

The Platinum Catalyst Prepared from Platinum Carbonyls

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Abstract: Pt catalysts for methanol electro-oxidation were prepared by thermal decomposition of platinum carbonyls. $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ were synthesized from inorganic platinum compounds (PtCl_4 or $(\text{NH}_4)_2\text{PtCl}_4$) in H_2O - MeOH solutions using carbon monoxide as a reducing agent. The progress of the platinum carbonyls synthesis reaction and its performance were monitored using UV-Vis spectroscopy. The obtained results clearly indicate the possibility of using platinum carbonyls as intermediates for the synthesis of pure and finely divided platinum particles. The electrochemical tests of the platinum powders performed in the polymer-electrolyte low-temperature methanol fuel cells (DMFC) indicated good electrocatalytic properties of these materials.

Keywords: platinum catalysts, platinum carbonyls, DMFC

1. INTRODUCTION

The use of the carbonyl intermediates in the synthesis of metallic, finely divided platinum (or its mixtures with other metals), is very attractive taking into account not complicated synthesis procedure. In view of the fact that the platinum carbonyls are the multi-platinum systems $[\text{Pt}_3(\text{CO})_6]_n^{2-}$, where $n = 1, 2, \dots, 6 \sim 10$, they can be relatively easily synthesized[1] and decomposed at elevated temperature to nano-size platinum powders[2]. Our previous measurements indicated that this reaction takes also place in liquid media[3]. The preparation of nano-size Pt-Cr particles from decomposition of platinum/chromium carbonyls (synthesized in methanol) were also performed by Yang et al[4]. But the influence of water content in methanol on the efficiency of this reaction did not presented. For the first time platinum carbonyls were synthesized and characterized in the seventies of the XX century[5]. $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ consists of a complex clusters of $\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3$. The spatial structure of a single cluster is based on a triangular ring Pt atoms. It turns out that the value of “n” depends critically on the conditions of synthesis. Generally, the higher the basicity / nucleophilicity of the reaction solution, the lower degree of aggregation is observed.

Due to the fact that solutions of individual oligomers absorb UV-Vis light in different ranges, it is possible to detect the prod-

ucts of the reaction between carbon monoxide and inorganic platinum compounds. For the lower degree of aggregation ($n = 3$) the absorption bands are observed at $\lambda_{\text{max}} = 358 \text{ nm}$ and 542 nm . The oligomers with the degree of aggregation of $n = 6$ absorb light in the visible range at $\lambda_{\text{max}} = 420 \text{ nm}$. Further increase in the number of the Pt-CO clusters (for $n \sim 10$) results in a shift in the absorption band to higher wavelength[5].

2. EXPERIMENTAL

To obtain platinum carbonyls, chemically pure platinum compounds $(\text{NH}_4)_2\text{PtCl}_4$ (99%) and PtCl_4 (99.9%) from Sigma Aldrich were used. Carbon monoxide (99.99% AirProducts) was used as a reducing agent. For the preparation of water-methanol solutions of platinum salts used water ($18.2 \text{ M}\Omega\text{cm}^{-1}$) and methanol (anhydrous, 99.8%) from Sigma Aldrich. The progress of the reaction was measured using a UV-Vis spectrophotometer Multispec 1500 Shimadzu. Raman spectra measurements were performed on a FT-IR Spectrometer Perkin Elmer 2000. SEM pictures of platinum powders were on the electron microscope JEOL JSM-6490L. All the experiments were performed under atmospheric pressure. The decomposition of the platinum carbonyls was performed in the porcelain crucibles.

