Comparison of high surface Pt/C catalysts by cyclic voltammetry

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Abstract

A detailed procedure for comparing high surface Pt/C catalysts was pointed out. Platinum dispersed carbon was prepared from carbonaceous material and chloroplatinic acid solution using sodium formiate. The real platinum metal surface area was evaluated by cyclic voltammetry on a thin porous coated disk electrode. The performance of catalysts prepared in our laboratory were similar to those of a well-known commercial one. The results show that electrochemical active surface (EAS) measurement is strongly influenced by the gas diffusion electrode (GDE) preparative method. It is only by means of a well-defined preparative procedure and data analysis that it is possible to use this technique to compare different carbon supported platinum catalysts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs), could provide, in a near future, a primary power source for terrestrial electrical vehicles fed with reformed hydrogen-rich gas, thanks to the high power density achievable at low temperature (70–90 °C). The direct evaluation of various catalysts for their activity in the gas diffusion electrodes (GDEs) of PEFCs is, however time consuming and expensive: hence it would be useful to devise a simple half-cell technique, which could mimic the complete polymer electrolyte fuel cell. Cyclic voltammetry (CV) has been frequently used to estimate the surface area (as electrochemical active surface (EAS)) of Pt/C catalysts by adsorption of atomic hydrogen in acidic media [1–6]. Nevertheless, the results obtained by different authors on a commercial Pt/C in the same or in different operative conditions are very discordant. All authors referred in Table 1 used the same catalyst, a Pt/C 20 wt.% catalyst (ETEK). The operative conditions were different: a conventional three-electrodes cell with an inert gas saturated solution of H_2SO_4 at 25 °C or full cell test station at 80 °C. The calculated active surface area are in a wide range 14–87 $m^2 g^{-1}$. A loss of 19–87% of surface area is observed in the literature data, as compared to the surface area calculated from the XRD for a Pt/C 20 wt.% ETEK

catalyst. The preparative method of the GDE appears to be important. In the past (Table 1), three methods were utilized for the preparative of catalyst layer of GDE: PTFE incorporated, Nafion[TM] incorporated, Nafion[TM] impregnated.

Perez et al. [1] used a PTFE incorporated Pt/C electrodes adapted on graphite substrate (1 cm^2); the low surfaces values obtained by CV was mainly explained by the low catalyst utilization due to the presence of PTFE in the electrode.

Tamizhmani et al. [2] and Fournier et al. [3] spread a very low volume of a catalyst ink (Pt/C + Nafion[TM] 5 wt.%) on the surface of a vitreous carbon electrode (0.196 cm^2). Also, using the same preparative method (but different Pt/C loading), the difference of calculated EAS was about 34%. Tamizhmani et al. [2] pointed that to obtain reproducible results using a sensitive technique as CV, it was important to maintain a constant Pt/C powder loading on the electrode surface. Nevertheless this method appears hardly reproducible and with a great possibility of uncertainties; in fact a very low volume (10 μl) of catalyst ink, not easily homogenized, must be spread on a very small electrode surface. The authors [2] attributed the loss of surface area on the Nafion[TM] impregnated Pt/C catalyst to the blocking, by the recast Nafion[TM] on the surface, of the Pt sites and to the inaccessibility of the protons to the Pt surfaces which are present between the Pt crystallites and the carbon support.

Gloaguen et al. [4] used a ultrasonically homogenized mixture of Pt/C 20 wt.% ETEK, Nafion[TM] and

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Table 1
Comparison of electrochemical active surface obtained using cyclic voltammetry by different authors

Authors	GDE structure ink composition/support	[Pt] (mg cm^{-2})	EAS (m^2 g^{-1})
Perez et al. [1]	Pt/C + PTFE/graphite	–	58
Tamizhmani et al. [2]	Pt/C + Nafion^{TM}/glassy carbon	0.165	87
Fournier et al. [3]	Pt/C + Nafion^{TM}/glassy carbon	0.042	57
Gloaguen et al. [4]	Pt/C + Nafion^{TM} + TEP/glassy carbon	–	88
Ciureanu and Wang [5]	Pt/C/teflonized carbon paper	1.700	14
Ticianelli et al. [6]	Pt/C + PTFE + Nafion^{TMa}/carbon paper	0.450	53
Giorgi and coworkers [7]	Pt/C + Nafion^{TMb}/carbon paper	0.22	68–115

