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THE FEASIBILITY OF ELECTROPLATING
PLATINUM-IRIDIUM ALLOY OUT OF FUSED
CHLORIDES

PDO 6984728, Topical Report

W. B. Harding, Project Leader

Published August 1976

Prepared for the United States Energy
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**Kansas City
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Project Leader:
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Department 812

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THE FEASIBILITY OF ELECTROPLATING PLATINUM-IRIDIUM ALLOY OUT OF FUSED CHLORIDES

BDX-613-1227, UNCLASSIFIED Topical Report, Published August 1976

Prepared by W. B. Harding, D/812, under PDO 6984728

The feasibility of electroplating platinum and platinum-iridium alloys out of mixtures of molten chloride salts was studied by means of constant-current electrolysis and cyclic voltammetry. Platinum anode and cathode efficiencies were 100 percent. The deposits were coarsely crystalline, dendritic, and noncoherent. Only platinum deposited from melts containing both iridium and platinum because the deposition potential of iridium is 50 to 100 mV more cathodic than that of platinum. It was concluded that deposition of these metals from chloride melts was not feasible.

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SUMMARY

The feasibility of plating platinum and platinum-iridium alloys out of molten chloride salts was tested. Chlorides have lower melting temperatures and are less corrosive than the cyanide salts that have been used. They therefore have potential advantages both in the design of equipment and fixtures and in the chemical stability of the melt. This work was conducted during May and June 1974.

Electrolysis and cyclic voltammetry studies were made of the eutectic mixture of lithium chloride and potassium chloride with and without additions of potassium tetrachloroplatinite (II) (K_2PtCl_4) and potassium hexachloroiridite (III) (K_3IrCl_6).

Platinum was deposited at 100 percent efficiency from melts containing it. The deposit was dendritic, coarsely crystalline, non-coherent, and nonadherent. Deposits from melts containing both platinum and iridium were pure platinum--the iridium did not deposit--and had the same undesirable form as those from the melts containing platinum only: the deposition potential for iridium was found to be about 100 mV more negative than platinum.

No future work is planned.

DISCUSSION

SCOPE AND PURPOSE

As part of the process development project on the fused salt plating of platinum and platinum-iridium alloy, a feasibility study was made of the use of chloride electrolytes for the plating bath. The work previously done on the project was with cyanide electrolytes, and, although satisfactory deposits can be obtained using cyanides, chlorides offer significant potential advantages. Chlorides have lower melting points and so might operate at a lower temperature, as much as 150 K lower. This reduces the power and insulation requirements. The thermal shock to fixtures is less, and problems arising from differential thermal expansion are less. Pyrex borosilicate glass can be used for plating fixtures and for containers because of the lower temperature and because the chloride melts do not attack glass as do the cyanides.

The platinum cyanide electrolyte is unstable, slowly breaking down into platinum metal at the operating temperature. Chlorides, by virtue of the lower operating temperature, might be stable.

Chloride salts are readily obtainable in high purities. Iridium cyanide, an ingredient in the cyanide system, is hard to synthesize and therefore not normally available from chemical suppliers. Melts of sodium and potassium cyanide contain impurities that interfere with the interpretation of experimental data and may interfere with the desired plating reactions.

Finally, chloride melts have been extensively studied, so there is a large body of literature on properties, reactions, and experimental techniques. There is virtually no information on molten cyanides.

PRIOR WORK

It was not known whether platinum and iridium could be plated out of chlorides melts. The only reference found¹ reported obtaining deposits, but the purpose of that study was purification of the raw metals by electrolysis rather than electroplating of the metals. For this reason, the report contains little information about electroplating.

ACTIVITY

Atkinson¹ used a ternary eutectic (50.6, 22.7, and 26.7 mole percent, respectively, of lithium chloride, sodium chloride, and potassium chloride). He learned that the melting point of the binary

eutectic of lithium and potassium chloride was as low as that of the ternary and, therefore, that the sodium chloride was not needed.

