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# Platinization assisted by Keggin-type heteropolytungstates<sup>\*</sup>

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### Abstract

Chronoamperometry and cyclic voltammetry (CV) were used to address the platinum deposition kinetics on glassy carbon and polycrystalline Pt supports from H<sub>2</sub>PtCl<sub>6</sub>-containing solutions with and without additives of different Keggin-type heteropoly acids (HPAs) of tungsten. The effect of addition of these polyoxometallates manifested itself in the pronounced disturbance of instantaneous nucleation and it can be interpreted in terms of strong HPA adsorption on certain nucleation centers followed by the modification of their activity. HPA additives decreased the current efficiency for Pt deposition despite the fact that the reduction of HPA additives was thermodynamically forbidden at the potentials chosen for electrodeposition. The latter fact can be explained as selective inhibition of the intermediate Pt<sup>II</sup> reduction by tungstates. CV of Pt deposits in sulfuric acid solutions indicated a noticeable increase in the deposit roughness if P- and Si-containing HPA were added in the course of platinization. More complex behavior was found for *B*-dodecatungstate that most likely originated from its tendency to undergo codeposition with Pt. Ex situ scanning tunneling microscopy (STM) images demonstrate more pronounced globular structure and smaller crystal sizes for HPA-affected deposits as compared with usual platinized platinum. These features can be explained by HPA effects on deposition kinetics assumed on the basis of electrochemical data and demonstrate that HPA can act in template-like manner.

Keywords: Platinum deposition; Polyoxotungstates; Adsorption; Nucleation; Scanning tunneling microscopy

## 1. Introduction

Heteropoly acids (HPAs) of tungsten containing electrochemically inert hetero atoms exhibit the redox properties attractive for electrocatalysis and nanotechnology [1-4]. A group of well-characterized Keggin-type complexes is among the most studied HPAs because of their unique stability at low pH and the possibility to tune the potentials of subsequent electron transfer processes in a wide range.

Polyoxo acids, including HPAs, tend to undergo spontaneous adsorption from aqueous solutions on various electrode substrates, namely Hg, Au, Ag, glassy carbon (GC), and highly oriented pyrolytic graphite (HOPG) (see [5-8] for example). This phenomenon provides a simple tool for the modification of the surfaces [9-18]. While the adsorption interactions of HPAs with platinum electrodes are commonly accepted, they have not been studied in detail until recently. For example, it has been demonstrated for a smooth and platinized platinum [19] that Keggin-type adsorbed HPAs interact with hydrogen adatoms. This interaction leads to the appearance of new highly reversible redox features that should be attributed to mixed hydrogen/tungstate adlayers and interpreted in terms of spillover effect. Similar features were found for multilayers formed by isopolytungstates on smooth Pt [20].

It is plausible to expect that it is just the interaction of immobilized tungstates with hydrogen adatoms<sup>2</sup> (H-

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 $<sup>^{2}</sup>$  Here and below we use notations H-upd and O-upd for the corresponding regions of underpotential deposition.

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upd) (and/or fairly specific tungstate effect on oxygen adatoms (O-upd) [2,21]) which is responsible for the pronounced electrocatalytic activity of platinized films of tungsten oxides,  $WO_3 \cdot nH_2O$  (1 < n < 2), and Keggin-type heteropoly tungstic acids [22,23]. Consequently, the activity of the resulting system should be sensitive to the mutual location of tungstate and platinum nanosize fragments in the mixed materials, and the latter feature is expected to be sensitive to the choice of deposition (codeposition) mode.

Polyoxotungstate reduction at low pH values proceeds at potentials being hundreds of millivolts more negative in comparison to the Pt<sup>IV</sup>/Pt<sup>0</sup> formal potential. Hence, contrary to polyoxomolybdate acids which undergo multielectron reduction simultaneously with Pt<sup>II</sup> and Pt<sup>IV</sup> complexes [24], a wide region of potentials is available for the Pt cathodic deposition in the absence of any parallel tungstate reduction. The purpose of this work is to address the most general kinetic peculiarities of Pt electrodeposition from polytungstate-containing media in the absence of parallel reduction of the HPA additive. We have also considered the effect of tungstate adsorption in the course of deposition by using traditional approaches to the analysis of nucleation growth phenomena in terms of current transients. Finally, we compared deposit's roughness as estimated from conventional cyclic voltammetry (CV) with the structural features imaged by means of ex situ scanning tunneling microscopy (STM).

