formation at that potential. Pt(I) must then be formed at a lower potential. Fig. 4 shows Pt(I) dissolution and its subsequent reduction (scan c). By extending the anodic limit to 1.9 V and holding it there, Pt(II) is formed (scan a). Comparison of scans a, b and c shows that the more anodic the scan, the smaller the height of the second reduction wave. This is perhaps not so surprising since all the Pt(II) has just been reduced to Pt(O), leaving only Pt(I) to be further reduced. Spectroscopic measurements showed Pt(II), Pt(I) and Pt(O) complexes to be present in the melt after Pt(II) was added [3, 4]. Pt(I) is reported to be the least stable complex [3, 4].

An interesting feature of multicycling between 0.0 and 0.9 V was that at platinum working electrodes both anodic and cathodic peak heights increased with each additional cycle. At titanium electrodes the original reduction peak was preceded by a much narrower peak, the height of which subsequently increased, as did the corresponding stripping peak (Fig. 5). In some cases the original reduction peak was not retraced during later scans. While a single stripping peak occurred more often, composite stripping peaks have been observed as well. As soon as the anodic limit of, for example, 0.9 V was changed to 1.9 V, the sharp peaks disappeared during succeeding scans. Limiting the potential range to 0.9 V would once again reintroduce the narrow peaks. Increases in peak heights have been attributed to an increase of the surface area of the electrode due to a roughening effect [15, 16]. It may explain the steady increase in peak heights, but it certainly does not explain the narrow peak formation at titanium electrodes. They could be due to a TiPt compound being stripped and deposited again during succeeding scans. However, these explanations remain speculative.

