



# PLATINUM POWDER FORMATION AT POLARIZATION INDICED BY IMPULSE ALTERNATING CURRENT IN THE PRESENCE OF QUADRIVALENT TITANIUM IONS

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## ABSTRACT

Platinum (IV) ions reduction process was firstly studied at polarization induced by pulsed cathode current in the presence of titanium ions (IV). It was demonstrated that at the current density variation between 1000 and 6000 A/m<sup>2</sup> and sulfuric acid concentration between 50 and 300 g/L, current output is reduced, and with increasing of the platinum concentration (IV) and temperature of the solution is elevated. It also has been established that with increasing of the cathode current, the mean particle size is decreased and achieves 20 nm. It was demonstrated, that in the presence of the titanium (IV)-titanium (III) oxidation-reduction system, the platinum powder dispersion is increased.

**Key words:** Platinum, Powder, Oxidation-reduction system, Impulse current.

## INTRODUCTION

Platinum; one of the main catalysts in the production of nitric acid, the restoration of car exhaust, oil cracking, proton-exchange membrane fuel cells. In all of these processes, platinum is generally used in a highly dispersed form<sup>1-3</sup>.

Among platinum reduction techniques the main two are emphasized: chemical and electrochemical with powders and spongy black platinum formation<sup>4</sup>. In the chemical process usually formaldehyde, hydrazine, and hydrogen serve as reducing agents. Platinum (IV) might also be reduced using following reagents: ascorbic acid, Zn, Hg (I), Cu (I), Cr (II), Ti (III), HCOONa, NH<sub>2</sub>OH, and NaBH<sub>4</sub><sup>5,6</sup>.

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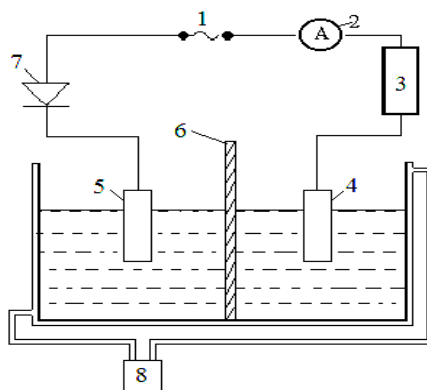
However, listed techniques possess peculiar disadvantages is that worked-out reductors hereafter could not find a use and create particular problems, associated with the need of their disposal.

Platinum (IV) reduction process at polarization induced by impulse alternating current in the presence of quadrivalent titanium ions with the purpose of the current output (CO), increasing and facilitating of the instrument component is investigated. Facilitating of the instrument component was carried out by rectifier replacement with brand D 248 diode. As is known, diode is able to pass the current in one direction, and as a result of passage of the industrial alternating current through the diode an impulse cathode current is created at the titanium.

## EXPERIMENTAL

Electrolytic reduction was performed using chloroplatinic acid solutions in sulphated environment in electrolyzer with volume 50 mL with separated by CM-40 membrane electrode spaces. Titanium used as cathode, and platinum electrode used as anode. Platinum powder formation is occurred in the result of immediate discharge of its ions at the cathode (reaction 1), as well as in cathodic area of the electrolyte according to reaction 2.

Installation diagram is illustrated in Fig. 1.



1- Power supply; 2- Amperemeter; 3- Rheostat; 4- Titanium electrode; 5- Platinum electrode;  
6- Cation-exchange membrane MK-40; 7- Diode; 8- Thermostat

**Fig. 1: Installation diagram for electrochemical platinum reduction with diode**

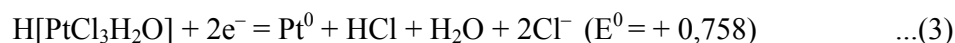
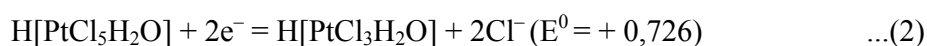
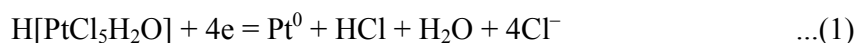
After electrolysis the platinum powder picked up from cathode, and separately by means of decantation and filtration the powder was collected in solution. Therefore, we have

assessed an influence of electrolysis parameters on the current output platinum powder formation at the cathode and in electrolyte bulk.

