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Studies of platinum electroplating baths Part VI: Influence of some experimental parameters on deposit quality

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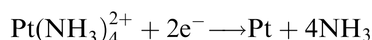
The influence of the conditions on the rate of Pt electroplating and the quality of the deposited layers are reported for the Pt 5Q bath (26 mM $Pt(NH_3)_4HPO_4$ + ≈30 mM sodium phosphate buffer adjusted to pH 10.4 with NaOH). It is confirmed that much higher rates of deposition can be achieved using constant potential control and the resulting deposits are less stressed than those formed by constant current plating. Deposition with high current efficiency is possible at 358 K but again it is more readily achieved at constant potential; the rate of deposition is, however, lower and the plate quality is not as good as observed at 368 K. Finally it is reported that three types of deposit can be identified by scanning electron microscopy (almost featureless, hemispherical growth centres leading to "cauliflower" deposits, and angular crystallites) depending on the cathode potential.

Keywords: *platinum electroplating*, *deposit structure*

1. Introduction

Platinum electroplating is extensively used in the engineering industry, particularly when components are subject to the risk of high temperature corrosion. In these applications, it is necessary to electroplate thick layers of Pt, typically more than ~5 μm, and this is conveniently achieved with a high rate plating bath such as the Pt Q solutions supplied by Johnson Matthey [1, 2]. This plating solution contains $Pt(NH_3)_4^{2+}$ (Pt concentration 5–20 g dm^{-3}) in a dilute phosphate buffer, pH 10.3–10.5 and gives high quality, thick Pt deposits when it is operated at a temperature above 363 K. Previous papers [3–5] have defined the influence of the conditions on the voltammetry of the bath and discussed the complex mechanism for the reduction



$$Pt(NH_3)_4^{2+} + 2e^- \longrightarrow Pt + 4NH_3$$

In particular, it has been shown that voltammograms for Q bath at Pt, C or Cu cathodes, each show a reduction peak for this reaction at a potential close to −740 mV vs Ag/AgCl. The reduction is, however, never mass transport controlled and the peak current density is very sensitive to temperature, no peak or wave being observed close to room temperature. On the other hand, although the recommended operating temperature for Q bath is above 363 K [1], the voltammograms show significant reduction peaks at temperatures in the range 340–360 K. This paper, therefore, considers further the effect of temperature on the deposition of Pt from Q bath. In addition, the influence of the rate of plating and surface preparation on the type and quality of the platinum layers formed in this bath is discussed.

2. Experimental details

The solution was the Pt 5Q electroplating bath, containing 5 g dm^{-3} Pt(II) in ~30 mM sodium phosphate buffer adjusted to pH 10.4 with NaOH and supplied by Johnson Matthey Materials Technology Division. Plating solutions were replaced regularly (each experiment, when thick deposits were formed and daily for other experiments). Although similar results could be obtained with copper panel substrates, the results reported here were obtained with Cu disc cathodes (area 0.08 cm^2). Polished Cu surfaces were prepared by abrading with 600 grade emery paper and then polishing with alumina powder (1.0, then 0.3 and 0.05 μm grades) on a moist polishing cloth (materials from Buehler Inc.), followed by thorough washing with deionized water. Rough surfaces were prepared only by abrading with emery paper and washing. In one set of experiments, freshly machined discs were used and these retained the circular tool marks from their fabrication on a lathe. In all experiments, the counter electrode was a Pt gauze. Scanning electron microscopy employed a Joel analytical instrument, type JSM 6400. All other experimental information can be found in the earlier publications in this series [3–5].

