



Short communication

# Platinum oxidation in alkaline electrolyte under potentiostatic conditions



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## ABSTRACT

Oxidation of a polycrystalline Pt electrode under potentiostatic conditions is examined in an aqueous 0.1 M KOH electrolyte at potentials lower than the oxygen evolution onset. When a potential step is applied, the kinetics of the oxidation and stability of the oxidised layer formed depend on the potential applied during the first oxidation step. The results also show that Pt surfaces with a high degree of surface coverage with an oxide are stable at potentials significantly lower than applied for the oxide formation.

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## 1. Introduction

A submonolayer oxidation of noble and non-noble metals is amongst the most often studied aspects of electrochemical formation of surface oxides/hydroxides [e.g., 1–15]. Several questions related to this process, however, remain still open. This includes potential influence on the oxidation rate [4,6,15], stability of the oxidised layer at potentials different than applied for their formation [16] and existence of a limiting oxide/hydroxide thickness [4,5]. The potential influence on the oxidation rate may be related to many factors, such as the charge transfer step, adsorption of ions, chemical/physical structure of the oxidised layer formed or oxidation of various crystallographic planes of a polycrystalline surface [3,4,6,12]. Apparently constant thickness of the oxidised layer obtained for long oxidation times [5] may suggest existence of a limiting thickness of the oxide/hydroxide or a very low rate of the oxidation process which decreases with the oxidation progress. Intuitively, existence of the limiting thickness can be related to limited thermodynamic stability of very thick oxidised layers at a certain potential. In general, thin metal oxides/hydroxides play an important role in many electrocatalytic processes [17–19] hence; thorough understanding of the surface oxidation processes is required.

In Shrestha et al. [20], differences in the structure of products of Pt oxidation under potentiodynamic and potentiostatic conditions were discussed. The purpose of submitted manuscript was to explore that further influence of the order of applied potentials affects surface oxidation processes. Platinum/alkaline electrolyte system was selected for the studies due to low solubility of the electrode and reversibility of the surface oxidation processes [21–24]. Oxidation of Pt in alkaline

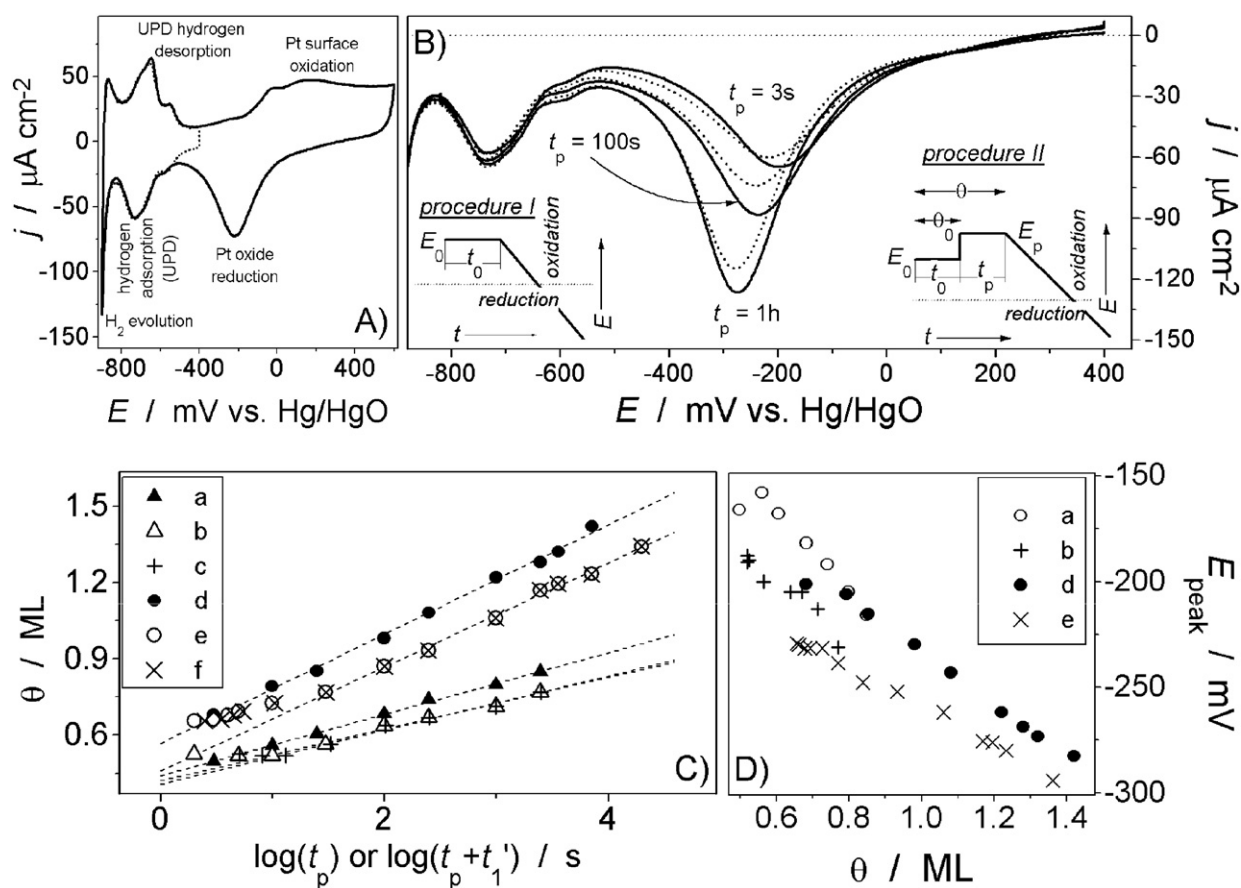
electrolytes at potentials between ca. 200 mV vs. Hg|HgO and the oxygen evolution onset lead to formation of a 2D layer containing PtO [7,22].