In the first step of the platinum powder preparation from the platinum carbonyl, the solution was heated in the porcelain crucibles. The solvent was evaporated and the resulting precipitate was

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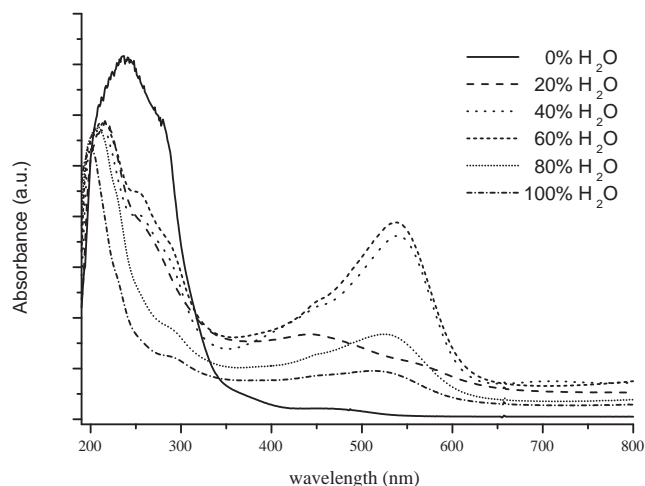


Figure 1. UV-Vis spectra recorded after the end of synthesis of platinum carbonyls in solutions of PtCl_4 ($0,5\text{mgPt}/\text{cm}^3$) with different ratios of methanol to water.

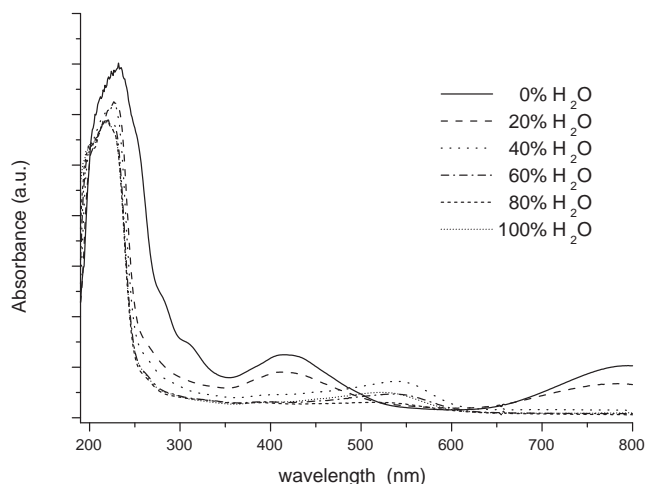


Figure 2. UV-Vis spectra recorded after the end of synthesis of platinum carbonyls in solutions of $(\text{NH}_4)_2\text{PtCl}_4$ ($0,5\text{mgPt}/\text{cm}^3$) with different ratios of methanol to water.

then roasted. After completion of these operations, the platinum powder was again quenched with methanol, filtered and dried. The obtained precipitates were then analyzed.

The fineness of platinum was examined using photon scattering spectroscopy (Zetasizer Nano S90).

The catalytic properties of platinum powders were examined in the low-temperature fuel cells with polymer electrolyte constructed at the Institute of Industrial Chemistry (IChP). The obtained platinum catalysts were used for the preparation of the cathode, while the anode catalyst was always black Pt-Ru (1:1 atomic) from E-TEK (now part of BASF). The prepared catalyst layer were deposited on the Nafion 117 membranes (Du Pont, USA) using coating ink prepared as a slurry of catalyst particles in deionized water with the addition of Nafion emulsion (Ion Power, Inc., USA). The same procedure was used for the preparation of the cathode cell with a commercial Pt black (E-TEK) having an average particle size (X-ray diffraction) to 5.3 nm. Load of the platinum on the cathode of each cell was 4 mg cm^{-2} , while the load Pt-Ru at the anode was 10 mg cm^{-2} . Geometric surface area of the anodes and cathodes were from 1.28 to 5 cm^2 . The prepared membrane-electrode assemblies were mounted in housings (diffusion layers of E-TEK: LT1400W - anode and LT2500W - cathode flow field plates and the end of its IChP production) and tested in methanol power regime. Air was used at the cathode.

3. RESULTS AND DISCUSSION

In order to obtain platinum powder with the most developed area, a number of experiments involving the reduction of PtCl_4 and $(\text{NH}_4)_2\text{PtCl}_4$ in various water-methanol solutions were performed. Depending on the composition of the solution (volume ratio of methanol to water), the platinum carbonyls with various degree of aggregation were obtained. The results are shown in Fig. 1 and Fig. 2 for PtCl_4 and $(\text{NH}_4)_2\text{PtCl}_4$ respectively.