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3. Results and discussion

3.1. *Influence of temperature at constant potential*

The deposition of Pt onto Cu from Pt 5Q bath (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer adjusted to pH 10.4 with NaOH) was carried out at a series of potentials at 368 K and 358 K, above and below the minimum recommended temperature. In fact, the potential was stepped from −400 mV to a value in the range −650 to −900 mV and the potential was then held constant for 3 h (368 K) or 5 h (358 K). After a rising current at very short times (<60 s) while the nuclei of Pt form, pass through an initial growth phase and then overlap into a continuous layer [5], a steady state current was observed at each potential while the deposit thickens. At the end of the depositions, the current efficiency was calculated from the increase in weight of the copper cathode and the appearance of the Pt layers was examined. Table 1 reports the steady state currents and the current efficiencies for Pt deposition. It can be seen that there is little difference in the current efficiencies for Pt deposition at the two temperatures. They are high until hydrogen gas evolution begins on the electroplated Pt negative to −800 mV. At all potentials, the rate of deposition is, however, clearly lower at 358 K; the maximum rate at 358 K corresponds to a current density of 4.2 mA cm^{-2} compared to 13.2 mA cm^{-2} at 368 K. On the other hand, the shape of the steady state current density vs potential responses for the Pt(II) → Pt reaction are similar with a peak at around −700 mV. The steady state currents were also independent of the mass transport regime confirming that the rate of Pt deposition was limited by a chemical step. All these observations are consistent with the voltammetry reported earlier [3–5]. It should be emphasized that, at both temperatures, the rate of deposition declined over the potential range −700 to −800 mV although there was little change in the current efficiency. This is an unusual feature and clearly indicates a change in surface conditions which adversely influences the rate of deposition. The adsorption of H atoms seems the only process likely to occur over this range of potentials.

Table 1. Steady state current densities, $j_{s.s.}$, and current efficiencies, ϕ, for the constant potential deposition of Pt onto Cu from 5Q bath (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer adjusted to pH 10.4 with NaOH)

	368 K		*358 K*	
$-E$ *vs Ag/AgCl*/mV	$j_{s.s.}$/mA cm^{-2}	ϕ/%	$j_{s.s.}$/mA cm^{-2}	ϕ/%
650	6.0	92	2.4	77
700	13.2	97	4.2	90
750	6.6	97	3.6	89
800	4.4	79	1.9	79
850	3.7	46	1.8	40
900	7.2	4	3.2	20

Deposition charges 20–130 C cm^{-2}.

Although the adhesion (as judged by repeated bending of plated foils as well as the degree of pressure required to remove layers with emery paper) of all the electroplates was excellent, their appearances did depend on the plating conditions. At 368 K, positive to −700 mV, the electrodeposits were metallic and highly reflecting. Then to more negative potentials they became less reflecting until, beyond −800 mV, the layers were matt and black. At 358 K, the deposits were never highly reflecting although uniform in appearance. The same general trend with potential was apparent. At potentials positive to the peak in the current/potential response, the deposits were metallic but grey while at more negative potentials the deposits darkened and were eventually matt black. It should be noted that the matt black deposits do not arise from mass transport controlled deposition; the currents for Pt deposition are below 10% of the predicted mass transport controlled current in these conditions.

Figure 1 illustrates the scanning electron microscopy of these deposits. At both temperatures, the micrographs show the same trends. At the most positive potentials, the deposits appear relatively flat although underlying hemispherical features can be seen. At slightly more negative potentials, the deposits had a 'cauliflower' appearance with the deposit being made up of closely spaced, dense hemispherical centres; each of these centres can be seen to be made up of smaller and densely packed, overlapping centres. Beyond −800 mV, the structure changed entirely and the deposit then consists of many, overlapping angular crystallites with sharp edges growing out into solution.

The micrographs for the plates formed in the range −600 to −800 mV at 368 K are clearly different from those reported in an earlier paper [5]. The micrographs reported there show the deposits to be rather featureless but also highly cracked. It was postulated that the difference lies in the degree of polishing, the more polished surface leading to the featureless and more reflecting deposit. This was confirmed by two types of experiment. Figure 2 shows scanning electron micrographs for thinner deposits formed under identical deposits on a well polished copper surface and a surface which had been deliberately scratched. The former is featureless while the latter deposit shows linear features reflecting the substrate preparation. Another interesting feature of the experiments was that the steady state current densities at the scratched surfaces were lower than at the polished surfaces; this surprising result must arise from the different nucleation patterns at the two types of surface. Figure 3 shows a low sensitivity scanning electron micrograph for a plate onto a disc which retained the circular tool marks from its machining during fabrication on a lathe; on the lower magnification, this thick deposit clearly shows that the growth centres collect within the defects caused by the machining. It is, however, worthwhile to note that cracks only appear in the deposits which are

