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The mild anodic oxidation of platinum in organic solvents of low acidity

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Abstract

Platinum cathodes maintained at very negative potentials in dimethylformamide (DMF) containing tetramethylammonium salts (TMAX) lead specifically to the decomposition of TMA^+ cation and the protonation of electrogenerated bases with the residual water. Therefore the electrogeneration in situ of TMAOH can yield a charging reaction with platinum at such reducing potentials. Sudden changes of potential (not larger than +0.3 V vs. the saturated calomel electrode (SCE)) allowed anodic reactions to occur, affording the superficial formation of platinum oxide. Voltammetric and chronocoulometric measurements strongly suggest that the platinum surface is uniformly covered by a compact monolayer of oxide, which can be reduced further according a well-defined adsorption-like step. This mode of superficial oxidation conducted on several types of platinum surfaces (smooth and platinized) allowed area changes to be followed in the course of multistep electrolyses.

Keywords: Platinum electrodes; Platinum oxide; Tetramethylammonium salts

1. Introduction

The electrochemical superficial oxidation of platinum electrode in rather strongly acidic and/or basic aqueous solutions is now a well-documented field [1–9]. The nature of the resulting platinum oxide (PtO or/and PtO_2) would seem to depend on the applied potential. The oxidation of platinum appeared to occur under rather drastic conditions [10–12]. More precisely, the growth of platinum oxide in 0.25 M aqueous H_2SO_4 aqueous solution at room temperature was recently described as being achieved within a potential range from 1.80 to 2.30 V vs. RHE [13]. Attention has also been drawn to the formation of an initial oxide film that would seem to correspond to two nominal monolayers of "PtO". However, with time the oxide growth did not reach a limit. The oxide was claimed to be formed concomitantly with dioxygen evolution, according to a process apparently of a high complexity.

The fine control of the formation of such superficial oxide layers may be of interest when the use of modified surfaces is considered in catalysis and in electrochemistry (not only within the oxidation range but also at fairly negative potentials) when the reduction of platinum oxide should yield a kind of "native" platinum surface in situ.

Thus, it is hereby proposed to apply the very peculiar behaviour of platinum cathodes in superdry conditions already described by our group [14,15]: let us recall that in the absence of a strong hydrogen evolution process, platinum reacts cathodically with a large palette of salts (in particular tetraalkylammonium salts NR_4X) at rather negative potentials (often beyond −2 V vs. SCE). Quite generally, the formation of thin "ionometallic" layers of structure $[Pt_n^-, NR_4^+, NR_4X]$ have been recognized. In general, the parameter *n*, which is dependent on R and X, was found to be equal to 2 or 4.

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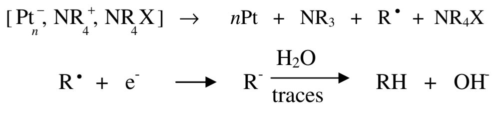
Thus, when tetramethylammonium (R = CH_3) salts are used as electrolytes in fairly aprotic dimethylformamide (DMF), specific behaviour occurs. Owing to the high cathodic reactivity of tetramethylammonium cations, hydrogen evolution does not occur prior to the implication of the salt, especially when solvent moisture is present only at very low levels. A slow decomposition of the layer could occur, rendering the electrode interface basic (see Scheme 1).

The in situ formation of OH^- led concomitantly to the consideration of a "basic" ionometallic layer at the platinum interface. Such a feature (concept of a "probase" cathode) allowed deprotonation and subsequent reaction of very weakly acidic substrates. Thus, primary alkyl halides could be transformed into alkenes in high yield [16].

If now the "basic" ionometallic layer electrochemical reactivity is considered specifically, we expect it to be oxidized anodically to liberate simultaneously platinum microaggregates and native OH^- which may be transformed smoothly into the strongly reactive $OH^\bullet$ radical.