[a] Thin film of 5 wt.% Nafion^{TM}.
[b] Nafion^{TM} in the range 0–1.46 mg cm^{-2}.

triethylphosphate (TEP), heat treated and dropped on a glassy carbon surface (1 cm^2). The authors pointed that by using TEP it was possible to heat above the glass transition temperature of Nafion^{TM}, which was necessary to obtain a well recast ionomer. The platinum loading in the active layer was not reported; nevertheless also their calculated EAS was 20% lower than XRD values. Others authors utilized a full cell configuration to obtain EAS. Ciureanu and Wang [5] used a 1 cm^2 single cell with a thin film catalyst layer of 1.7 mg cm^{-2} pressed on a gas diffusion backing of teflonized Toray carbon paper, but the EAS they founded was surprisingly low. Also, Ticianelli et al. [6] performed measurements on a single cell with a PTFE incorporated electrode (5 cm^2) and impregnated on the surface with a Nafion^{TM} solution. As the authors [6] pointed, the results showed great uncertainties due to the presence of a large double-layer charge.

Giorgi and coworkers [7] showed that in a GDE with a catalyst layer, obtained by mixing Pt/C and Nafion^{TM}, EAS was function of (Pt/C)/ Nafion^{TM} ratio. Using a constant platinum loading (0.22 mg cm^{-2}) and different Nafion^{TM} loading, the authors found EAS in the range 68–115 m^2 g^{-1}. This last result indicates that, using this preparative method, Nafion^{TM} loading should be carefully controlled to obtain comparable results.

Some conclusion can be drawn. The CV appears to be a good electrochemical method to obtain information on EAS, but attention must be dedicated to establish a well-defined procedure. In particular the GDE preparative method appear to be fundamental and some critical points can be defined: (a) the catalyst ink must be prepared preferentially without a binding agents (PTFE, Nafion^{TM}, etc.) that can decrease or change the catalyst utilization; (b) an exact control of platinum loading it is necessary before and after the electrochemical measurements; (c) a constant volume of Nafion^{TM} solution must be utilized to cover electrode surface; (d) the simplest and reproducible measurement configuration seem to be a half-cell three-electrodes set-up (with a working electrode geometric area of 1 cm^2). Our experiments have shown that the presence of an inert gas flowing on the back of the electrode (as in a full cell configuration) affects the hydrogen adsorption/desorption processes thus influencing the CV experiment.

2. Experimental

2.1. Catalyst preparation

Carbon black powder (Vulcan XC-72, Cabot International) with a specific surface area (BET) of 250 m^2 g^{-1} was used as a support for all catalysts. Three different Pt/C catalysts 20 wt.% (ENEA2, ENEA3, ENEA4) were prepared using a proprietary method briefly explained here. The carbon black was impregnated with H$_2$PtCl$_6$ in water, adjusting pH to 5–6 using a Na$_2$CO$_3$ solution. The ink was ultrasonically blended for 20 min and heated at 90–95 °C. A solution of the reducing agent HCOONa at three different concentration (0.1 M for ENEA2, 1 M for ENEA3 and 2 M for ENEA4) was heated at the same temperature and added at three different stirred ink. The mixtures were dried, cooled and washed repeatedly with distilled water. The three different catalyst powders were heated overnight at 110 °C in an air-oven. The platinum percentage (wt.%) in the catalyst powders were controlled by means of a spectrophotometric method described elsewhere [8] and sample absorption at ($\lambda = 403$ nm was measured using a UV–VIS spectrophotometer Beckman Model, DU65. Commercial available Pt catalyst powder 20 wt.% on carbon black (Vulcan XC-72) was obtained from ETEK Inc. as a reference material.