## RESULTS AND DISCUSSION

As is known from published literature<sup>7,8</sup>, hexachloroplatinate (IV) in sulfated solutions less than 3 M exists in the form of:  $\text{H}[\text{PtCl}_5\text{H}_2\text{O}]$ .

Cathodic process of the chloroplatinate ions reduction to metal might be presented as follows:



Herewith at the cathode hydrogen ions are reduced:

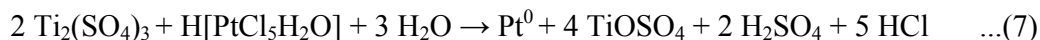


According to the data, presented in the paper<sup>9</sup>, precipitation is possible also at disproportionation of the complex Pt(II) (or other partial reduction products  $[\text{PtCl}_6]^{2-}$ ), for instance according to reaction:



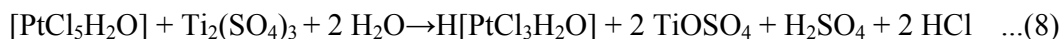
Certainly, that due to side reaction (4), current output of the main process (1) is always well below 100%. Therefore, the landmark decision is required, allowing to process current yield increasing, without negative influence of the product quality.

With the purpose of current output form a powder of platinum powder formation, we have used the reduction-oxidation catalyst system titanium (IV)/(III). Its operating principle consists in following: into solution, containing platinum ions (IV) and sulphuric acid, quadrivalent titanium sulphate was added. Upon reaching the current density exceeding the maximum allowable, at the cathode, the current part previously consumed for hydrogen ions reduction according to reaction 4, will be consumed for titanium (IV) ions reduction (reaction 6). Thereafter, titanium (III) ions within cathode space of the solution a chemically reduce the platinum (IV) to metallic state (reaction 7), oneself oxidizing to titanium ions (IV). Latter are reduced again at the cathode with titaniuma (III) formation.



Therefore, the scheme described allows to provision of the continuous cycle of the platinum (IV) ions reduction, as well as increasing the CE. Titanium ions render, at the certain scale, catalytic effect. To establish the optimum conditions for powder formation with high current output, an influence of various parameters on the current output reduction of the platinum (IV) ions was assessed: catalyzer concentration, cathode current density, electrolysis duration, sulfuric acid concentration, Pt (IV) concentration, and electrolyte temperature.

Examination of the electrocatalyzer, i.e. titanium ions (IV), concentration influence, showed (Table 1) that if it's content is elevates to 10 g/L, the CY at the cathode increased 1.7-fold. It was found, that at the current density of 1000 A/m<sup>2</sup> platinum powder formation in the bulk solution doesn't occur. According to our assumptions, this phenomenon could be explained as follows: at the current density of 1000 A/m<sup>2</sup>, the quadrivalent platinum complex containing in the solution, under the action of the formed in the cathode space titanium (III) ions, is reduced to bivalent state, according to reaction 8.



Obtained bivalent platinum complexes at the cathode are more easily reduced to elementary state, according to reaction 3, than quadrivalent, resulting in increasing the CE at the cathode. With increasing of the quadrivalent titanium concentration to 15 g/L at following conditions:  $i = 1000 \text{ A/m}^2$ ,  $\tau = 9 \text{ min}$ ,  $t = 20^\circ\text{C}$ ,  $\text{Pt (IV)} = 4 \text{ g/L}$ ,  $\text{H}_2\text{SO}_4 = 100 \text{ g/L}$ , the current output at the cathode is 36,4%. At the current density 2000 A/m<sup>2</sup> with increasing of the titanium (IV) ions concentration to 20 g/L, the cumulative current output achieves 46,5%. In the Table 1 the dependence of the current output of platinum reduction from quadrivalent titanium concentration is presented.