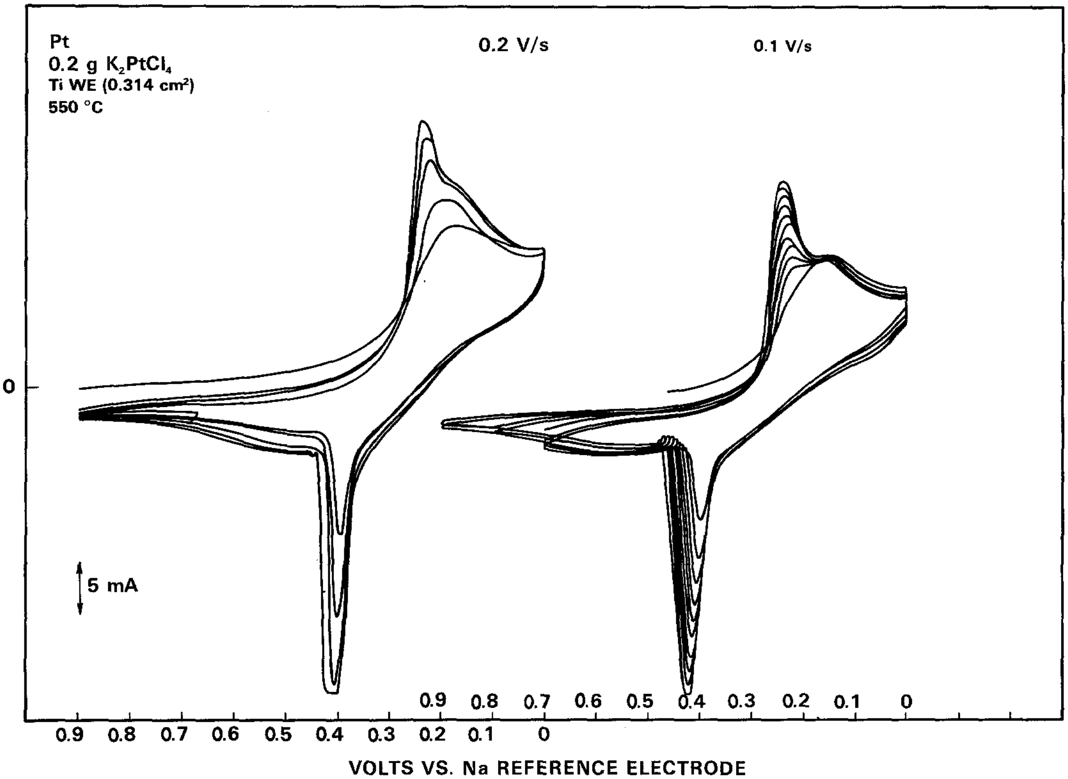

Fig. 5. Cyclic voltammogram of a cyanide melt containing platinum, cycled repeatedly between 0.9 and 0.0 V at 0.1 and 0.2 V s^{-1}.

3.5. *Rhodium*

This element anodizes at 1.8 V but also at 1.0 V. At titanium working electrodes two sets of reactions become apparent. The first set, at more anodic potentials, represents a reversible ox-red reaction between two soluble complexes (Table 1). The second set, i.e. the irreversible part, is pictured in Fig. 6. It shows two successive reduction peaks (of which the first one showed the same half-peak to peak potential difference of about 80 mV as the corresponding platinum reduction wave) and a composite re-oxidation peak, implying two oxidation and reduction reactions. However, the second reduction peak was not always prominent, while a completely symmetrical re-oxidation peak was rarely observed. Spectroscopic measurements revealed the presence of Rh(III), Rh(I) and Rh(O) species [3, 4]. From these results, and knowing that rhodium plates well from a cyanide melt, a possible explanation for the peaks is offered. Reactions taking place may be the reduction of Rh(I) to Rh(O), both soluble species, and the deposition-stripping of Rh(I). On the other hand, interference of the titanium working electrode during the stripping process cannot be excluded. Obviously a more detailed study would be required to settle this part of the rhodium voltammogram.

3.6. *Palladium*

The palladium cyclic voltammogram shows a reversible reaction between two soluble species and an ill-defined reduction peak at the cathodic limit (Fig. 7). Particulars of the reversible reaction are given in Table 1. Palladium working electrodes dissolved anodically at about 0.15 V and at the anodic limit of 1.9 V, suggesting the formation of Pd(I) and Pd(II) complexes. Three species, characterized as Pd(II), Pd(I), and Pd(O) were found in cyanide melts by spectroscopic means [3, 4].

