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Review

Electrochemical CO stripping on nanosized Pt surfaces in acid media: A review on the issue of peak multiplicity

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ABSTRACT

This manuscript reviews the complex behavior of the electrochemical oxidation of adsorbed CO (CO stripping) on Pt nanoparticles in acid media. While on low-index Pt single crystals the so-called CO stripping generally exhibits a single, narrow, and well-defined oxidation peak, its oxidation on Pt nanoparticles may produce multiple peaks instead, whose origin is still not fully understood. The issue of peak multiplicity is reviewed based on published articles in the field of electrocatalysis and also on new experimental results. The aim of the present contribution is to highlight the extreme sensitivity of this reaction with respect the state of the surface, microstructure and discuss some other important related features, including the role played by the experimental protocol itself. The influence of the index of crystallografic planes exposed to the electrolyte, particle size, particle agglomeration, CO surface diffusion, adsorbed anions, catalyst support, among other factors on the CO electro-oxidation are presented and discussed. In turn, the ideas presented herein would help scientists to avoid misinterpretation of the experimental results, better design experimental procedures and thus advance in the required knowledge for tuning the Pt nanoparticles to fulfill the requirements for specific applications, such as fuel cell catalysts resistant to CO poisoning.

1. Introduction

The electrochemical oxidation of carbon monoxide (CO) pre-adsorbed on Pt electrodes, the so-called “CO stripping”, is one of the most studied electrochemical reactions. Despite the importance of this reaction for gas sensors and surface science studies, the oxidation of CO is of paramount importance for the development of low-temperature Fuel Cells [1–4]. In these systems, such as H_2-fed Polymer Electrolyte Membrane Fuel Cells (PEMFC), even trace amounts of CO as low as 10 ppm may drastically reduce the ability of the Pt-based electrocatalyst to efficiently oxidize H_2. Due to the intrinsic mechanism of the reaction and the rather high enthalpy of adsorption on Pt (values up to 140 kJ mol^{-1} at low coverages were measured on Pt (111) single crystals [5]), in Pt electrodes the oxidation of CO to CO_2 only starts at a significant rate at rather high potentials (above ≈ 0.6 V vs. reversible hydrogen electrode), making CO a catalytic poison for hydrogen/oxygen PEMFCs. Thus, the long-term operation of such Fuel Cells depends critically on the understanding of the fundamental parameters that control the oxidation of CO in real Pt-based electrocatalysts. Other types of low temperature Fuel Cells based on the oxidation of organic fuels such as formic acid, methanol, ethanol also depend on the kinetics of CO oxidation, since it has been found as an adsorbed intermediate of such reactions [6,7].

As it will become clear in this manuscript, in contrast to the narrow single peak usually found using low Miller index well-defined Pt single crystals electrodes, such as Pt (111), Pt (110), and Pt (100), CO stripping on Pt nanoparticles usually shows multiple peaks in addition to the well-known pre–ignition peak also present on single crystal and smooth Pt electrodes. In such materials, especially carbon-supported Pt nanoparticles (the actual electrocatalysts used in Fuel Cells), the origin of such peak multiplicity is still an open question.

A survey of the published works in the literature revealed several explanations for the occurrence of multiple peaks in the CO stripping voltammetry, such as the effect of crystallography of surface planes [8], surface defects (edges and terraces) which are particle size dependent [9], particle size distribution [10], particle agglomeration [11], [12–14], and CO surface diffusion on the facets of a nanoparticle [15,16], among others.

The aim of the present paper is to provide an overview of the major ideas regarding the origin of the peak multiplicity on Pt nanoparticles

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(both supported and unsupported) in acidic media and discusses some important related features, including the role played by the experimental protocol itself. We believe this manuscript might be helpful to support scientists to conduct more in-deep interpretation on their results concerning this complex reaction and highlight its extreme surface-sensitivity. It is clear that a comprehensive knowledge of the reaction is needed for the design of new electrocatalytic materials for Fuel Cells applications. However, only by understanding the fundamental aspects of the CO oxidation on real electrocatalysts, it will be possible to improve the performance (particularly, the CO tolerance) of these nanomaterials and contribute to scale-up the use of Fuel Cells.

1.1. Fundamental background

From the mechanistic point-of-view, the electrochemical oxidation of CO is believed to occur by adsorbed CO and oxygen-containing molecules (generally ascribed to be OH). A simplified version of the mechanism of the reaction is given according to the reactions below:

$$H_2O + Pt \rightleftarrows Pt - OH_{ads} + H^+ + e^- \tag{1}$$

$$Pt - CO_{ads} + Pt - OH_{ads} \rightarrow CO_2 + H^+ + e^- + 2Pt \tag{2}$$

In the first step (1) oxygen-containing species (denoted here as OH_{ads}) are formed through the oxidation of water on free Pt sites; the conversion of CO to CO_2 is accomplished as described by Reaction (2): adsorbed CO molecules interact with adsorbed OH_{ads} molecules yielding CO_2, H^+, electron, and two free Pt sites. The overall process involves 2 Faradays per mol of reaction. Since Reaction (2) is a surface reaction between two adsorbed molecules, it belongs to the so-called Langmuir-Hinshelwood type of reaction. Therefore, the mobility of the adsorbed species at the surface as well as the active sites for the reaction are of extreme importance for the overall understanding of the process [10,13,15] as it will be later discussed in the text. As we shall see, these features determine the strong dependence of the reaction with structural characteristics of the electrode. Although Reactions (1) and (2) provide a good overview of the mechanism for CO oxidation, a more complex mechanism (i.e., involving an adsorbed intermediate such as $COOH_{ad}$) has also been proposed, as reviewed in ref. [1].

Fundamental electrochemical studies regarding the oxidation of CO can be carried out under three distinct situations: i) oxidation of a monolayer of CO adsorbed on the electrode (CO stripping) and, ii) continuous (bulk) CO oxidation and iii) CO-contaminated H_2 gas. Only the first situation (CO stripping) will be considered here since our main focus is to discuss the issue of the peak multiplicity observed in the oxidation of a pure adsorbed CO layer in a CO-free solution. In a typical electrochemical experiment of CO stripping in aqueous solution, CO is introduced in the electrochemical cell and allowed to adsorb on Pt electrode surface at a controlled potential where no oxidation occurs, i.e., close to the thermodynamic potential. Next, dissolved CO molecules are removed from the solution by purging the system with the aid of some inert gas, usually nitrogen or argon. Then, a potential sweep (or a potential step for chronoamperometric experiments) is initiated and the behavior of the current as function of potential (or the current as function of time) is recorded. Fig. 1 illustrates a typical CO stripping experiment on a carbon supported Pt electrocatalysts (Pt/C) recorded with cyclic voltammetry (Fig. 1a) and, on a separate experiment, with chronoamperometry at a constant potential (Fig. 1b).

As depicted in Fig. 1a, CO oxidation currents above the base voltammogram (the subsequent scan after the CO stripping) are observed only above 0.6 V, defining a single peak centered at 0.79 V (RHE, reversible hydrogen electrode in the same solution). If CO stripping is carried out at a constant potential (Fig. 1b) it is observed a current decay at short times followed by a broad peak centered at about 12 s, with levels off at about 50 s indicating the end of the reaction. Peak-shaped transients are generally expected in process involving nucleation and growth of reacting centers. For the specific case of the oxidation of adsorbed CO, this is a consequence of the Langmuir-Hinshelwood mechanism, where the reaction rate (and therefore, the current) is expected to be proportional to the product of the surface coverage of CO_{ads} and OH_{ads}. The reader is referred to ref. [1] for further details on the mechanism of the reaction. However, in contrast to the behavior shown in Fig. 1, where a well-defined single peak develops in the positive-going sweep, CO stripping on Pt-based electrocatalysts can also depict multiple peaks in both potentiodynamic and potentiostatic experiments [10,11,17].