2.2. Electrochemical measurements

The cyclic voltammetries were carried out in a conventional airtight three-electrode cell containing 1 M H$_2$SO$_4$ electrolyte at 25 °C. The working electrode was a GDE disk inserted/mounted into a Teflon holder with a 1.1 cm diameter cavity that was adapted to a rotating disk electrode system EG&G Model 616. The active layers on the GDEs were prepared using a proprietary method briefly explained here. A mixture containing about 0.1 g of Pt/C catalyst powder and 1–4 ml ethanol was ultrasonically blended in a glass vial for 15 min to obtain the catalyst paint. A volume of 100–200 μl of this paint was spread on the surface of a weighted carbon paper (Toray TGPH090) disk (0.95 cm^2) using a micropipette and dried in an argon oven at 80 °C for about 20 min to eliminate solvent and obtain a thin active layer. The GDE was weighted again and the Pt loading was

calculated for every sample. A volume of 40 µl of 5 wt.% Nafion™ solution (Du Pont) was spread on the active layers and dried in an argon oven at 80 °C for about 30 min. Nafion™ acts as a protective layer and avoid loss of catalyst powder in the electrolyte. The electrode geometric area exposed to the electrolyte was 0.95 cm². A large area platinum flat electrode was used as counter electrode. An Ag/AgCl reference electrode was placed externally to the cell and connected to the main compartment through a Luggin capillary whose tip was placed as closest as possible to the working electrode surface. The potential values are reported with reference to the normal hydrogen electrode (NHE). The electrochemical cell was connected to a Solartron 1287 potentiostat/galvanostat interfaced with a GPIB card to a personal computer.

The experimental procedure [9] was as follows: the three-electrode cell was purged with argon for 15 min prior to electrochemical measurements. Subsequently, five consecutive CV (sweep rate 10 mV s⁻¹) were performed in the potential range 0–1400 mV versus NHE. For CO stripping measurements, pure CO was bubbled into the electrolyte for 15 s and then its adsorption on the electrode was driven under potential control at 200 mV versus NHE for 1 min. The electrolyte was purged for 25 min with argon, keeping

electrode potential at OCP to eliminate CO reversibly adsorbed on the surface. Three cyclic voltammmetry (sweep rate 10 mV s⁻¹) were recorded from 0 to 1400 mV versus NHE. The first anodic sweep from 0 to 1400 mV versus NHE was performed to electro-oxidize the irreversibly adsorbed CO and the subsequently voltammetries in order to verify the completeness of the CO oxidation.

2.3. X-ray diffraction analysis

The X-ray diffractograms were recorded using a Cu Kα source radiation in a Philips diffractometer, with a graphite monochromator on the diffracted beam and operating in the Bragg Brentano parafocusing geometry. The diffractometer was operated in the step scan mode with a 0.05 step and in the range of 15–90° (2θ). The high tension generator, a Philips Model PW1729, was operating at 40 kV and 30 mA.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the commercial Pt/C 20 wt.% ETEK and of the three Pt/C 20 wt.% ENEA catalysts. All the patterns clearly shows the five
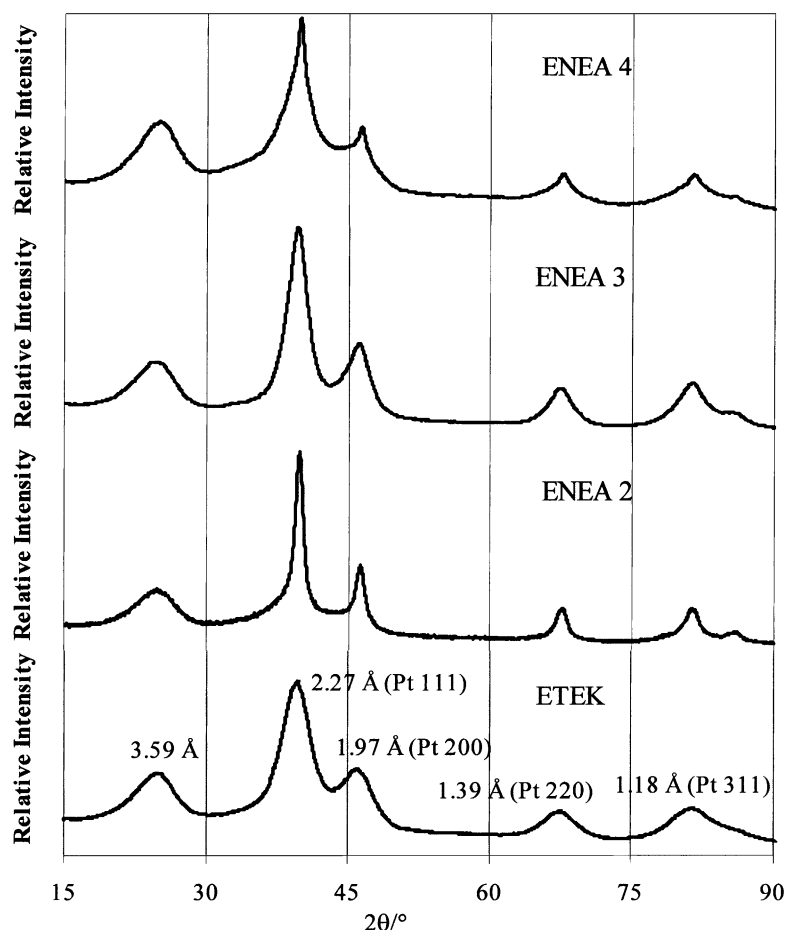