**Table 1: Influence of the titanium (IV) concentration on the current output of platinum powder formation**

C Ti(IV), g/L	2,5	5	10	15	20
CO at the cathode, %	23.2	20.0	17.3	15.8	10.2
CO in the bulk solution, %	6.9	12.1	28.0	30.2	36.3
Total CO, %	10.6	18.1	45.3	46.0	46.5

Note:  $t = 20^\circ\text{C}$ ,  $\tau = 15 \text{ min}$ ,  $\text{Pt (IV)} = 4 \text{ g/L}$ ,  $\text{H}_2\text{SO}_4 = 100 \text{ g/L}$ ,  $i = 2000 \text{ A/m}^2$

An influence of the current density in the presence of Ti (IV) ions at the following conditions: Ti (IV) = 10 g/L,  $\tau = 9$  min,  $t = 20^{\circ}\text{C}$ , Pt (IV) = 4 g/L,  $\text{H}_2\text{SO}_4 = 100$  g/L was assessed. As consistent with the table 2, net current and cathode current output are decreased with increasing of the cathode current density, and comprises 31,3% at  $1000 \text{ A/m}^2$ , and 21,5% at  $6000 \text{ A/m}^2$ . Herewith, the CE ratio, accounted to chemical reduction, rises from 0% at  $1000 \text{ A/m}^2$  to 14,0% at  $6000 \text{ A/m}^2$ .

**Table 2: Influence of the current density at the titanium cathode on the current output of the platinum powder formation**

<b>i, A/m<sup>2</sup></b>	<b>1000</b>	<b>2000</b>	<b>3000</b>	<b>4000</b>	<b>5000</b>
CO at the cathode, %	31.3	30.0	19.8	13.0	5.6
CO in the bulk solution, %	0.0	6.0	9.3	12.2	14.0
Total CO, %	31.3	36.0	29.1	25.2	21.5

Note: Ti (IV) = 10 g/L,  $\tau = 9$  min,  $t = 20^{\circ}\text{C}$ , Pt (IV) = 4 g/L,  $\text{H}_2\text{SO}_4 = 100$  g/L

In the Table 3, the data, presenting the character of the influence of sulfuric acid concentration on the current output of the platinum powder formation. Maximum CE is observed at 100 g/L and is 45, 3% (at concentration Ti (IV) = 10 g/L,  $\tau = 15$  min,  $t = 20^{\circ}\text{C}$ , Pt (IV) = 4 g/L,  $i = 2000 \text{ A/m}^2$ ). With further increase in the acid concentration in solution, the CE falls down.

Results of our experiments consistent with data presented in article<sup>5</sup>, where an increasing of the complexes resistance is observed at the sulfuric acid concentration elevation.

**Table 3: Influence of the sulfuric acid concentration at the cathode current output of the platinum reduction (IV)**

<b>H<sub>2</sub>SO<sub>4</sub>, g/L</b>	<b>50</b>	<b>100</b>	<b>150</b>	<b>200</b>	<b>300</b>
CO at the cathode, %	22.2	17.3	16.1	6.4	3.8
CO in the bulk solution, %	18.0	28.0	26.8	25.7	25.2
Total CO, %	40.2	45.3	42.9	32.1	29.0

Note:  $i = 2000 \text{ A/m}^2$ , Ti (IV) = 10 g/L, Pt (IV) = 4 g/L,  $t = 20^{\circ}\text{C}$ ,  $\tau = 15$  min

As Table 4 shows, increasing of the initial Pt (IV) ions content in the solution to 5 g/L promotes the growth of the net CE to 47.0%.