## 2. Experimental

HPAs  $(H_3PW_{12}O_{40} (PW_{12}), H_4SiW_{12}O_{40} (SiW_{12}), H_5BW_{12}O_{40} (BW_{12}))$  and  $H_2SO_4$  were for analysis grade quality (Merck). All solutions were prepared from ultrapure water (Millipore). High-purity grade  $H_2PtCl_6 \cdot H_2O$  was provided by both Merck and Reakhim (Russia).

A three-electrode cell was used for all electrochemical measurements. Polycrystalline Pt foil (apparent area: 1 cm<sup>2</sup>) and a commercial GC electrode (Mineral, Warsaw, Poland) with a diameter of 0.3 cm were used as the supports. The auxiliary electrode was a Pt wire. During CV experiments, the potentials were measured with respect to reversible hydrogen electrode (RHE), consisting of Pt/Pt wire immersed in hydrogen-saturated 0.5 M  $H_2SO_4$  and connected with working electrode compartment by Luggin capillary. Saturated calomel electrode was used as a reference electrode in deposition experiments. All potentials are reported below in RHE scale.

Before each deposition experiment, Pt support was etched in hot aqua regia, washed with water, and subsequently polarized by anodic and cathodic current (current density: 20 mA cm<sup>-2</sup>) in 0.5 M H<sub>2</sub>SO<sub>4</sub>. GC electrode was thoroughly polished prior to each deposi-

tion (powdered glass) and washed before use. If to compare the pretreatment mode with the modes applied in Ref. [25], the surface of the present GC corresponds to the less-oxidized GC.

Platinum was electrodeposited from  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub>+0.5 M H<sub>2</sub>SO<sub>4</sub> solution and in the presence of  $10^{-2}$  M HPAs at 0.25 V.

The solutions were deaerated thoroughly for 30 min with pure argon. Experiments were carried out at room temperature.

To obtain deposition current transients and to fabricate the deposits, the electrode potential was first maintained at 0.9 V (which corresponds to the potential region in which chloroplatinate complex is not reduced, provided that  $E^0$  values are equal to 0.726 and 0.758 V for Pt<sup>IV</sup>/Pt<sup>II</sup> and Pt<sup>II</sup>/Pt<sup>0</sup>, respectively [26]) for 1 min and then switched to the electrodeposition potential of 0.25 V. In the preparative experiments on Pt supports, the deposition charge was controlled and the process was interrupted after attaining 13 C cm<sup>-2</sup>. This charge formally corresponded to the deposition of 3 µm of Pt layers under assumption of the 100% current efficiency. To check the real current efficiency, the supports were weighted before and after deposition with the accuracy of 0.2 mg.

To study H-upd and O-upd on resulting platinized platinum samples, the potential was scanned in the range 0.05–1.3 V in supporting electrolyte solution. Prior to these measurements, the deposits were thoroughly washed by water. The real surface area  $S_r$  was calculated from H-upd charge by normalizing it to 210  $\mu$ C cm<sup>-2</sup> value. As some difference of anodic and cathodic H-upd charges was observed, we calculated two  $S_r$  values (denoted below as 'an' and 'cat') for each deposit. The exact  $S_r$  value finds itself within the interval limited by these values.

Both CV and current transients were measured with BAS Model 100B Electrochemical Analyzer and EG&G PAR Model 173 Potentiostat/Galvanostat equipped with a Model 175 Universal Programmer and Model 179 Digital Coulometer.

Polarographic experiments were carried out on the dropping mercury electrode, as it is described in detail in Ref. [8].