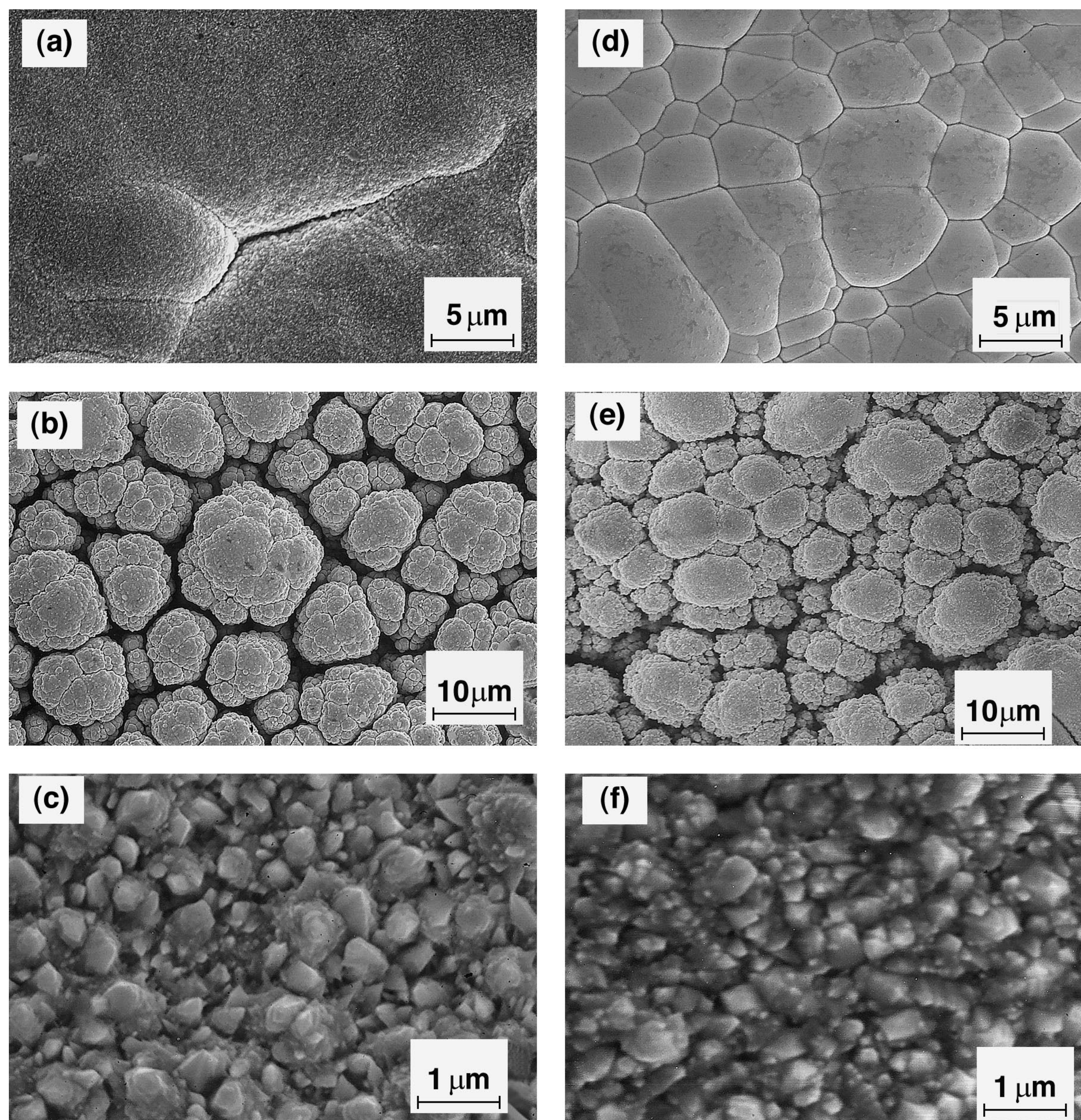

Fig. 1. SEM of thick deposits plated from Pt 5Q bath under constant potential control. Bath temperature: (a)–(c) 368 K and (d)–(f) 358 K. Potentials: (a) −650, (b) −700, (c) −850, (d) −700, (e) −750 and (f) −850 mV vs Ag/AgCl.

otherwise featureless. Insufficient stress is present in all deposits where grain boundaries are observed or the deposit can be seen to be made up of many centres.