Fig. 1. X-ray diffraction patterns of ETEK 20 wt.% Pt/C and ENEA catalysts.

characteristic peaks of face centred cubic crystalline Pt [10] namely the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) (not resolved in the ETEK sample). The first broad peak at 25° is associated with the Vulcan XC-72 support material as demonstrated from XRD recorded only on the carbon not shown here. The average crystallite size was calculated from the broadening (β) of XRD peaks using the Williamson and Hall method [11] to separate strain (ε) and size (d) contribution to the line breadth

$$\beta \cos(\beta) = \frac{\lambda}{d} + 2\varepsilon \sin \theta \qquad (1)$$

when the strain is negligible (as it is for our samples), this equation can be reduced to the Scherrer formula and the surfaces areas of catalyst can be estimated from the X-ray diffraction peaks using the following equations:

$$d = \frac{k\lambda}{\beta_{1/2} \cos \theta} \qquad (2)$$

$$S = \frac{6000}{\rho d} \qquad (3)$$

where d is the average particle sizes (nm), S the surface area (m^2 g^{-1}), λ the wave-length of X-ray radiation (1.54 Å), ρ the Pt density (21.4 g cm^{-3}), θ the angle at the position of the peak maximum, $\beta_{1/2}$ the width (in radians) of the

Table 2
Average particle size of catalysts from XRD data of Fig. 1

Catalysts	Average particle size (nm)	Surface area (m^2 g^{-1})
ETEK	2.6 ± 0.4	108 ± 16
ENEA4	3.0 ± 0.5	93 ± 14
ENEA3	3.5 ± 0.5	81 ± 12
ENEA2	5.7 ± 0.9	49 ± 7

diffraction peak at half height, and k is the coefficient taken here as 1. Table 2 lists calculated average particle sizes for all the catalysts on the basis of the strongest diffraction peaks Pt (1 1 1).

It is important to remember that the crystallite size, calculated from XRD data, is related to the area of coherent diffraction and, in general, can be smaller than the true particle size. The crystallite size of sample ENEA2, as calculated from XRD, is nearly two times bigger than ENEA3 and thus the specific surface area is two times smaller. We believe that undetected Pt may have an important role in our case; the integrated intensity of the crystalline platinum reflection in XRD of sample ENEA2 are 23% smaller than ENEA3, this means that in ENEA2 there is 23% of undetectable non-crystalline Pt; this metal may be aggregated in small cluster with high catalytic activity. The line profile of sample ENEA4 is characteristic of a bimodal crystal size distribution. With Rietveldt analysis we have fitted the experimental XRD with two different lorentzian components: a major component (87%) with large peak associated to small crystal size (2 nm) and a minor component associated to bigger crystal (10 nm).