In the case of the solutions containing platinum tetrachloride as a reactant, the water concentration plays intermediate role on the

observed carbonyl products. The performance of the synthesis of platinum carbonyl with $n = 3$ can be inferred from the strong band with the maximum at 548 nm. This strongly misshapen and broad band covers the characteristic absorbance at 358 nm which can indicate the co-existence of other platinum carbonyls in the solution. Synthesis occurred most efficiently (the highest absorption at $\lambda_{\text{max}} = 548\text{ nm}$) for the MeOH/ H_2O solution with a water concentration equal to 60 percent.

The water content in the solution containing $(\text{NH}_4)_2\text{PtCl}_4$ plays far greater role on the obtained products than in the case of PtCl_4 . For $(\text{NH}_4)_2\text{PtCl}_4$, depending on the composition of the solution, various carbonyls oligomers are observed.

Only for the solutions containing $(\text{NH}_4)_2\text{PtCl}_4$ with the highest concentration of methanol (100% and 80%), the higher aggregated oligomers ($n \geq 5$) are generated. For these forms the characteristic absorption maximum at 430 nm develops. For PtCl_4 such tendency is not so well marked and only weak shoulders at 450 nm for intermediate concentrations of the methanol (from 40 to 60%) are observed. At higher than 20% water concentration in the solution containing PtCl_4 , the absorption maximum at 548 nm is detected. Such tendency is also observed for the solution containing $(\text{NH}_4)_2\text{PtCl}_4$. Generally, for the same time of the reaction the highest absorbance (related with the generation of the platinum carbonyls with $n = 3$) is observed in the solutions with water content of 40 and 60 percent for $(\text{NH}_4)_2\text{PtCl}_4$ and PtCl_4 , respectively. In both analyzed systems a large excess of water or methanol, affects adversely the performance of the synthesis of platinum carbonyls with the low degree of the aggregation.

Additional experiments were conducted to determine the optimal time for the platinum carbonyls synthesis. The results are presented in Fig. 3 and Fig. 4.

The reduction of PtCl_4 (Fig. 3) in the methanol/water solution occurs practically complete after 70 min from the start of the platinum carbonyl synthesis. Spectra recorded after this time are practically the same.

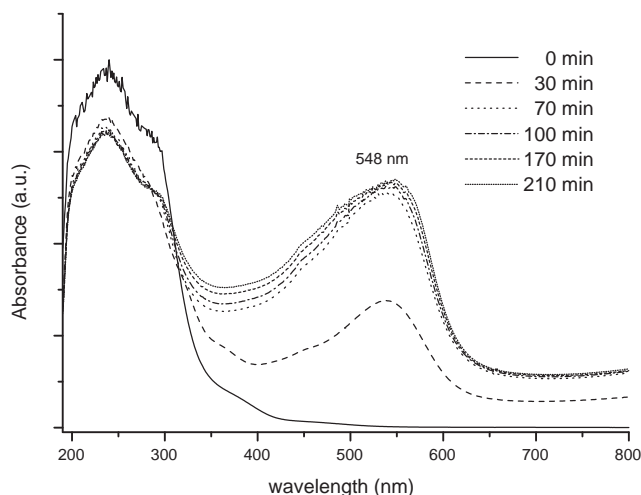


Figure 3. Time dependence UV-Vis spectra recorded during passing carbon monoxide through methanol-water solution (volume ratio 3:2) containing PtCl_4 ($0.5\text{mgPt}/\text{cm}^3$).