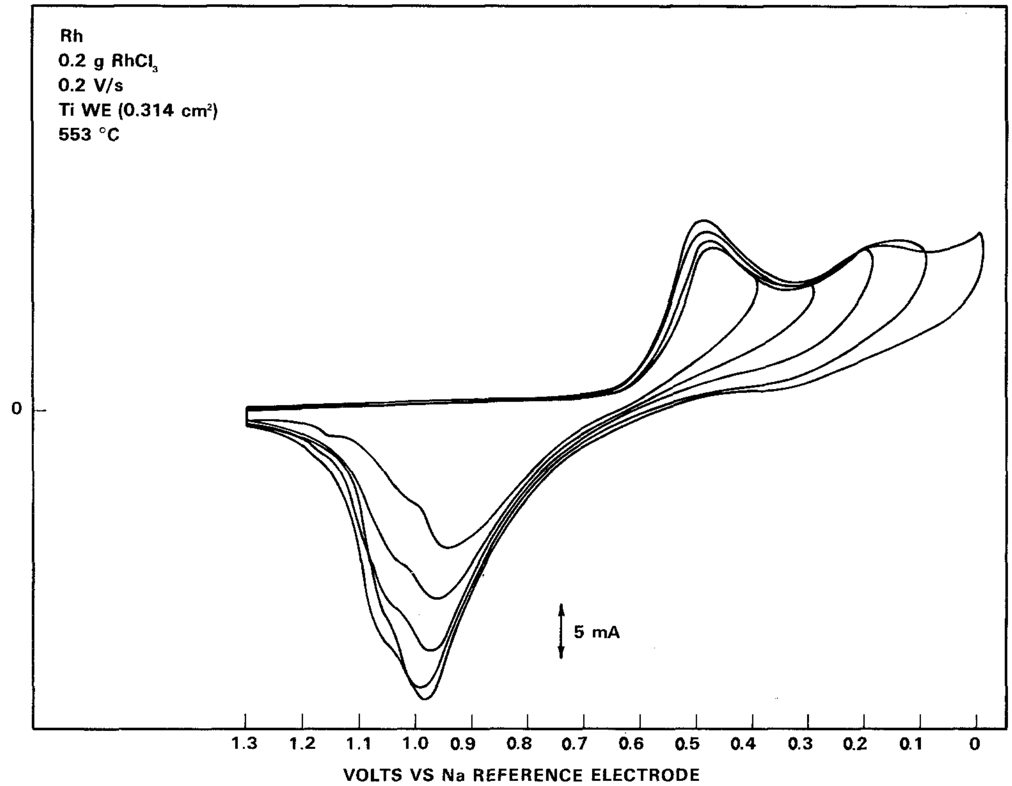

Fig. 6. Cyclic voltammogram of a cyanide melt containing rhodium, cycled between 1.3 and varying cathodic potentials.

3.7. *Iridium*

Iridium working electrodes dissolved readily at 1.9 V, but not at any lower potential. Irrespective of the type of working electrode, each cyclic voltammogram showed a reaction between two soluble species, followed by a reduction peak. For the reaction between the soluble species, half-peak to peak potential differences increased rapidly with increasing scan rate at a titanium working electrode (Table 2). At iridium working electrodes the results were similar to those obtained for platinum, rhodium and palladium melts at titanium working electrodes (Table 1). The same applied to anodic–cathodic peak potential differences ($E_{ap} - E_{cp} = 2.22\,RT/nF$, 79 mV at 550° C for $n = 2$) [17].

Given the similarity between rhodium and iridium, the second reduction peak could also be due to Ir(I) being reduced to iridium metal or to Ir(O). By scanning between 1.9 and 0.8 V, a reaction between two soluble species is revealed, while by extending the cathodic limit to 0.6 V and 0.2 V, respectively, the anodic oxidation peak becomes 'distorted'. First of all the anodic peak height increases, indicating an additional amount of oxidized material, and secondly, the peak becomes broader and tends to shift anodically. Some re-oxidation takes place, which must be related to the second reduction peak (Fig. 8). Further evidence that the irreversible reduction

Table 2. Scan rate, peak potential, half-peak to peak potential and anodic–cathodic peak potential difference for a melt containing 0.670×10^{-3} mol Ir *dissolved as* IrCl$_3$ *in* 30 g (Na, K)CN *eutectic at a titanium working electrode*

Scan rate $(V\,s^{-1})$	E_p (V)	$E_p - E_{p/2}$ (mV)	$E_{ap} - E_{cp}$ (mV)
0.05	1.055	98	131
0.1	1.040	111	152
0.2	1.028	119	172
0.5	1.000	138	216