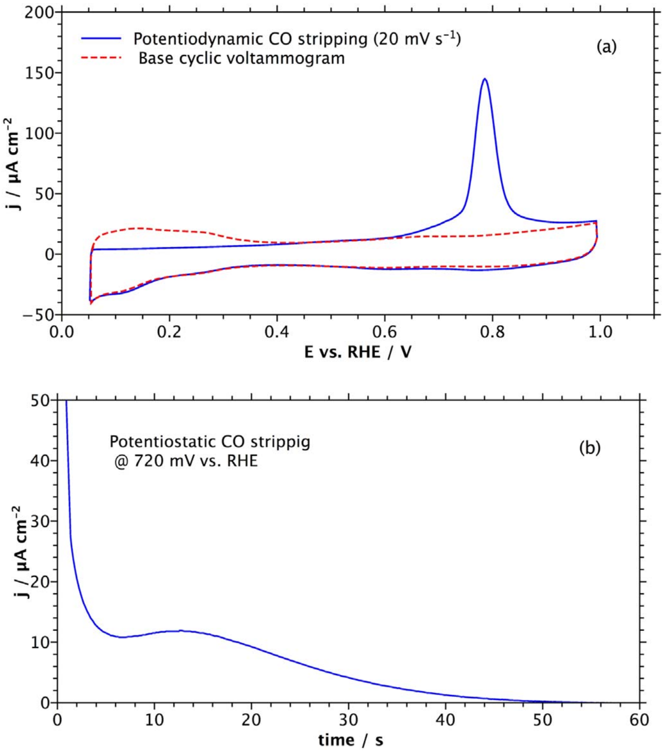

Fig. 1. Electrochemical CO stripping obtained for a carbon-supported Pt nanoparticles (Pt/C, average particle size of 2.8 nm determined by Transmission Electron Mycroscopy, see ref. [37]) in 0.1 mol L^{-1} $HClO_4$; $T = 25\,°C$. a) Potentiodynamic CO oxidation at 20 mV s^{-1} (line) and subsequent cycle (dashed); b) Potentiostatic CO stripping at 0.72 V (RHE).

Herein, we focus on the origin of the peak multiplicity generally observed on carbon-supported Pt electrodes and other high-surface area electrocatalysts, such as Pt blacks and platinum electrodeposits. Although the discussion concerning the several effects that can lead to peak multiplicity will be made separately, it has to be clearly stated that all of them may be somehow interconnected and thus a careful analysis is required to understand the factors governing the peak multiplicity for each particular case.

2. The effect of the surface crystallographic planes and surface defects

Innumerous published papers have shown that CO electro-oxidation belongs to the family of the so-called structure-sensitive reactions (see, for instance refs [5,18] for a detailed review). Fig. 2 best illustrates this behavior, where the CO stripping voltammetry was carried out at two Pt single crystals electrodes presenting distinct crystallographic planes, namely Pt (111) and Pt (100) [19].

As it can be clearly observed in Fig. 2, two important features are highlighted: i) only a single CO stripping peak develops on the low index Pt(*hkl*) surfaces, and ii) the potential at which the peak appears depends on the surface crystallographic plane. It is well known that the chemical activity of a metallic surface is strongly dependent to the surface crystallography. For instance, the (100) surface crystalline

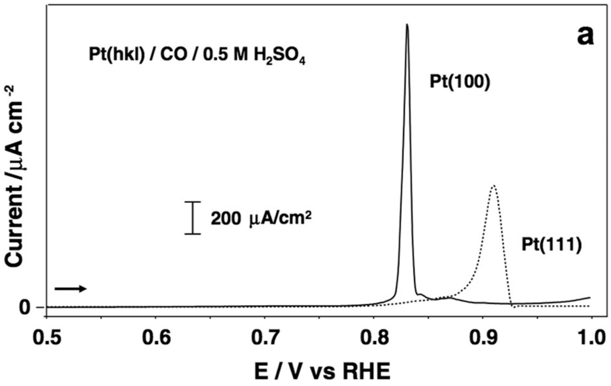

Fig. 2. CO stripping voltammetry on low-index Pt single crystals. Experimental details: scan rate = 50 mV s^{-1}; Electrolyte: 0.5 mol L^{-1} H_2SO_4. Figure from Inkaew et al. [19] [Electroanal. Chem, 614 (2008) 93–100]. Reproduced with permission.

plane of Pt has atomic arrangement of 4-fold symmetry; the Pt(111) surface plane has 6-fold symmetry; and the Pt(110) surface plane has 2-fold symmetry. Moreover, depending on the symmetry of the crystalline plane at top surface, the exposition of the sub-surface atomic layer will also vary which will also influence the activity of the metal surface. For more detailed information on the surface structure of clean metals, the interested reader may consult the review paper of Markovic and Ross Jr. [5].

Among the low Miller index Pt(111), Pt(100), and Pt(110), the oxidation of CO on the Pt(111) exhibits the highest overpotential for the oxidation of the adsorbed CO molecules, while Pt(100) presents the lowest one. The reason for such behavior is generally ascribed to the distinct behavior of the surfaces planes for the formation of OH-like species [18] which is crucial for the reaction.

Although the influence of the crystallographic planes is evident it should be recalled that the structure of the surface is not only related to the crystalline plane on the top layer but also to the presence of crystalline surface defects such as terraces, steps, kinks, surface vacancies, etc. Some of these defects have large equilibrium concentration in any real material and might influence the activity of the catalyst [20]. Specifically on the CO oxidation reaction, much research has been conducted aiming to depict the play rolled by steps and terraces in this reaction. The same line of arguments abovementioned for different surface crystalline planes was used to explain the activity of stepped surfaces for CO oxidation. Lebedeva et al. [21] showed by means of potential step measurements conducted on a series of Pt[*n* (111) × (111)] stepped surfaces (where *n* is the number of rows of Pt atoms at the terrace) that the presence of steps has a significant effect on the rate of CO oxidation. In their experiment, only a single peak was observed in the current-time response. The (apparent) rate constant for the reaction was found to be proportional to the step fraction (1/n) of the surface. In another work, Lebedeva et al. [22] showed that the position of the peak for CO stripping on Pt(111) electrodes was influenced by the preparation procedure of the single crystal electrode. It was shown that the cooling atmosphere of flame-annealed electrodes (H_2/Ar versus air), the air-annealed surface exhibited a less positive potential by c.a. ~80 mV for CO oxidation with respect to that of H_2/Ar Pt(111) surfaces, attributed to a higher amount of defects in the former. Similar findings on the influence of the cooling atmosphere on the "quality" of single crystal surfaces was reported by van der Vliet et al. [23] for Pt(100) electrodes, altering significantly the CO stripping profile in alkaline media. Earlier work of Vielstich and co-workers found that an "disturbed" Pt(111) electrode (i.e., a single crystal presenting high amount of surface defects) was able to oxidize CO at more negative potentials (low overpotential), than that a "undisturbed" (almost defect-"free") Pt (111) single crystal [24]. All cited studies highlight the effect of the structure (e.g., the presence of surface defects) on the CO stripping voltammetry.

Despite the fact that only a single peak behavior was observed in these works for both potentiodynamic and potentiostatic experiments, single crystals may also present multiple peaks during the oxidation of an adsorbed monolayer of CO. Feliu and co-workers [25] studied the role of steps in a Pt[(n-1)(100) × (110)] stepped surfaces i.e., (100) terraces with (110) step sites. They found that for surfaces presenting short terraces, such as Pt (210) and Pt(310), a shoulder at more positive potentials can be observed in the voltammograms in addition to the main peak (surprisingly only one peak was observed in the corresponding chronomperometric experiments); however, potentiostatic current transients during CO oxidation recorded for Pt(510) single crystal electrodes clearly showed two peaks, ascribed to the reaction taking place at two distinct type of sites, i.e., sites with distinct OH adsorption isotherms.