CV was employed to obtain the electrochemical active area of the different catalysts. As an example, Fig. 2 shows the cyclic voltammograms obtained in 1.0 M H$_2$SO$_4$ for Pt/C (ETEK) electrode. The coulombic charge for hydrogen desorption (Q_H) was used to calculate the active platinum surface of the electrodes. The value of Q_H was calculated as the mean value between the amounts of charge exchanged during the electro-adsorption (Q') and desorption (Q'') of H$_2$ on Pt sites. The contribution of "double layer" charge was evaluated for every sample as shown in Fig. 2.

Table 3 summarize the charges Q_H, Q' and Q'' for some of the catalysts tested. Results show that the values Q' and Q'' obtained for every electrode are always similar but the ratio
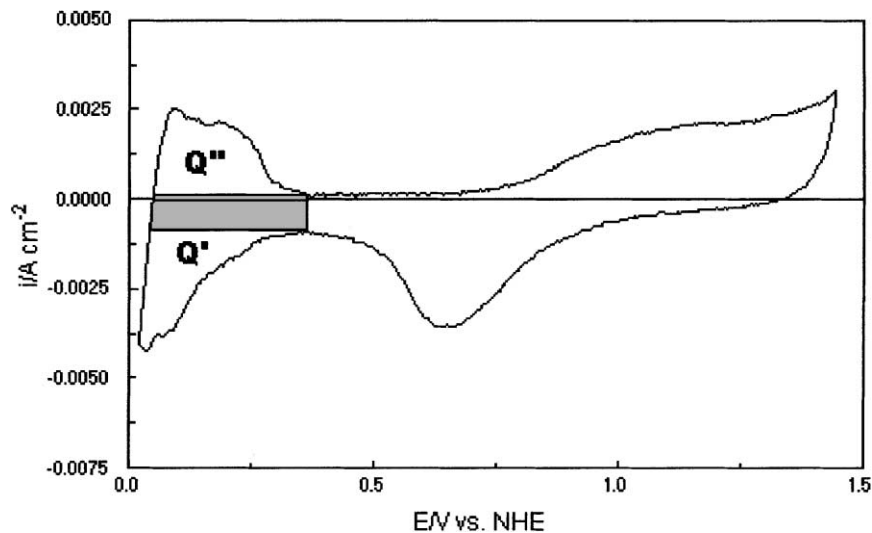

Fig. 2. Cyclic voltammograms (10 mV s^{-1}) at 25 °C on Pt/C (ETEK) in the potential range 0–1400 mV vs. NHE. Q' and Q'' represent the amount of charge exchanged during the electro-adsorption and desorption of H$_2$ on Pt sites and the fill area is the contribution of double layer charge.

Table 3
Hydrogen adsorption and desorption charges and mean values at different platinum loading

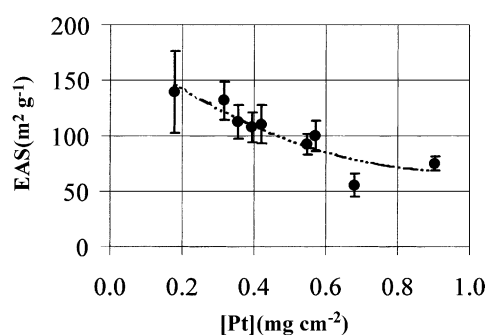| Catalyst	[Pt] (mg cm^{-2})	Q' (mC cm^{-2})	Q'' (mC cm^{-2})	Q_H (mC cm^{-2})	Q_H/[Pt] (mC g^{-1})
ETEK	0.32	87	87	87	276
ETEK	0.42	91	104	97	231
ETEK	0.55	109	103	106	193
ETEK	0.90	147	136	142	157
ENEA4	0.36	90	92	91	255
ENEA4	0.56	110	113	112	200
ENEA4	0.85	110	99	104	123
ENEA3	0.28	72	67	69	246
ENEA3	0.35	74	80	77	217
ENEA3	0.83	82	63	72	87
ENEA2	0.41	71	73	72	176
ENEA2	0.51	70	73	71	141
ENEA2	0.74	85	90	88	118

Fig. 3. Calculated (Eq. (4)) electrochemical active surface based on hydrogen adsorption vs. platinum loading for ETEK catalyst.