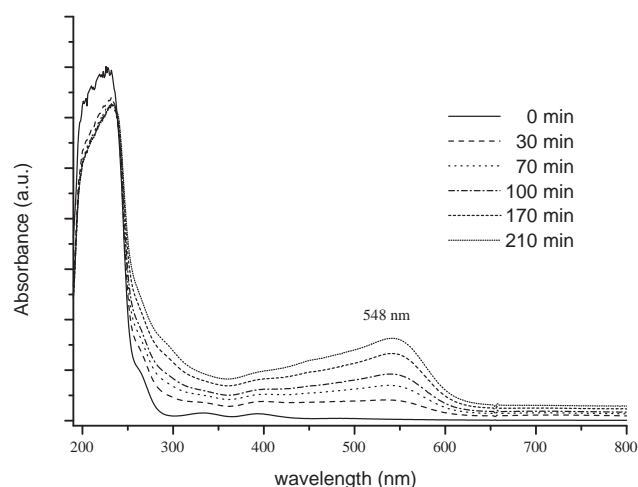


Figure 4. Time dependence UV-Vis spectra recorded during passing carbon monoxide through methanol-water solution (volume ratio 3:2) containing $(\text{NH}_4)_2\text{PtCl}_4$ ($0.5\text{mgPt}/\text{cm}^3$).

The reduction of PtCl_4 by carbon monoxide (Fig. 3) results in far more rapid appearance of a suspension in the solution. On one hand, the appearance of the slurry may indicate the formation of metallic platinum, but on the other hand, taking into account literature data[5,8], the generation of the $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ is also possible.

During the reduction of $(\text{NH}_4)_2\text{PtCl}_4$ the characteristic for these ions absorption with maxima at 335 and 395 nm decrease (Fig. 4). After about 30 min from the start of passing carbon monoxide through the solution, the absorbance were poorly selected and strong misshapen band with the maximum at 548 nm developed. This misshapen can indicate that during the reduction process not only platinum carbonyls with the degree of the aggregation equal to 3 but also higher aggregated platinum carbonyls were generated in

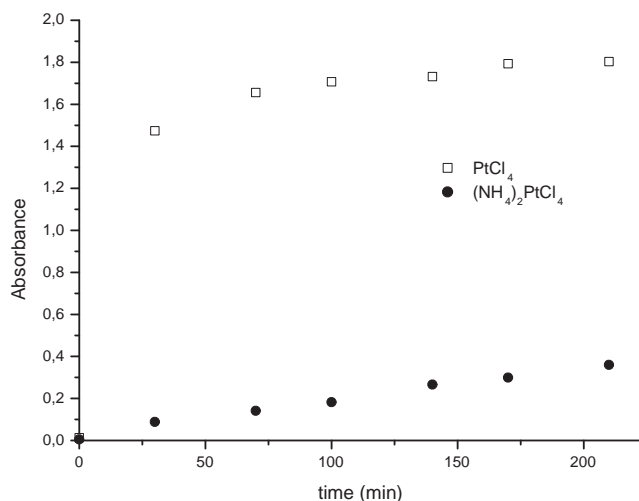


Figure 5. Changes in the absorbance ($\lambda = 548 \text{ nm}$) recorded during passing carbon monoxide through methanol-water solution (60% v/v methanol) containing $(\text{NH}_4)_2\text{PtCl}_4$ or PtCl_4 ($0.5\text{mgPt}/\text{cm}^3$).

the solution.

Observed red color of the solution would indicate the appearance of the carbonyl platinum with low degree of the aggregation. Calabrese et al.[5] and Longoni et al[8], indicated that for this color, $[\text{Pt}_3(\text{CO})_6]_3^{2-}$ is responsible. Although in an acidic environment (produced by the hydrolysis of platinum compounds) a mixture of oligomers with the degree of aggregation equal to 5 or higher are also postulated[1,9,10]. These conclusion are in line with UV-vis spectra where broad misshapen band with the maximum at 548 nm is observed. The weak developed shoulder near 450 nm would also indicate the presence in the solution the platinum oligomers with the degree of aggregation of $n = 6$ ($\lambda_{\text{max}} = 420 \text{ nm}$).

