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CO-Stabilized Supported Pt Catalysts for Fuel Cells: Radiolytic Synthesis

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In a CO-saturated water/2-propanol mixed solvent, K_2PtCl_4 salt can be radiolytically reduced either into molecular carbonyl clusters of the $[Pt_3(CO)_6]_n^{2-}$ series or into colloidal metal particles by varying the CO : Pt ratio. The reduction occurs by a combined effect of CO and radicals produced by radiolysis, giving rise to unusually high reduction yields. The colloidal platinum and also the molecular clusters can easily be impregnated on carbon black. The particle size of the supported catalyst prepared in this way lies in the 2–3 nm range and is independent of the catalyst loading and support surface area, even for high loadings (3-nm particles have been deposited up to a 60 wt% loading on a Printex powder). These catalysts are found to be efficient for methanol or hydrogen electrooxidation and for oxygen electroreduction. The CO-stabilized colloids have been characterized by electron microscopy and UV–visible spectroscopy.

INTRODUCTION

Highly dispersed noble metals (platinum and platinum alloys) on high surface area supports such as carbon powders are the most popular electrocatalysts recommended for application in low-temperature fuel cell systems such as PEMFC and PAFC (protonic exchange membrane and phosphoric acid fuel cells).

Many attempts have been made to optimize the platinum efficiency. Particle size, platinum alloying, and catalyst loading on the support are the main relevant factors on which to work. It is now agreed that the 2–3 nm size range appears to be the best for catalytic efficiency, a size which ensures the metallic character of the element while optimizing the surface : mass ratio. However, a controversy exists concerning the necessity of further lowering the particle size (1). In fact, one of the most important parameters seems to be platinum loading on carbon powders. When the thickness of the active layer in fuel cell electrodes is lowered, a high platinum loading must be combined with a high utilization coefficient of the catalyst in the electrode (effectiveness factor) (2–5). However, particle size usually increases with platinum loading. For instance, the commercially available platinum-loaded Vulcan series (E-TEK Inc.) is quoted as having particle sizes of 2.0 nm at 10% loading, 3.2 nm at 30%, and 8.8 nm at 60%.

A second point, for oxygen reduction and methanol oxidation reactions, is that the activation polarization is very high, thus leading to a dramatic power drop. In the case of methanol oxidation, a reaction intermediate such as CO is known to be a poison. However, good catalytic results have been obtained with Pt-carbonyl compounds (6).

There are several methods for preparing supported catalysts, among which colloidal techniques offer the opportunity to maintain a low particle size dependence in regard to platinum loading. The radiolytic process has been used for a long time in our laboratory to reduce metal ions to small metal particles (7–10). Exposure of aqueous solutions of metal ions to ionizing radiation often leads to the formation of colloidal metals, the reduction being brought about by the hydrated electron $[E^0(n\mathrm{H_2O}/e^-_{\mathrm{aq}}) = -2.9$ V/SHE] and other radicals formed as primary or secondary radiolytic species. The first reduction product of metal ions is atoms in unusual valence states which undergo further reduction, dismutation, and finally coalescence until larger metal particles are formed. Various means can be employed to limit the size of the particles, such as a support or a dispersing agent such as polyvinyl alcohol (PVA) or polyacrylic acid (PAA). More recently, we used ligands (CO, phosphine) as size-limiting agents which give access to stoichiometrically well-defined molecular metal clusters (11, 12) or, as we report here, to very fine colloids.

The production of either molecular metal clusters or colloidal platinum with regard to the [CO] : [Pt] ratio is described in the first part of this paper. In the second part, the preparation of platinum-based supported catalysts by colloid impregnation and their characterization by microscopy and electrochemistry techniques, including a test in a complete fuel cell, are reported.

EXPERIMENTAL

The solutions contained K_2PtCl_4 (Aldrich) dissolved (10^{-3}–10^{-2} *M*) in a water/2-propanol solvent saturated with CO under 1 atm pressure (Alphagaz, 99.94% purity). The mixed solvent was chosen in order to combine platinum

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salt solubility (higher in water) and CO solubility (higher in alcohol). Since CO solubility is 10 times higher in ethanol ($\approx 10^{-2}$ *M*) than in water ($\approx 10^{-3}$ *M*), its concentration can be varied by modifying the proportions of the solvents. The solubility hypothesis has been based on linear interpolation. Among other alcohols, 2-propanol has been chosen because under irradiation it generates many radicals which are known to be highly reducing species, namely $(CH_3)_2C^\bullet OH : [E^0((CH_3)_2CO, H^+/(CH_3)_2C^\bullet OH) = -1.8$ V/SHE] (13). The solubility of CO is assumed to be close to that of ethanol/water mixtures.