STM imaging was carried out ex situ with the use of Litscan-2 device [27] with bias voltage of 0.2–0.3 V and typical tunneling currents up to 0.2–0.3 nA. To obtain representative images, we scanned 2–3 samples of each type, approaching 3–5 macroscopic regions of each sample (total size of samples was ca.  $5 \times 10 \text{ mm}^2$ ). For each tip approach, about 10–20 images were registered, both in µm- and nm-size scales. The sign of tunneling current and scan direction did not affect the images. The smallest size of particle which we were able to visualize at available resolution was ca. 2 nm.

#### 3.1. Current transients

The choice of electrodeposition potential was based on the previously reported data concerning platinization from H<sub>2</sub>PtCl<sub>6</sub>-based electrolytes [26,28,29]. The deposits obtained earlier at 0.25 V exhibited fairly high current efficiency for the Pt<sup>IV</sup>/Pt<sup>0</sup> process (up to 90%), high stability, and their cyclic voltammetric (CV) responses were typical for conventional polycrystalline Pt. The latter observation can be interpreted in terms of the absence of any specific defectiveness, which arises when one is depositing Pt at more cathodic potentials or, on the contrary, at very low overvoltages. Additional forcible argument involved the possibility of avoiding the reduction of tungstate because, for even the most easily reducible  $PW_{12}$ , the polyoxometallate reduction starts only at potentials more negative than 0.25 V  $(E^0 = 0.15 \text{ V (SHE) for } PW_{12}^{VI}/PW_{11}^{VI}W^V$  [30]). Electroreduction of SiW<sub>12</sub> and BW<sub>12</sub> starts at even more negative potentials [30].

The transients measured on Pt foil in all deposition solutions (Fig. 1a) exhibit sharp current growth after application of the deposition potential followed by current decrease, which is more and more monotonous with time. Transients flatten at sufficiently long times (>30 s). The initial current values are very close to one another in solutions containing HPA additives and seem to be slightly higher for  $PW_{12}$  and  $SiW_{12}$  and lower for BW<sub>12</sub> than those in the  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub>+0.5 M H<sub>2</sub>SO<sub>4</sub> solution studied here for comparison (curve 1 in Fig. 1a). The transients in the presence of HPAs most likely reflect the sum of several current transients corresponding to various nucleation processes, and this fact can be explained in terms of Pt nucleation at the centers of various activities (or with various induction periods). The transients replotted as *i* vs.  $t^{-1/2}$  (i.e. according to the model of diffusion to the planar electrode surface rather realistic for supports under study) might be



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Fig. 1. (a) Current transients for Pt deposition at 0.25 V at Pt foil from solutions: (1)  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub>+0.5 M H<sub>2</sub>SO<sub>4</sub>, and (2) H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, (3) H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, and (4) H<sub>5</sub>BW<sub>12</sub>O<sub>40</sub> in the presence of  $10^{-2}$  M HPAs; (b) the analysis of *i* vs.  $t^{-1/2}$  transient responses for Pt deposition at 0.25 V at Pt foil from solutions: (1)  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub>+0.5 M H<sub>2</sub>SO<sub>4</sub> and (2) the same in the presence of  $10^{-2}$  M H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

approximated by two straight lines with non-zero intersects corresponding to the points appearing at low t (Fig. 1b). As before [29], the change of the slope can be explained by inhibitory effect of Cl<sup>-</sup> anions generated in the course of chloroplatinate reduction. This inhibitory effect manifests itself at longer times in HPA-containing solutions as compared with conventional platinization electrolyte.

The transients obtained on Pt are rather featureless due to the presence of a large number of nucleation centers. Typical nucleation maxima, if any, are expected to appear at millisecond-range time and they superimpose a region of a sharp current decrease induced by double-layer charging. It appeared to be possible to obtain reliable non-monotonic transients for a slower nucleation process taking place on GC (the example involving PW<sub>12</sub> is given in Fig. 2a). In the latter case, by analogy to HPA-free solutions [25], the more detailed analysis of nucleation kinetics can be carried out.

The current maxima preceding plateau currents appeared on i-t curves recorded on GC in all deposition solutions under study following t = 8-20 s (Fig. 2a). Their positions were affected by both reagent concentration in the absence of additive (curves 1 and 2 in Fig. 2a) and by the presence of HPA (curves 1' and 2' in Fig.