The aim of this review is not to provide a deep description of the oxidation of CO in single crystals; instead, we focus on the results obtained when using real fuel cell electrocatalysts, i.e., Pt nanoparticles. Nevertheless, from the discussion above, it is clear though that the kind and amount of surface (hkl) planes exposed to the electrolyte play a key role in the electrochemical oxidation of CO. Therefore, taking into account that the surface of a polycrystalline material consists of randomly distributed (*hkl*) planes, the behavior of polycrystals during the oxidation of adsorbed CO was thought to be proportional to the amount of planes exposed. In fact, polycrystalline Pt electrodes can yield single or multiple peaks in CO stripping voltammetry. Already in the 80s, Santos et al. [26] found that both potentiodynamic and potentiostatic CO stripping at polycrystalline Pt in 0.05 mol L^{-1} $HClO_4$ revealed 4 processes, all of them also observed on line in the mass signal (charge to mass ratio of 44) via the Differential Electrochemical Mass Spectrometry (DEMS) technique, as shown in Fig. 3. As we shall discuss later, the use of a non-adsorbing electrolyte such as perchloric acid is also of importance when dealing with the issue of peak multiplicity in the CO stripping experiments.

Increasing the level of complexity from platinum single crystals, stepped surfaces, and polycrystalline surfaces to nanoparticles, several studies have shown peak multiplicity in CO stripping. Solla–Gullón et al. [8] prepared four samples of unsupported Pt nanoparticles with different shapes (semi-spherical, cubic and tetrahedral-hexagonal – presenting distinct relative amount of low index crystallographic planes exposed to the electrolyte) and studied their physical and electrochemical properties. They found that even for similar (average) particle sizes, CO stripping voltammetries exhibited multiple peaks, in which the current profile and peak positions varied differently from one sample to another, as reproduced in Fig. 4. Authors explained the behavior of the peak multiplicity in terms of the number (quantity) and nature (crystallography) of the surface sites. However, it should be recalled that even for nanoparticles with similar average particle sizes, the particle size distribution has to be taken into account, given that the surface planes exposed to the electrolyte may be related to the size of the particles (smaller particles tend to present more closed packed surface planes, as discussed in ref. [27]).

3. Size effects

3.1. Particle-size effects

The effect of the size of the particles in catalysis and electrocatalysis has been extensively investigated over the years. Keeping in mind the mechanism for the oxidation of CO – where the presence of oxygen-containing species is crucial – it is interesting to note that according to experimental results and some theoretical calculations, a decrease in the particle size increases the affinity for oxygen atoms. Therefore, a quick view of this feature leads us to conclude that smaller particles would be more reactive for CO oxidation than larger ones. Therefore, there is an almost general trend in scientific community for trying to

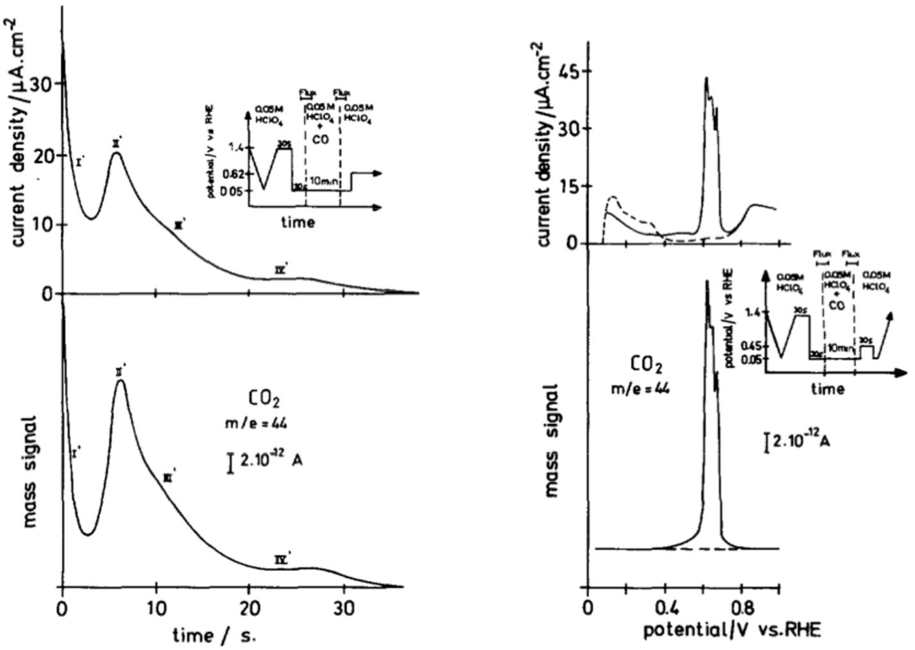

Fig. 3. CO stripping at polycrystalline Pt electrodes with the simultaneous detection of the mass signal (charge-to-mass ratio 44) by DEMS technique. Left: potentiostatic pulse to 620 mV (RHE); Right: Potentiodynamic sweep at 10 mV s^{-1}. Experimental details: Electrolyte: 0.05 mol L^{-1} HClO$_4$. Figure from Santos et al. [26] [*J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *227*, 199–211]. Reproduced with permission.

synthesize nanoparticles as small as possible in order to increase the surface area of the catalyst, decrease the mass of Pt and, consequently, the cost of the catalyst, which is a key issue for technological applications such as fuel cells. However, the reduction in nanoparticle size not necessarily lead to an optimal performance of the electrocatalyst, as the electrocatalytic activity not always increases linearly with the surface area of the nanoparticle [28]. In fact, as it will be discussed in the following, some experimental results regarding CO oxidation on particles with different sizes have shown that CO oxidation starts at lower potentials at larger particles than at smaller ones (in contrast to the theoretical findings abovementioned). Therefore, the discussion on the effect of the particle size in the electrochemical CO stripping will be done in sub-sections, as follows.

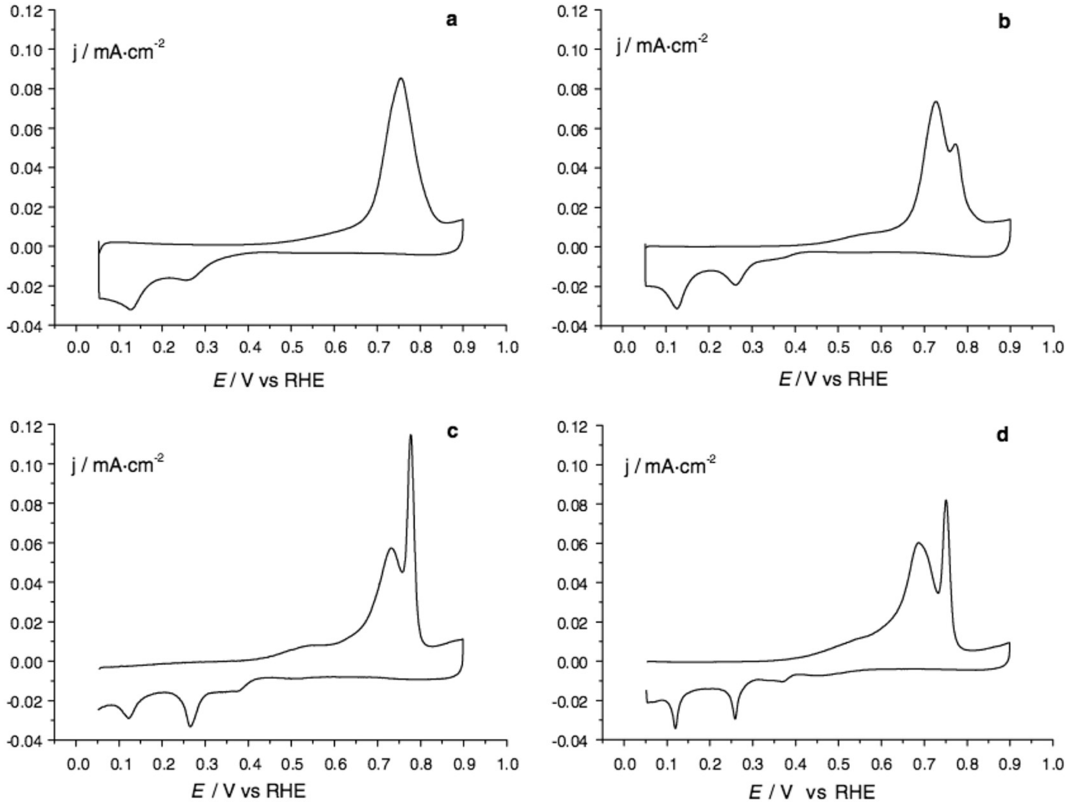

Fig. 4. CO stripping at unsupported Pt nanoparticles with different shapes (that resulted in distinct nature and amounts of crystallographic planes exposed to the electrolyte). Conditions: 0.5 mol L^{-1} H$_2$SO$_4$, 20 mV s^{-1}.Particle sizes a) 4.5 ± 0.8 nm, b) 4.0 ± 0.6 nm; c) 9 ± 3 nm; d) 9.7 ± 1.6 nm. Results from Solla-Gullón et al. [8] [*Electrochem. commun.* **2006**, *8*, 189–194]. For the corresponding blank CV, the reader is referred to the original paper. Reproduced with permission.