The reduction of $(\text{NH}_4)_2\text{PtCl}_4$ methanol/water solutions, as it was mentioned, does not proceed so rapidly in comparison to PtCl_4 , Fig. 5. The increases of the absorbance characteristic for platinum carbonyls ($\lambda_{\text{max}} = 548 \text{ nm}$) is much faster for PtCl_4 than for $(\text{NH}_4)_2\text{PtCl}_4$. During the first 30 min of the process the rapid increase of the absorbance and later on slowdown this increase is observed only for PtCl_4 . This tendency observed not only for the band characteristic for the platinum carbonyls but also in a whole range of the visible spectrum (see: Fig. 3) can indicate the generation of the platinum suspension in the solution. Pt^{4+} (PtCl_4) is a simple ion which can be easy reduced by the CO molecules and create Pt-CO bonds. In contrast to platinum tetrachloride, for $(\text{NH}_4)_2\text{PtCl}_4$ the linear increase of the absorbance at 548 nm with respect to time throughout the experiment is observed. In this case, in the first step of reaction the Pt-Cl bonds must be dissociated[3] and subsequent products with the Cl-Pt-CO core are created. These intermediate products are later reduced to platinum carbonyls.

In order to confirm the existence of platinum carbonyls in the solutions further spectroscopic measurements were carried out using Raman spectroscopy (Fig. 6). For the solutions containing initially $(\text{NH}_4)_2\text{PtCl}_4$ and PtCl_4 as a precursors, a strong band at 483

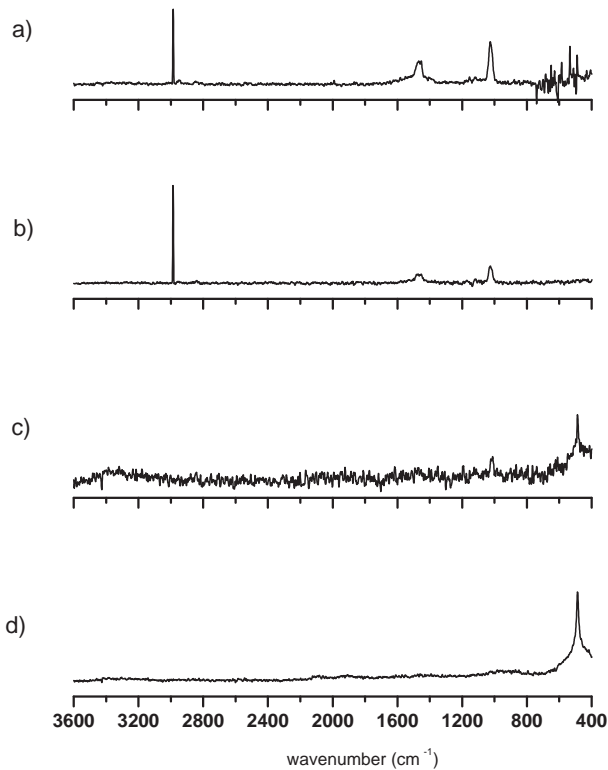


Figure 6. Raman spectra recorded: a) in the MeOH/H₂O (40% H₂O) solution containing PtCl₄ (0,1 mgPt/cm³), b) in the MeOH/H₂O (40% H₂O) solution containing (NH₄)₂PtCl₄ (0,1 mgPt/cm³), c) 100 min after start of the synthesis of platinum carbonyls in the MeOH/H₂O (40% H₂O) solution containing (NH₄)₂PtCl₄ (0,1 mgPt/cm³), d) 100 min after start of the synthesis of platinum carbonyls in the MeOH/H₂O (40% H₂O) solution containing PtCl₄ (0,1 mgPt/cm³)

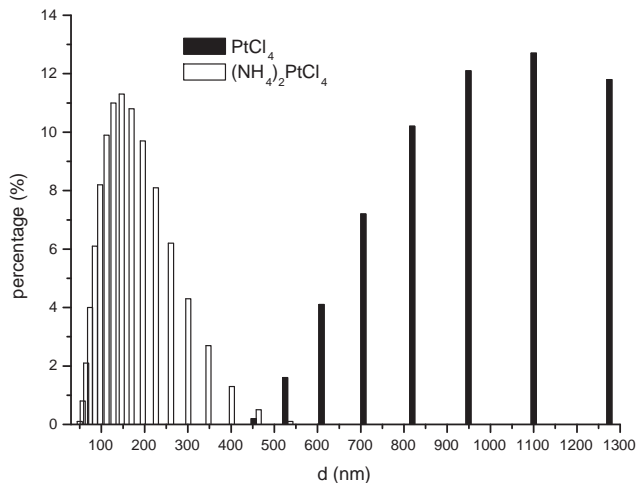


Figure 7. The platinum particle size obtained from the solution containing (NH₄)₂PtCl₄ and PtCl₄ as the substrates.

