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Electrochimica Acta 52 (2007) 2775–2784
ELECTROCHIMICA Acta
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Pt-Ru electrodeposited on gold from chloride electrolytes

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Received 16 May 2006; received in revised form 27 July 2006; accepted 15 August 2006

Abstract

Voltammetric behavior of submicron-thick electrodeposited Pt-Ru on gold support is studied in sulfuric acid solution as a function of deposition potential and Pt:Ru ratio in chloride bath. In contrast to Pt-Ru, deposition of pure Ru is observed only at potentials of hydrogen evolution. The reason is found to be of kinetic nature, namely an inhibition of Ru deposition in presence of chloride. Chloride ions remain adsorbed on Ru at more negative potentials than on Pt and Au because of more negative ruthenium potential of zero free charge. Cu-UPD is applied to test the surface content of the oxidized Ru on pure Ru and various Pt-Ru surfaces. An enhancement of Ru oxohydroxides reduction in presence of Pt is observed. The electrocatalytic activity of Pt-Ru in respect to methanol oxidation correlates with the content of rechargeable surface Ru oxide. Ageing and 'training' of Pt-Ru electrodeposits under various modes is studied in order to determine the conditions of irreversible Ru oxidation. No manifestations of Ru dissolution from Pt-Ru electrodeposits in 0.5 M H_2SO_4 are found for anodic potential limits up to 1.1 V (RHE), in agreement with thermodynamic predictions. Electrodeposited Pt-Ru can be considered as a convenient model system for the study of Ru dissolution and crossover, as well as for determining the nature of the active surface species in the real composite catalysts for methanol oxidation.

Keywords: Electrodeposition; Platinum-ruthenium catalyst; Copper underpotential deposition; True surface area; Ruthenium crossover

1. Introduction

The unique electrocatalytic activity of Raney Pt-Ru alloys [1,2] and electrodeposited Pt-Ru [3] in methanol electrooxidation were discovered independently in mid 60s. Slightly later carbon supported Pt-Ru [4], Pt-Ru powder prepared via borhydrade technique and Pt-Ru electrodeposited on TiC support were reported [5]. These original studies are rarely available, as compared to review [6] or original study [7] mentioning high activity of Pt-Ru.

Despite of fantastic number of the consequent studies concerning Pt-Ru system there are very important particular aspects [5,8–13], never studied for any type of these materials except electrodeposits. Now the latter found themselves at the periphery of Pt-Ru mainstream (immobilized colloids, electroless deposits, sputtered films, isolated nanoparticles, modified single crystalline materials and templated deposits attract the main attention).

A large number of reactions had been studied in experiments with electrodeposited Pt-Ru. Besides widely discussed oxidation of methanol, formaldehyde and formic acid [5], the hydrogenation of methanol, ethanol, propanol, acetaldehyde [8] and methane [9] electooxidation were also tested. As for the studies around methanol oxidation reaction, a versatile mechanistic information had been obtained, namely the steady-state Tafel plots, pH and reactant concentration effects, and comparison of initial, steady-state reaction and strongly bonded adsorbate electrooxidation rates [5]. These data were supplemented by the analysis of oxidation products for various fuels. The important contributions to the problem of optimal Pt:Ru ratio were based on temperature effects [10] and ^{106}Ru radiotracer experiments [13]; structural effects in Pt-Ru electrocatalysis and corrosion were also considered in a comparative study of dispersed and smooth samples [5,11]. The most specific point [12], rarely considered but being of great basic importance, was the experimental estimation of the Pt-Ru potential of zero free charge (pzfc).

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doi:10.1016/j.electacta.2006.08.025

Galvanostatically electrodeposited Pt-Ru layers (several μm thick) studied in Refs. [5,8–13] certainly had an extremely complex and non-uniform structure. The interplay of various structural effects (crystal size, distribution and geometry of pores, intergrain boundaries, lattice defectiveness, etc.) makes it difficult to extend automatically any previous conclusions to currently studied well-characterized Pt-Ru materials. Recent interest to electrodeposited Pt-Ru is not limited to a search for model systems, but has some practical aspects [14], namely the pulse galvanostatic deposition mode is found providing catalysts on dispersed carbons with the activity exceeding the activity of commercial Pt-Ru.

Typical platinum group metals electrodeposited from chloride bath are complex materials containing nm-size crystals, as it follows both from the width of XRD reflections and from direct microscopic studies (see Ref. [15] and references therein). To improve the characterization level of nanocrystalline electrodeposited materials, one should first deal with potentiostatic deposition, as the nanostructural features responsible for interfacial peculiarities are very sensitive to deposition potential (and, correspondingly, to its changes in the course of galvanostatic deposition). This statement was recently illustrated in experiments with electrodeposited Pt [15,16]. An important distinction of electrodeposits from, to say, high-surface-area powder blacks (like Johnson-Matthey Plc. catalysts [17]) is the pronounced degree of nanocrystals coalescence.

The influence of the electrodeposition potential on the structure and properties of Pt-Ru is still not studied systematically. Moreover, despite a wide variety of Pt-Ru deposits on Pt, Au and carbon was prepared from chloride and chloride-less electrolytes, and numerous microscopic and spectroscopic techniques were applied to characterization of these materials, no general tendencies of the effect of deposition conditions on Pt-Ru nanostructure and/or electrocatalytic properties are understood at this stage.

Pt-Ru potentiostatic deposition from acidic solution reported in the literature usually corresponds to 50 mV (NHE) [18–21]. Deposition at 200 mV [22] and even 240 mV [23] was also reported. Deposition at 0 V (NHE) is less favorable because of parallel hydrogen evolution disturbing the formation of new metallic phase. Galvanostatic [3,18,24–26] and pulse [14] deposition also typically induce a shift of potential towards hydrogen evolution region. In addition to crystal size, lattice compression, the volume of the intergrain boundaries and microstrains found to be potential-dependent for Pt electrodeposits, the dependence of Pt:Ru content on deposition potential for any fixed composition of plating solution cannot be ruled out.

The role of ruthenium content in the deposits as a factor determining their catalytic efficiency is still unclear. We consider the distribution of Pt and Ru atoms along the surface and Ru oxidation degree as at least the factors of comparable importance.

This paper presents a necessary preliminary step of general characterization of a series of Pt-Ru films deposited from chloride solution. Our goal was to apply these materials as the model systems to clarify some principal problems known for real DMFC catalysts.

2. Experimental

Electrodes under study were prepared by electrodeposition of Pt or Ru, as well as Pt-Ru codeposition on Au foil support with usual rolled texture (4 cm^2 geometric area). Gold was chosen to avoid the interplay of the deposit/support voltammetric responses. It was possible because of very high potential at which oxygen adsorption starts on gold. Our previous experimental tests [15,27] confirm that no contribution from gold in cyclic voltammograms appears when the anodic potential limit is below 1.3–1.4 V RHE. We should also mention that the true surface area of our deposits is always 10–50 times higher as compared to the surface of gold support, with its roughness factor never exceeding 2, leading to very low gold contribution (if any) in the double layer region.

Pt deposition from chloride bath takes place with a noticeable rate at deposition potential (E_d) below 0.5–0.6 V (NHE) [27]. The highest current efficiency (85–90%) is observed for 0.05–0.2 V interval.

The electrodeposition of Pt and/or Ru was performed at constant potentials 50 and 200 mV *versus* RHE or at constant current density[2] $j = 1.25\ mA\ cm^{-2}$. Total charge spent for any electrodeposition procedure was 7.8 C. By varying the ratio of Na_2PtCl_6 and $RuCl_3$ in 1 M HCl solution (total concentration of both salts was $10\ g\ l^{-1}$) the electrodeposited layers of different composition were fabricated. The molar Pt:Ru ratios in deposition solutions were 4:1; 2:1; 1:1; 2:3; 1:2; 1:3. For comparative experiments with pure Pt and Ru, $10\ g\ l^{-1}$ H_2PtCl_6 and $10\ g\ l^{-1}$ $RuCl_3$ (both in 1 M HCl) were used. All the samples were deposited at 0.05 and 0.2 V, excluding pure Ru (see below).[3] Current efficiency decreased with the increase of Ru content, but in general the weight of all deposits was of one and the same order ($mg\ cm^{-2}$), i.e. all deposits were of comparable thickness. This was also confirmed by our preliminary reflection XRD tests demonstrating the comparable intensities of the deposit reflections as normalized per typical intensities of Au reflections.

