



## Review

# Electron transfer kinetics of the ferrous/ferric redox system on the platinum deposits on gold



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## ABSTRACT

Electron transfer rate constant decreases gradually for a  $\text{Fe}^{2+/3+}$  redox system as platinum deposition covers a gold surface. This effect is assumed to be conditioned by reconstruction of double electric layer on a platinum deposit which increases reorganization energy and decreases the redox reaction rate constant.

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## 1. Introduction

Articles on analysis of deposits [1–4] of catalytically active metals, hold an important place among a great number of works on electrocatalytic activity of transition metals [5,6] and metals of platinum group, their alloys [2,7–9] and nanoparticles [10,11]. Many catalytic phenomena in irreversible reactions are explained in the Hammer-Norskov model [12,13], which associates catalytic activity with electronic structure of a catalyst and a depolarizer adsorbed on an electrode. Whereas, standard redox systems often used to compare electrodes electroactivity are characterized by different kind of electron transfer (ET). First, these systems have no strong adsorption capacity; second,

the molecules of a solvent fill space between an electrode and a redox system. These factors make ET rate dependent on the electrode material and the redox system specification, a solvent structure and a background electrolyte, as well.

Today the quantum mechanical theory [14,15] is widely applied to describe a process of heterogeneous ET. However, because of complexity of calculations for systems with great number of particles, only specific solutions obtained *via* simplifications are available for comparison with experimental data.

In our previous work [16], we have found that characteristics of an electric double layer (EDL) on a Ag monolayer deposit on Au are close to that of solid silver, and the parameters of electron transfer for a model redox system  $\text{Fe}(\text{CN})_6^{3-/4-}$  correspond to a gold electrode. In the present work, our further research concerns platinum deposits on gold with the  $\text{Fe}^{2+/3+}$  couple as a model. This system is characterized

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by strong dependence of ET rate constant on material of an electrode and adatoms of metals present on its surface [17,18]. Unlike silver, platinum is deposited on a gold surface not as a monolayer but as small islands made up of several atomic metal layers [19,20], which is caused by a considerable difference in lattice constants and surface tension of Au and Pt. In this work modified experimental procedures [19,20] developed for Pt monolayer deposition on basal planes of gold single-crystals were used to obtain platinum deposits maximum close to a monolayer. With electrode reaction rate measured for  $\text{Fe}^{2+/3+}$  on a gold electrode with different platinum deposits, effect of electronic structure of the electrode and EDL structure on electron transfer was analyzed for the system under consideration.

## 2. Materials and methods

Electrochemical measurements were performed with potentiostat P-30I (Elins, Russia) in a three-electrode cell with separated spacing between working and auxiliary electrodes. Gold plates of about  $0.5 \text{ cm}^2$  in area were used as the working electrodes. Silver chloride electrode (saturated KCl) with the Luggin capillary was taken as the reference electrode. A 10 cm-long capillary was filled with a working solution, thus the possibility of contamination with chloride was eliminated. All solutions were prepared from salts and sulfuric acid of chemical grade and triply-distilled water. Solution of sulphuric acid was additionally radiated with ultraviolet of 253.7 nm in wavelength. The solutions were deaerated with argon flown through a column with activated carbon and a heated pipe with fine copper to refine from impurities and oxygen traces. Scanning electron microscopy was performed with Zeiss LEO SUPRA 2S.

ET kinetics was carried in 5 mM  $\text{FeSO}_4$  solution in 0.5 M  $\text{H}_2\text{SO}_4$ . Estimation of the rate constant for  $\text{Fe}^{2+/3+}$  heterogeneous reaction was carried out by comparison of the experimental data with calculated  $\Delta E_p(\nu)$ -dependencies obtained from model cyclic voltammograms (CVs) [16]. The latter were calculated with the parameters as follows: transfer coefficient  $\alpha = 0.5$ , diffusion coefficients for both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$   $D = 6 \cdot 10^{-6} \text{ cm}^2/\text{s}$  [21].

## 3. Results and discussion

Pt deposits maximum close to monolayer were obtained from 0.2 mM solution of  $\text{H}_2\text{PtCl}_6$  in 0.5 M  $\text{H}_2\text{SO}_4$  on the basis of deposition techniques [19,20]. Linear potential sweep was applied from 890 mV (open-circuit potential) to 400 mV at rate of 2 mV/s; then the electrode was potentiostated at 400 mV for 10–200 s. Surface coverage with Pt was calculated as ratio of gold surface covered with Pt to surface area of the electrode. True surface area of gold was estimated from oxygen desorption at potential scanning with anode limit of 1.4 V on the assumption that an oxygen monolayer is formed on gold at charge of  $\sim 420 \mu\text{C}/\text{cm}^2$  [22]. Surface area of platinum was estimated from hydrogen desorption [23]. Typical CV measured in 0.5 M  $\text{H}_2\text{SO}_4$  solution on an Au electrode with Pt deposit is presented in the Fig. 1. Curves for pure gold and platinum are also demonstrated in the Figure. It can be seen that CV for deposit possesses peaks of oxygen desorption from parts of uncovered gold support and parts of platinum deposit. These observations are in agreement with the data of other authors [24,25].