The samples were prepared as previously described in (14). Solutions containing the metal salts were prepared in Pyrex flasks (10 to 100 cm^3 size, ratio of solution volume/gas free volume = 1), carefully degassed, and saturated with carbon monoxide at atmospheric pressure by bubbling. The time of bubbling was 25 min.

Four different carbon powders were used: Vulcan XC 72 (Cabot), specific surface area 254 $m^2\ g^{-1}$, grain diameter 30 nm, 1.5% ashes; Printex XE 2 (Degussa), specific surface area 1000 $m^2\ g^{-1}$, grain diameter 35 nm, 1.2% ashes; Black Pearls 2000 (Cabot), specific surface area 1475 $m^2\ g^{-1}$, grain diameter 15 nm; and Ketjenblack (Akzo), specific surface area 930 $m^2\ g^{-1}$, grain diameter 30 nm. The carbon powders were pretreated under a CO_2 atmosphere at 930°C for 30 min (1 h for the Vulcan powder), leading to a weight loss of about 30%.

The γ-irradiation was carried out in a panoramic ^{60}Co source. The usual dose rate was 5 kGy h^{-1}.

Once synthesized, the colloid solution is added to the desired amount of carbon powder. The ensemble is then thoroughly mixed for the impregnation step, then filtered and abundantly washed with pure water and dried. The impregnation is considered to be complete when the solution is colorless after filtration. The impregnation step is easy, and loadings as high as 60 wt% platinum on Printex XE 2 are obtained. Such a surprisingly high impregnation ratio is likely to be due to the specific interaction between carbon and Pt-bonded CO molecules. Let us recall that the carbon surface received an oxidative pretreatment with CO exhaust.

The spectroscopic analyses were carried out on a Varian DMS 100 spectrometer for the UV–vis spectra and on a Perkin–Elmer 883 spectrometer for the IR spectra.

TEM (transmission electron microscopy) measurements were conducted on a JEOL 2000 EX apparatus and STM (scanning tunneling microscopy) measurements on a Nanoscope III digital instrument.

Electrochemical characterization was done by cyclic voltammetry, either a half cell test or a complete cell test (this last test performed by the Sorapec Co.). For the cyclic voltammetry measurements, a suspension containing 10 mg ml^{-1} of platinized carbon powder and 10 mg ml^{-1} of soluble Nafion (5 wt% solution in aliphatic alcohol, Aldrich) was prepared by sonication. A few microliters of this suspension was deposited on a mirror-polished glassy carbon electrode. The ensemble was heated at 150°C for 15 min in order to recast the Nafion. The electrode thus prepared consisted of a thin film of less than 10 μm thickness.

For pure platinum catalysts, the particle size can be estimated upon deposition by cyclic voltammetry in a 1 *M* H_2SO_4 electrolyte (Fig. 1a). The coulombic charge Q corresponding to the oxidation and the reduction of adsorbed hydrogen on platinum can be measured by the area of the corresponding waves (hatched surfaces). On the basis of 210 μC per cm^2 of platinum, it is possible to determine the total platinum surface area in the film. Knowing the platinum mass in the initial drop, the mean particle size (Ø) can be estimated with the hypotheses of spherical and homogeneously sized particles, according to the relation

$$\text{Ø(nm)} = \frac{6 \times 10^3}{S_{Pt}\rho_{Pt}},$$

where S_{Pt} is the platinum specific area in $m^2\ g^{-1}$ and ρ_{Pt} is the platinum density in g cm^{-3}, supposed close to the bulk density (for instance, $S_{Pt} = 100\ m^2\ g^{-1}$ implies that Ø = 2.8 nm).