Q_H/[Pt] decrease as the platinum loading increase. Figs. 3 and 4 show EAS calculated at different platinum loading for ETEK and ENEA catalysts by means of Eq. (4) [12]

$$EAS = \frac{Q_H}{[Pt] \times 0.21} \tag{4}$$

where [Pt] represents the platinum loading (mg cm^{-2}) in the electrode, Q_H the charge for hydrogen desorption (mC cm^{-2}) and 0.21 represent the charge required to oxidize a monolayer of H_2 on bright Pt [1–7]. These results clearly
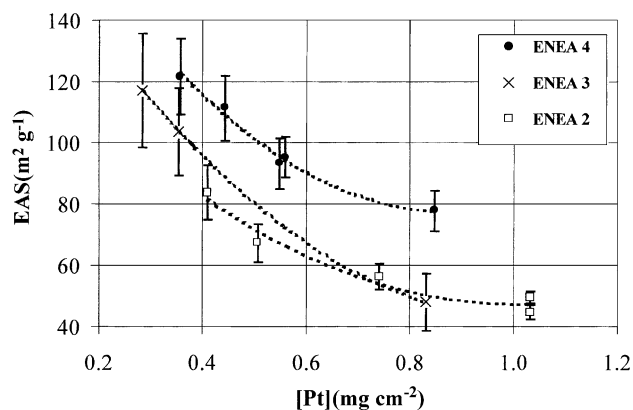

Fig. 4. Calculated (Eq. (4)) electrochemical active surface based on hydrogen adsorption vs. platinum loading for ENEA catalysts.

demonstrate that wide range of EAS are obtainable simply by changing the platinum loading.

The observed trend for EAS obviously depends by the fact that, in our calculation, all platinum loaded on the electrode is considered electrochemically active. This assumption can be considered exact only in a well-established range of platinum loading. In fact, as the platinum loading increase, the electrode thickness grows; as a consequence some platinum particles are blocked in the carbon substrate and not exposed to the electrolyte solution. On the other side, a too small amount of catalyst powder does not cover uniformly the electrode geometric area, so the EAS appear to be oversized. Besides the EAS standard deviation, calculated by means of Eq. (5) (obtained by differentiating Eq. (4)), is a function of the inverse square of platinum loading, for this reason a too small platinum amount should be avoid.

$$\Delta EAS = \left| \frac{\Delta Q_H}{[Pt] \times 0.21} \right| + \left| \frac{\Delta [Pt] Q_H}{[Pt]^2 \times 0.21} \right| \tag{5}$$

It must be considered that platinum loading on these powder catalysts is obtained by known the Pt/C wt.% so, a control of this parameter, by means of analytical method, needs to avoid a systematic error of calculated EAS.

Figs. 3 and 4 show that an exact control of platinum loading it is necessary to compare different catalysts; for ETEK catalyst a values comparable with XRD data can be obtained using a platinum loading in the range 0.35–0.45 mg cm^{-2} (Table 4). The comparison between the three

Table 4
Electrode surface obtained by means of different techniques

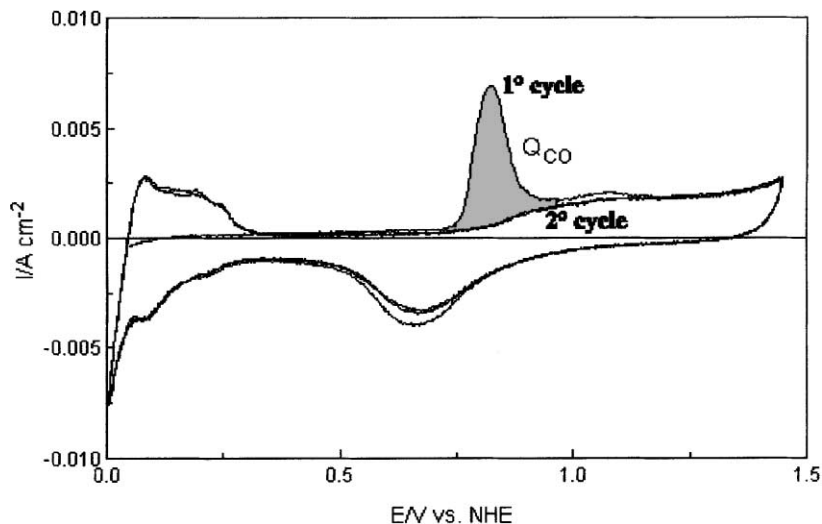| Catalysts	EAS (m^2 g^{-1})		Surface area XRD (m^2 g^{-1})
	H_2 adsorption	CO stripping	
ETEK	106 ± 17	97 ± 23	108 ± 16
ENEA4	100 ± 9	92 ± 13	93 ± 14
ENEA3	90 ± 12	79 ± 13	81 ± 12
ENEA2	60 ± 5	66 ± 15	49 ± 7