$[RuCl_5]^{2-}$ ion is expected to predominate in all deposition solutions under equilibrium conditions [28]. No manifestations of formation of Pt-Ru binuclear species were found in detailed UV–vis absorption tests (KFK-3, wave lengths 320–600 nm). Electronic absorption spectra were also applied to estimate Pt-Ru ratio in the deposits [29,30]. Prior to analysis the deposits were dissolved in aqua regia (ca. 1 mg of metal per 2 ml of liquid). Absorptions were compared at 350 nm (Pt), 380, 450 and 510 nm (Ru). For calibration, 1:5–1:50 Pt-Ru mixtures were used. The total quantity of metals calculated from the spectra was in satisfactory agreement with the deposit weight (determined with the low accuracy because of too low thickness). Gold dissolution in aqua regia was unavoidable, and the interplay of its absorption band with Pt and Ru responses induced additional complications. This is why we limited the analysis of deposits prepared on glassy carbon from the same deposition solutions.

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[2] All the values of current density are reported per geometric surface area.

[3] All potentials are reported versus RHE.

The electrochemical measurements were conducted on an automated setup based on a PARC-273 potentiostat at room temperature 20 ± 2 °C using a cell with separated compartments. A Pt wire served as a counter electrode. A reversible hydrogen electrode (RHE) in 0.5 M H_2SO_4 was employed as reference electrode during electrochemical measurements, and saturated calomel electrode was used as a reference for electrodeposition (potentials were then recalculated into RHE scale).

Cyclic voltammograms (CV) were measured in the potential intervals 0.05–0.8, 0.05–0.9 or 0.05–1.1 V, scan rate 5–50 mV s^{-1}. These anodic limits were chosen as preceding and succeeding the Ru_2O_3/RuO_2 redox potential value [31] (0.937 V).

We assumed that for anodic 0.8 and 0.9 V limits a chance to avoid Ru(IV) formation was rather high, and looked for qualitative difference with the data for 1.1 V limit. In contrast to Ru_2O_3 (or $Ru(OH)_3$), stoichiometric oxide RuO_2 does not tend to reversible reduction at potentials above zero (RHE) [28]. Besides the partial dissolution of Ru is possible at the potentials above 0.9 V [14].

Cu-UPD stripping voltammograms were measured in 0.01 M $CuSO_4$ + 0.5 M H_2SO_4 solution within the potential interval of 0.33–0.9 V (to avoid three-dimensional Cu growth, reported in Ref. [32]), scan rate 10 mV s^{-1}.

The following notations are used below for Pt-Ru electrodes treated under various modes:

I. freshly deposited electrodes;
II. electrodes aged in air for 10 months;
III. electrodes cycled in 0.5 M H_2SO_4 in the region of 0.05–0.9 V;
IV. electrodes cycled in 0.5 M H_2SO_4 in the region of 0.05–1.1 V.

For each electrode, Pt:Ru molar ratio in deposition solution is indicated in parentheses.

2.1. Chemicals

Solutions were prepared from MilliQ water, H_2SO_4 (Merc, GR for analysis), HCl (Merc, GR for analysis), $CuSO_4$ (GR for analysis), $RuCl_3$ (Wako, min. 99.9%) and Na_2PtCl_6 (GR for analysis).

3. Results and discussion

3.1. Electrodeposition and general characterization of freshly prepared deposits

3.1.1. Single-component deposits

The shape of voltammograms measured on Pt electrodeposits in 0.5 M H_2SO_4 was typical for platinized platinum [33] and platinum on gold obtained under similar modes [15,27], with negligible effect of deposition potential (50 and 200 mV).

For Ru, no bulk deposition on gold was observed at $E_d \geq 0.05$ V. We were able to form Ru deposits only at $E_d = -0.05$ V or under galvanostatic mode (1.25 mA cm^{-2}). For the latter mode, the steady-state potential value was −0.045 V. It is not so easy to judge about the real nature of deposit because of the absence of reliable information on $Ru/[Ru(III)Cl_x]^{n-}$ redox potentials. The experimental determination of those values is complicated by the formation of intermediate Ru(II) chloride complex and its fast hydrolysis. According to Ref. [28], for

$$Ru^{2+} + 5Cl^- \leftrightarrow RuCl_5{}^{2-} + e^-$$

the equilibrium potential is given by equation

$$E = 0.239 - 0.295 \log[Cl^-] + 0.059 \log\left(\frac{(RuCl_5)^{2-}}{Ru^{2+}}\right)$$

This means that for real systems with low content of Ru(II) intermediate the formation of metallic Ru is forbidden at $E > 0.3$ V, and inability to deposit metal at $E > 0$ met kinetic, not thermodynamic complications. Strong inhibition of Ru(II) reduction at potentials 0.3–0.35 V more negative than equilibrium potential can be explained, like for $[PtCl_4]^{2-}$ [34], by high surface coverage with chloride anion. The region of chloride adsorption on Ru (Ru-modified Pt) is expected to coincide with the supposed inhibition region: according to Ref. [12], the adsorbed chloride was found at Ru electrode at $E = 0$ V because the pzfc of ruthenium (ca. −0.1 V)[4] is more negative as compared to pzfc of both Pt and Au. We assume that the initial deposition step is Ru-UPD on gold [35]. It can be enough to shift pzfc, i.e. to charge the surface positively, and by these means to induce the pronounced adsorption of chloride initially absent at the negatively charged surface of the support.

The wave of Ru(III) reduction at positive potentials (RHE) on platinum is reported in Ref. [26]. However no metal deposition was found at the potentials of this wave. The authors proposed no special interpretation, but most probably this wave corresponds to Ru(III)/Ru(II) reduction. This situations looks typical for electrodeposition from exclusively chloride Ru complexes [14,18–20,22–24,36–39], but not for nitroso-containing plating solutions [5,8,10–13,25,40] with more positive Ru/Ru(III) redox potentials.

For comparison with Pt-Ru, we studied Ru electrodeposit prepared at −0.05 V. Cyclic voltammograms of this sample in 0.5 M H_2SO_4 (Fig. 1) demonstrate one anodic maximum at 0.05–0.2 V assigned earlier to hydrogen adsorption–desorption [8]. The subsequent broad maxima at 0.35–0.40 V are typical for Ru-containing electrodes and usually related to formation of various surface oxides/hydroxides, namely $Ru(OH)_3$ (0.65–0.8 V) and hydrated RuO_2 (0.8–1.2 V) [41] (peak position and shape are very sensitive to the anodic potential limit, scan rate and electrode prehistory [35]). Three curves in Fig. 1 are normalized per scan rate increasing from 5 (solid curve) to 50 (dotted curve) mV s^{-1}. Even in this narrow range of low scan rates the decrease of “hydrogen” peak with scan rate is pronounced, in contradiction with a typical kinetics of hydrogen UPD at platinum group metals. Scan rate affects also the cathodic reduction of surface oxide, but not its formation at 0.3–0.6 V (anodic scan).

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[4] This value was obtained [12] by extrapolation of the potential dependence of the surface excess of hydronium ion in chloride-containing solution.