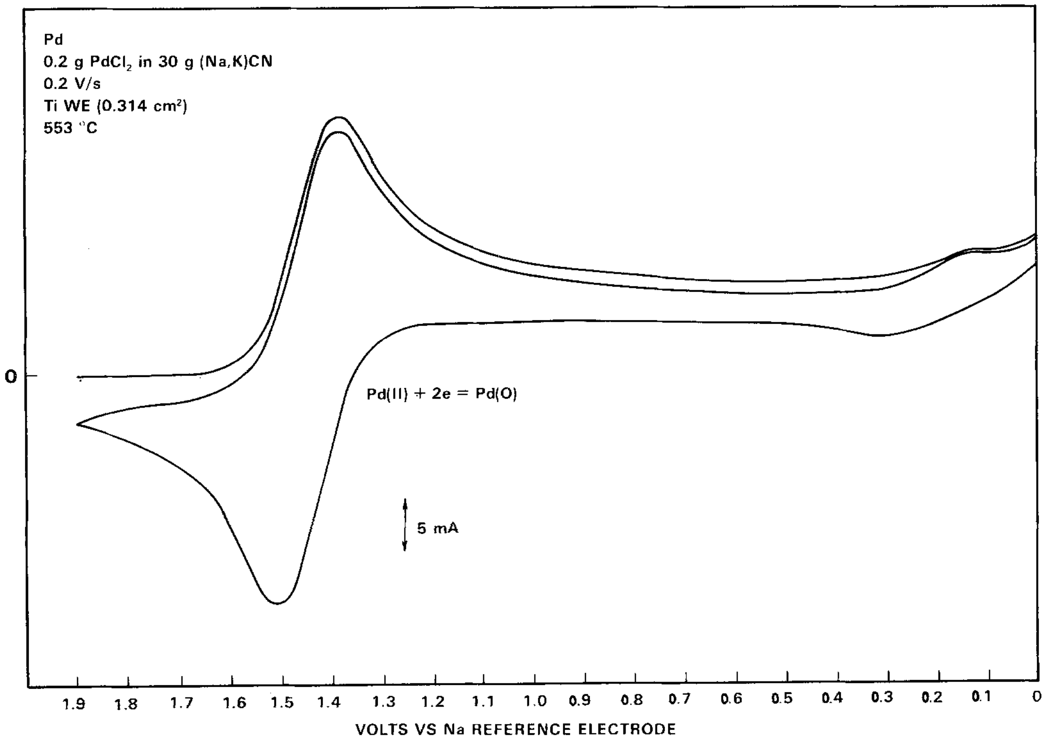

Fig. 7. Cyclic voltammogram of a cyanide melt containing palladium.

peak is related to Ir(I) comes from melts subjected to both infrared and cyclic voltammetric measurements: by increasing the Ir(I) concentration, the height of the reduction peak increased [18].

4. Discussion

From a review of the cyclic voltammograms of platinum, rhodium, palladium and iridium in molten cyanides, it becomes clear that in each case there is an equilibrium between two soluble species. For these reactions a plot of peak-current density against the square root of scan rate yielded straight lines for scan rates up to 1 V s^{-1}. Half-peak to peak potential differences indicate a two-electron transfer (Table 1). It is significant that for all four elements the potential differences are similar (although slightly larger than the theoretical predicted values), implying that electrochemically the same reaction must take place. The above-mentioned similarity and the evidence that for one of them, platinum, the number of electrons transferred was found to be two [5], also points to a two-electron transfer for the other three elements.

No oxidation states can be inferred from these results. However, from spectroscopic work [3, 4] it is evident that Pt(II) and Pt(O), Rh(III) and Rh(I), Pd(II) and Pd(O) and, finally Ir(III) and Ir(I), are the dominant and stable species in cyanide melts.

As mentioned in the introduction, the redox potential of the melt causes these equilibria to establish themselves. The species reduced in the reversible reactions represent the highest oxidation state of the metal in the melt.

Cyclic voltammograms of platinum, rhodium, palladium and iridium reveal two steps. The first step, i.e. the reversible reaction, has already been discussed. The second shows less uniformity. In the case of platinum there can be little doubt that deposition-stripping takes place. The same probability applies to rhodium. Both metals plate easily from cyanide melts. Palladium deposition is obscured due to its proximity to sodium and potassium deposition. The reaction between two soluble species in iridium is flanked on the cathodic side by a reduction peak, while an indication of an oxidation peak is found at more

