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Quantitative determination of dispersed platinum in carbon by cyclic voltammetry

A. ESSALIK, K. AMOUZEGAR, O. SAVADOGO*

Département de Métallurgie et de Génie des Matériaux, École Polytechnique de Montréal, B. P. 6079, succ. Centre-ville, Montréal, Québec H3C 3A7

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The application of cyclic voltammetry to the evaluation of the platinum content of carbon-supported platinum catalysts was investigated. The results were compared to those obtained by INAA and FAAS. A good linear relationship between the hydrogen deposition charge and platinum loading in the catalyst was found for platinum of different particle size. This method has the advantage of being readily available in many laboratories in addition to providing the real surface area of the metal at the same time.

1. Introduction

The overall bulk atomic composition of a catalyst is an important characteristic [1]. The determination of the metal content of supported metal catalysts is essential in the determination of other characteristics of the catalyst used in the control of the quality and reproducibility of new catalyst batches before loading into a reactor [2]. For example, the determination of the average particle size of the metal in a supported metal catalyst using a selective chemisorption gas requires an exact knowledge of the metal content of the catalyst [3].

Different analytical techniques may be used to determine the metal content of a supported catalyst. Some of these techniques, such as neutron activation analysis (NAA) or X-ray fluorescence spectrometry (XRF), are very sensitive although costly and not readily available. Other techniques, such as flame atomic absorption spectrometry (FAAS), are more readily available but require a lengthy procedure of prolonged acid dissolution and sample preparation [4]. In the case of platinum-supported catalysts, cyclic voltammetry (CV) has been used both for the characterization of the catalyst surfaces [5] and for the measurement of the metal real surface area [6, 7]. The CV technique is now successfully used for the determination of the catalyst specific surface area associated with high-area carbons [8–16]. It seems that the large double-layer capacity associated with these high-area carbons has no significant effect on the use of this method. Very recently it has been shown that CV provides more consistent results than TEM for the evaluation of the electrode active area when an electrochemical system is considered [16]. In this paper, we report on the application of cyclic voltammetry to the determination of the metal content of platinum supported on graphitized carbon black. NAA and FAAS were also used and the results are compared to those obtained with cyclic voltammetry.

2. Experimental details

The carbon-supported platinum catalysts were prepared by reducing a chloroplatinic acid solution in the presence of graphitized carbon (Vulcan XC-72R from Cabot Canada) by the addition of sodium formate to the slurry. The metal content of the fabricated catalysts was examined by NAA and the results were used to correct the theoretical values. For the NAA analysis, the details of the experiments and the measurements have been described elsewhere [17–21]. The sample was shuttled to and from a reactor using a pneumatic system. Thus, the sample was irradiated three times with a maximum flux of 10^{12} neutrons $cm^{-2} s^{-1}$ and counted four times with the gamma-ray detector. Several measurements were performed in order to optimize the conditions. For each measurement an appropriate decay time, the time between irradiation and counting, was chosen. The germanium detector used had a volume of 65 cm^3 and a resolution of 1.65 keV at 1332 keV and was surrounded by 5 cm of lead shielding. To avoid contamination the sample was handled with clean polyethylene gloves. After irradiation and before counting, it was transferred into a new plastic vial so that elements in the vial were not detected. The FAAS analysis was performed using a 5000 Perkin–Elmer-flame atomic absorption spectrophotometer. The sample preparation consisted of the following: 50 mg of the powder was treated with 20 ml of hot aqua regia. The slurry was evaporated to dryness and another 20 ml of aqua regia was added. This was repeated four more times, evaporating to dryness each time. Then, 9.5 ml of water, 0.25 ml of

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* Author to whom correspondence should be addressed.

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Table 1. Theoretical and INAA-measured platinum content of the catalysts

Sample	*Pt content* (*theoretical*) /% (w/w)	*Pt content* (*INAA analysis*) /% (w/w)
1	0.5	0.49
2	1.0	0.89
3	2.0	1.85
4	5.0	4.75
5	10.0	9.50

concentrated HCl and 0.25 ml of Triton X-100 were added. The Triton was added to assist the wetting of the powder and to ensure a uniform dispersion. Sample slurries were aspirated into the flame in the normal manner. The absorbance of each sample was measured five times at 265.9 nm.

The cyclic voltammetry measurements were carried out in a three-compartment cell with an Ag/AgCl reference electrode and a platinum screen as the counter electrode. A PAR 273A potentiostat monitored by PAR M270 software was used. The electrolyte consisted of 1 M H_2SO_4 prepared from concentrated acid purified by electrolysis and 18 MΩ cm water. The preparation of the electrodes from the catalysts consisted of the following: 10 mg of the catalyst was mixed with enough volume of a suspension of Teflon-30 (Dupont Canada) to give 10% (w/w) content in the Teflon. Once the water and the wetting agent contained in the Teflon suspension are evaporated, each paste was pressed at 345 °C on a platinum perforated sheet. The electrode was then treated with hot nitric acid for 30 s and washed with boiling water. It was then placed in the electrode compartment using a platinum wire and submitted to 10 potential sweeps between 0.27 and 1.1 V vs Ag/AgCl at a sweep rate of 50 mV s^{-1}. Finally, the voltammogram was obtained after five potential sweeps at 8 mV s^{-1}.