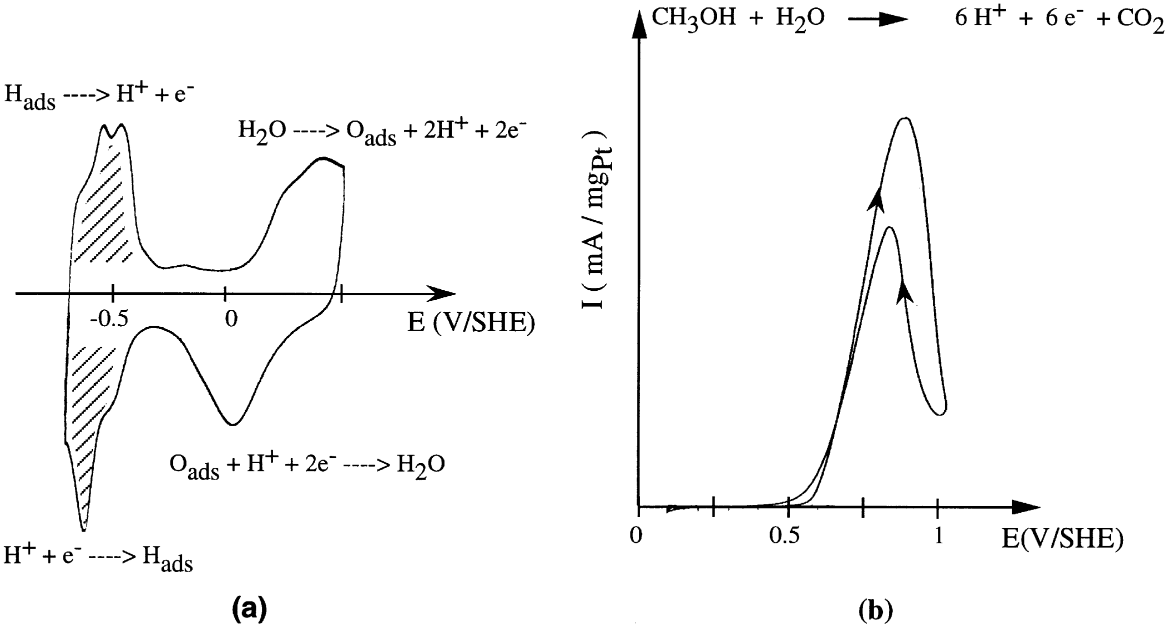
This method has the advantage of measuring only those platinum atoms that are accessible to electrochemical reactions. The electrocatalytic activity (oxidation current density) of the catalysts for the methanol oxidation reaction is determined by cyclic voltammetry under the following conditions: CH_3OH 1 *M*, H_2SO_4 1.5 *M*, 60°C, and 5 mV s^{-1} (Fig. 1b). In order to compare the different samples, activities are given in milliamperes per unit mass of platinum at 0.55 V/SHE potential.

RESULTS

Radiolytic Reduction of Platinum in CO-Saturated Solution

CO is well known to spontaneously reduce platinum salts to molecular carbonyl clusters of the $[Pt_3(CO)_6]_n^{2-}$ series (15). We have shown that γ-irradiation can considerably accelerate the reaction (14). When CO is in excess, carbonyl clusters are synthesized with a dose-dependent nuclearity: the higher the dose, the lower the *n*. When the [CO] : [Pt] ratio decreases, a colloid is obtained.

Molecular carbonyl clusters $[Pt_3(CO)_6]_n^{2-}$ of the series have been observed with STM after the drying of a drop of solution deposited on a HOPG (highly oriented pyrolytic graphite) carbon surface. The deposit appears to be preferential at the steps (Fig. 2a) and atomic resolution can be seen on an isolated cluster (Fig. 2b). Both length and width (1.0 × 0.5 nm) are compatible with the known rod-shaped structure (15, 16).



(a) **(b)**

FIG. 1. Voltammograms recorded on platinized powder in (a) H_2SO_4 1*M*, 20°C electrolyte, sweep rate 50 mV s^{-1}; (b) CH_3OH 1 *M*, H_2SO_4 1 *M*, 60°C electrolyte, sweep rate 5 mV s^{-1}.

A solution of 2×10^{-3} *M* Pt^{II} in a CO-saturated 50% v/v water/2-propanol solvent ($[CO] \approx 5.10^{-3}$ *M*), has been irradiated with different doses. At low doses, brightly coloured carbonyl clusters (such as are described in Ref. 15) are obtained until roughly half of the platinum is reduced, while at higher doses they turn to colloidal platinum (a brown solution) when the reduction is complete (Fig. 3). Actually, this transition is progressive: molecular carbonyl clusters and colloidal platinum can coexist. As can be seen in Fig. 4, for constant platinum concentration, after complete reduction the cluster concentration increases with increasing CO concentration. Consequently, conditions can be adjusted so that the radiolytic reduction finally turns either towards carbonyl clusters or towards colloidal metal. When there is not initially enough CO to stabilize all of the reduced platinum ions as carbonyl clusters, the system evolves towards colloidal metal. In fact, whatever the initial CO : Pt^{II} ratio, in the early stages of the reduction CO is always in excess compared to the reduced platinum ions so that carbonyl clusters are always synthesized at the beginning of irradiation. Carbonyl clusters can be considered as precursors of this particular CO-stabilized colloidal platinum and, once the CO has reacted, the further-reduced platinum ions appear to react with the earlier synthesized clusters to give the colloidal metal. Let us note that in Fig. 4 two isosbestic points appear at 390 and 490 nm, which correspond to a quantitative conversion of molecular clusters to the colloid. These are only pseudo-isosbestic points, however, since the molecular clusters are not a unique species, but their 400-nm band is practically nuclearity-independent.