In the work reported here, the lithium chloride-potassium chloride eutectic was used. Lengthy purification of this mixture is required to eliminate oxygen-containing compounds, but the need for this was avoided through buying a purified mixture.* The salt is supplied in about 300-gram quantities under argon in sealed glass ampoules.

Complex iridium and platinum chlorides were used, potassium chloroiridate (III) (K_3IrCl_6), potassium chloroiridate (IV) (K_2IrCl_6), potassium chloroplatinate (II) (K_2PtCl_4), and potassium chloroplatinate (IV) (K_2PtCl_6), supplied by Research Organic/Inorganic Chemical Corp., Sun Valley, California. The eutectic was used as received. The iridium and platinum compounds were vacuum dried, typically at 30 inches of mercury (100 kPa) vacuum at 423 K for 1 hour. The weight loss during drying, presumably water, ranged from 0.05 to 0.2 percent. All of the experiments were performed under nitrogen drawn from the plant system and passed through phosphorous pentoxide to assure dryness.

Two kinds of experiments were run, simple electrolysis and cyclic voltammetry. In the electrolysis experiments, platinum was added as K_2PtCl_6 but the salt did not appear to dissolve in the melt. Therefore, in all but one of the subsequent experiments, K_2PtCl_4 was used. Atkinson¹ reported that although he added K_2PtCl_6 to his melt, electrolysis converted it to K_2PtCl_4 .

Platinum, only, was present in the melt in half of the electrolysis experiments. Both platinum and iridium were present in the others. The ranges within which the process variables were examined are these: temperature--650 to 840 K; metal concentration of platinum--0.2 to 4 w/o; metal concentration of iridium--1 w/o; anode and cathode current densities--10 to 980 A/m²; and natural convection agitation.

In most of the electrolysis experiments, a 1.6-mm platinum wire was immersed in the electrolyte and used as a reference against which the anode and cathode potentials were measured.

Platinum anodes and nickel and Inconel** cathodes were used in two experiments. In each, the cathode was etched and there was no deposit. Apparently the melt's corrosive attack upon these metals is substantially greater than the deposition process and completely

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dominates the cathode reaction. Carbon, platinum, and gold cathodes were used in the other experiments with no apparent difficulties.

In all of the experiments (except the aforementioned ones with nickel and Inconel cathodes), the cathode deposits were coarsely crystalline, dendritic, noncoherent and nonadherent. In the straight platinum runs, the cathode efficiency ranged from 80 to 108 percent. Because the deposits were dendritic, some platinum may have been lost from the cathode, so it seems probable that the cathode efficiency was essentially 100 percent in all cases. Anode efficiency was essentially 100 percent at low current densities, such as 60 A/m². At higher current densities (300 to 1000 A/m²) the anode became passive because of the formation of a slowly soluble film of platinous chloride (II) (PtCl₂) and the efficiency dropped to nearly zero. The cell potentials, except for the runs in which the anode became passive, ranged from about 10 to 110 mV.

In all of the experiments in which both platinum and iridium were in the melt, the deposit was pure platinum. Iridium could not be detected using an electron microprobe. This was indirectly confirmed because the deposits were soluble in aqua regia. On the basis of platinum alone, the cathode efficiencies in these mixed electrolytes were essentially 100 percent.

The chemical reactions occurring during electrolysis were studied by means of cyclic voltammetry (CV). This technique has been discussed in detail in an earlier report² and will be only briefly described here.

In CV, the potential on an electrode is swept at a selected rate from some starting value to a second value and then swept back to the beginning, usually at the same rate. The potential on the electrode is measured against that of a reference electrode--in this case, a platinum wire. A counter electrode in the electrolyte completes the circuit. The current flowing through the cell is measured and the potential-current relationship is plotted by an X-Y recorder.

When the potential is swept through a value at which an electrode reaction occurs, the resulting current flow produces a peak. Cathodic reactions produce cathode peaks (upward in the convention used in this study) and anode reactions produce anodic peaks (downward). The locations, shapes, and sizes of the peaks yield information on the thermodynamics and kinetics of the reactions. In the present study, CV was used only to locate the potentials at which the electrode reactions of interest occurred.