3. Results and discussion

The platinum catalysts containing different platinum loading were analysed using instrumental neutron-activation analysis. The theoretical and the measured values of platinum loading in the catalysts prepared from a 10% platinum catalyst are listed in Table 1. The values determined by NAA are slightly lower than the theoretical values. This is because some platinum is lost during preparation of the catalyst. Since NAA is noted for its precision (e.g., the detection limit for platinum is 5×10^{-4} μg g^{-1} [7]), it is frequently used as the reference technique for the development of reference materials. Furthermore, carbon is among the elements that do not activate upon irradiation with thermal neutrons to produce gamma-rays and thus it will not affect the analysis of platinum. Therefore, the platinum percentages determined by NAA have been used in this study in the evaluation of the other techniques.

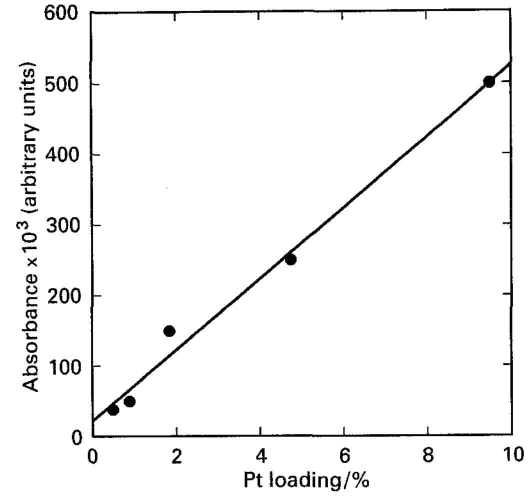

Fig. 1. Platinum absorption intensities of catalysts containing varying platinum loadings.

3.1. *Flame atomic-absorption spectrometry (FAAS)*

Figure 1 shows the variation of the measured absorbance at 265.9 nm as a function of the platinum percentage in the catalyst. All the samples were prepared from the catalyst containing 10% Pt. A linear relationship was found. The detection limit for the supported platinum was found to be 1%, since the absorbance of the catalyst containing 0.5% Pt (w/w) is the same as that of the blank. The most important disadvantage of this technique in the analysis of carbon-supported platinum is that, prior to the analysis, a time-consuming procedure of dissolution of the sample in aqua regia followed by dispersion using a surfactant is required. On the other hand, the direct atomic absorption analysis of the solid samples, as described by O'Reilly *et al.* [22], was not possible due to the fact that the measured absorbances were neither reproducible nor stable.

3.2. *Cyclic voltammetry*

Cyclic voltammetry is a suitable electrochemical method for characterizing catalysts. This method has been used to determine the real surface area of the different noble metal catalysts [6, 23] by measuring the coulombic charge associated with the deposition or removal of a chemisorbed monolayer of a species, usually hydrogen. The present communication describes the determination of the Pt loading of carbon-supported catalysts by this technique. Figure 2(a) shows the potentiodynamic sweep curve obtained at a smooth platinum electrode in 1 M H_2SO_4 at 25 °C at a sweep rate of 50 mV s^{-1}. The typical peaks associated with hydrogen deposition and desorption and with oxide formation and reduction can be observed. The CV corresponding to a carbon-supported platinum catalyst with a platinum loading of 5% prepared from the sample of 10% (w/w) Pt is shown in Fig. 2(b). The voltammogram was obtained under the same conditions as that in Fig. 2(a), except for the sweep rate which was 8 mV s^{-1}. The very large double layer observed is due to the

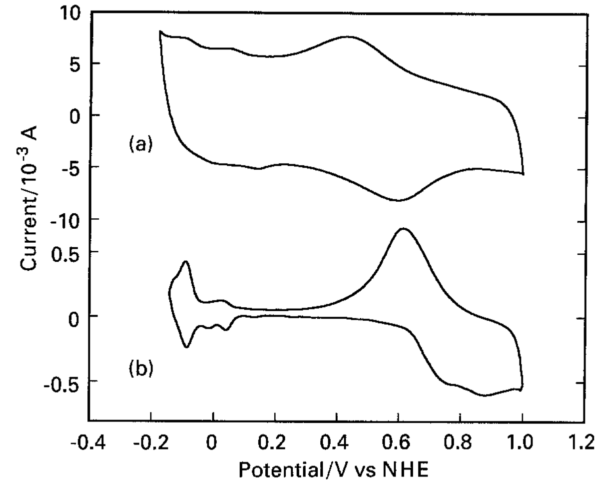

Fig. 2. Cyclic voltammograms of (a) 5% Pt on carbon at 8 mV s^{-1} in 1 M H_2SO_4, and (b) smooth platinum electrode at 50 mV s^{-1}.