Such an interconversion between platinum–carbonyl cluster anions $[Pt_3(CO)_6]_n^{2-}$ and fine platinum particles has already been observed through laser excitation (17). It has been suggested that this process occurs through decarbonylation and rearrangement of the metal core: the $[Pt_3(CO)_6]^{2-}$ units are known to be labile.

The reduction yields have been found to be exceptionally high: values such as 4.4 μmol J^{-1} have been found at the beginning of the reduction (based on the optical absorption of the coloured clusters) and (though more difficult to estimate at this point) remain relatively high for the colloid. A recent study by Henglein *et al.* (18) on radiolytic platinum reduction also mentions high yields.

A TEM observation of our colloids shows a homogeneous dispersion of 1.0–2.0-nm particles (Fig. 5a). The mean size is much higher than the known high nuclearity (17, 19) molecular cluster sizes (in their narrow dimension) so the particles are probably metal aggregates, roughly spherically shaped. However, the size distribution suggests that particles with diameters lower than the microscope resolution are present (Fig. 5b).

A question arises as to whether the radiolytic product could also include high nuclearity carbonyl clusters such as those reported in the literature ($[Pt_{26}(CO)_{32}]^{-2}$ or $[Pt_{38}(CO)_{44}]^{-2}$ as brown solutions can be synthesized by thermal (19) or laser (17) degradation of $[Pt_3(CO)_6]_n^{2-}$ ($n = 4$) clusters). For this reason, colloids have been dried:

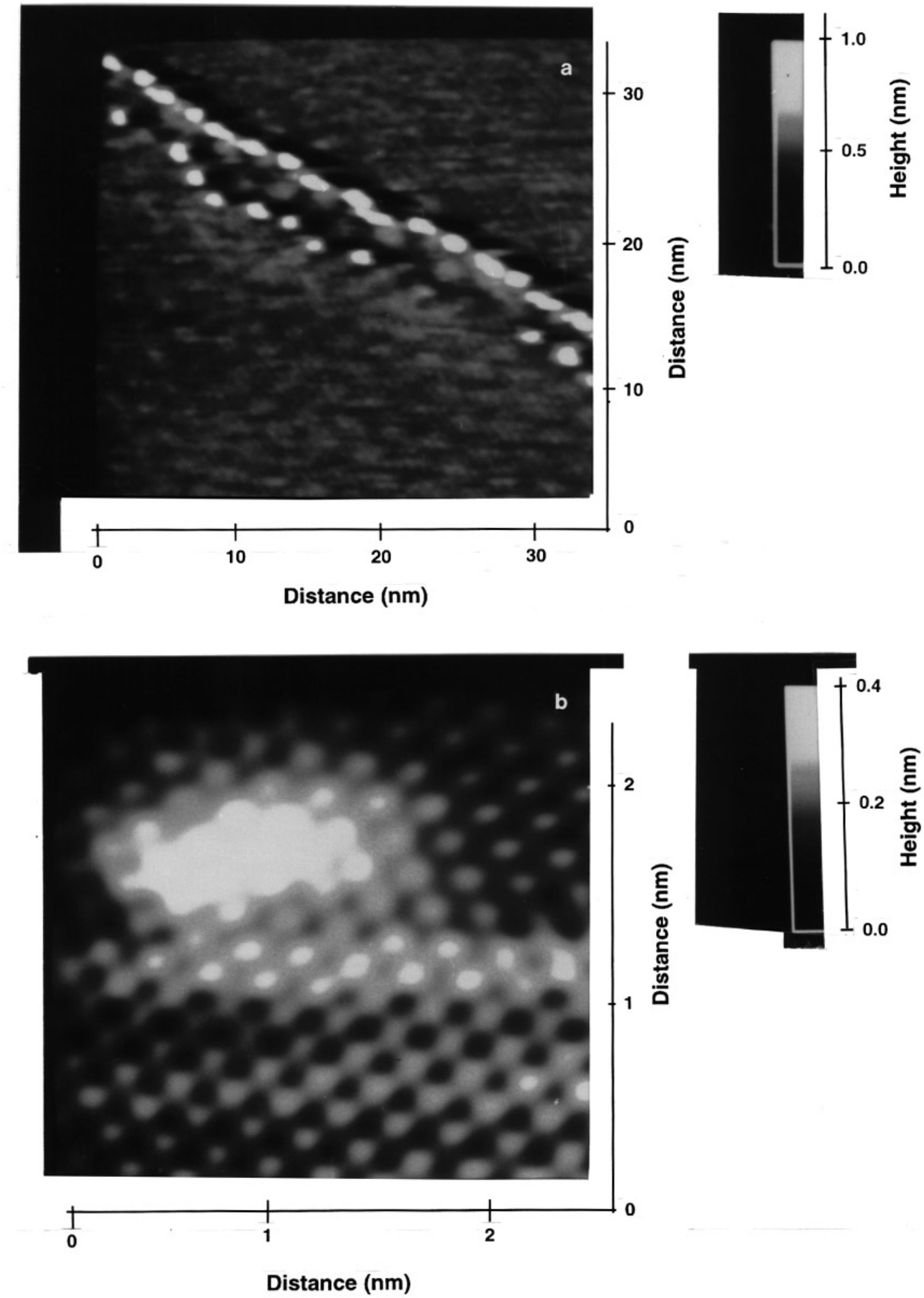


FIG. 2. STM micrographs of a cluster solution deposited on a HOPG graphite surface: (a) preferential deposit at a step, (b) isolated particle showing bidimensional character (length ≈ 1 nm, height ≈ 0.5 nm).

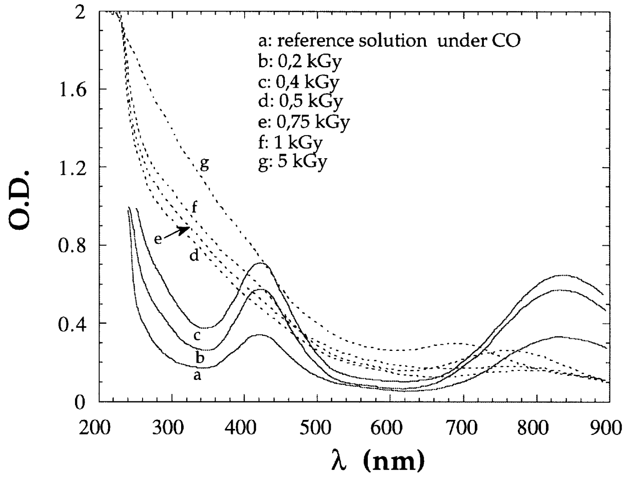


FIG. 3. UV-vis spectra of K_2PtCl_4 2.10^{-3} M in CO-saturated 50/50% v/v water/2-propanol solvent irradiated with increasing doses. Optical path is 2 mm.

only a small part is soluble in acetonitrile and displays an IR spectrum with the characteristic bands of linear and bridged CO (Fig. 6). These are twin bands which indicates that there are probably two kinds of species in the solution. One pair of bands at 1803 and 2058 cm^{-1} (for bridged and linear CO, respectively) can be attributed to $[Pt_{38}(CO)_{44}]^{-2}$, as Roth *et al.* (19) have reported. The other bands cannot be attributed from the literature and may be due to either molecular clusters or metal aggregates. Actually, the colloidal platinum seems to be a mixture containing a minor quantity of high nuclearity molecular carbonyl clusters (made up of a few tens of atoms) and a majority of metal aggregates (made up of a few hundreds of atoms).

Care must be taken to prevent the formation of clumps in the colloid. This problem can be overcome by increasing the CO concentration close to the limit of the cluster-formation range. Such clumps have been observed by TEM and have led to overestimated coulometric size measurements.