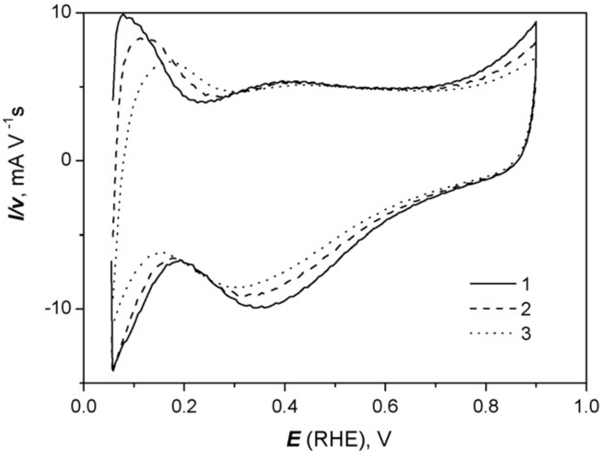

Fig. 1. Cyclic voltammograms normalized per scan rate of freshly deposited Ru ($E_d = -0.05$ V) in 0.5 M H_2SO_4 solution. Scan rate (mV s^{-1}): 1–5; 2–20; 3–50 (see text).

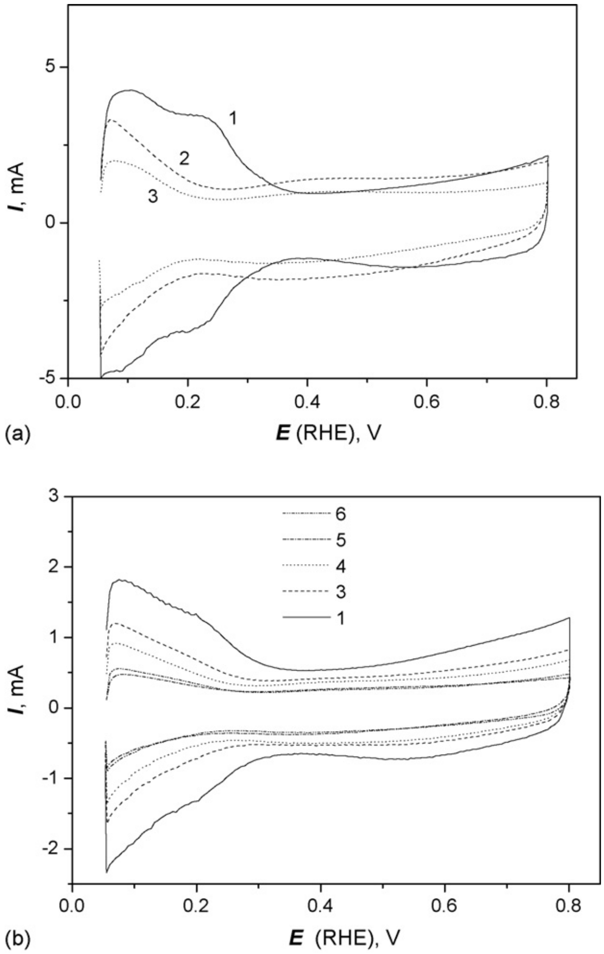

Fig. 2. Cyclic voltammograms of electrodeposited Pt-Ru electrode (type II) in 0.5 M H_2SO_4. Scan rate 10 mV s^{-1}. Deposition potential: (a) 0.05 V and (b) 0.2 V. Pt-Ru (mol.%): 1—4:1; 2—2:1; 3—1:1; 4—2:3; 5—1:2; 6—1:3.

Similar voltammograms were reported earlier for Ru electrodeposited under galvanostatic mode from nitrosyl-chloride [11] and chloride [26,35] solutions, as well as for Ru potentiostatically deposited from chloride [26] and formed by electroless deposition from $RuCl_3$ [17], as well as for bulk polycrystalline Ru [11,25,42]. Voltammograms with similar features were also published for Ru submonolayers on Au(1 1 1) and Pt(1 0 0) [43]; for these materials, separation of three cathodic peaks (0.5, ∼0.4 and ∼0.2 V) was found.

The observed voltammetric behavior, like for other Ru materials mentioned above, cannot be unambiguously referred to pure Ru metal, it is affected at least by surface oxide/hydroxide formation. Moreover, one cannot exclude the presence of more bulky oxidized fragments.

3.1.2. Fresh binary deposits (type I)

When deposition was carried out from mixed $RuCl_3 + Na_2PtCl_6 + HCl$ solutions, Ru codeposition appeared to be possible at positive RHE potentials, i.e. in the region where no evidence of pure Ru deposition was found. This principal difference can be hardly attributed formation of mixed reactants (spectroscopic tests are mentioned in Section 2).

Facilitation of $[RuCl_5(H_2O)]^{2-}$ discharge under condition of parallel discharge of $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ ions can be considered as a possible kinetic reason. This factor works if the formation of platinum nuclea simultaneously with Ru adatoms prevents or weakens the pzfc shift discussed above and by these means prevents the adsorption of chloride inhibitor.

Acting in parallel is an important thermodynamic reason, Pt-Ru alloy (solid solution [44,45]) formation. Additional deposit stabilization due to formation of ternary alloy with gold support is also possible because of mobility of gold surface atoms, like observed earlier for platinum electrodeposits on gold [46].

The voltammograms of fabricated Pt-Ru electrodes in 0.5 M H_2SO_4 solution are given in Fig. 2. The shape of these curves demonstrates the essential changes with Ru concentration in deposition solution. Two quasireversible peaks of hydrogen adsorption in interval 0.05–0.3 V are observed only for the sample deposited from Pt-Ru (90:10) solution. For all other electrodes with higher Ru content there is only one asymmetric peak. Currents in the "double layer" region increase, oxygen desorption peak is weakly pronounced. The values of currents in the overall potential region decrease systematically with Ru content in deposition solution, independently on deposition potential. For the highest Ru contents, the cathodic voltammograms are rather smooth and contain no peaks, even feebly marked. Similar tendencies were observed for Pt-Ru layers deposited under galvanostatic [12,25] and potentiostatic (at $E = 0.05$ V) [18,39] modes, as well as for Pt and Ru impregnated into carbon support [47]. The quantitative comparison with these data is complicated by the absence or conditional character of the true surface area values.

If one assumes that the current efficiency of deposition is independent on bath composition, the observed decrease of the total charge calculated by integrating the anodic part of voltammograms with Ru content can be interpreted as the decrease of the specific surface area with Ru content grow. For one and the same bath composition, the total charge is higher when deposition potential is lower. Again, if the current efficiency does not depend on deposition potential (the latter is evidently true for Pt [34]), this means that the specific surface area is higher for deposits formed at 0.05 V as compared to deposition at 0.2 V. However another interpretation is also possible (see below).

The ratio of Pt and Ru at the surface is a key characteristic of Pt-Ru any catalyst. This ratio depends on both segregation effects and bulk ratio of metals, the latter being dependent on the bath Pt:Ru ratio. According to direct radiotracer data [13], Pt:Ru molar (atomic) ratios in deposition solution and in galvanostatic deposit are approximately equal. The problem of surface/bath Pt:Ru ratio was later studied by EDX [14,25], AAS [14] and XPS [18,38]. Various types of segregation were observed, the most reliable seems to be XPS data [18,38] on 10–30 at.% surface excess of Pt resulting from potentiostatic deposition from the bath of any composition. We failed to find the reliable data on the bulk composition of the deposits of our type which we consider as very important for deposition controllability and more correct understanding of segregation problem.

Any spectral analysis of Pt and Ru in the presence of gold results in serious uncertainties. We made a number of attempts to apply UV–vis absorption spectroscopy to solutions obtained by dissolving our electrodeposits in aqua regia with subsequent dilution. To get at least a rough estimate we deposited Pt-Ru (4:1) on glassy carbon. Deposition rate was sufficient only at rather negative potential −0.05 V, assumed to be close to the steady-state potential value under galvanostatic mode used in Refs. [5,7–13]. The analysis demonstrated that even under these conditions favorable for Ru codeposition the ratio of Pt:Ru in the deposit is certainly higher than in deposition solution. There is no direct contradiction with analytical data of Ref. [13], as ruthenium nitrosochloride was used in this study instead of purely chloride complex. The presence of nitroso ligand shifts Ru/Ru(III) redox potential towards more positive values favoring higher Ru content in the deposit.