## 2. Experimental

A polycrystalline Pt wire (Mint of Poland, 4 N), Pt gauze-wire and Hg|HgO served as a working, counter and reference electrode, respectively. The electrolytes were prepared from Millipore water (18.2 MΩ cm) and analytical grade reagents (POCh). The experiments were carried out at room temperature, before the experiments the electrolyte was deoxygenated with Ar (Air Products, 5.0 N), during the experiments the gas stream was directed above the solution level. A CHI 660D potentiostat (CH Instruments) was used in the experiments. The real surface area, used for current density calculation, was determined by integration of voltammetric currents due to desorption of underpotential deposited (UPD) adsorbed hydrogen [25–27] recorded with negative potential limit of –800 mV (typically adopted surface coverage with adsorbed hydrogen of 0.77 [27] although the value of unity is also considered [26]) and with assumed specific charge density of 210 μC cm<sup>-2</sup> for full coverage with adsorbed hydrogen [26–28].

Fig. 1A presents typical cyclic voltammetry curve recorded for a polycrystalline Pt electrode in 0.1 M KOH<sub>aq</sub> with indicated potential regions of hydrogen adsorption/desorption, hydrogen evolution and surface oxidation. The oxidised layers were formed during a constant potential polarisation at potential region of surface oxidation for various oxidation times. In order to reduce influence of possible evolution of the electrode surface, longer and shorter oxidation times were applied alternately. Various potential sequences were applied with different numbers and orders of potential steps applied during potentiostatic oxidation. In all cases the surface oxidation procedure was followed by

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**Fig. 1.** A): cyclic voltammetry of a polycrystalline Pt in 0.1 M KOH<sub>aq</sub> (50 mV s<sup>-1</sup>). Shown are curves recorded in a limited potential region of hydrogen adsorption/desorption and the double layer charging and in potential range extended to the surface oxidation region. B): Insets: potential programmes applied in procedures I and II, details in the text. Main panel: examples of cathodic voltammetric currents (50 mV s<sup>-1</sup>) for  $E_p = 400$  mV for procedures I (solid lines) and II (dotted lines) for  $\theta_0 = 0.55$  ML ( $E_0 = 100$  mV) and  $t_p$  values of 3 s, 100 s and 1 h. C)  $\theta$  vs  $\log(t_p)$  plots for: a) procedure I for  $E_p = 300$  mV; b) procedure II for  $E_p = 300$  mV,  $\theta_0 = 0.55$  ML ( $E_0 = 100$  mV); c) same as b) but plotted vs.  $\log(t_p + t_p')$ ; d) procedure I for  $E_p = 400$  mV; e) procedure II for  $E_p = 400$  mV and  $\theta_0 = 0.51$  ML ( $E_0 = 100$  mV); f) same as e) but plotted vs.  $\log(t_p + t_p')$ . D) Potentials of Pt oxide reduction peak vs.  $\theta$ ; a), b), d) and e) have the same meaning as for panel B).