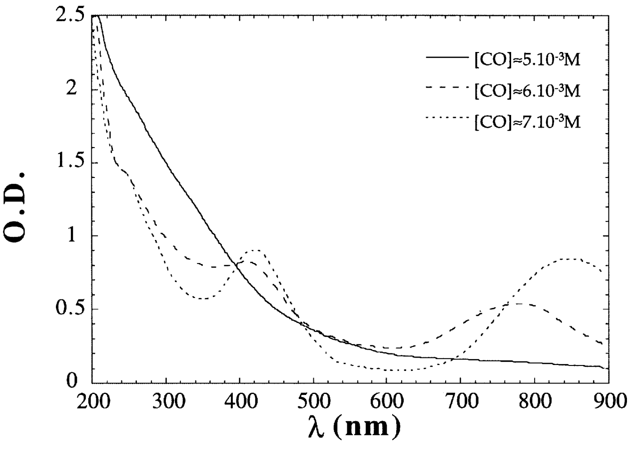


FIG. 4. UV-vis spectra of K_2PtCl_4 2.10^{-3} M in CO-saturated water/2-propanol mixtures. CO concentration is modified by solvent composition. Irradiation dose is 9 kGy, optical path 2 mm.

TABLE 1

Particle Size in nm Measured by H_{ads} Oxidation/Reduction Coulometry for Various Platinized Powders with Various Platinum Loadings

Loading (wt% Pt):	20	25	30	40	50	60
Vulcan (250 $m^2\,g^{-1}$)	3	2.5	2.8	2.6	—	—
Printex (975 $m^2\,g^{-1}$)	3	2.4	2.4	2.4	3	3
Ketjenblack (1000 $m^2\,g^{-1}$)	—	2.3	—	—	—	—
Black Pearls 2000 (1475 $m^2\,g^{-1}$)	—	2.2	—	—	—	—

Carbon-Supported Platinum Electrocatalysts

High platinum loadings (up to 60%)[2] have been obtained as reported in Table 1 and Fig. 7: the particle size (2–3 nm) and the mass electroactivity ($\approx$150 mA mg^{-1} Pt at +0.55 V/SHE under the conditions of Fig. 7) are roughly independent of the platinum loading and the specific area of the support. Coulometric measurements lead to sizes in good agreement with TEM observations (Fig. 5). This means that during the measurements almost all of the platinum surface atoms are electrochemically active in the film.

Thus carbon monoxide reveals itself to be very efficient in stabilizing small platinum particles. Although carbon monoxide is known to be one of the most important poisons of platinum catalyst, no poisoning effect is observed here. It is concluded that CO must have been partially displaced from the platinum surface during the thermal treatment.

Tests have been conducted on a complete H_2/O_2 PEMFC with our catalysts at both electrodes. Results with the catalysts not yet completely optimized are summarized in Table 2 and Fig. 8. However, the curves in Fig. 8 have been obtained after several operating cycles over a total of more than 200 hr. The catalysts remain very efficient at this stage, probably due to the strong interaction between the support and the CO-stabilized particles mentioned above. It is worth noting that the characteristics of the electrodes after a break of one night, for example, are immediately recovered on the following day. The mass activity clearly increases with the catalyst loading. The thinner the active layer, the better the use of the catalyst.

The electrocatalytic activities are very satisfactory. The higher the platinum loading, the higher the activity. This last point is very promising because, as we have seen, it is now possible to keep the size in the 2–3-nm range while increasing the platinum loading up to 40 or 60 wt%.

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[2] Such a high Pt/C ratio has never been obtained either for platinum colloids (polymer stabilized) deposited on carbon or for platinum salt solutions radiolytically reduced in the presence of carbon supports.