To summarize the data obtained here and published by other groups, a general tendency is platinum enrichment of electrodeposits as compared to metals ratio in deposition solution. This tendency looks to manifest itself in rather wide range of deposition parameters. We can assume that a number of segregation effects reported earlier on the basis of comparing surface/bath ratios were overestimated, i.e. the difference of surface and bulk deposit compositions was less pronounced.

The pronounced difference of pure Ru (Fig. 1) and all Pt-Ru deposits (Fig. 2) is seen from the scan rate dependence. For Pt-Ru, there is no noticeable changes of normalized voltammograms in the same scan rate interval, 5–50 mV s^{-1}, when for pure Ru the kinetics of charging processes in the ‘hydrogen region’ (<0.2 V) is much slower. We assume that the processes observed at Ru in this region do not present pure hydrogen adsorption in its usual classical sense, but some recharging of the surface oxide, the process known to be strongly catalyzed in the presence of Pt. Similar effect is known for Pt-oxotungstate compositions, it consists in catalysis of W(VI/V) redox transformations when oxotungstate species coexist with Pt [27]. Taking into account these manifestations one can assume that the increase of total charge with Pt content in deposition solution (i.e. in the deposit also) results not only from higher specific surface area but also from the involvement of the higher portion of surface ruthenium oxides into reversible recharging.

There is no chance to study this problem in detail for freshly deposited Pt-Ru because of the instability of their voltammetric features. It is evident that the properties of stabilized electrodes presented in the next section are of higher importance for understanding the electrocatalytic events in Pt-Ru system.

3.2. Closer to real catalysts: aged and ‘trained’ binary deposits

In the majority of papers devoted to Pt-Ru system, the authors consider the evolution of electrode properties in the course of relatively short periods (few hours or days). We observed that the properties of electrodeposited samples can continue to change for much longer time (type III and type IV, ‘trained’ electrodes), the same is for ageing in air (type II electrodes).

Evolution of voltammetric behavior in the course of stabilization of type III and type IV electrodes prepared from 4:1 Pt-Ru bath at 0.05 V is demonstrated in Fig. 3a and b respectively. For both 0.9 V (type III) and 1.1 V (type IV) anodic limits, the potential cycling decreases the total charge in the overall potential region. Single broad peaks in the “hydrogen region” are transformed into couples of peaks most typical for platinum. For type IV electrodes (Fig. 3b), oxygen desorption peak is also dividing into two, one is still at 0.5 V, and the second appears at

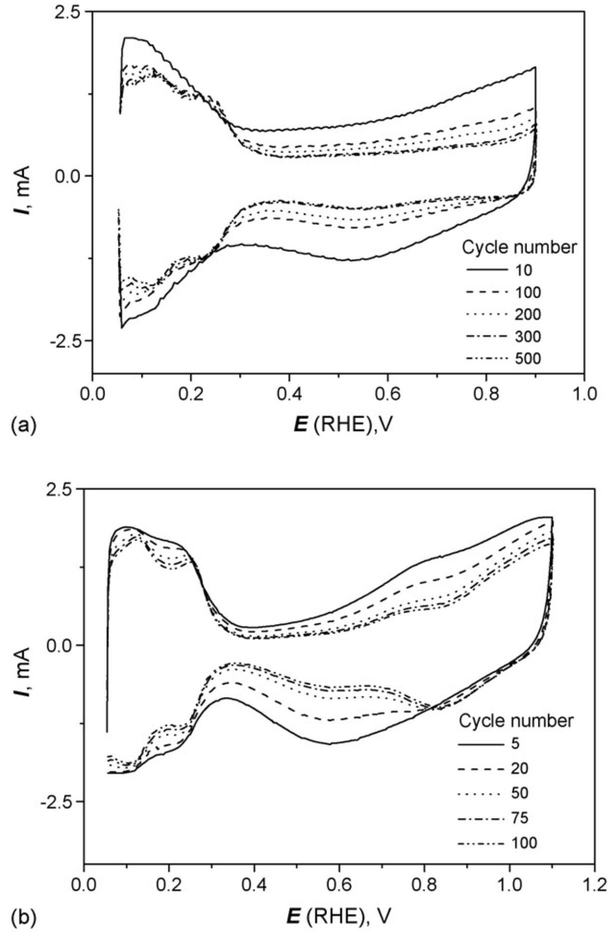

Fig. 3. Cyclic voltammograms of Pt-Ru (4:1) electrodeposited at 0.05 V in 0.5 M H_2SO_4. Scan rate 10 mV s^{-1}. (a) Electrode III and (b) electrode IV.

0.8 V. The same tendencies are observed for other deposits. The appearance of oxygen desorption peak at 0.8 V and separation of “hydrogen peaks” was earlier reported for annealed Pt-Ru alloys (heated at 850 °C for 3 h) [11] and was interpreted as the diffusion of surface Ru atoms to the bulk with corresponding surface enrichment by Pt. Similar results were obtained later in Ref. [48]. This process was assumed to be advantageous because of lower Pt free surface energy and cannot be ignored when interpreting room temperature ageing.

Our study of Pt-Ru deposits demonstrates that really no essential Ru dissolution takes place even if potential is cycled up to 1.1 V RHE. Neither analysis of solution, nor experiments with cathodic polarization in solution after prolonged cycling manifest the appearance of dissolved ruthenium. At the same time, if the anodic limit is increased up to 1.25 V, it is easy to notice the dissolution product. We can conclude that evolution of response results mostly from stabilization of Ru oxidation state in the surface layers, with negligible change of Ru content. Note that voltammogram of type IV deposits stabilizes much faster than for type III electrodes cycled with a lower potential limit. The steady-state voltammograms resulting from application of 0.9 and 1.1 V anodic limits are not identical, but in both cases do not demonstrate disappearance of Ru from the surface.

Steady-state voltammograms corresponding to different ageing modes are compared in Fig. 4 for one and the same initial deposit (4:1 plating solution), curve 1 represents the initial voltammogram. Minor changes take place when we age the electrode in air (type II). Dissolution is completely excluded in the course of type II ageing process, which can only consist of formation of various oxygen-containing ruthenium compounds (in particular irreversibly oxidized forms). The decrease of total charge induced by ageing does not exceed 15% for type II electrode and amounts 40 ± 5% for type III and type IV electrodes. There is no qualitative difference in the features of electrodes aged or ‘trained’ under various modes. The most pronounced feature is the preferential decrease of current in the mid ‘double layer’ region of voltammograms. This means that the decrease of surface area is a minor consequence of ageing, when the major changes are related to the decrease of contribution from recharging of ruthenium surface oxides.

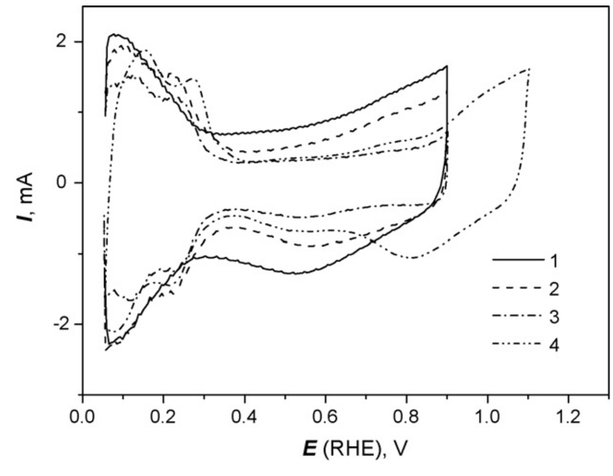

Fig. 4. Cyclic voltammograms of Pt-Ru (4:1) electrodeposited at 0.05 V in 0.5 M H_2SO_4. Scan rate 10 mV s^{-1}. 1—Type I; 2—type II; 3—type III; 4—type IV. Electrodes of II–IV types were stabilized completely.