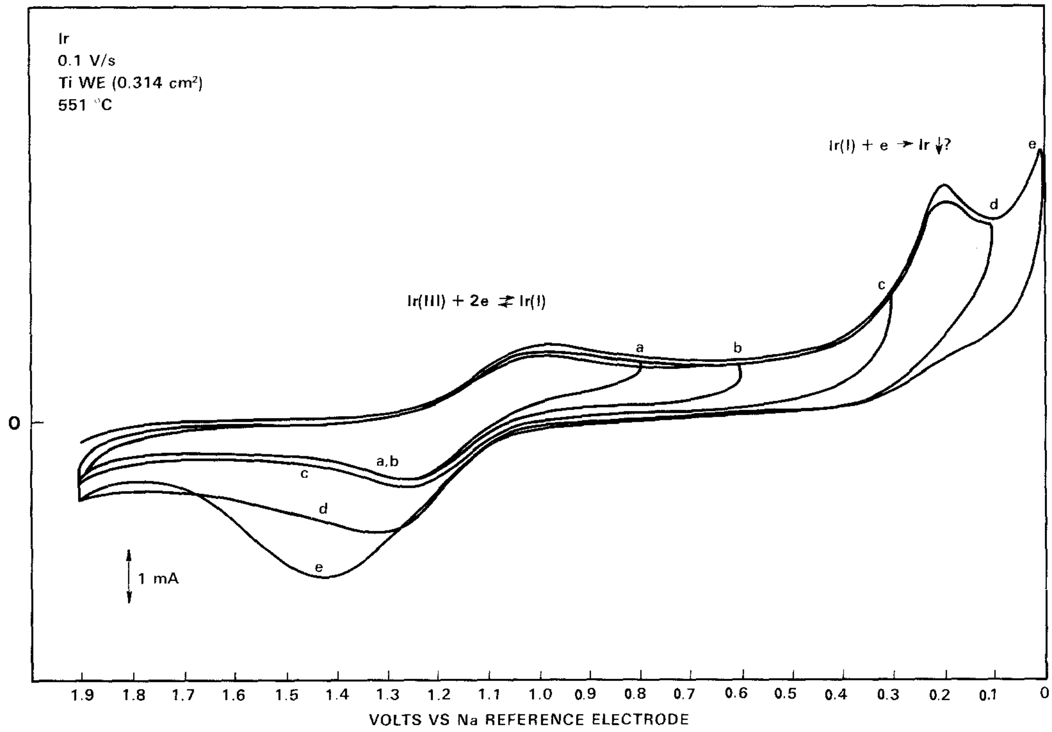

Fig. 8. Cyclic voltammogram of a cyanide melt containing iridium, cycled between 1.9 V and varying cathodic potentials.

anodic potentials (Fig. 9). Is the reduction peak due to the formation of Ir(O), which is reported to be very unstable [3, 4], or, more likely, due to the reduction to metal?

Additions of sodium dicyanamide (oxidant) should result in a greater concentration of the higher oxidation states, while sodium cyanamide (reductant) favours the lower oxidation states. Cyclic voltammograms with such additions were obtained, but the inevitable introduction of new peaks led to overlapping and the distortion of existing peaks, especially at the extreme cathodic potentials. A small amount of these compounds will be present in the melt in any case, due to the reaction of the solute(s) with the melt.

All the metal working electrodes dissolved rapidly at the extreme anodic limit of 1.9 V as their weight loss testified. At this potential, dicyanamide is formed and rapid dissolution, therefore, not surprising. Since it represents therefore, is not surprising. Since it represents should also lead to the highest oxidation state possible in the melt. In order to find out whether anodic dissolution takes place at lower potentials as well, scans were started at 0.0 V and gradually increased to higher anodic potentials. At lower potentials metal dissolutions were found for palladium, platinum and rhodium, but not for iridium. The low potential dissolution must then be evidence for the generation of Pd(I), Pt(I) and Rh(I) complexes. (No Rh(II) species have ever been detected in cyanide melts.) Coulometric experiments were also conducted for spectroscopic measurements, where anodizing at low current densities led to the low oxidation state, while above certain current densities the high oxidation state became prevalent [3, 4]. The only other element present in more than one oxidation state was nickel. Its cyclic voltammogram resembled that of platinum and rhodium, but in a 'compressed' form, i.e. it showed a reaction between two soluble species, directly followed by a deposition-stripping reaction. No consistent *n*-values could be obtained for the nickel reactions. Other elements investigated were iron,