Fig. 2. (a) Current transients for Pt deposition on GC at 0.25 V from 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions containing (1, 1')  $10^{-3}$  M and (2, 2')  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub> and also (1', 2')  $10^{-2}$  M H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>; (b) non-dimensional (*I*/ $I_{m}$ )<sup>2</sup> vs. *t*/ $t_{m}$  plots for progressive (1) and instantaneous (2) nucleation as compared with the transients of Pt deposition on GC from  $10^{-3}$  M H<sub>2</sub>PtCl<sub>6</sub>+0.5 M H<sub>2</sub>SO<sub>4</sub> solutions without additive (3, 4) and in the presence of  $10^{-2}$  M H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (5); curve 4 corresponds to preliminary treatment of GC with H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-containing solution under open circuit with subsequent washing.



2a). Most pronounced difference was observed in the vicinity of maxima, manifesting the preferential HPA effect on primary nucleation. It should be mentioned that deposition current in the absence of HPA is not exactly proportional to reagent concentration, and the shift of maximum with concentration does not follow usual tendencies, as it shifts towards higher time value. This behavior demonstrates self-inhibition of reaction in more concentrated solution.

In accordance with the theoretical models of the mass transport controlled nucleation and growth of hemispherical clusters, we carried out the analysis of current transients plotted in non-dimensional coordinates (I/  $I_{\rm m}$ )<sup>2</sup> vs.  $t/t_{\rm m}$  (Fig. 2b), where  $t_{\rm m}$  is the time at current maximum  $I_{\rm m}$ , in order to recognize qualitatively the progressive or instantaneous nucleation (corresponding theoretical curves (solid) are numbered 1 and 2, respectively) [31]. In the absence of HPA (curve 3 in Fig. 2), the reduced transient for more diluted  $10^{-3}$  M H<sub>2</sub>PtCl<sub>6</sub> solution finds itself between theoretical curves for progressive and instantaneous nucleation (curves 1 and 2 in Fig. 2b) in the region of deposition times shorter than 50 s; further deviations can be explained by secondary nucleation [25]. The reduced transient recorded in  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub> solution coincides with the model curve for instantaneous nucleation in the same time interval. Similar instantaneous behavior was observed for Pt nucleation on HOPG from  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub> solution [32].

After preliminary contact of GC with HPA-containing solution under open-circuit conditions (i.e. before the actual measurements) the reduced transient looks much closer to progressive behavior (curve 4 in Fig. 2b). The nucleation in the presence of PW<sub>12</sub> (curve 5 in Fig. 2b) follows most precisely the theoretical transient for progressive nucleation in a relatively wide time interval. These observations for both  $10^{-3}$  and  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub> solutions are in agreement with the general idea of the existence of various types of active centers on HPAmodified surface. Deviations of transients observed at longer deposition times are of the same type as in HPAfree solution but they start at higher times. It can be concluded that the secondary nucleation is slightly slower in the presence of HPAs.

Let us stress that close shape of curves 4 and 5 which both differ from curve 3 in HPA-free solution confirms strong bonding of adsorbed HPA and impossibility to delete it by washing the electrode under open circuit.

For instantaneous nucleation, the diffusion coefficient  $D \pmod{s^{-1}}$  can be estimated [32] from the following equation:

$$i_{\rm m}^2 t_{\rm m} = 0.1629 D(zFc)^2 \tag{1}$$

where z = 4, F is Faraday's constant (96 500 C mol<sup>-1</sup>), and c (in mol cm<sup>-3</sup>) is the PtCl<sub>6</sub><sup>2-</sup> concentration in solution. When progressive nucleation occurs, D can be estimated according to