This observation supports indirectly our statement concerning negligible dissolution of Pt-Ru, additionally substantiated below by Cu-UPD experiments.

For stabilized electrodes, the effect of Ru content in deposition solution is qualitatively the same as for freshly deposited Pt-Ru within the same series. Ageing effect is more pronounced for Pt-Ru deposited at 0.05 V. This fact can be probably assigned to the higher initial Ru content in this series as compared to a series of Pt-Ru films deposited at 0.02 V.

3.3. Is it possible to determine Pt-Ru surface area?

The techniques to measure (or, more exactly, to estimate) the true surface area of Pt-Ru materials were widely discussed in relation to the values of specific electrocatalytic activity. It is evident that coulometric analysis of H-UPD region usually applied to determine Pt surface area is unlucky in the case of Pt-Ru, because of the absence of separated H-UPD region. The technique assuming the reversible formation and reduction of the surface Ru(II) hydroxide as proposed by Watanabe and Motoo [49] was later found to be suitable only for low surface concentrations of ruthenium (see Ref. [25] for example). Another (most widely used) technique is CO stripping [50–52], its limitations and estimates of accuracy were discussed by many authors. Recently proposed Cu-UPD technique [17,40] was applied up to now to freshly prepared Pt-Ru materials and found to give an additional information on the surface Pt:Ru ratio due to separation of Cu-UPD responses on Ru (desorption peak at more negative potentials) and Pt. It was mentioned in Refs. [17,40] that no Cu-UPD occurs at oxidized Ru surface.

We attempted to apply two independent techniques (with their rather different approximations) to aged and ‘trained’ electrodeposits under study. Our set of samples represents a wide range of compositions and surface oxidation states.

First, we assumed that the surface area is proportional to voltammetric charge in the region 0.05–0.4 V. This is the same what was done in Ref. [10] with the use of galvanostatic charging curves and resulted in good correlation with BET data for the same materials.

The second approach was based on Cu-UPD. We found that the shape of Cu desorption voltammograms, and especially the key value of desorption charge are crucially dependent on the adsorption potential and time. These experiments provide an important information about ruthenium oxidation at the surface.

For pure Pt and Ru deposits, Cu-UPD responses differ strongly (Fig. 5a), and the difference is qualitatively the same as reported in Refs. [17,40] for other materials. At least three copper desorption peaks are observed for Pt in the region 0.45–0.75 V, with a broad adsorption peak at 0.65 V at cathodic branch. The value of maximum desorption current at 0.72 V is not affected by adsorption time, when other peaks continue to increase with time within the interval of 30–600 s. The final value of desorption charge achieved at 600 s (corresponding to curve 1 in Fig. 5b) gives the surface area value very close to the area calculated

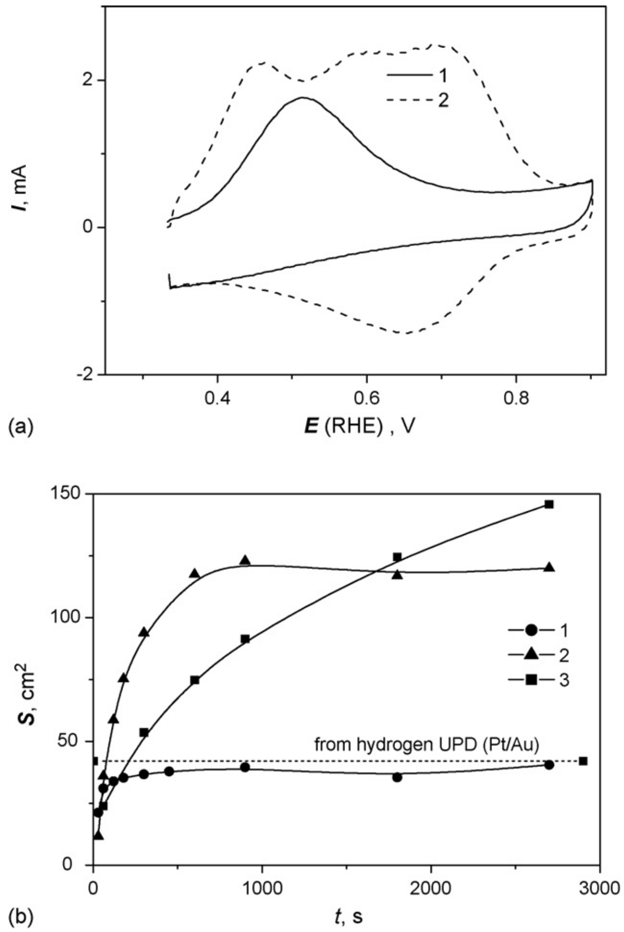

Fig. 5. Cu-UPD stripping results in 0.5 M H_2SO_4 + 0.01 M $CuSO_4$. (a) Stripping voltammograms (10 mV s^{-1}) for freshly deposited Ru/Au (1) and Pt/Au (2); adsorption time 900 s. (b) Surface area of Pt/Au via H-desorption in 0.5 M H_2SO_4 (1) and surface areas of Pt/Au (2), Pt-Ru (4:1) (3), Ru/Au (4) via Cu-UPD stripping as a function of adsorption time. Scan rate 10 mV s^{-1}.

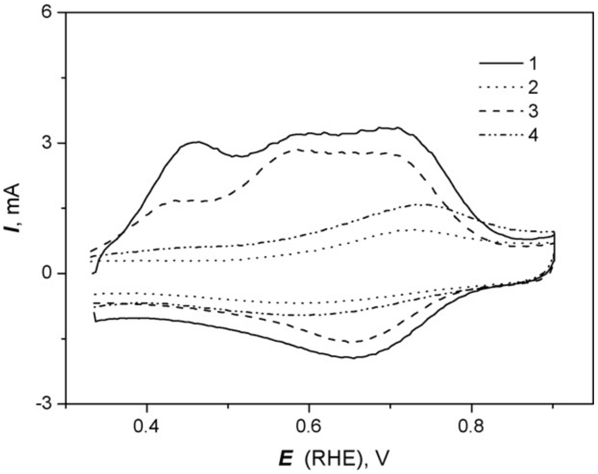

Fig. 6. Cu-UPD stripping voltammograms in 0.5 M H_2SO_4 + 0.01 M $CuSO_4$, t_{ads} = 300 s, for Pt-Ru (4:1) electrodeposited at 0.05 V. 1—Type I; 2—type II; 3—type III; 4—type IV.

from H-UPD response of the same Pt sample (dashed straight line in Fig. 5b).

A single desorption maximum of Cu-UPD for Ru is observed at 0.5 V, and no features of adsorption are found at the cathodic scan in a wide range of scan rates. The anodic response continues to increase with adsorption time up to 3000 s, i.e. Cu adatoms formation on Ru is a very slow process (curve 3 in Fig. 5b). It is rather natural to assume that the observed phenomenon results from slow reduction of surface ruthenium oxides at potential of Cu adsorption (0.33 V) accompanied by involvement of freshly reduced Ru atoms into Cu-UPD process.

For Pt-Ru electrodes of type III, the characteristic time to reach the limiting value of Cu desorption charge is close to the same value for Pt (see curve 2 in Fig. 5b for a sample deposited from 4:1 chloride electrolyte). It looks like reduction of surface ruthenium oxides is catalyzed by Pt, at least for the samples escaping deep irreversible oxidation. The relatively fast accumulation of Cu adatoms was also observed for the samples aged in air for several days, but not for longer period. For deeper oxidation (type IV electrodes), the quantity of Cu adsorbed at the surface remained negligible even after several thousands seconds, i.e. the major portion of ruthenium at the surface was irreversibly oxidized. Typical responses of the electrodes under study are collected in Fig. 6.