Figure 1 is a CV made of the as-received chloride eutectic in which the reference, working, and counter electrodes were 1.6-mm diameter platinum wires. The sweep started at the left (+500 mV on the working electrode versus the reference electrode) and proceeded in a

clockwise direction. There was very little current initially because at the moment this high potential was applied, high current momentarily flowed producing insoluble PtCl_2 faster than it could be converted into soluble K_2PtCl_4 . The salt formed a high resistance film on the anode.

As the potential was swept to the right the point was reached (+280 to +300 mV) where the rates of dissolution and formation were the same, the film dissolved, and anodic current flowed. Continuing the sweep, the point was reached (+210 to +240 mV) at which the reaction reversed, the current became cathodic, and the previously formed K_2PtCl_4 was now reduced back to platinum metal. The cathodic current reached a peak, and then fell to essentially zero when all of the K_2PtCl_4 produced in the anodic side of the cycle had been reduced back to platinum.

The sweep reversed at -300 mV and the current remained zero until approximately +50 mV. Then the platinum started to go into solution again and an anodic current began to flow. The current increased rapidly until the potential reached about +420 mV, at which point the electrode once again passivated. The anodic current at this point (about 1900 A/m^2) was substantially greater than that of the cathodic peak (about 350 A/m^2) because whereas in the cathode reaction there was a limited amount of reactant present, all of it coming from the anodic part of the cycle, the supply of raw materials for the anodic reaction, platinum and chloride, was essentially unlimited.

A second sweep was made immediately following the first giving essentially the same pattern. The reason for the displacement to the left of the cathode peak on the second sweep was not known. Possibly it was a result in a change in the working electrode surface produced by the first sweep.

From CV, therefore, it was learned that a platinum anode will passivate if the current density is high. The upper limit was substantial and therefore not likely to occur in practice. The smooth transition from the anodic to the cathodic side of the sweep showed that little or no over-voltage was required to initiate either the anode or cathode reaction. Finally, there was only one anode and only one cathode reaction in the voltage range swept. These reactions, therefore, should have occurred at 100 percent efficiency.

A CV run was made of the same electrolyte after the addition of K_2PtCl_4 to give a platinum concentration of about 1 percent by weight. The shape of the curve obtained (Figure 2) was essentially the same as in Figure 1, but there were meaningful differences. The curve in Figure 2 shifted to the right. The cathode peak was now at about -90 mV instead of about +150 mV. The potential at which the anode passivated moved from +420 mV to +350 mV.

Figure 1. Cyclic Voltammogram of LiCl-KCl Eutectic at 729 K, Using Platinum Wire Electrode

Figure 2. Cyclic Voltammogram of LiCl-KCl Eutectic Containing One Percent by Weight of Platinum as K_2PtCl_4 , Using Platinum Wire Electrode

These shifts were caused by a shift in the potential of the reference electrode resulting from the addition of the K_2PtCl_4 . In the first run, the platinum ion concentration in the electrolyte surrounding the reference electrode was essentially zero. In the second run, the concentration was about one percent by weight, which shifted the reference electrode in the positive direction. Actually, the reference electrode was a pseudo-reference electrode because its potential was a function of the electrolyte composition. A true reference electrode would be independent of such minor change in composition.

A net current flowed at the potential to the right of the cathode peak in Figure 2 (as compared to zero in Figure 1) because there was a supply of platinum ions in the electrolyte to support a current, whereas in the other run all of the platinum ions were produced during the anodic cycle and were quickly exhausted. The level portion of the curve at the cathode end showed that with a 1-percent platinum content the limiting current density was about 300 A/m^2 .

It was not known why the current density at which anode passivity set in was so much higher (4250 A/m^2 versus 1950 A/m^2) in Figure 2. Nor was the significance understood of the discontinuity in the small anodic peak appearing in the forward sweep. The discontinuity was reproducible and therefore real. It appeared that another passive film formed briefly.