**Table 4: Dependence of current output of the platinum powder formation from initial platinum concentration (IV)**

Pt (IV), g/L	1	2	3	4	5
CO at the cathode, %	1.2	3.1	10.1	17.3	17.8
CO in the bulk solution, %	5.2	7.0	12.2	28.0	29.2
Total CO, %	6.4	10.1	22.3	45.3	47.0

Note:  $t = 20^{\circ}\text{C}$ ,  $\tau = 15$  min,  $\text{Ti (IV)} = 10$  g/L,  $\text{H}_2\text{SO}_4 = 100$  g/L,  $i = 2000$  A/m<sup>2</sup>

As is shown in the Table 5, with elevation of temperature of the solution, current output of the platinum powder formation in all cases passes through the maximum. Maximum net CE is equal 58.0% at 40<sup>0</sup>C. Further decreasing of the CE resulted from the hydrogen release process intensification.

**Table 5: Influence of the electrolyte temperature on the current output of the platinum powder formation**

$t^{\circ}, \text{C}$	20	30	40	50	60
CO at the cathode, %	17.3	18.4	19.2	18.2	17.8
CO in the bulk solution, %	28	32	38.8	34.1	33
Total CO, %	45.3	50.4	58	52.2	50.8

Note:  $\text{Ti (IV)} = 10$  g/L,  $\tau = 15$  min,  $\text{Pt (IV)} = 4$  g/L,  $\text{H}_2\text{SO}_4 = 100$  g/L,  $i = 2000$  A/m<sup>2</sup>

At the platinum powder formation particle size and particle size distribution are critical. Undoubtedly, these indices are substantially influenced by current density, temperature, acidity, and solution concentration. Powder particle size and particle size distribution are determined, primarily, by the current density. Herewith, generally, increasing of the current density promotes the fine-grain precipitate at the cathode. In the Tables 6 and 7 data regarding influence of various parameters on platinum powder particle size.

**Table 6: Influence of the various parameters on platinum powder particle size deposited at the cathode surface**

Influence of the current density at the cathode		Influence of the concentration Ti (IV)		Influence of the sulfuric acid concentration		Influence of the Pt (IV) concentration	
A/m <sup>2</sup>	Particle size at the cathode	g/L	Particle size at the cathode	g/L	Particle size at the cathode	g/L	Particle size at the cathode
1000	800 <sub>HM</sub>	0	100-200 <sub>HM</sub>	50	300 <sub>HM</sub>	1	50 <sub>HM</sub>
3000	20-100 <sub>HM</sub>	5	10 <sub>HM</sub>	150	100 <sub>HM</sub>	3	50 <sub>HM</sub>
6000	20 <sub>HM</sub>	20	10 <sub>HM</sub>	300	100 <sub>HM</sub>	5	100 <sub>HM</sub>

**Table 7: Influence of the various parameters on platinum powder particle size formed in the bulk solution**

Influence of the current density at the cathode		Influence of the concentration Ti (IV)		Influence of the sulfuric acid concentration		Influence of the Pt (IV) concentration	
A/m <sup>2</sup>	Particle size in the bulk solution	g/L	Particle size in the bulk solution	g/L	Particle size in the bulk solution	g/L	Particle size in the bulk solution
1000	80 nm	0	Powder is not formed	50	30 nm	1	2,5 nm
3000	20 nm	5	10 nm	150	10 nm	3	10 nm
6000	3 nm	20	3 nm	300	10 nm	5	30 nm

## CONCLUSION

An influence of the titanium (IV)-titanium (III) oxidation-reduction system on the cathode platinum (IV) ions reduction process with formation of its powder from sulfated solution at polarization using cathode impulse current was studied. An influence of various parameters (current density, acid concentration, solution composition, electrolysis duration and electrolyte temperature) at the current output of powder formation was assessed. It was found that in the presence of titanium ions (IV) current output of the platinum powder formation is increased, and its dispersivity is increased.

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