When comparing the surface areas determined by abovementioned techniques we found that the difference can reach 100%. The following typical situations are observed: when Pt content is high, the total charge gives higher values of the surface area; when Pt content is lower, the values resulting from Cu-UPD become higher than the values obtained from the total charge. It is easy to understand in terms of rechargeability processes, being faster for higher Pt contents.

To work correctly, Cu-UPD technique should be applied with variation of adsorption time. At low time, this technique discovers only Pt atoms and Ru atoms initially existing in metallic state. At longer times, it becomes sensitive to all forms of recoverable (reversibly oxidized) Ru. In contrast, the total charge can fix only the surface species recharging in a certain timescale. The main prospect of Cu-UPD measurements is more detailed analysis of the ensemble of surface ruthenium oxides.

The tendencies found for the change of surface area within each series of Pt-Ru samples do not depend on applied technique and look as follows:

1. The increase of Ru content in deposition solution results in the decrease of true surface area.
2. The surface areas of Pt-Ru deposits fabricated at 0.2 V are always lower than for the samples deposited from the same solutions at 0.05 V.

One cannot exclude that these differences result from the decrease of current efficiency (deposit weight), but another reason also looks realistic: the increase of the content of irreversibly oxidized Ru with formation of species invisible for both coulometric techniques.

To conclude this section, we would like to mention the correlation found recently in Ref. [53] for equimolar Pt-Ru: CO stripping charges measured in Ref. [53] correlated with voltammetric current values at 0.1 V for scan rates 10–50 mV s^{-1}. This was the reason why this value of current at fixed potential was proposed [53] as a measure of true surface area. We attempted to formally apply such a correlation to the deposits under study and found a number of dramatic deviations from Cu-UPD results (up to 200% excess as compared to Cu-UPD surface areas).

We would like to stress that using the CO stripping charge for surface area determination in the context of specific catalytic activity looks basically doubtful, as this value is already dependent on electrocatalytic properties of the sample.

3.4. *Electrocatalytic activity*

Optimization of Pt:Ru ratio in fuel cell catalysts is one of the most popular and contradictory problems. For methanol and CO oxidation, the optimal compositions are different, and for both reactions rather contradictory values of Pt:Ru ratios can be found in the literature, indicating the important role of structural and other factors. Most typically the highest activity is reported either for close Pt and Ru contents of ca. 50 at.% [25,39,49], or for materials with Ru content of 10–20 at.% [10,14,25,39,54]. The latter conclusion is more typical for electrodeposited materials, usually more active as compared to metallurgical alloys [55], chemically reduced bimetallic materials [19] or platinum modified by ruthenium adlayers [17,35,40,55]. In this study, we tested the activity in methanol oxidation under steady-state conditions in a wide compositional range.

Steady-state polarization curves (Fig. 7) demonstrate the pronounced electrocatalytic activity of all deposits under study (2–2.5 orders higher than the activity of pure Pt deposit of comparable thickness, at least in the region of 0.35–0.5 V). Simultaneously, the slopes of Tafel-like curves on Pt-Ru were much higher as compared to the slope for Pt.

The highest activity increase (about two orders of magnitude as compared to Pt) was found for Pt-Ru (4:1). The difference in activities for Pt-Ru (4:1) and Pt-Ru (2:1) surely exceeds a possible mistake of the surface area determination, i.e. the difference in surface areas obtained by two different techniques, and even more so for comparison of Pt-Ru (4:1) and Pt-Ru (1:1) activities. These conclusions are true for electrodeposits obtained at both 0.05 and 0.2 V potentials. Further increase of Ru content results in the pronounced decrease of activity. Similar decrease of activity with Ru content was found earlier in Ref. [3]. We found that the decrease is sharper for the series of samples deposited at 0.05 V. Most probably these samples contain higher portions of Ru than our deposits prepared at 0.2 V, so the observed difference does not contradict the results mentioned in Ref. [3].

Thick electrodeposited films studied in Refs. [3,10] had very high surface area and allowed to measure methanol oxidation current starting from very low potential ∼0.22 V. Probably this gave an opportunity of observation of low Tafel slope (close to 60 mV). Our measurements at less rough electrodes start at higher potentials, and give ∼100 mV slope in 0.4–0.5 V region, in satisfactory agreement with the slope in the same region found in Refs. [3,9] (∼90 mV). This inhibition can result from oxygen adsorption, a factor decreasing the rate of methanol dissociative adsorption.

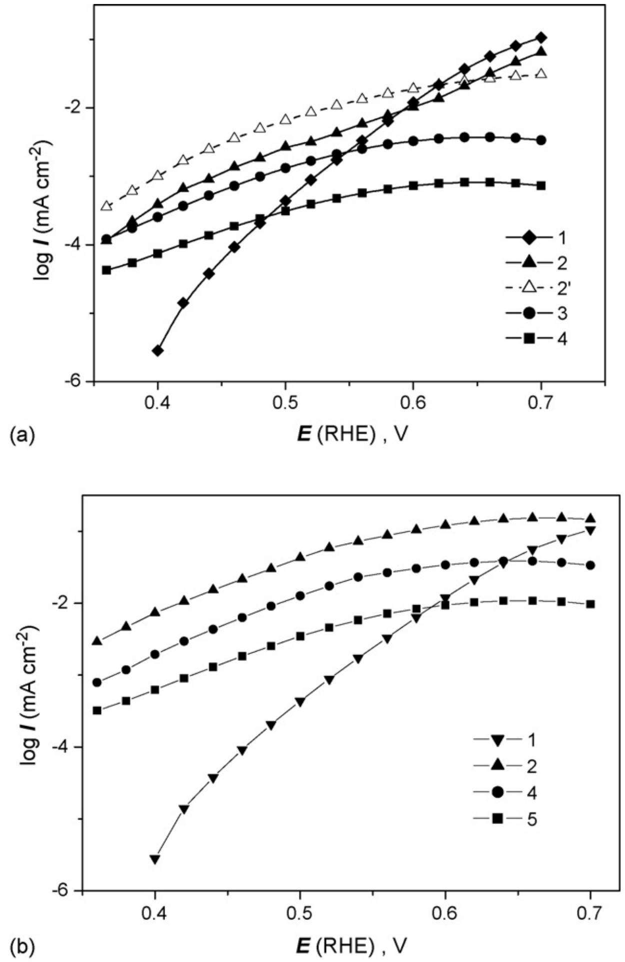

Fig. 7. Steady-state polarization curves of various Pt-Ru electrodes in 0.1 M CH_3OH + 0.5 M H_2SO_4. Deposition potential: (a) 0.05 V and (b) 0.2 V. 1—Pt; 2, 2′—Pt-Ru (4:1); 3—Pt-Ru (2:1); 4—Pt-Ru (1:1); 5—Pt-Ru (2:3). Curves 1–5: type III; curve 2′: type I.

We observed also a slight decrease of activity with ageing or ‘training’ (Fig. 8). The lowest activity for potentials 0.35–0.6 V was found for type III deposit. All changes do not exceed two times activity difference, when the reproducibility of the activity for any certain type of Pt-Ru is much better.

Composition effects discussed in this section should not be straightforwardly interpreted as a lack of activity with the decrease of Ru content. More likely, Ru content (Pt:Ru ratio) is a factor affecting Ru oxidation state and/or the rate of establishing a certain oxidation state at given potential. Early data on Pt-Ru and Ru electrodeposits should be concluded by mentioning a high catalytic activity of pure Ru at elevated temperatures [10]. This fact should be taken into account in mechanistic discussions around Pt-Ru. Actually, according to a classical bifunctional mechanism Pt and Ru are equal parties supplementing the limited catalytic abilities of each other. This is the same for the most conventional versions of ‘electronic effect’, ‘ligand effect’ and other relative mechanisms under current discussion, as well as for various ‘geometric’ interpretations of Pt-Ru electrocatalysis.