Figures 3 and 4 are CV curves, again on the same electrolyte but now after the addition of K_3IrCl_6 to give 1 percent by weight of iridium along with the like amount of platinum. The working electrode is platinum in Figure 3 and iridium in Figure 4. Two cathodic peaks corresponded to the reduction of platinum and of iridium. Comparison of Figure 2 and 3 suggested that the first cathodic peak reached during the sweep was that for platinum and that iridium was the second peak, at roughly 100 mV more cathodic value. Figure 4 was the same form except the potentials were displaced in the anodic direction. Why it was displaced is not known. Problems such as that demonstrated the importance of a reliable reference electrode with which real potential changes could be distinguished from apparent ones.

The presence of the iridium peak to the cathodic side of the platinum peak was consistent with the findings of the electrolysis experiment: only platinum deposited from electrolytes containing both platinum and iridium. The deposition potential for iridium was 50 to 100 mV more cathodic than that of platinum. In the electrolysis runs the overall potentials were about 10 to 100 mV. So it appeared that in none of the electrolysis runs did the cathode potential reach the value necessary for the deposition of iridium. Codeposition of the two metals would require much higher current densities and operation at the diffusion control level for platinum.

Figure 3. Cyclic Voltammogram of LiCl-KCl Eutectic Containing One Percent by Weight of Platinum as K_2PtCl_4 and One Percent by Weight of Iridium as K_3IrCl_6 , Using Platinum Wire Electrode

Figure 4. Cyclic Voltammogram of LiCl-KCl Eutectic Containing One Percent by Weight of Platinum as K_2PtCl_4 , and One Percent by Weight of Iridium as K_3IrCl_6 , Using Iridium Wire Electrode

Only one anode reaction was revealed--platinum dissolution in the first and iridium dissolution in the second.

In Figure 5 and 6, the anode potential was carried well beyond the point of anode passivation. In Figure 5, the working electrode was platinum; in Figure 6 it was iridium. In Figure 5, the passivation of the anode still occurred but not as abruptly (review Figures 1 and 2) and the subsequent return sweep contained what appeared to be noise. It might have been that, by the time this run was made, the platinum electrode had developed surface roughness that prevented the formation of the tight, uniform passive film obtained in earlier runs.

Figure 6, more complex, was not completely understood. There appeared to now be four cathode peaks with a new one at +100 mV and the one at 0 mV splitting into two. A new, small, anodic peak showed up at +230 mV. This shows that the iridium system was more complex, possibly because iridium was present in more than one valence state. In this case, the anodic peak at +230 mV might have represented oxidation of iridium from a +3 to a +4 valence and the cathode peak at +100 mV the reduction of the +4 back to the +3. There was no explanation of the new peak around 0 mV..

Experience with the fused cyanide system² showed that iridium had a complex behavior there, too.

ACCOMPLISHMENTS

The study of the chloride system, for feasibility only, indicated that the system is not feasible without substantially more work.

Platinum was deposited at 100 percent efficiency from a chloride melt containing potassium platinum chloroplatinite (II) (K_2PtCl_4). The deposits were dendritic, coarsely crystalline, noncoherent, and nonadherent. Chloride melts containing both platinum (K_2PtCl_4) and iridium as potassium chloroiridite (III) (K_3IrCl_6), upon electrolysis, yielded similar deposits that were pure platinum. Platinum anodes run at moderate current densities had 100 percent efficiency.

Cyclic voltammetry showed that the deposition potential of iridium in fused chlorides was about 100 mV more cathodic than platinum.

FUTURE WORK

No future work is planned.

Figure 5. Cyclic Voltammogram of LiCl-KCl Eutectic Containing One Percent by Weight of Platinum as K_2PtCl_4 , and One Percent by Weight of Iridium as K_3IrCl_6 , Using Platinum Wire Electrode

Figure 6. Cyclic Voltammogram of LiCl-KCl Eutectic Containing One Percent by Weight of Platinum as K_2PtCl_4 , and One Percent by Weight of Iridium as K_3IrCl_6 , Using Iridium Wire Electrode

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