Table 2. Electrochemical by active surface area ($m^2\ g^{-1}$) for platinum electrocatalysts prepared under different conditions

Electrode	*Electrochemical surface area*/$m^2\ (g\ Pt)^{-1}$
2% Pt prepared from 2% Pt	169
2% Pt prepared from 5% Pt	111
2% Pt prepared from 10% Pt	52
2% Pt prepared from 30% Pt	17

presence of the high-area carbons. The platinum oxide reduction peak is shifted to more cathodic potentials. This has been attributed to a possible metal-support interaction [5, 11, 24, 25]. Figure 3 shows the cathodic waves corresponding to hydrogen deposition at electrodes prepared with catalysts containing different platinum loadings ranging from 10% to 1%. The charge associated with the cathodic deposition of both the strongly and the weakly adsorbed hydrogen was measured by integrating the current under the peaks associated with these processes. The base line is taken by extrapolation of the double-layer region of the voltammogram. The endpoint for the integration was set at the potential at which the cathodic current reaches a minimum as the hydrogen atom deposition and molecular hydrogen evolution merge [26]. The measured electrochemically active surface area ($m^2\ g^{-1}$) calculated from the measured charges (mC) for a 2% Pt electrocatalyst prepared from 2% (w/w) Pt, 5% (w/w) Pt, 10% (w/w) Pt and 30% (w/w) Pt, respectively, is shown in Table 2. The electrochemical surface area decreases as the particle size increases. The measured charges are presented in Fig. 4 as a function of the Pt loading for different platinum-dispersed samples prepared with different particle sizes or active surface areas. As may be seen, a very good linear relationship between the measured charge and the platinum percentage is observed for the platinum-dispersed samples prepared under these different conditions. The detection limit of this technique was found to be $\sim 1\%$ of platinum for the samples prepared under different conditions. Thus, the interferences from the double-layer capacitance of the carbon did not allow the hydrogen deposition peaks to be distinguished in the case of the catalyst with 0.5% Pt.

4. Conclusion

Compared to FAAS, cyclic voltammetry (CV) seems to be more precise in the determination of the platinum loading of carbon-supported catalysts. Moreover, the CV technique is readily available and does not require any lengthy sample preparation. On the other hand, CV allows the simultaneous determination of other important characteristics of the catalyst, such as the real surface area of the metal. This technique has, in fact, been successfully used in the determination of electrochemically active surface areas of the catalyst [9–16] in high-area carbon. This may be used to determine the platinum concentration in the electrodes to be identified or the platinum lost after performance tests of the electrodes with the same particle sizes.

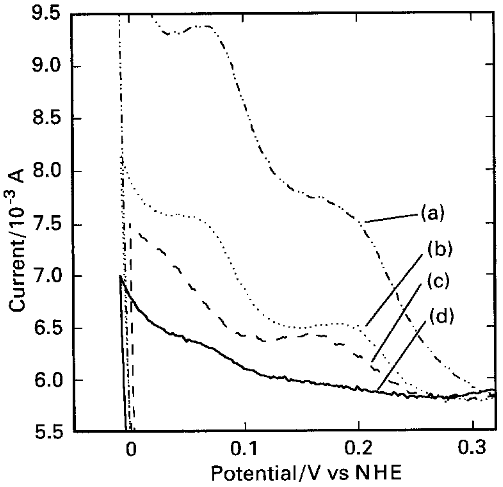

Fig. 3. Hydrogen deposition peaks obtained in 1 M H_2SO_4 at 8 mV s^{-1} at (a) 10% Pt, (b) 5% Pt, (c) 2% Pt and (d) 1% Pt electrodes prepared from 10% Pt.

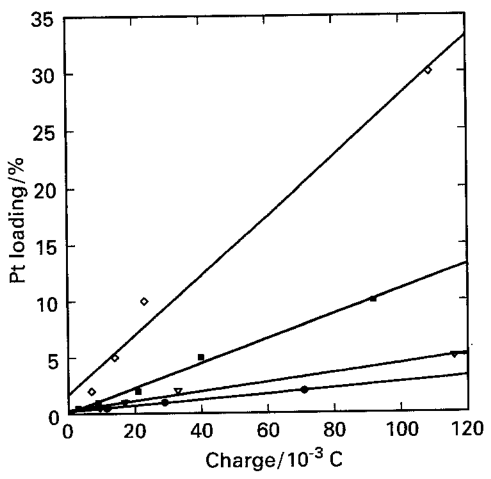

Fig. 4. Charge under the hydrogen deposition peaks as a function of platinum loading in the catalyst for different conditions of catalyst preparation: (◇) 30% Pt; (■) 10% Pt; (▽) 5% Pt; and (●) 2% Pt.

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