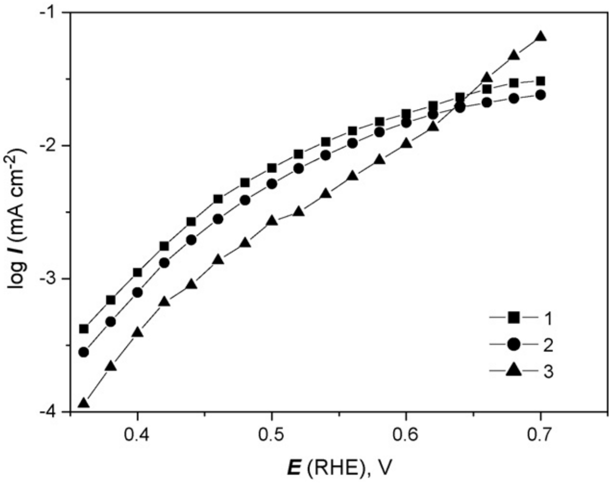

Fig. 8. Steady-state polarization curves of Pt-Ru (4:1) electrodes of various types in 0.1 M CH_3OH + 0.5 M H_2SO_4. 1—Type I; 2—type II; 3—type III. Deposition potential 0.05 V.

3.5. Pt-Ru electrodeposits in the context of Ru crossover

During the recent years the increasing attention is observed to ruthenium crossover phenomena in DMFC and Ru deposition on the DMFC cathode, with resulting decrease of cathode activity in oxygen reduction and simultaneous deterioration of the polymer electrolyte membrane [56,57]. There is still no satisfactory explanation of all these phenomena and ideas how to prevent it. Formally it contradicts ruthenium Pourbaix diagram in both its classical [31] and modified [58] versions. One should remember that ruthenium dissolution from thermodynamically stable Pt-Ru solid solution is even less probable than from pure Ru. The unique quantity of papers concerning various Pt-Ru materials induced a number of widely accepted illusions, and Ru dissolution from Pt-Ru is just the illusion of this sort: its nature is automatic extending of conclusions for certain Pt-Ru materials to other, of rather different type.

The following structural and chemical factors can affect the stability and dissolution rate of Pt-Ru and its partly oxidized forms: two-phase composition; defectiveness of small particles; oxide non-stoichiometry. All these features are expected at least for some of deposits with a wide compositional range studied in this paper, but no pronounced dissolution is observed for any of them. For instance, the electrodeposits are in general more defective and their fabrication conditions favor codeposition of less stoichiometric oxohydroxides. If despite of these facts Ru dissolution is not observed, it is all the more doubtful for more ordered Pt-Ru materials. Our preliminary XRD tests confirm that thin electrodeposits of our series are either single- (fcc) or two-phase (fcc + hcp at higher Ru content). As dissolution is not observed for both types, this factor is hardly very important.

According to our hypothesis, the dissolution reported for more complex Pt-Ru materials of PEMFC under similar polarisation conditions can result from the specific interaction with the foreign fragments, like carbon surface groups or polymer groups. The latter was already discussed in the literature [59] in terms of ionic exchange with Nafion membranes. Another reason specific for certain material or medium can be disintegration and chemical dissolution. We believe that the comparison with electrodeposited Pt-Ru escaping the phenomena specific for electrode-membrane configuration can be useful to clarify better their nature and to improve the catalyst and membrane lifetime. In this context and wider the nanostructural study of the thin electrodeposits and the oxidation state of Ru in these materials is of interest for a number of the key problems of electrocatalysis by the binary alloys.

An important phenomenon absent from usual laboratory experiments is the potential distribution at fuel cell anode. Recent double layer modeling of metal/solid polymer electrolyte interface demonstrates a possibility of dramatic potential fluctuations along the surface, with the amplitudes up to 0.3 V [60]. This situation should be specially modeled in experiments on ruthenium dissolution.

4. Conclusions

We reported above a number of the properties of thin Pt-Ru electrodeposited layers. Due to potentiostatic deposition mode and submicron thickness these layers present the relatively simple type of dispersed Pt-Ru, with minimal structural inhomogeneity induced by the changes of nucleation-growth peculiarities in the course of subsequent deposition of nm-size crystals.

Thus obtained deposits behave as a typical Pt-Ru material. Their specific feature is a high stability in acidic solutions at room temperature under cycling, up to relatively high value 1.1 V (RHE). More thick galvanostatic deposits studied earlier [5,7–13] were also rather stable for a long time.

Further development of techniques to determine the surface composition and the true surface area of dispersed Pt-Ru requires special attention. Our comparison demonstrated that the difference in true surface area obtained by various electrochemical techniques is not dramatic, at least for comparing the specific activities of various Pt-Ru materials towards methanol electrooxidation. Cu-UPD seems very promising because of its sensitivity to Ru oxidation state. This aspect should be probably considered also for technique proposed in Ref. [61], based on determination of the true surface area from the rate of oxalic acid oxidation. The data of this sort are of crucial importance for the basics of Pt-Ru electrocatalysis, as the role of metallic and oxidized Ru still remains one of the most controversial problems in the area [62–64].

Re-examination of the early data on Pt-Ru electrodeposits should be concluded by mentioning a high catalytic activity of pure Ru at elevated temperatures [10]. This fact contradicts from the first glance some mechanistic discussions around Pt-Ru. Actually, according to a classical bifunctional mechanism Pt and Ru are equal parties supplementing the limited catalytic abilities of each other. This is the same for the most conventional versions of ‘electronic effect’, ‘ligand effect’ and other relative mechanisms under current discussion, as well as for various ‘geometric’ interpretations of Pt-Ru electrocatalysis.

Some advanced interpretations of bifunctional catalysis assume inequality of components, by considering Ru as an oxophylic additive (inactive itself) for generation of OH species. We would like to stress that an opposite view is also possible: if some specific forms of oxidized Ru are exclusively responsible for electrocatalysis (in a widely understood mediating sense), this is just platinum which improves Ru activity by catalyzing the surface redox transformations, not vice versa. The nature of Pt catalytic role requires further examination, it can be in particular related not to direct mediator-like catalysis, but to electronic effects (changes of d-bands known already from 1960s [65]).

Acknowledgement

The study is supported by the Russian Foundation for Basic Researches, project 05-03-32381a.