3.2. *Influence of temperature at constant current*

Table 2 reports data for the deposition of Pt from the same solution at a series of constant current densities, again using temperatures of 358 K and 368 K. In each experiment, the electrode quickly takes up a constant potential and this is reported in the table along with the current efficiencies for deposition. At both temperatures, it is clearly impossible to achieve rates of deposition comparable to those carried out at constant potential deposition; with current densities above 2.5 mA cm^{-2}, the potential for deposition is shifted into the region where the current efficiency is decreased by hydrogen evolution. It is not surprising that, for a system with a current density/potential characteristic with a large peak, with constant current control the cathode always takes up a steady state potential well to one side of the peak.

At highly polished copper surfaces and 368 K, the deposits formed at 1.0 and 2.5 mA cm^{-2} (and using a deposition charge of 1 or 10 C cm^{-2}) were both strongly adherent and highly reflecting while at 358 K, reflecting deposits were only obtained at 1.0 mA cm^{-2}. At higher current densities, the deposits were metallic but grey and poorly reflecting. When examined by scanning electron microscopy, it could be seen that the highly reflecting surfaces were all featureless except for extensive cracks. It appeared that these deposits are formed with a high degree of stress and that they crack as they are cooled since there is no evidence for renucleation and growth of Pt within the cracks. Above the current densities where a shift in potential to beyond −800 mV is observed, the

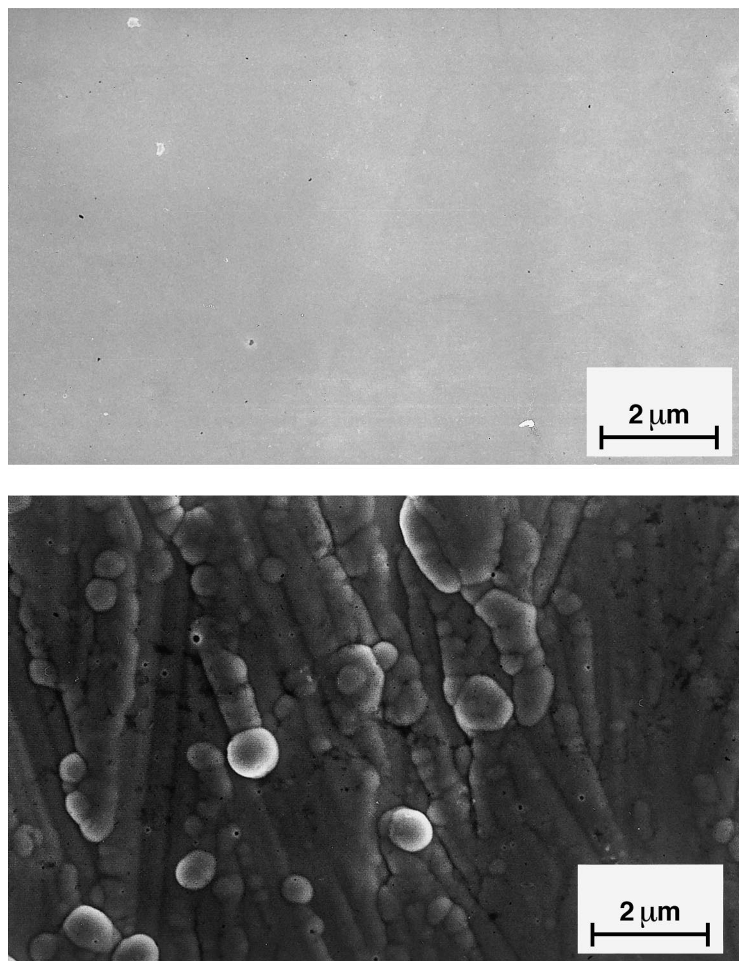

Fig. 2. SEM of thin deposits ($\sim$2 C cm^{-2}) plated from Pt 5Q bath under constant potential control. Bath temperature: 368 K (a) highly polished Cu surface, $E = -600$ mV vs Ag/AgCl (b) abraded Cu surface, $E = -700$ mV vs Ag/AgCl.

deposit always consists of angular crystallites. For example, Fig. 4 compares the scanning electron micrographs for deposits formed at 2.5 mA cm^{-2} at the two temperatures.