Fig. 5. Cyclic voltammograms (10 mV s^{-1}) at 25 °C in the potential range 0–1400 mV vs. NHE on Pt/C (ETEK) with (first cycle) and without (second cycle) a CO adsorbed ad-layer. The filled area represents the charge related to the CO oxidation reaction.

ENEA catalysts shows that by increasing 10 times the concentration of the reducing agent HCOONa (0.1 M for ENEA2 and 1 M for ENEA3), the active surface grows about 50%. Increasing the concentration of sodium formiate to 2 M (ENEA4) the growth of EAS is about 66% respect to ENEA2. The results pointed out that the platinum particles dimensions (Table 2) are strictly related to concentration of reducing agents. This can be explained considering that formiate concentrations influence the reduction kinetic of Pt(IV) to Pt(0) and the higher reaction rate produces smaller catalyst particles. The decrease in EAS indicates that an increasing fraction of the Pt surface becomes screened as Pt loading is increased.

Fig. 5 shows two cyclic voltammograms obtained on Pt/C (ETEK) with a CO adsorbed ad-layer. The peak at about 0.87 V versus NHE, in the first cycle, represents the electro-oxidation of the irreversibly adsorbed CO. The calculated peak charge Q_{CO}, is related to the reaction

$$Pt - CO + H_2O \rightarrow Pt + CO_2 + 2e^- + 2H^+ \qquad (6)$$
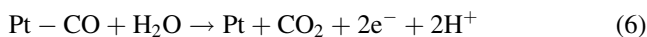
the charge Q_{CO} was used to compare the active surface of the catalyst, calculated by means of the following equation:

$$EAS_{CO} = \frac{Q_{CO}}{[Pt] \times 0.484} \qquad (7)$$

where the value 0.484 represents the charge density, required to oxidize a monolayer of CO on bright Pt [5,13]. The active surfaces so obtained show the same trend of those obtained by means of hydrogen adsorption (mean value) and XRD data (Table 4), but the values are generally lower. The fractional coverage of adsorbed CO molecules to surface Pt atoms ((θ_{CO}), calculated by the ratio EAS_H/EAS_{CO}, was about 90% in good agreement with the corresponding values obtained by other authors [13,14]. Active surface calculated by means of CO adsorption seem to be not dependent from platinum loading, but further investigation are in progress

about this aspect. Table 4 summarizes data obtained with the three different techniques. The trend appears to be the same for all techniques, only the ENEA2 catalyst shows a higher EAS value respect to XRD data. The presence of a high fraction of not XRD detectable platinum particles in this sample can justify this difference.

4. Conclusions

In conclusion the following considerations can be drawn.

1. A simply preparative method for the realization of platinum on carbon catalysts for PEFC electrodes was pointed out. The method is based on reduction with formiate and it appears to be easily scaled up to manufacture level.
2. The obtained electrochemical performance are comparable to those of commercial catalysts.
3. A detailed procedure for comparing high surface Pt/C catalysts by means of CV was pointed out and the results were in good agreement with XRD data.
4. The results show that EAS measurement are strongly influenced by the GDE preparative method and in particular by the platinum loading.
5. The electrochemical technique can substitute XRD characterization, giving more specific information taking in account crystalline and amorphous particles.

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