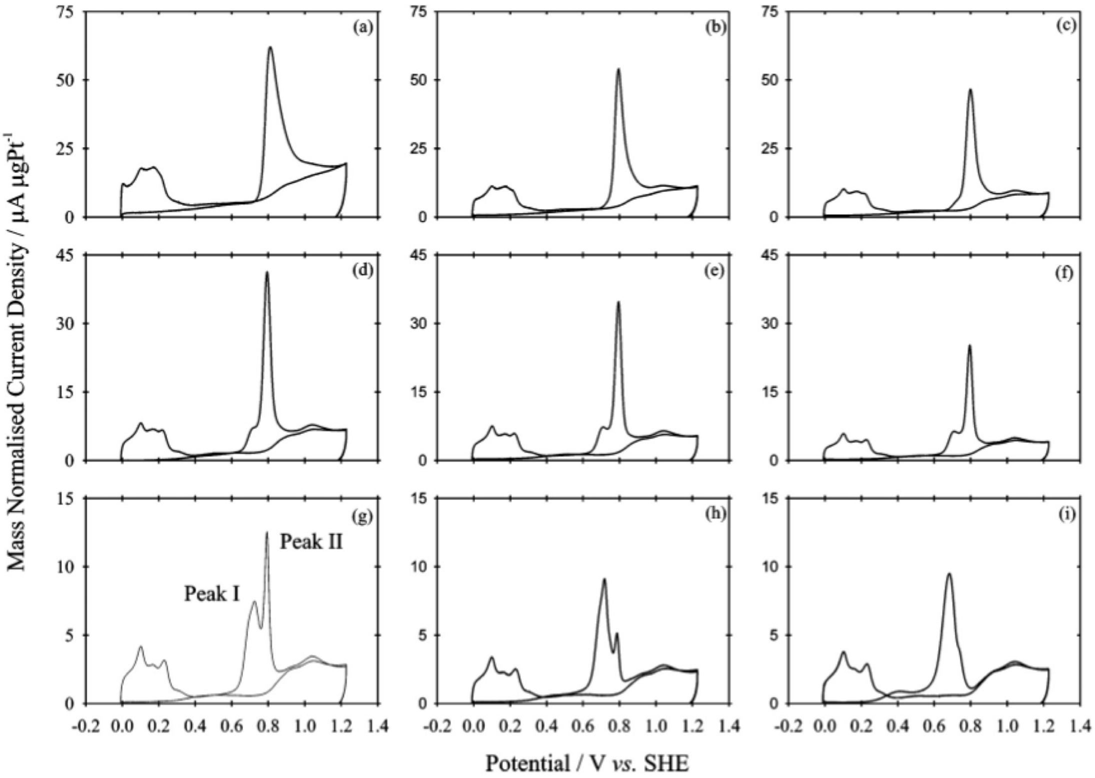

Fig. 5. CO stripping voltammetries obtained for glassy carbon-supported Pt electrocatalysts with distinct Pt to carbon weight percent: a) 10, b) 20, c) 30, d) 40, e) 50, f) 60, g) 70, h) 78 wt % Pt and of (i) Pt black. Potential sweep of 10 mV s^{-1} in 0.5 mol L^{-1} H_2SO_4. Currents normalized to the mass of Pt. The average crystal size (determined by X-ray diffraction) for the 10 to 78% wt Pt/C ranged from 1 to 6.5 nm. From Guerin et al. [9]. Reprinted with permission from Journal of Combinatorial Chemistry. Copyright (2017) American Chemical Society.

3.1.1. *Particle size effects I: surface facets as function of particle size*

Guerin et al. [9] prepared several catalysts comprised of Pt nanoparticles supported on glassy carbon (GC), where the Pt content was systematic changed from 10 to 78 wt%. CO stripping voltammetry carried out at 10 mV s^{-1} in 0.1 mol L^{-1} H_2SO_4 (Fig. 5) showed only a single peak at 0.79 V (SHE) for 10, 20, and 30 wt% Pt, and two well-–separated peaks for catalysts containing more than 30 wt% of Pt where, in addition to the peak at 0.79 V, a lower potential peak centered at 0.69 V was observed. In addition, they found that increasing the content of Pt, which increased the average particle size (see the caption of Fig. 5 for details), the lower potential peak at 0.69 V increases in intensity at the expenses of the high potential peak (at 0.79 V). They also showed CO stripping voltammograms on (unsupported) Pt black catalysts which presented the lowest overpotential, with the main peak at 0.69 V while the high potential peak (Ep = 0.79 V) appeared only as a shoulder in the current–potential profile. Then, based on the work of Kinoshita related to the oxygen reduction reaction (who showed a significant decrease in the number of edge and corner sites as the fraction of terrace domains increases with particle size), the authors interpreted their results in terms of the oxidation of CO taking place on terrace sites (expected to be predominant at larger nanoparticles) being responsible for the low potential peak, while the high potential peak was due to the reaction occurring on or near edge and corner sites, present preferentially at smaller nanoparticles. Maillard et al. [10] also reported a positive shift of CO stripping peak as the size of Pt nanoparticles decrease, with more pronounced effect between 1 and 4 nm. These results were explained suggesting a limited mobility of CO_{ads} for small nanoparticles (up to 2 nm). In their work, the diffusion coefficient of CO_{ad} onto the Pt surface was found to be strongly dependent to the particle size. According to the authors, above a particle size of 3 nm, a transition from a slow to fast diffusivity may take place. The play rolled by surface diffusion on peak multiplicity in CO stripping will be detailed in a further section, but the work of Maillard et al. [10] is a very interesting example on the interdependence of the features governing peak multiplicity in CO stripping.

Electronic effects that also change with particle size were not taken into account in the abovementioned works. More important, the effect of agglomeration of the particles with the increase of the metal loading was also not considered. As it will be discussed latter in this paper, agglomeration effects play a pivotal role in the CO stripping voltammetry.

3.1.2. *Particle size effects II: the effect of the size distribution*

Maillard et al. carried out a series of studies concerning the influence of the size of carbon–supported Pt nanoparticles on CO oxidation [10,29,30]. One of their results is reproduced in Fig. 6 (ref. [6]). They concluded that the peak splitting observed in CO stripping voltammetry on carbon–supported Pt nanoparticles occurs due to CO oxidation on nanoparticles with different sizes and not to differences in their terraces and edges, as proposed by Guerin et al. [9]. It has also been proposed that CO stripping voltammetry could be used as a probing technique for the particle size distribution of the catalyst, being described as a fingerprint of this feature. Furthermore, according to the authors, the reaction occurring at larger particles and at particle agglomerates yield the low overpotential peak, while individual nanoparticles lead to higher overpotential peaks [29]. In another interesting work, by using in situ FTIR (Fourier Transform Infrared Spectroscopy) and double-potential step measurements they showed that CO could be oxidized selectively from large to small nanoparticles, highlighting their previous findings that peak multiplicity results from the oxidation of CO on particles presenting distinct sizes [31].