4. Conclusion

Constant potential control has the advantage over constant current control electroplating in Pt Q baths; it is possible to achieve significantly higher rates of Pt deposition. This is the case at 358 K as well as 368 K although the absolute rate of deposition is substantially decreased at the lower temperature. Moreover, the use of a constant potential permits high current efficiencies to be obtained at temperatures of 358 K as well as 368 K. Indeed, it is now clear that the step increases in current efficiency with temperature reported earlier [1, 3] result only from the use of constant current control, the particular current density selected and the peaked form of

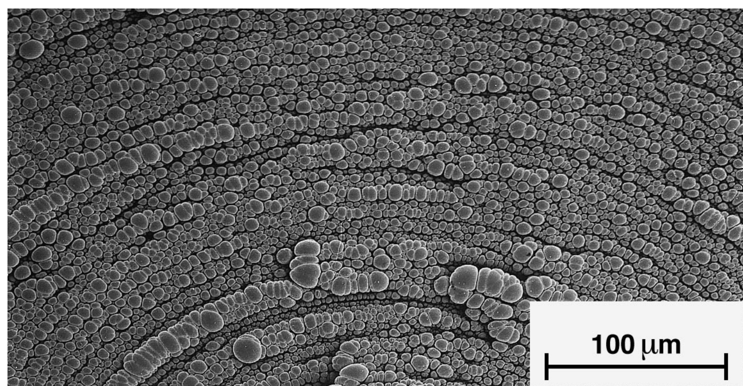

Fig. 3. Low sensitivity SEM of a thick deposit (76 C cm^{-2}) on a copper disc retaining the circular tool marks on its surface from its fabrication on a lathe. Electroplated from Pt 5Q bath at -700 mV vs Ag/AgCl. Temperature 358 K.

Table 2. Steady state potentials, E, and current efficiencies, ϕ, for the constant current deposition of Pt onto Cu from 5Q bath (26 mM $Pt(NH_3)_4$ + ~30 mM sodium phosphate buffer adjusted to pH 10.4 with NaOH)

	368 K		358 K	
$j_{s.s.}$/mA cm^{-2}	−*E vs Ag/AgCl*/mV	ϕ/%	−*E vs Ag/AgCl*/mV	ϕ/%
1.0	610	67	615	67
2.5	620	88	880	61
5.0	880	18	925	8
10.0	940	10	1010	4

Deposition charges 10 C cm^{-2}.

the steady state current density/potential characteristic.

The overall structure of the deposit is principally determined by the cathode potential. At the most positive potentials where Pt plating occurs, the SEM are always almost featureless. Then over a range of potentials positive to about −750 mV, the deposit can be seen to be made up of essentially hemispherical centres; depending on the conditions, these centres may be merged into a uniform flat deposit (particularly with constant current control where a high nucleation overpotential at the instant the constant current is applied leads to a high nucleation density) or may lead to the 'cauliflower' appearance. Negative to −750 mV, the deposit is always made up of the angular crystallites. This marked change in deposit structure must reflect a significant change in the electrode/solution interface and, as previously proposed [5], it would seem that it is the adsorption of hydrogen atoms on the Pt surface that leads to a change in the shape of the Pt nuclei and growing centres as well as decreasing the rate of deposition. The deposits with appearances ranging from shiny and highly reflecting to matt black as well as quite