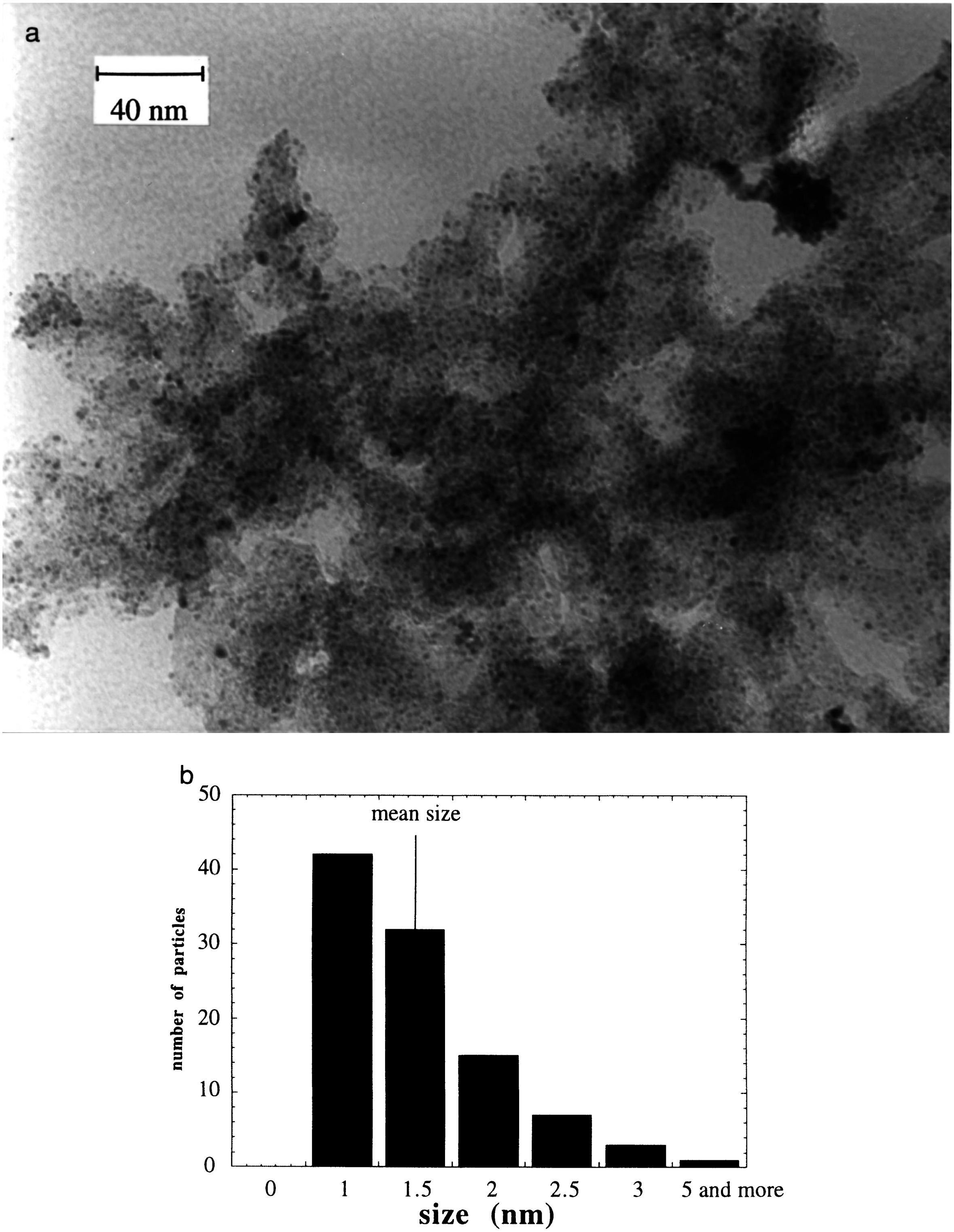

FIG. 5. (a) TEM micrograph and (b) size distribution of a Pt colloid stabilized by CO (2×10^{-3} *M*). A few clumps can be observed. Pt loading is 15 wt% on Printex powder.

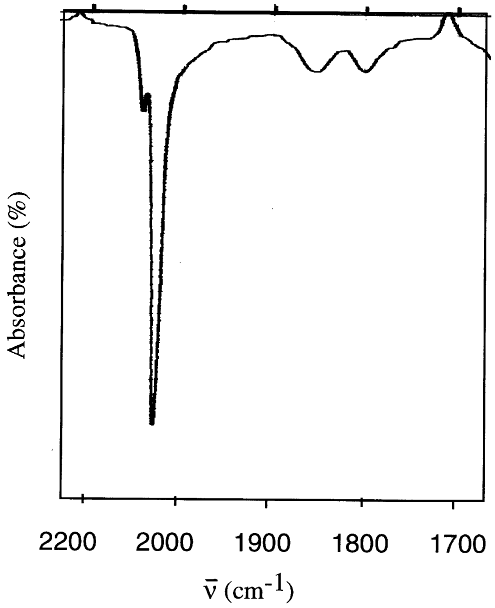

FIG. 6. IR spectrum of 2×10^{-3} *M* Pt/CO colloid in acetonitrile.