Further evidence on the correlation between the several peaks observed in CO stripping with the particle size was provided by using the DEMS technique. Behm and coworkers prepared model Pt catalysts supported on glassy carbon via colloidal lithography and studied the CO stripping voltammetry coupled with a DEMS apparatus [32]. The

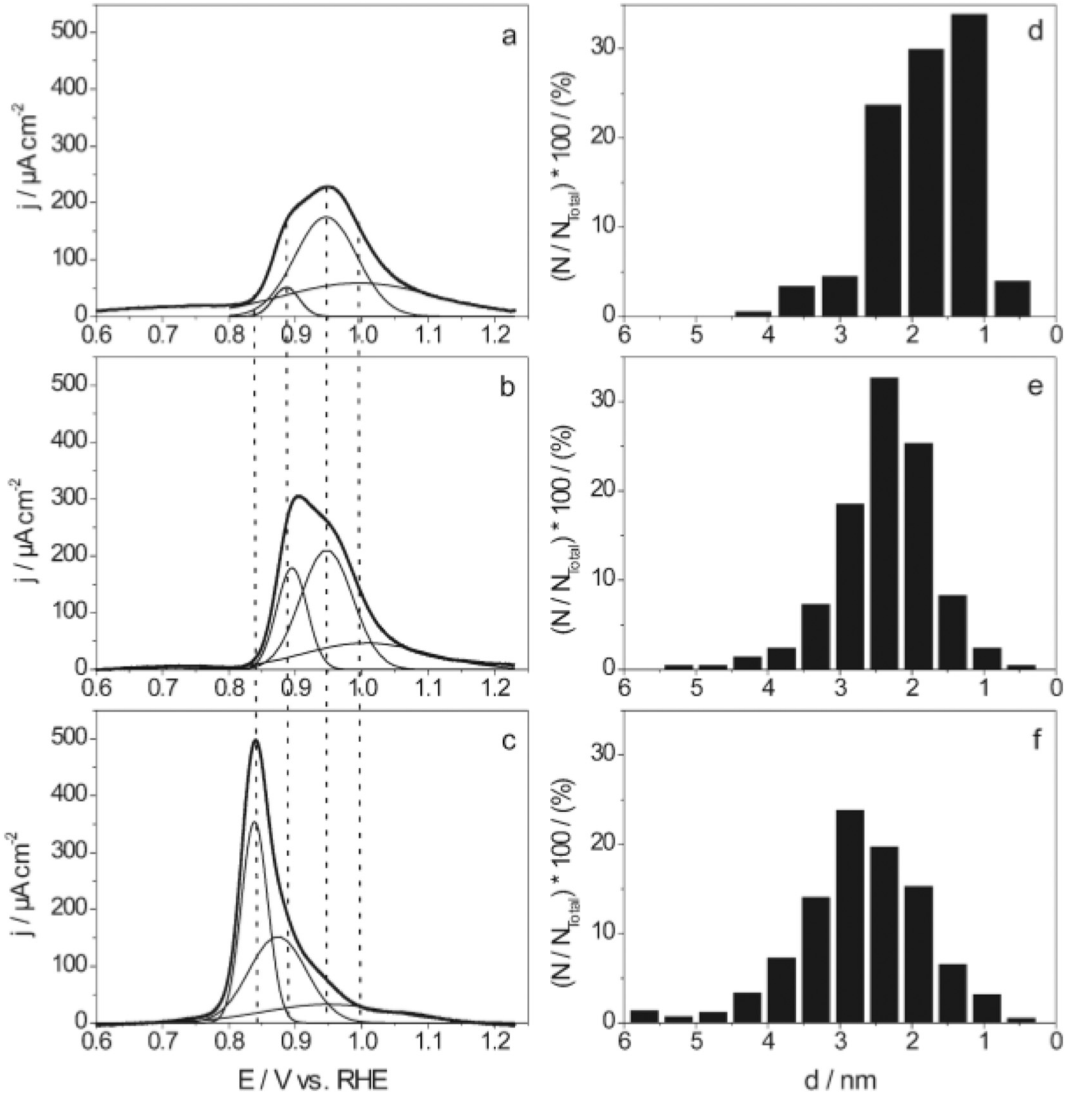

Fig. 6. CO stripping voltammetry carried out in glassy carbon supported platinum nanoparticles (Pt/C) with distinct particle sizes and the corresponding particle size distributions. (a, d) Mean particle diameter = 1.9 ± 0.7 nm, Pt loading 1.8 µg cm^{-2}; (b, e) Mean particle diameter = 2.4 ± 0.7 nm, Pt loading 3.6 µg cm^{-2}; (c, f) Mean particle diameter = 3.1 ± 1.2 nm, Pt loading 5.4 µg cm^{-2}. Electrolyte: 0.1 mol L^{-1} H_2SO_4; sweep rate of 100 mV s^{-1}. Reproduced from ref. [10] with permission from the Royal Society of Chemistry.

synthesis was designed to fabricate Pt nanodisks of 100–140 nm and, as a part of the electrochemical characterization of the electrodes, CO stripping experiments were conducted, which were reproduced in Fig. 7. Interestingly, when the preparation method yielded the formation of small (~5 nm) particles in addition to the desired Pt nanodisks (of about 100–140 nm), a high potential peak (at ~0.75 V, versus RHE in 0.5 mol L^{-1} H_2SO_4, see caption for details) was developed in the CO stripping voltammetry in addition to the main (low potential) oxidation peak, at ~0.7 V. These voltammetric features were also clearly visible in the mass signal (mass to the charge ratio, $m/z = 44$), shown in Fig.7b. In contrast, when they modified the synthesis procedure in order to avoid the formation of such small nanoparticles, that is, forming solely the Pt nanodisks (samples named HCL-20 and HCL-10 in Fig. 7) only a single peak was observed at ~0.7 V, which is less positive than those ascribed to the oxidation of CO on small Pt nanoparticles. Therefore, they concluded that the high potential peak could be used for the unambiguous detection of small Pt nanoparticles on such surfaces.

As a final word regarding "particle-size effects", we would like to stress that the definition of "particle size effect" could be somewhat arbitrary, since it may comprise several related phenomena; recall that particles with the same "average size" could show different amounts of surface facets and defects, distinct electronic structure (i.e., 5d band filling), diverse particle size distribution, etc., all of them contributing to the CO stripping features in electrochemical experiments for which the separation of the role of each effect may not be straightforward.

3.2. The effect of the size of the (hkl) surface plane

Coutanceau and coworkers have also investigated the issue of peak multiplicity on CO stripping experiments and obtained very interesting insights on the origin of such behavior [33–35]. In one of their work [34] by using different preparation procedures, unsupported Pt nanoparticles with distinct morphologies were obtained, yielding preferentially oriented nanoparticles. The amount of (100) and (111) surface domains were also estimated by the irreversible adsorption of germanium and bismuth method developed by Feliu's group [36]. Similar to the findings of Solla-Gullon discussed in Section 2, CO stripping results exhibited multiple peaks, as shown in Fig. 8a. The four distinct oxidation processes were ascribed to the oxidation of CO on (111) surface domains (peak 1a), low-coordinated surface sites (peak 1b), while peak 2 was assigned to the CO oxidation on (100) domains. Thus, in this regard, their work could have been described in Section 2, where the effect of the surface planes were discussed. However, in a latter