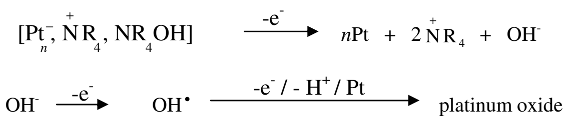
The concept of the formation of "PtO" from pulse electrolyses by using a neutral starting solution and apparently limited to a monolayer is hereafter described preliminarily (see Scheme 2).



$$[Pt_n^-, NR_4^+, NR_4X] \rightarrow nPt + NR_3 + R^\bullet + NR_4X$$

$$R^\bullet + e^- \longrightarrow R^- \xrightarrow[\text{traces}]{H_2O} RH + OH^-$$

Scheme 1.



$$[Pt_n^-, \overset{+}{N}R_4, NR_4OH] \xrightarrow{-e^-} nPt + 2\overset{+}{N}R_4 + OH^-$$

$$OH^- \xrightarrow{-e^-} OH^\bullet \xrightarrow{-e^- / -H^+ / Pt} \text{platinum oxide}$$

Scheme 2.

2. Experimental

2.1. Salts and solvent

In most of the experiments, the tetramethylammonium salts (TMAX) concentration was fixed at 0.1 M. All salts studied here were purchased from Fluka. Their purity was at least 99% and they were all employed without any additional purification after being thoroughly dried under vacuum at 60 °C (except perchlorate, which used as purchased, just for safety reasons). DMF (anhydrous, for analysis) was purchased from SDS; its percentage of water was claimed to be 0.005%. Nevertheless DMF was kept continuously over alumina activated at 340 °C under vacuum for at least 4 h before preparation of the solutions. All experiments were performed under an argon atmosphere and the total absence of dioxygen in liquid electrolytes was carefully checked. The continuous use of alumina (acidic, Brockmann I, standard grade from Aldrich) in solutions and in situ in the electrochemical cell during the experiments allowed moisture levels to be maintained no higher than 50 ppm.

2.2. Electrochemical instrumentation and procedures

All potentials are given vs. Ag|(a)gI|0.1 M $nBu_4N^+I^-$ in DMF. This electrode has a potential of −0.52 V vs. SCE at 25 °C. A three-electrode cell was used without a separator. The counter electrode was a carbon or a graphite rod. Different sized platinum electrodes were used (diameters of 0.5, 1 or 10 mm). In the present study, the electrodes were polished using Norton polishing papers (02 and 03) or DP Paste M from Struers alumina (particles for the finest polishing). After polishing operations, the electrode was always sonicated for 10 min and then rinsed twice with alcohol and acetone and dried at about 60 °C. Chrocoulometric and EQCM operations procedures have been already fully described in a recent paper [15].

2.3. Electrode plating

Coulometric experiments were carried out on platinized platinum electrodes, which were prepared by depositing the metal from an aqueous solution of $10\ g\ l^{-1}$ H_2PtCl_6 (Aldrich) in 0.1 M HCl onto a platinum disk (apparent area: $8 \times 10^{-3}\ cm^2$). The plating was achieved at a constant current density ($30\ mA\ cm^{-2}$). The changes in the morphology of the plating layer in the course of experiments were followed by SEM analysis.

3. Results

3.1. Voltammetric results

The cathodic response of polished platinum in a very carefully dried (<50 ppm) solution of TMAX salts (with $X^- = BF_4^-, ClO_4^-, I^-$) in DMF exhibits only a cathodic step Ic ($E_{1/2}$ at about −1.8 V) immediately associated with an anodic counterpart Ia (Fig. 1A). With tetraalkylammonium salts in general and with TMAX in particular, this quasi-reversible step at quite a reducing potential was assigned to a charging/discharging process. Such a feature (occurring only in quasi-superdry conditions) could be confirmed by means of EQCM and microcoulometry by forming very thin layers of platinum until the total electrochemical charging of the layer was completed. This behaviour has already