References

[1] J.G.E. Cohn, O.J. Adlhart, Fuel Cells, Belg. Pat. 650,651, January 18, 1965; US Appl., July 17, 1963, 33 pp. (Citation from CA 65:P8352g).
[2] O.J. Adlhart, H. Shields, S. Pudick, Engelhard Ind. Tech. Bull. 6 (2) (1965) 37 (Citation from CA 64:3011g).
[3] O.A. Petrii, Doklady AN SSSR 160 (1965) 871.
[4] O.J. Adlhart, A.J. Hartner, Engelhard Ind. Tech. Bull. 6 (4) (1966) 37 (Citation from CA 65:14828e).
[5] V.S. Entina, O.A. Petrii, Elektrokhimiya 3 (1967) 1237.
[6] J.O'M. Bockris, H. Wroblowa, J. Electroanal. Chem. 7 (1964) 428.
[7] O.A. Petry, B.I. Podlovchenko, A.N. Frumkin, Hira Lal, J. Electroanal. Chem. 10 (1965) 253.
[8] V.S. Entina, O.A. Petrii, Yu.N. Zhitnev, Elektrokhimiya 3 (1967) 344.
[9] R.V. Marvet, O.A. Petrii, Elektrokhimiya 3 (1967) 116.
[10] V.S. Entina, O.A. Petrii, Elektrokhimiya 4 (1968) 678.
[11] V.S. Entina, O.A. Petrii, Elektrokhimiya 4 (1968) 111.
[12] V.S. Entina, O.A. Petrii, Elektrokhimiya 4 (1968) 457.
[13] O.A. Petrii, V.E. Kazarinov, Elektrokhimiya 1 (1965) 138.
[14] C. Coutanceau, A.F. Racotondrainibe, A. Lima, E. Garnies, S. Pronier, J.-M. Leger, C. Lamy, J. Appl. Electrochem. 34 (2004) 61.
[15] L.M. Plyasova, I.Yu. Molina, A.N. Gavrilov, S.V. Cherepanova, O.V. Cherstiouk, N.A. Rudina, E.R. Savinova, G.A. Tsirlina, Electrochim. Acta 51 (2006) 4477.
[16] J.J. Whalen III, J.D. Weiland, P.C. Searson, J. Electrochem. Soc. 152 (2005) C738.
[17] C.L. Green, A. Kucernak, J. Phys. Chem. B 106 (2002) 1036.
[18] F. Richards, B. Wohlmann, U. Vogel, H. Hoffschuls, K. Wandelt, Surf. Sci. 335 (1995) 361.
[19] C. Cattaneo, M. Sanchez de Pinto, H. Mishima, D. Lescano, L. Cornaglia, J. Electroanal. Chem. 461 (1999) 32.
[20] V.M. Schmidt, R. Iannielo, J. Phys. Chem. 100 (1996) 17901.
[21] H. Chan, Ch. Takoudis, M. Weaver, J. Catal. 172 (1997) 336.
[22] R.B. de Lima, V. Paganin, T. Iwasita, W. Vielstich, Electrochim. Acta 49 (2003) 85.
[23] C.H. Lee, C.W. Lee, D.I. Kim, D.H. Jung, C.S. Kim, D.R. Shin, J. Power Sources 86 (2000) 478.
[24] M.A. Quiroz, I. Gonzalez, Y. Meas, E. Lami-Pitara, J. Barbier, Electrochim. Acta 32 (1987) 289.
[25] T. Frelink, W. Visscher, J.A.R. van Veen, Surf. Sci. 335 (1995) 353.
[26] M.A. Quiroz, Y. Meas, E. Lami-Pitara, J. Barbier, J. Electroanal. Chem. 157 (1983) 165.
[27] L.M. Plyasova, I.Yu. Molina, S.V. Cherepanova, N.A. Rudina, O.V. Sherstyuk, E.R. Savinova, S.N. Pron'kin, G.A. Tsirlina, Russ. J. Electrochem. 38 (2002) 1116.
[28] O.E. Zviagintcev, N.E. Kolbin, A.N. Riabov, T.D. Avtokratova, A.A. Gorunov, The Chemistry of Ruthenium, Nauka, Moscow, 1965 (in Russian).
[29] Analytical chemistry of elements. Platinum metals, Nauka, Moscow, 1972.
[30] J. Kirkland, J. Yoe, Anal. Chim. Acta 9 (1953) 441.
[31] M. Pourbaix (Ed.), Atlas d'equilibres electrochimiques, Gauthier-Villars, Paris, 1963, p. 345.
[32] A.I. Danilov, E.B. Molodkina, Yu.M. Polukarov, Elektrokhimiya 34 (1998) 1387.
[33] B.I. Podlovchenko, R.P. Petukhova, Elektrokhimiya 6 (1970) 198.
[34] O.A. Petrii, G.A. Tsirlina, S.N. Pron'kin, F.M. Spiridonov, M.L. Khruscheva, Russ. J. Electrochem. 35 (1999) 12.
[35] S. Strbac, F. Maroun, O. Magnussen, R.J. Behm, J. Electroanal. Chem. 500 (2001) 479.
[36] R. Iannielo, V.M. Schmidt, J.S. Rodrigues, E. Pastor, J. Electroanal. Chem. 471 (1999) 167.
[37] M. Metikos-Hukovic, S. Omanovic, J. Mol. Catal. A 136 (1998) 75.
[38] N. Fujiwara, K.A. Friedrich, U. Stimming, J. Electroanal. Chem. 472 (1999) 120.
[39] B.A. Lopez de Mishima, H.T. Mishima, G. Castro, Electrochim. Acta 40 (1995) 2491.
[40] C.L. Green, A. Kucernak, J. Phys. Chem. B 106 (2002) 11446.
[41] R.O. Lenza, N.R. de Tacconi, A.J. Arvia, J. Electroanal. Chem. 151 (1983) 193.
[42] H.A. Gasteiger, M. Markovic, P.N. Ross, J. Phys. Chem. 99 (1995) 8290.
[43] W. Chrzanowski, A. Wieckowski, Langmuir 13 (1997) 5974.
[44] V.A. Nemilov, A.A. Rudnitski, Izvestia AN USSR Ser. Chim. 1 (1937) 33.
[45] J.M. Hutchinson, Platinum Met. Rev. 16 (1972) 88.
[46] L.M. Plyasova, I.Yu. Molina, S.V. Cherepanova, N.A. Rudina, O.V. Sherstyuk, E.R. Savinova, S.N. Pron'kin, G.A. Tsirlina, Russ. J. Electrochem. 38 (2002) 1116.
[47] C. Roth, N. Mertz, F. Hahn, J.-M. Leger, C. Lamy, H. Fuess, J. Electrochem. Soc. 149 (2002) E433.
[48] E.D. McNicol, R.T. Short, J. Electroanal. Chem. 81 (1977) 249.
[49] M. Watanabe, S. Motoo, J. Electroanal. Chem. 60 (1975) 267.
[50] T.J. Schmidt, M. Noeske, H.A. Gasteiger, B.R. Behm, P. Britz, W. Brijoux, U.H. Bönnemann, Langmuir 13 (1997) 2591.
[51] H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Cairns, J. Phys. Chem. 98 (1994) 617.
[52] N.H. Dinh, X. Ren, F.H. Garzon, P. Zelenay, S.J. Gottesfeld, J. Electroanal. Chem. 491 (2000) 222.
[53] A.N. Gavrilov, E.R. Savinova, P.A. Simonov, V.I. Zaikovskii, S.V. Cherepanova, G.A. Tsirlina, V.N. Parmon, in preparation.
[54] H. Hoster, T. Iwasita, H. Baumgatner, W. Vielstich, J. Electrochem. Soc. 148 (2001) A496.
[55] M.-S. Loffler, H. Natter, R. Hempelmann, K. Wippermann, Electrochim. Acta 48 (2003) 3047.
[56] P. Pila, C. Eickes, E. Brozha, F. Garzon, P. Zelenay, J. Electrochem. Soc. 151 (2004) A2053.
[57] W. Chen, G. Sun, J. Guo, X. Zhao, S. Yan, J. Tian, S. Tang, Z. Zhou, Q. Xin, Electrochim. Acta 51 (2006) 2391.
[58] G. Barral, J.-P. Diard, C. Montella, Electrochim. Acta 31 (1986) 277.
[59] J.L. Weininger, R.R. Russell, J. Electrochem. Soc. 125 (1978) 1482.
[60] V.P. Zhdanov, B. Kasenno, Electrochem. Commun. 8 (2006) 561.
[61] C. Bock, B. McDougall, J. Electrochem. Soc. 150 (2003) E377.
[62] J.W. Long, R.M. Stroud, K.E. Swider-Lyons, D.R. Rolinson, J. Phys. Chem. B 104 (2000) 9792.
[63] H. Kim, I. Rabelo de Morals, G. Trimilosi-Filno, R. Haasch, A. Wieckowski, Surf. Sci. 474 (2001) L203.
[64] S.C. Thomas, X. Ren, S. Gottesfeld, J. Electrochem. Soc. 146 (1999) 4354.
[65] D.W. MkKee, F.J. Norton, J. Catal. 3 (1964) 252.