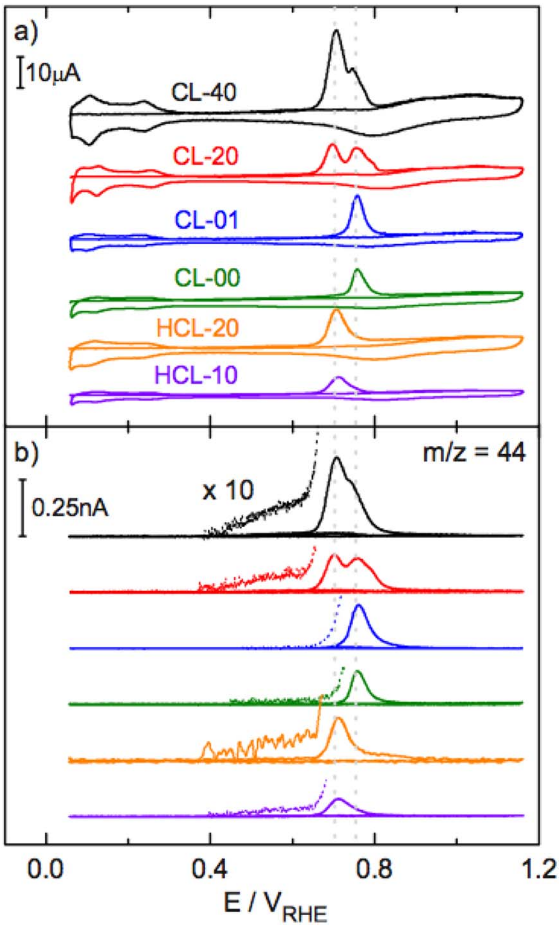

Fig. 7. CO stripping and subsequent cyclic voltammetries on nanostructured Pt/GC model electrodes (disk-like morphology of about 100–140 nm) obtained in 0.5 mol L^{-1} sulfuric acid; scan rate 10 mV s^{-1}. Faradaic currents as measured and b) mass spectrometric currents at $m/z = 44$. Figure from Behm et al. [32]. See text for details. Reprinted with permission from J. Electrochem. Soc., 155 (10), K171 (2008). Copyright 2008, The Electrochemical Society.

work, further evidences on the role played not only by the relative amount but the size of such domains were obtained. By using a rather simple (and elegant) strategy, the surface properties of those preferentially oriented unsupported Pt particles were altered by cycling the electrode potential up to 1.2 V (RHE), promoting a surface reconstruction due to the continuous formation/reduction of Pt oxides/hydroxides. The characteristic cyclic voltammetric features of the Pt particles in 0.5 mol L^{-1} H_2SO_4 as function of the number of "reconstruction voltammetric cycles" showed a change in the nature and relative amount of (100) and (111) surface planes. CO stripping voltammetries carried out after distinct states of such surface reconstruction are shown in Fig. 8b for three samples of preferentially-oriented (unsupported) Pt nanoparticles. Notice that after progressive surface reconstruction, there is a change in the relative intensity of the peaks. As an example, for the pristine sample "Pt-nc" (chart *a* in Fig. 8b) presenting 38% of (100) and 16% of (111) surface sites, peak II (at ~0.76 V, ascribed to (100) surface domains) is higher than peak I (assigned to (111) surface planes and low coordination sites); in contrast, when the electrode was subjected to 12 reconstruction voltammetric cycles in a CO-free electrolyte, the CO stripping curve is drastic altered, being peak I the most intense, whereas peak II now appears only as a small peak. Moreover, they observed that both peaks are shifted towards more positive potentials as the long-range order terraces are disrupted (i.e., become shorter) due to surface reconstruction, highlighting an effect of the size of the (hkl) surface domains.

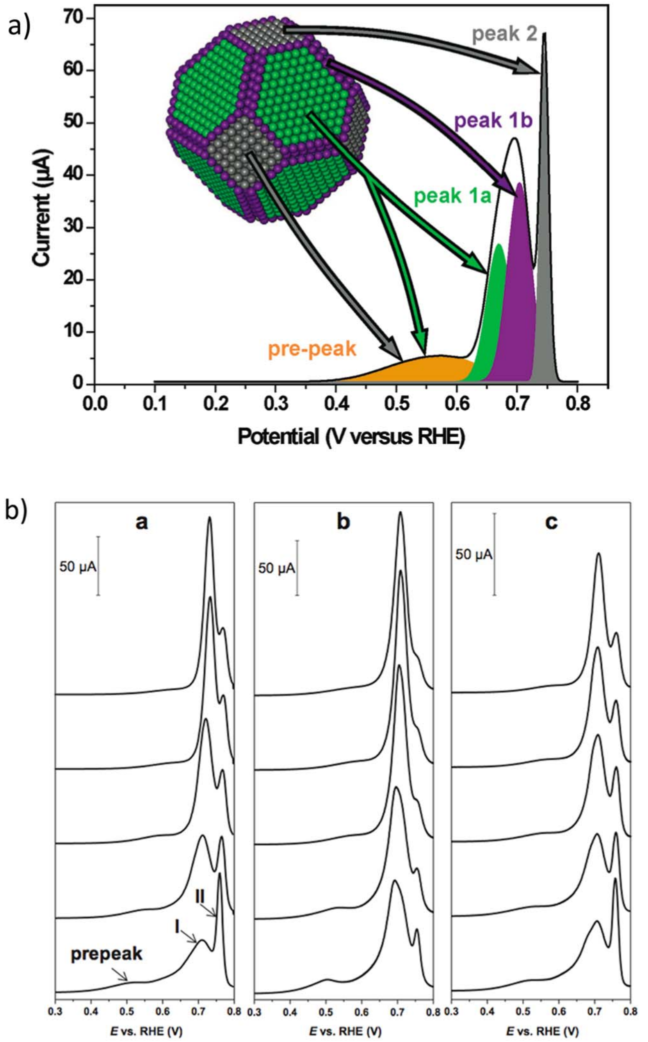

Fig. 8. (a) CO stripping voltammetry on (unsupported) preferentially-shaped Pt nanoparticles and the corresponding assignment of the multiple peaks with the surface sites (see text for details). Experimental conditions: 0.5 mol L^{-1} H_2SO_4; sweep rate = 20 mV s^{-1}. Reprinted with permission from Langmuir. Copyright (2017) American Chemical Society. (b). The effect of the progressive surface reconstruction on the CO stripping voltammetry on three unsupported Pt nanoparticles presenting distinct (111) and (100) surface planes. Experimental conditions: 0.5 mol L^{-1} H_2SO_4; sweep rate = 20 mV s^{-1}.Results from Urchada et al., refs [33,34], respectively. Reproduced with permissions.

The cited works from Coutanceau et al. could be used to tentatively unify the "particle-size effects" discussed in previous sub-section. For example, the high potential peak observed for Behm et al. (Fig. 7) ascribed to the oxidation on small nanoparticles (i.e., rather than on the "large" 100 nm nanodisk) could be related to a shorter (100) domain size on such small nanoparticles than on the nanodisks. However, this effect of the size of the (hkl) surface plane may not explain the peak multiplicity that appears on samples of carbon-supported Pt nanoparticles of the same size (and nearly the same size distribution) presenting distinct metal-to-carbon ratio during the CO stripping, to be described in the next section.

4. Agglomeration effects

Carbon-supported electrocatalysts for fuel cells are generally tailored to present well-dispersed metallic nanoparticles to provide high surface area to maximize the rate of the electrochemical reactions. However, depending on the method employed in the synthesis or even due to the degradation of the supporting material, particle growth and agglomeration may develop. For long time, the agglomeration of metal nanoparticles was considered a deleterious microstructural change in Fuel Cell electrocatalysts, despite the lack of specific investigations concerning this particular feature. In many investigations, agglomeration was observed in degradation tests of the electrocatalysts. Therefore, this feature is observed accompanied by particle coarsening, corrosion of the carbon substrate (loss of electrical contact between the particle), and so on, making difficult a precise analysis on the play rolled by agglomeration in some electrochemical reactions. Thus, if agglomeration favors or not relevant fuel cells reactions is still an open question, although some recent studies have shown that agglomerates and other porous structures enhance the electrochemical activity in certain cases [37–39].

The effect of agglomeration of Pt nanoparticles in carbon-supported Pt electrodes on the CO stripping voltammetry was investigated by Maillard et al. [29]. They showed that Pt agglomerates, with a high concentration of surface defects (steps, kinks, impinging nanoparticles in complex agglomerate structures) presented enhanced activity towards CO electrooxidation. This was demonstrated by the appearance of a less positive peak in the CO stripping voltammetry, if compared to the main peak found in experiments conducted with samples composed mainly of isolated small nanoparticles.