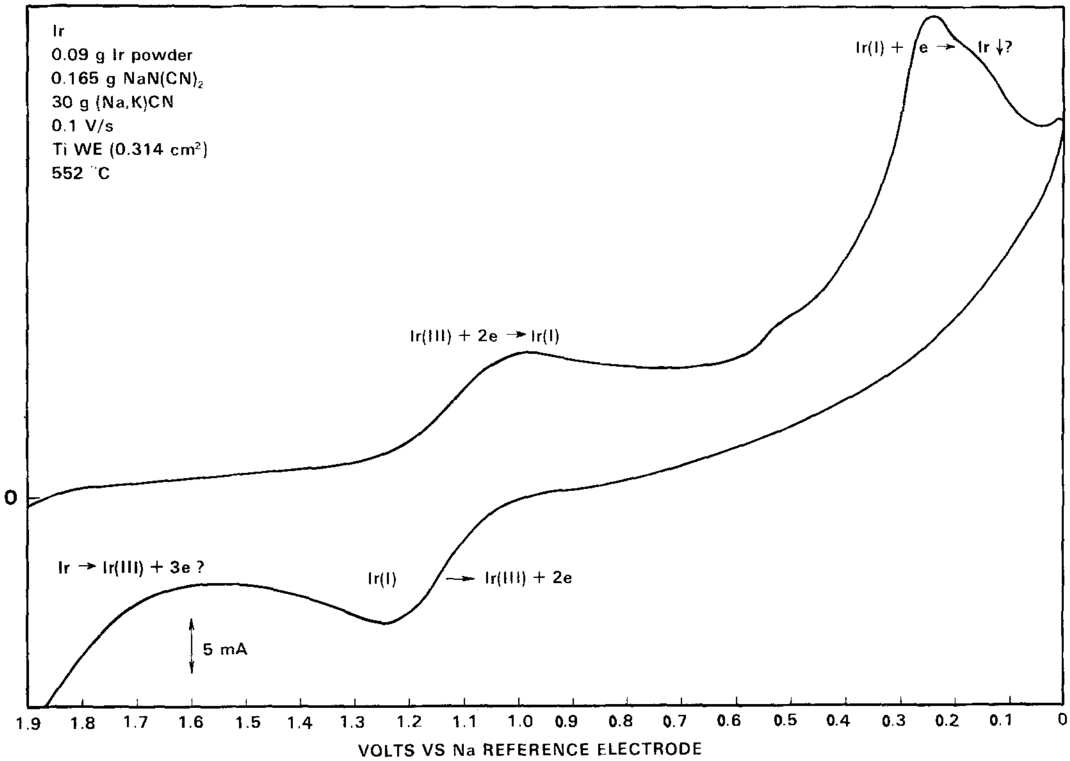

Fig. 9. Cyclic voltammogram of a cyanide melt containing iridium. Ir powder was dissolved by means of sodium dicyanamide.

chromium and manganese, but their cyclic voltammograms were not reproducible.

To summarize, the reactions between soluble species (step-one reactions) could be treated reasonably well quantitatively, but step-two reactions could not. There may be kinetic or other reasons for this behaviour, but a complicating 'incompatible' titanium working electrode may also play a role. The composite rhodium stripping peaks and the behaviour of platinum melts after multiple scanning seem to point to such a role.

5. Conclusion

Ru(II), Os(II) and Cu(I) were all stable in cyanide melts and occurred in one oxidation state only. Silver and gold precipitated from their melts. Platinum, rhodium, palladium, iridium and nickel were present in more than one oxidation state. Their cyclic voltammograms indicated the presence of at least two soluble species for these elements. No ideally reversible depositions of an insoluble product were observed.

Acknowledgements

Helpful discussions with Dr K. F. Fouché are gratefully acknowledged. This paper was originally presented at the Fall Meeting of the The Electrochemical Society, Inc. held in Denver, Colorado.

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