TABLE 2

Platinum Activities for O_2 Reduction in PEMFC Fuel Cell at 0.85 V (Considering That There Is No Polarization for H_2 Anode). Experimental Conditions: Nafion 117 Membrane, $p(H_2) = 3$ bar, $p(O_2) = 5$ bar at 80°C

Sample	Pt specific area (m^2 g^{-1})	Pt mass activity (A g^{-1})	Pt surface activity (μA cm^{-2})	Pt loading (mg cm^{-2})
Printex XE2 (9%)	80 (3.5 nm)	69	87	0.36
Printex XE2 (15%)	100 (3 nm)	182	182	0.44
Printex XE2 (25%)	100 (3 nm)	207	207	0.4
Vulcan XC72 (25%)	100 (3 nm)	227	227	0.55
Vulcan XC72 (20%)[a]	112 (2.5 nm)	289	258	0.45

[a] Commercial data.

CONCLUSION

The radiolytic process used in the presence of CO leads to very homogeneous platinum colloids made up of particles ca 2 nm in size. These colloids can be impregnated onto carbon supports at loadings as high as 40 to 60% in weight without a noticeable increase of the particle size. The deposits proved to be excellent electrocatalysts for fuel cells (methanol or hydrogen), and even higher performance results are expected from highly loaded electrodes. Electrochemical cell tests demonstrate the stability of the catalysts over periods longer than 2 weeks. Further investigation is needed of longer term performance. Among several tested carbon supports, Vulcan XC72 seems to be better than Printex XE2, probably due to the microporosity of the latter (reactants cannot reach the Pt sites located inside the micropores).

Further studies concerning the structure of the nanoparticles are in progress.

An important way to improve the catalyst for methanol electrooxidation is to overcome the anode overvoltage by combining platinum with some other metal(s). We have applied the radiolytic process described here to a series of Pt/Ru, Pt/Sn, and Pt/Ru/Sn salts. The results will be given in detail in a forthcoming paper.

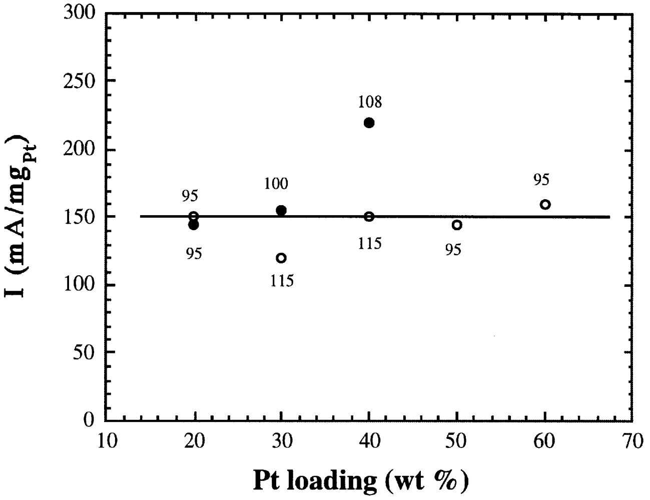

FIG. 7. Platinum mass activity (voltammetric measurements) at 0.55 V/SHE for methanol oxidation for CO-stabilized colloidal deposits on two carbon blacks with different catalyst loadings: (●) Vulcan XC72, (○) Printex XE 2. Experimental conditions: CH_3OH 1 *M*, H_2SO_4 1.5 *M*, 60°C, 5 mV s^{-1}. The data points refer to the specific areas (in m^2 g^{-1}) measured by coulometry, from which the apparent sizes are deduced.

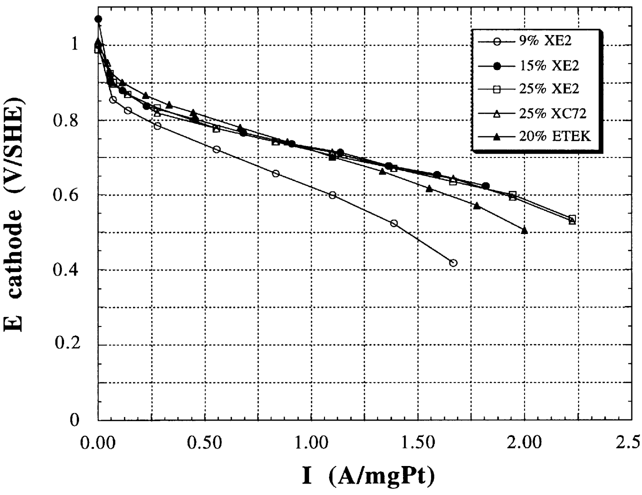

FIG. 8. Polarization curves of cathodes corresponding to Table 2 samples. Measurements were performed by the Sorapec Co.

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