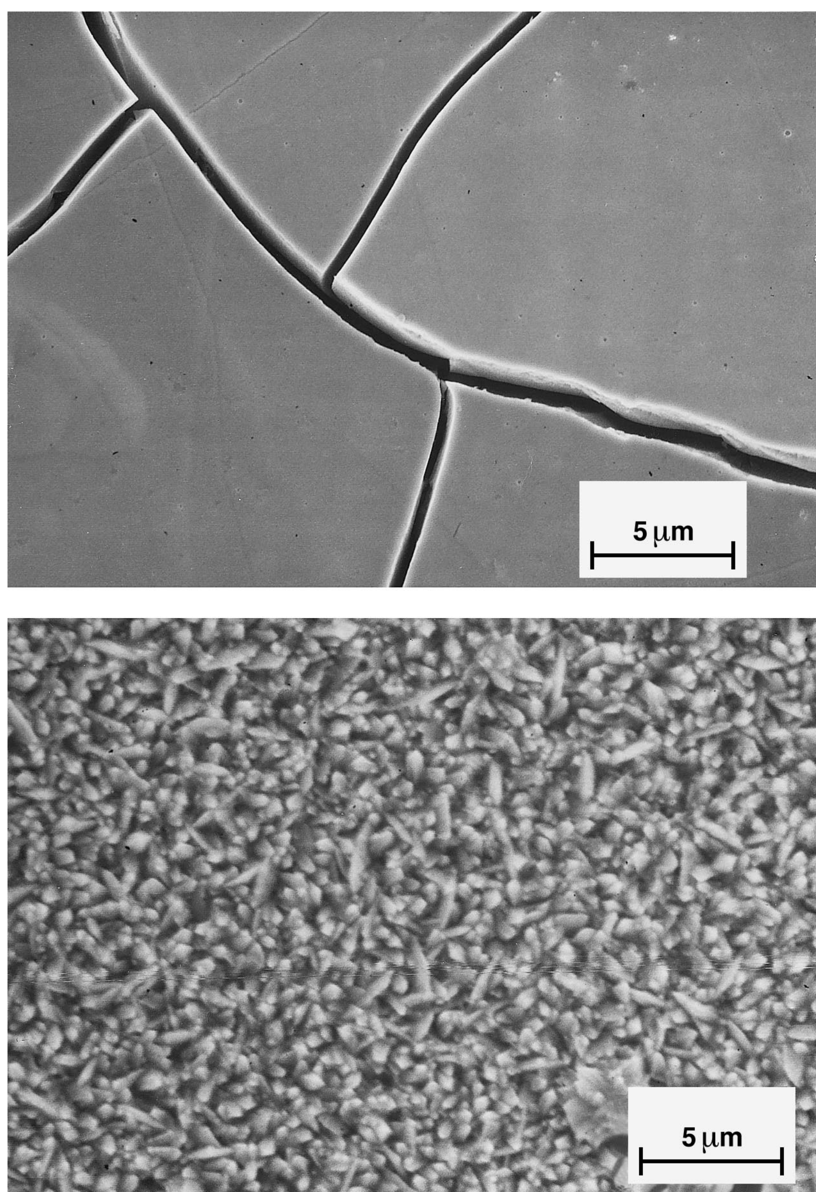

Fig. 4. SEM of deposits (10 C cm^{-2}) plated from Pt 5Q bath onto polished Cu discs with a constant current density of 2.5 mA cm^{-2}. Temperature: (a) 368 K and (b) 358 K.

different structures are certainly all formed in conditions where the current densities are much below mass transport control.

Surface preparation also influences the properties and appearance of the deposits (although not the basic type of structure). Not surprisingly, highly polished copper surfaces are essential to the deposition of Pt layers with a high reflectivity.

It is interesting to note that stress related cracking of the electroplates is only observed for deposits which appear to be almost featureless by scanning electron microscopy. The extent of cracking increases with deposit thickness and is also most prevalent with constant current deposition. Unfortunately, the deposits with highest reflectivity are also those which are most stressed although a compromise of reasonable reflectivity without cracking can be achieved with constant potential deposition. When individual hemispherical centres or the angular crystalline structure are observed by SEM, the stress in the deposit is relieved at the grain boundaries.

The plating solution was replaced regularly to avoid changes in the bath composition (i.e. there was no depletion of Pt(II) or accumulation of Cu(II), anode products or byproducts of the deposition process). Such variations inevitably occur in commercial operation and it would be interesting to define their influence on the quality and morphology of the Pt deposits.

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