$$i_{\rm m}^2 t_{\rm m} = 0.2598 D (zFc)^2 \tag{2}$$

For  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub> solution, the calculated value of D (4.25 × 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup>) from Eq. (1) is in satisfactory agreement with the value  $D = 4.5 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> reported earlier [33], but it is slightly higher than the effective D value obtained for the deposition on HOPG  $(3.74 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ [32]})$ . For  $10^{-3} \text{ M H}_2\text{PtCl}_6$ solution the choice of Eq. (1) or Eq. (2) for D calculation looks ambiguous because of pronounced deviations of the transient from both theoretical curves. Under rough approximation we calculated formal Dvalues using both Eqs. (1) and (2) and found that in both cases these values are rather high  $(1 \times 10^{-5} - 1.5 \times 10^{-5})$  $cm^2 s^{-1}$ ). The same very high D value calculated for the progressive nucleation (Eq. (2)) corresponds to deposition from  $10^{-3}$  M H<sub>2</sub>PtCl<sub>6</sub> solution with PW<sub>12</sub> additive ( $1.6 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>), when for  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub>+PW<sub>12</sub> solution a reasonable value of  $4.7 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> is obtained.

Close D values for solutions with and without additive of one and the same H<sub>2</sub>PtCl<sub>6</sub> concentration allow us to conclude that the degree of conformity in respect to a simple models of mass transport controlled nucleation is not affected by the additive. For more concentrated solution, this degree of conformity is evidently higher than for more diluted solutions, as for the latter the D values are overestimated. However, under these circumstances qualitative comparison of curves with and without additive looks correct, even if the real mechanism is more complex and probably corresponds to comparable rates of nucleation and growth or to the mixed control [34]. Detailed elaboration of this mechanism is beyond the statement of this study. What we demonstrate here is the qualitative HPA effect, namely the fact that the presence of HPAs in the deposition solutions results in higher heterogeneity of nucleation centers. In the limiting case it results in the transfer from instantaneous to progressive nucleation, but in general case it is more correct to state the decrease of nucleation rate at certain centers induced by adsorbed tungstate.

#### 3.2. Current efficiency

When the Pt electrodeposition was performed in presence of HPAs additives, the mass (m) of deposit corresponding to constant deposition charge appeared to be lower in comparison to the situation where deposition was achieved from tungstate-free solution. In both cases, the electric charges consumed were equal (Table 1). The current efficiency values (w) somewhat differ for Pt/Pt electrodes that were deposited from H<sub>2</sub>PtCl<sub>6</sub> solutions with PW<sub>12</sub> and SiW<sub>12</sub> additives. It was found that *w* was higher in the case of deposition

Table 1

 $S_{\rm m} \,({\rm M}^2\,{\rm g}^{-1})$ Deposition solution  $S_r (cm^2)$ R w (%) m (mg)5.3 690 690 80 13.0 H<sub>2</sub>PtCl<sub>6</sub> (an) H<sub>2</sub>PtCl<sub>6</sub> (cat) 5.3 622 622 80 11.7  $H_2PtCl_6 + PW_{12}$  (an) 4.0 645 645 61 16.1 H<sub>2</sub>PtCl<sub>6</sub>+PW<sub>12</sub> (cat) 581 4.0581 61 14.3  $H_2PtCl_6 + SiW_{12}$  (an) 3.9 640 640 59 16.4 H<sub>2</sub>PtCl<sub>6</sub>+SiW<sub>12</sub> (cat) 3.9 581 581 59 14.9  $H_2PtCl_6 + BW_{12}$  (an) 2.0 180 180 30 9  $H_2PtCl_6+BW_{12}$  (cat) 2.0252 252 30 12.6

Survey of data related to Pt deposition from  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub>+0.5 M H<sub>2</sub>SO<sub>4</sub> with and without  $10^{-2}$  M HPAs additives (Q = 13 C cm<sup>-2</sup>) and to CV measurements in 0.5 M H<sub>2</sub>SO<sub>4</sub>

from HPAs-free solution and it was lower for  $BW_{12}$ -containing solution (Table 1).

Consumption of charge during any Faradaic reaction with HPAs participation cannot be a reason for such a strong w decrease because the reduction of HPAs from the solution bulk at 0.25 V is impossible. Some redox processes involving adsorption of HPAs [19] cannot give so strong contribution to w decrease, at least for  $PW_{12}$ and  $SiW_{12}$  which are forming submonolayer adsorbates. A possible explanation of w decrease may take into account an additional accumulation of  $Pt^{II}$  intermediate in the reaction layer in the presence of HPA.