Obtained parameters of electrodes are summed up in Table 1. Notice that the gold substrates have rather low roughness factor  $R_f$  which is proved by SEM images (Fig. 2A). Low values of roughness factor  $R_{f,\text{Pt}}$  and Pt atomic layers in deposit  $n_{\text{Pt}}$  for  $\text{Pt}_1/\text{Au}$ – $\text{Pt}_3/\text{Au}$  samples demonstrate that the chosen technique provides mainly two-dimensional deposit growth.

As may be clearly seen in the SEM image, at 90% coverage (Fig. 2B) platinum is deposited in an island manner around the crystallization centers; the observable size of the clusters is  $< 30 \text{ nm}$ . As surface coverage increases (Fig. 2C), the platinum clusters start merging into one solid arrangement. Electrochemical measurements for deposits with

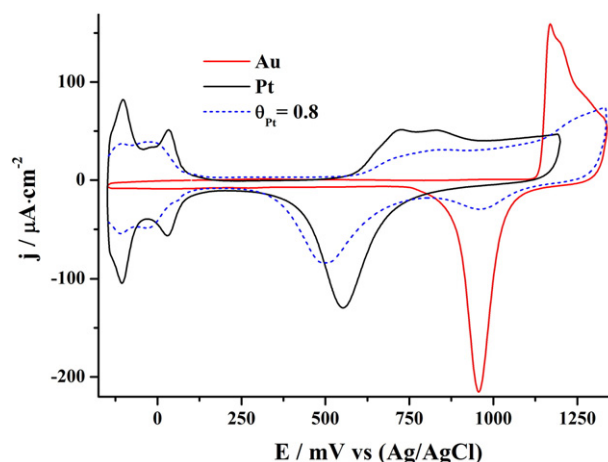


Fig. 1. CVs measured in 0.5 M  $\text{H}_2\text{SO}_4$  solution on pure Au and Pt and on an Au electrode covered with Pt by 80%. Potential scan rate  $\nu = 50 \text{ mV/s}$ .

great number of Pt atomic layers ( $\sim 19$ ) showed total coverage of gold substrates with platinum.

According to the purity grade of sulfuric acid and iron sulphate used in this study concentration of chloride in working solution must not exceed  $2.5 \cdot 10^{-6} \text{ M}$ . Even such small amount of chloride causes an increase in the apparent rate constant for  $\text{Fe}^{2+/3+}$  redox system in perchloric acid solution [17,28]. Reference experiments with the addition of  $\text{Cl}^-$  to the working solution were carried out to determine the effect of the presence of chloride-anion on the ET rate constant.  $\Delta E_p(\nu)$ -dependencies obtained at chloride concentration of  $10^{-5} \text{ M}$  demonstrated the absence of such an effect for Pt and Au electrodes. As to chloride adsorption on the electrode surface, according to the quantum chemical calculations [29–31] the energy of sulphate adsorption is noticeably higher than that of chloride on gold and platinum. It should result in the displacement of chloride ions by the sulphate-anions on the electrode surface. At the same time the adsorption of sulphate anions on platinum surface can affect substantially the ET kinetics. According to the literature data surface coverage of Pt (111) and Au (111) by sulphate anion in  $\text{H}_2\text{SO}_4 + 0.1 \text{ M HClO}_4$  solution equals to 0.16 and 0.18 for Pt and 0.02 and 0.04 for Au at sulphuric acid concentration of 0.5 and 5 mM, respectively [32–34]. These data reveal that sulphate adsorption on Pt (111) is noticeably greater than that on Au. However, surface coverage by sulphate-anions is not high and virtually doesn't depend on  $\text{H}_2\text{SO}_4$  concentration. In particular, the approximation of literature data by Temkin isotherm demonstrates that surface coverage by sulphate in 0.5 M  $\text{H}_2\text{SO}_4$  solution can be  $\approx 0.24$  and  $\approx 0.1$  for Pt and Au, respectively. According to these data one can suppose that a 20% decrease in experimental peak currents for Pt (Fig. 3) in comparison with the calculated on the basis of Randles-Sevcik equation ones can be explained by partial blockage of Pt electrode surface. Meanwhile the effect of surface blockage will be observed only in the case when sulphate-anions are adsorbed on a polycrystalline platinum in the form of islands with the dimensions that exceed the characteristic size of diffusion layer. Unfortunately, in the literature there is no evidence of such a manner of sulphate adsorption on Pt. Nevertheless, regardless any reason for the decrease in CV currents on platinum, in the present study the estimation of ET rate constant is based on the determination of peak potential differences that are not affected by not so large decrease in peak currents.

It is important to note that the presence of less electrochemically active parts (in our case Pt deposit) with surface coverage  $\leq 25\%$  doesn't lead to the substantial difference in experimental value of rate constant and the one typical for electrochemically uniform electrode [35,36]. Besides according to [17] the ratio of  $\text{Fe}^{2+/3+}$  redox reaction rates on gold and platinum in perchloric acid is close to the one obtained in the present work for sulphuric acid solution. This fact indicates a low influence

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