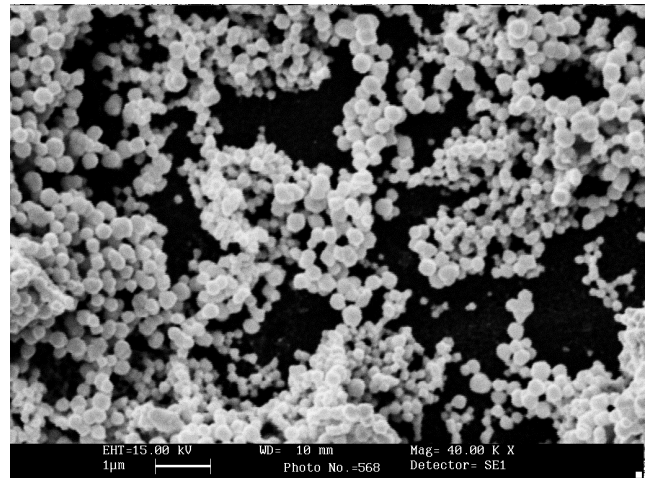


Figure 8. SEM imaging of Pt obtained after reduction of (NH₄)₂PtCl₄ (in MeOH:H₂O = 3:2) by carbon monoxide and decomposition of the platinum carbonyls Magnification 40 000 x.

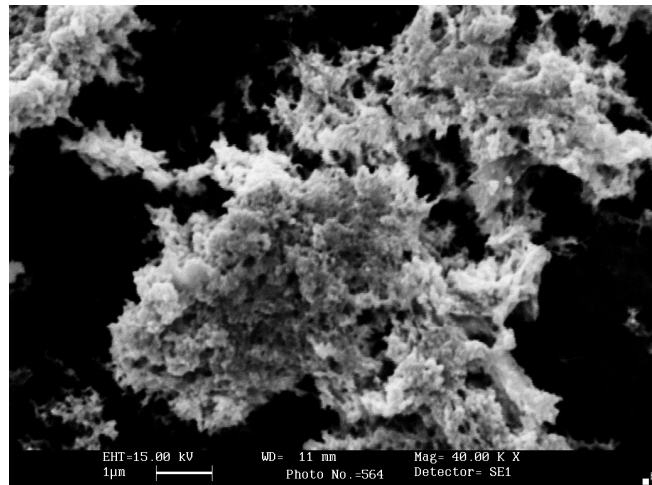


Figure 9. SEM imaging of Pt obtained after reduction of PtCl₄ (in MeOH:H₂O = 3:2) by carbon monoxide and decomposition of platinum carbonyls. Magnification 40 000 x.

cm⁻¹ was observed. This band clearly shows the appearance of platinum carbonyls and is characteristic for Pt-CO binding[10]. The bands at 1024, 1485 and 2986 cm⁻¹ observed in the other (tests) solutions are characteristic of methanol.

Literature data[3,11,12] indicate that platinum carbonyl decomposition occurs at low temperatures. This property was used in the preparation pure and nano-sized platinum.

On the basis of the elementary analysis, it was found that obtained platinum powders contain almost pure platinum. Analyzed nitrogen, carbon and chlorine content were on the limit of quantification (for both analyzed platinum samples: PtCl₄ and (NH₄)₂PtCl₄ as the precursors below 0.1%). The results show efficient reduction of (NH₄)₂PtCl₄ and PtCl₄ by carbon monoxide to form platinum and practically complete decomposition of carbonyls of platinum.