The electroreduction of  $PtCl_6^{2-}$  to metallic Pt is usually considered under the first approximation as a two-step reaction [35,36] having comparable redox potentials for two subsequent two-electron steps [26]. The observed splitting of the thermodynamically predicted united four-electron reduction wave has kinetic origin ([29] and references therein). One of the widely accepted explanations involves the inhibition of the first and/or the second two-electron steps by Cl<sup>-</sup> anion (in particular, by negligible amount of chloride generated in the course of reduction of platinum complexes). It is also known that the sensitivity of the second step to the chloride adsorption is more pronounced in comparison to the first one, thus resulting in the accumulation of  $PtCl_4^{2-}$  in solution and in corresponding decrease of the current efficiency [29]. In the tungstate-free solutions, the latter effect is potential-dependent and the rates of Pt<sup>IV</sup>/Pt<sup>II</sup> and Pt<sup>II</sup>/Pt<sup>0</sup> reactions become comparable as the overvoltage increases. Consequently, the inhibitory ability of Cl<sup>-</sup> anions at 0.25 V is not very high.

One can assume that adsorbed HPAs can act like chlorides but in a wider potential range, since the specific and strong adsorption of various polyoxometallates on various electrode materials has been demonstrated [1–18]. The adsorbed HPAs can form wellordered self-assembled monolayers [18,37–41] and some of them even have a tendency to undergo multilayer adsorption (for example, the number of layers reaches 6-7 on Hg for some systems at high positive surface charges [7]).

To verify indirectly the hypothesis about the more pronounced inhibition of the PtII/Pt0 reduction in comparison to the Pt<sup>IV</sup>/Pt<sup>II</sup> preceding process by adsorbed HPAs, we have applied polarography utilizing a dropping mercury electrode. The advantage of this electrode is the stable state of its surface during reaction and the possibility of overcoming mass transport limitations in a certain potential region. As it has been already demonstrated [8], the  $PtCl_4^{2-}$  reduction is strongly inhibited by tungstates at positive free electrode charges. This inhibition appears during electroreduction of many anions (e.g.  $S_2O_8^{2-}$ ,  $BrO_4^-$ ,  $Co^{III}(EDTA)^-$ ). The results obtained now for  $PtCl_6^{2-}$  imply some similarities between the reactions because the polarographic maximum is also suppressed and the currents at positive charges are also lower than the limiting diffusion current. However, the current growth that accompanies polytungstate charge-induced desorption (with the potential shift towards more negative values) has been found to be more pronounced for  $PtCl_6^{2-}$  rather than for  $PtCl_4^{2-}$  which is in agreement with our hypothesis about the stronger inhibition of the second step at a given tungstate surface coverage. This result cannot be extended automatically and quantitatively to solid electrodes and to lower overvoltages, but it seems to be at least qualitatively consistent with the abovementioned hypothesis. Further experiments are in progress and they should lead to final conclusions.

### 3.3. Roughness of deposited platinum

All deposits considered here were characterized by similar H-upd and O-upd voltammetric responses, which were separated by smooth double-layer region (Fig. 3). For all deposits studied, no additional peaks appeared in comparison to platinum deposited from the HPA-free solution. For  $PW_{12}$  undergoing one-electron reduction in the H-upd region, the result implies the absence of the dissolved additive in the bulk of deposit (for example, in the pores). In the case of the samples deposited from  $BW_{12}$ -containing solutions, the anodic



Fig. 3. Cyclic voltammograms recorded at 0.01 V s<sup>-1</sup> in the solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> on Pt/Pt deposited at 0.25 V ( $Q_{dep} = 13 \text{ C cm}^{-2}$ ) from (a)  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub>+0.5 M H<sub>2</sub>SO<sub>4</sub>, and (b) H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, (c) H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, and (d) H<sub>5</sub>BW<sub>12</sub>O<sub>40</sub> in the presence of  $10^{-2}$  M HPAs.

and cathodic charges were observed to be non-equivalent (the latter being higher).