a negative potential scan with reduction of the oxidised layer. The amount of the latter was calculated by means of integration of the Pt oxide reduction peak [1,2] (Fig. 1) with assumed two electron transfer and formation/reduction of Pt(II) compounds [7,22]. In contrast to acidic electrolytes [1–5,16,28–30], in alkaline solution currents due to UPD hydrogen adsorption and reduction of the oxidised layer partially overlap [7]. Voltammetry curves recorded in a limited potential range, covering only hydrogen adsorption/desorption and the double charging regions are helpful here (Fig. 1A). Hence, the first step was integration of the cathodic section of the voltammetric curve from the negative current onset to  $-800$  mV. The currents due to the double layer charging to be subtracted were extrapolated from respective double layer currents of the curve recorded in limited potential range (Fig. 1A) while correction for overlapping currents due to hydrogen adsorption and surface reduction was made by subtraction of respective hydrogen adsorption currents of the curve recorded in a limited potential range. Based on the charge of the hydrogen desorption (Fig. 1) the obtained Pt(II) reduction charge can be recalculated into the surface coverage with the oxidised layer,  $\theta$ , expressed in monolayer units (ML).

Insets in Figs. 1B and 2A schematically depict three of potential programmes applied in the oxidation procedures. Procedure I is the one typically applied in surface oxidation studies (e.g., [1,2]) and delivers information on the kinetics of the surface oxidation at a single potential value of  $E_p$ . In procedures II and III, the oxidation at  $E_p$  is preceded by preoxidation at  $E_0$  for a certain time of  $t_0$  allowing obtaining surface coverage with the oxidised layer of  $\theta_0$ . The  $E_0$  was lower (procedure II) or higher (procedure III) than  $E_p$ . During subsequent potential

jump to  $E_p$  the surface oxidation is continued for time of  $t_p$  and  $\theta$  further increases. Application of procedures II and III allows determination of influence of the order of applied oxidation potentials on kinetics of the surface oxidation.

### 3. Results and discussion

The results of application of procedures I, II and III are shown in Figs. 2 (I and II) and 3 (I and III). In order to take into account the overall oxidation time applied for the surface oxidation, i.e.  $t_0$  at  $E_0$  (oxidation to  $\theta_0$ ) and  $t_p$  at  $E_p$ , the  $t_0$  was also recalculated into the time required to obtain the same  $\theta_0$  value but during polarisation at  $E_p$ ,  $t_p'$ . This was accomplished on the basis of the results of procedure I for a certain  $\theta_0$ . The following features are noted:

- a positive shift in potential of Pt oxide reduction peak,  $E_{\text{peak}}$ , is observed for procedures II and III for a certain  $\theta$  (Figs. 2D and 3B)
- application of procedure II leads to a decrease in  $\theta$  for a certain value of  $t_p$  (or  $t_p + t_p'$ ) (Fig. 2C)
- $\theta$  vs  $\log(t_p)$  (or  $\log(t_p + t_p')$  for procedure II) plots are linear, in agreement with Refs. [1,2,4,6,10,11] (Figs. 2B and 3C), the detailed discussion of the oxidation mechanisms can be found elsewhere [1–4,13–15]. Application of procedure II leads to a decrease in the slopes of the plots, the effect is more pronounced for a lower  $E_p$  (ca. 14–19% for 300 mV vs. ca. 5% for 400 mV) (Fig. 2B)
- a departure from linearity is observed for procedure II for low  $\theta$  values (Fig. 2B)

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