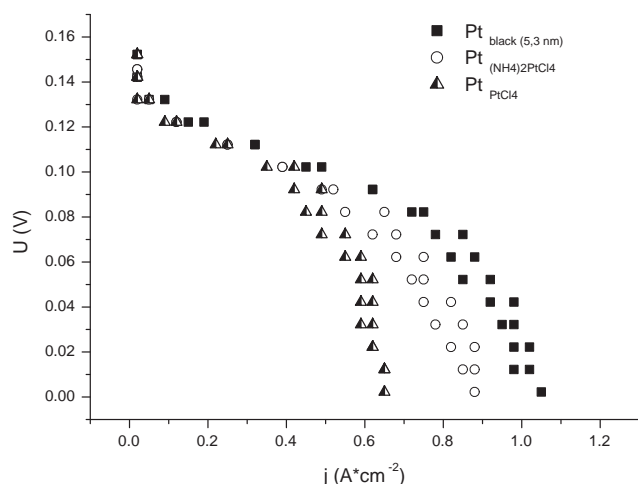


Figure 10. The polarization curves obtained for the commercial black and synthesized cathode materials (MeOH:H₂O = 3:2) in the direct methanol fuel cell.

The sizes distribution of the platinum particles obtained from (NH₄)₂PtCl₄ and PtCl₄ as precursors is shown in the Fig. 7. For both analyzed platinum salts, this distribution is broad: from 34 nm to 456 nm and from 259 nm to 2500 nm for platinum particles obtained from (NH₄)₂PtCl₄ and PtCl₄ respectively. The results of these analyzes indicate that the aggregation of the platinum particles took place during the decomposition of the platinum carbonyls.

Additional information concerning the structure of the platinum powders provided the SEM images. The microscopic images of the platinum obtained after thermal decomposition of platinum carbonyls showed a developed area of samples (Fig. 8 and Fig. 9).

The process of reduction of platinum compounds: (NH₄)₂PtCl₄ (Fig. 8) and PtCl₄ (Fig. 9) as precursors, leads to obtain the deposits of granular structures although in the case of (NH₄)₂PtCl₄ the level of the platinum particles aggregation is lower than for PtCl₄. It is worth noting that the particles are not uniform and are made up of smaller than 100 nm particles of Pt.

In order to characterization of obtained platinum materials, the experiments in the direct methanol fuel cell were performed (Fig. 10). In the experiments used flow rate of 0.3 M solution of methanol (1.3 mlmin⁻¹) and air flow rate (20 Ncm³min⁻¹). Analyzing the polarization curves obtained for commercial available platinum black and both synthesized platinum powders the identical electrochemical noises in the low current density were recorded. The differences are observed only for higher than 0.4 Acm⁻² current densities. The factor determining the catalytic properties of these materials is a potential drop in the area of concentration polarization. The decrease in current cell voltage starts earlier and faster for platinum powder obtained from PtCl₄ than in the case of (NH₄)₂PtCl₄. Better electrocatalytic properties has the platinum powder obtained from (NH₄)₂PtCl₄. For the 0.8 Acm⁻² the cell potential where the cathode was performed from the Pt ((NH₄)₂PtCl₄) equaled 0.04V and was two times lower than for the commercially available platinum black. This indicates that the cathode obtained from experimental black ((NH₄)₂PtCl₄) were slightly worse than the cathode prepared

from the commercial black. If we take into account that the size of the particles of the commercial platinum was 5.3 nm and the size of experimental black much higher the obtained results are good and indicated that the surface of obtained platinum particles are much more developed than observed using photon scattering spectroscopy or SEM techniques.

4. CONCLUSIONS

The reaction of carbon monoxide with inorganic compounds of platinum: PtCl₄ or (NH₄)₂PtCl₄ in methanol/water solutions leads to obtain the platinum carbonyls. The study indicates that the reaction proceeds at a satisfactory rate at room temperature and atmospheric pressure, which is of particular importance in the context of a highly toxic properties of carbon monoxide. Based on the obtained results, it can be concluded that the process is done with the greatest reaction rate in a mixture of methanol:water in the ratio 3:2. The electrochemical experiments shown better electrocatalytic properties of platinum powders obtained from (NH₄)₂PtCl₄ as the precursor.

5. ACKNOWLEDGEMENT

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