The real surface area of the deposits  $(S_r)$  was estimated from H-upd charges. Current was integrated in the potential range 0.05-0.45 V and corrected for double-layer charging by means of linear extrapolation. The values of  $S_r$  are listed in Table 1. There are some differences in the values obtained from anodic and cathodic portions of H-upd responses. For BW<sub>12</sub> cathodic charge is higher than corresponding anodic value, when for all other deposits the anodic charge is slightly higher. To clarify the reasons of these differences, the equilibrium charge values are necessary which can be obtained in future from more slow measurements. At this stage we limit ourselves by rough comparison of  $S_r$  values for various deposits based on the difference of only anodic or only cathodic H-upd charges. A general qualitative tendency can be formulated as follows: the additives of  $PW_{12}$  and  $SiW_{12}$ increase the specific areas of deposits, whereas the BW<sub>12</sub> additive probably slightly decreases it in comparison to the area of a usual deposit. The latter follows only from comparison of anodic H-upd charges for pure Pt/Pt and Pt deposited from BW<sub>12</sub>-containing medium. However, there are no doubts that  $BW_{12}$  is less effective for Pt roughening than  $PW_{12}$  and  $SiW_{12}$  (compare both anodic and cathodic values in Table 1).

It is noteworthy that the formation of rechargeable tungstate multilayers on Pt surface cannot be excluded [19]. Correspondingly, for this type of samples, the presence of solid polytungstate in the deposit bulk is feasible. Charge used for the formation of such films may be responsible for the abnormally low current efficiency observed (Table 1). If it is operative, the true Pt mass is expected to be lower in comparison to those given in Table 1.

It should be stressed that all above-mentioned CV data refer to stable deposit structures. The constant real surface area observed in 10 subsequent potentiodynamic cycles was taken as a criterion of stationarity. It took ca. 1 h to reach this state in the course of potentiodynamic aging. Characterization of the aging processes of deposits shall provide additional information on the deposit structure and stability.

Potentiodynamic aging in the potential region from 0.05 to 1.3 V resulted in the decrease of  $S_r$  for all deposits under study. It was observed that Pt/Pt electrodes deposited from HPA-free solutions were slightly more stable against aging (the decrease of  $S_r$  was ca. 12%, whereas it was ca. 14% for deposits obtained in the presence of HPAs additive). On the other hand, this difference does not seem to be significant enough to make any definite conclusion. Further, there are no special non-equilibrium features of HPA-affected deposits that induce their instability.

The aging affects the shape of H-upd response. To illustrate these results, we consider the  $h_2/h_1$  ratio (where  $h_2$  and  $h_1$  are the heights of H-upd current peaks related to strongly and weakly bound H adatoms, respectively). The  $h_2/h_1$  value of  $0.91 \pm 0.01$  was obtained for freshly deposited Pt/Pt and it exhibited no dependence on the presence or absence of HPAs. During the aging process, the parameter decreased and reached the values of 0.7 for Pt deposited from HPA-free solution (the result is consistent with the ratio for smooth Pt [29]) and 0.8 for the solutions with HPAs additives. Having in mind the earlier study [29], in which interpretation based on the preferential surface crystallographic orientation was provided, the present data imply the possibility of some specific structural features induced by tungstates.

## 3.4. STM measurements

In order to get the direct information about the surface morphology of electrodeposits under study, we compared ex situ STM images of three types of aged samples (Fig. 4): Pt/Pt (images a, d) and Pt deposited from PW<sub>12</sub>- and BW<sub>12</sub>-containing solutions (images b, e and c, f, respectively). Typical STM images of submicron regions (see Section 2 for statistical details) demonstrate the presence of globules consisting of nm-size crystals (Fig. 4a–c). For Pt/Pt the globules are more smooth and homogeneously distributed along the surface; the difference of deposit height in the vicinity of any globule does not exceed 100 nm and is comparable with the linear size of globule (typically 80–120 nm). This fact means that the globules inside the deposit bulk



Fig. 4. STM images of aged Pt/Pt deposited from (a, d)  $10^{-2}$  M H<sub>2</sub>PtCl<sub>6</sub>+0.5 M H<sub>2</sub>SO<sub>4</sub>, and (b, e) H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and (c, f) H<sub>5</sub>BW<sub>12</sub>O<sub>40</sub> in the presence of  $10^{-2}$  M HPAs; image scales: (a-c)  $240 \times 240$  nm<sup>2</sup> and (d-f)  $20 \times 20$  nm<sup>2</sup>.

are close-packed. Note that Pt/Pt images treated in Ref. [29] were obtained for slightly thinner deposits in which globules were rarely imaged because of more smooth morphology.