A very interesting work concerning the role of agglomeration was presented by Feliu and co-workers [11]. After the preparation of Pt nanoparticles by colloidal route, the particles were anchored on high surface area carbon (Vulcan, Cabot Co.) with different loadings of Pt on carbon, from 10 to 50 wt%, thus yielding materials with different loadings but formed with the same Pt nanoparticles. This latter aspect was demonstrated by the particle size histograms obtained from TEM images, which resulted in nearly the same particle size distribution. Such approach allowed the study on the effect of agglomeration in the electrocatalytic activity of Pt nanoparticles separate from other microstructural features, which were kept constant for all the investigated samples. As the amount of Pt anchored on carbon was increased, a low-potential peak was developed in the CO stripping voltammetry, as shown in Fig. 9. They explained this behavior by considering the interaction between CO and OH adsorbed in different nanoparticles, i.e., an inter-particle effect.

It is interesting to note that the abovementioned results are in line with those obtained by Maillard et al. [29] and suggest that particle agglomeration does influence the behavior of the electrochemical oxidation of CO on Pt nanoparticles. In fact, unsupported Pt agglomerates (e.g., Pt black nanoparticles) do show peak multiplicity in CO stripping experiments. In a previous publication we analyzed both potentiodynamic (cyclic voltammetry) and potentiostatic CO electrochemical oxidation in well-characterized unsupported Pt black nanoparticles [17]. The results clearly exhibited the presence of peak multiplicity in the CVs as reproduced in Fig. 10 for two samples of unsupported Pt blacks (see the Transmission Electron Microscopic images at the right side of the voltammograms). Based on a detailed structural characterization of the Pt agglomerates the behavior was ascribed to the occurrence of the reaction in particle with different sizes but we were able to show by several characterization techniques that this “size effect” can be understood as a combination of an altered electronic structure (i.e., amount of unoccupied Pt 5d–band states), crystallography, and morphology, as highlighted in Section 3.

5. The role of the catalyst support

As we have already mentioned in the Introduction section, real electrocatalysts for fuel cells generally rely on supported metal crystallites anchored onto a high surface area support, e.g., Pt/C. Several experimental studies have shown that the support material influence the eletrochemical behavior as a whole, including the CO stripping voltammetry. An interesting example of the support effect was presented in our previous work [37]. We showed that if unsupported Pt black particles (agglomerates) are anchored onto different supports such as Carbon, SnO_2 and RuO_2, the CO stripping voltammetry still presents peak multiplicity, as depicted in Fig. 11a. However, only the first (low potential) peak is significantly altered when using SnO_2 or RuO_2 as the support phases with respect to an “inert” support as Carbon. In contrast, the peak potential for the high potential peak ($Ep = 0.68\,V$) remains at the same position for all the investigated supports. The alteration of the first peak for SnO_2 or RuO_2 supports suggests that oxygen-containing species from the support phase modifies the way the reacting species interact (i.e., likely by CO molecules adsorbed on Pt sites with OH species from the support phase), thus modifying the shape of the peak. In contrast, the lack of alteration of the second (high potential) peak suggest that the related process of CO oxidation is taking place only at Pt sites, not being affected by the support phase. The reader is referred to ref. [37] for more details. Such behavior could be an indication that the assignment of the first peak due to solely (111) surface planes and low coordination sites (as suggested by Coutanceau et al.) may not be that straightforward, at least for the case of highly agglomerated Pt nanoparticles.

5.1. Functionalization and morphology of the carbon support

Carbon black is the most widely employed material as the support for Pt nanoparticles due to its high surface area (about $250\,m^2/g$) and conductivity [40,41]. Nevertheless, some studies have shown that functionalization of the carbon surface (i.e., the addition of specific functional groups with oxygen, nitrogen, sulfur, and phosphorous-containing species) and morphology of the material (e.g., microspheres, nanotubes, graphene, nanofibers, etc.) alter the electrochemical behavior of the whole Pt/C catalyst (see, ref. [2] for a review).

With regard to the issue of peak multiplicity during CO stripping and the modification of the physicochemical characteristics of the carbon support (chemical functionalization and morphology), interesting results are found in the literature. In general, they suggest that both factors may result in the appearance of multiple peaks in the CO stripping in such Pt/C electrocatalysts and also shifts in the peak potential for the oxidation of CO [42–46]. For instance, Pastor et al. [47] studied the influence of chemical treatments in samples of ordered mesoporous carbon that were further used to prepare carbon-supported Pt electrocatalysts. Their results for the CO stripping voltammetry are reproduced in Fig. 11b. For the samples subjected to a chemical treatment with concentrated HNO_3 (denoted as CMK-Nc0.5 and CMK-Nc2h), CO stripping curves revealed the presence of two peaks whereas for the untreated samples only one peak was observed. Moreover, a peak shift towards less positive potentials was also clearly visible, which was ascribed to the presence of hydroquinone/quinone on the carbon surface that promoted the reaction (lowering the CO peak potential). Similar potential shifts were also found for carbon functionalized with nitrogen and sulfur described by Kanninen et al. [44] and phosphorous-modified graphene [46]. In general, the explanation for the differences in the CO stripping peak potential among distinct samples of functionalized carbon support has been ascribed to changes in the interaction between Pt and the support (e.g., lowering the activation energy for the reaction, altering the electron density of Pt, shifts in the d-band center, etc.) [44,45,48] and also by some influence of oxygenated species provided by the support [47] in a similar manner as in the case of RuO_2 and SnO_2 described above. However, it should be borne in mind that funcionalization of the carbon support generally alter the size and distribution of the Pt nanoparticles [42,47] which, in turn, may produce multiple peaks in the CO stripping as discussed in previous sections.

Another important result coming from such studies on the influence of the support on the “active” phase of the electrocatalyst (Pt) is that some surface electrochemical reactions rather than the CO_2 formation may also generate a peak in the CO stripping voltammetry. Rizo et al. [43] have shown by a simultaneous electrochemical DEMS setup and also by FTIR spectroscopy that the faradaic current observed in the CO

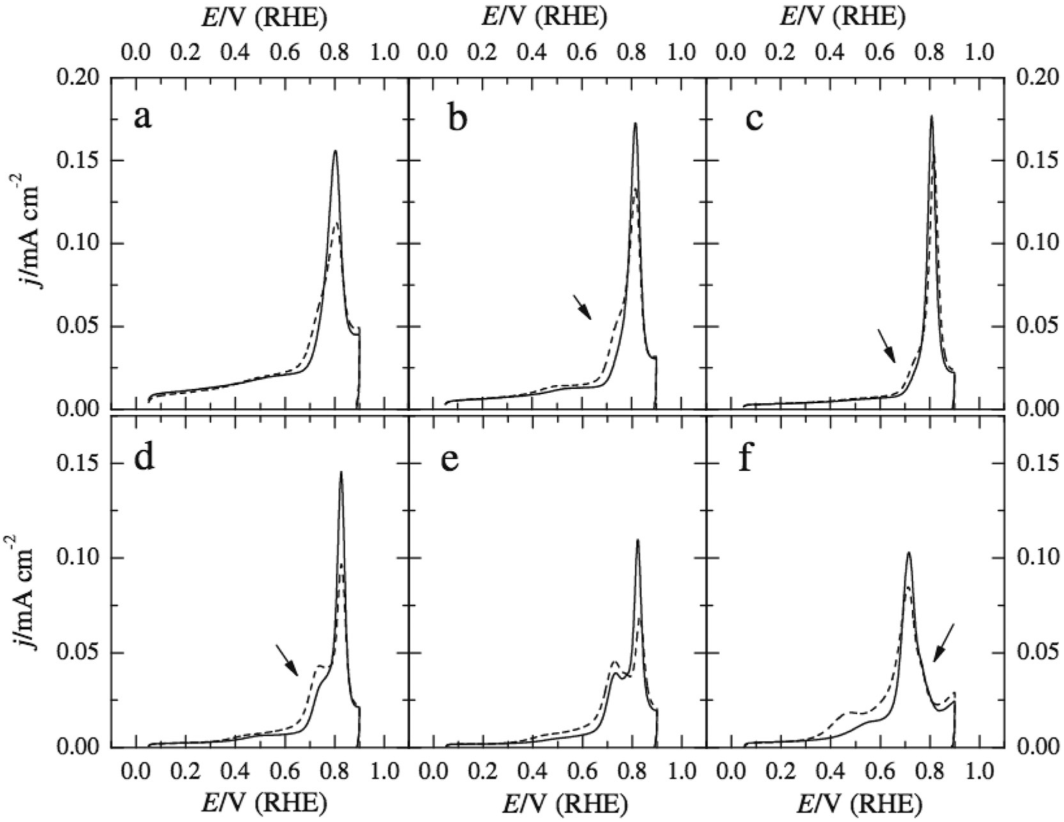

Fig. 9. Potentiodynamic CO Stripping carried out in carbon-supported Pt nanoparticles (Pt/C) with a average diameter of 2.2 ± 0.5 nm supported on carbon with different platinum loadings a) Pt/C (10% wt); b) Pt/C (20% wt); c) Pt/C (30% wt); d) Pt/C (40% wt); e) Pt/C (50% wt). Results from López-Cudero et al. [11]. Experimental conditions: 0.5 mol L^{-1} H_2SO_4; sweep rate = 20 mV s^{-1}. Reproduced with permission.