Images of samples deposited from  $PW_{12}$ - (Fig. 4b) and  $BW_{12}$  (Fig. 4c)-containing solutions demonstrate more pronounced surface heterogeneity. HPA-affected deposits contain more separated globules with the average diameter of 50–120 nm. In general, these aglomerates are chaotically located; however, there are the regions in which the globules look ordered, especially for  $BW_{12}$ -affected deposits (Fig. 4c). Differences of deposit height in the vicinity of globule are in general higher than for Pt/Pt and sometimes reach 350–400 nm. There are, however, some closely packed globules which look coalesced in  $BW_{12}$ -affected deposits.

The smallest imaged fragments of deposits are represented by nm-size particles (crystals) of elliptical shape, with average diameter ranging from 7 to 9 nm for Pt/Pt (Fig. 4d). This observation is in agreement with the data [29] for aged Pt/Pt. Similarly, aged deposits prepared in PW<sub>12</sub>-containing solutions also consist of elliptical particles (Fig. 4e). However, their elongation is less pronounced and their average diameter is noticeably smaller (5–7 nm). For deposit prepared in BW<sub>12</sub>containing medium the majority of particles look hemispherical, with diameter of ca. 4–5 nm (Fig. 4f). The smaller the particles in the globules, the higher pronounced is the order inside the globule. For BW<sub>12</sub>affected deposits, this order is most pronounced, as the globules consist of linear rows of particles.

Decrease of particle size and more pronounced globular growth with ordered location of crystals in the globules are the typical features of quasi-template deposition [42]. Qualitatively, all these features can be explained by adsorption of template molecule (HPA in the systems under discussion) on the support and newly formed nm-scale crystals. Adsorption-induced decrease in the number and/or activity of primary nucleation centers result in the start of secondary nucleation at lower surface coverage by the primary nuclei. As the latter appear to be more rarely distributed along the surface, the secondary nucleation growth takes place not only on top of the primary crystals but also at other positions, and separated globules start to form instead of iterative parallel layers. At a certain moment the adsorbate is also formed on already deposited crystals, affecting the growth rate and, probably, growth direction. As the size of HPA molecule is comparable with the size of nuclei, this effect results in above-mentioned structural difference not only for first and second but also for subsequent layers.

By analogy with Pt deposition of Pt [29] and GC [25], the lower concentration of primary active centers and corresponding preference of secondary nucleation lead to formation of smaller crystals and simultaneously increase the degree of crystal coalescence inside globules. The first feature should increase the specific surface area, when the second one is expected to decrease it. The interplay of both factors can finally lead to higher or lower  $S_r$ , so that STM data explain the effects discussed in the previous section.

### 4. Conclusions

Polytungstate-assisted potentiostatic electrodeposition of platinum proceeds under conditions of fixed nucleation growth, and the approach seems to result in higher morphological inhomogeneity of the deposits in comparison to those obtained from solutions not containing HPAs additives. Structural features result from the change of primary/secondary nucleation rates governed by the number of corresponding nuclear centers. This effect results in more pronounced globular structure of deposits and smaller size of crystals. The degree of crystal coalescence depends on the additive nature and can induce both increase and decrease of specific deposit area. From mechanistic point of view, strong adsorption of HPA on Pt nucleation centers is expected. This work has much in common with recent concepts of Pt codeposition with oxometallates and related species under galvanostatic and potentiodynamic modes. Applications in the field of electrocatalysis and analytical sensing can be envisioned. For example, it has been found recently that methanol electrooxidation on Pt/Pt is subject to less-pronounced self-poisoning in presence of  $PW_{12}$  [43].

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