stripping were not related to the production of CO_2 but rather to an electrochemical surface reaction in the carbon phase. In their case, a voltammetric peak centered at 0.66 V (0.5 mol L^{-1} H_2SO_4, 20 mV s^{-1}) was attributed to the formation of adsorbed C–OH species formed during the adsorption of CO at low potentials. Their result points out that care must be taken when interpreting a “pure” electrochemical result.

6. CO surface diffusion

The role of CO surface diffusion also needs to be included in the scenario of peak multiplicity. Simulations of CO stripping voltammetries on Pt nanoparticles conducted by Zhdanov and Kasemo [16] showed that CO surface diffusion onto different surface planes might dramatically influence both the current-potential profile and peak positions as well. In their study, a model nanoparticle formed by a (100) top surface facet surrounded by (111) lateral facets and a large (100) facet in contact with the catalyst support (contact interface) was considered (see the inset of Fig. 12a). Then, a mechanism for CO oxidation (similar to that described in the Introduction section) was proposed in which CO molecules were allowed to diffuse from one facet to another. For instance, CO molecules adsorbed on sites of (111) planes could diffuse and react predominantly at (100) facets. Authors showed that for relatively slow interfacet diffusion, the CO stripping peaks slightly overlap, giving rise to two well–separated peaks. In the case where the rate of the CO oxidation reaction is comparable to the CO interfacet diffusion, the current profile would appear as two peaks with considerable overlapping, as shown in Fig. 12a. Assuming that the (100) facet is more active than the (111), the larger integral intensity of the first (low potential) peak was explained in terms of CO diffusion from (111) towards (100) facets, while the shoulder observed occurs due to the reaction on (111) sites. In the third case, where CO diffusion is fast, the stripping of both facets would occur simultaneously, giving rise to a single narrow peak in the CO stripping voltammogram (Fig. 12a). Surprisingly, the shape of the currents predicted by Zhdanov and Kasemo are in agreement with our previously published results [17] and reproduced in Fig. 12b. The reader is encouraged to see ref. [16] for figures and details of simulations. The general resemblance between the simulated and experimental data is noteworthy (and also from other authors, see, for instance, Fig.8 from Coutanceau et al.). Thus, one may speculate that assuming a coupled effect, where the CO diffusion between the surface facets is taking place and also that the particle size distribution is playing a role (a particle size effect), it could be tentatively explained that the first peak and its shoulder occur due to the reaction taking place with a rate comparable to the CO diffusion between different facets. On the other hand, the second narrow peak could be due to the reaction on small nanoparticles, where the CO interfacet diffusion is very rapid due to the small mean free path if compared to the larger nanoparticles (i.e., according to the simulations, both (111) and (100) surfaces yields the current transient exhibited by the narrow, high potential peak). Obviously, this description is quite speculative and requires further investigation. Nevertheless, the simulation results from Zhdanov and Kasemo gives rise to a distinct point-of-view for the explanation of the current-potential profile if compared to the ideas of Coutanceau et al. (i.e., the low potential peak being assigned to (111) surface planes and low coordination sites and the high potential peak solely due to (100) surface planes).

Further knowledge of the issue of the CO surface diffusion was obtained in the works of Maillard et al. [10], Koper et al. [49], Savinova et al. [50], Wieckowski et al. [51,52], Feliu et al. [53], and others. In general, it was found that the diffusion coefficient of CO (D_{CO}) on Pt surfaces depends on the coverage of CO and particle size. Nevertheless, there is no consensus whether the diffusion of CO is fast or slow (or even immobile) on Pt electrocatalysts under electrochemical

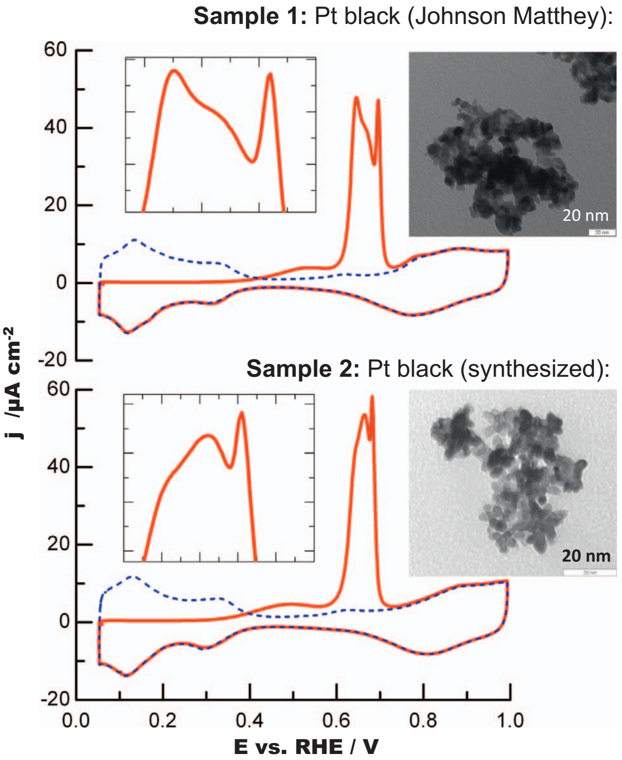

Fig. 10. CO stripping voltammetry at 10 mV s^{-1} recorded in 0.1 mol L^{-1} $HClO_4$ for two distinct samples of Pt blacks and their corresponding TEM images. Insets show the multiple features in the main peak of the voltammogram. Sample 1 (upper part): Commercial Pt black (Johnsom-Matthey Co) and Sample 2 (lower part): Pt black synthesized by chemical reduction. Details of the synthesis and structural characterization are given in Ciapina et al. [17].

environment. In fact, reported values for D_{CO} spread over three orders of magnitude, from 3.6 × 10^{-13} cm^2/s (measured by electrochemical nuclear magnetic resonance) as in ref. [51] to 4 × 10^{-15} cm^2/s (estimated from simulation and fitting of experimental data of electrochemical measurements), as in ref. [50]. Regarding the correlation between CO surface diffusion and the appearance of multiple peaks in CO stripping, a recent theoretical study was done by Zhang et al. [54] by means of Dynamic Monte Carlo (DMC) simulations and using the data obtained by Behm's group already discussed in Section 3 and shown in Fig. 7. They concluded that different CO stripping peaks could be rationalized in terms of a different CO surface diffusion (particle-size dependent) and CO initial configuration (i.e., the initial distribution of the CO molecules at the surface).

An interesting (and yet different) point-of-view was recently presented by Wang et al. [55]. In their work, the presence of peak multiplicity found in CO stripping was ascribed to the mobility of adsorbed oxygen molecules adjacent to Pt sites rather than related to the mobility of the CO_{ad} molecules. This explanation is quite unusual, since it is generally considered that the CO oxidation reaction takes place between CO_{ad} and adsorbed (fixed) OH molecules at defect sites, as discussed in previous section. However, given that the estimated value for the (apparent) diffusion coefficient for adsorbed oxygen in the form of OH_{ad} (D_{OH}) is considerable higher than that of CO (D_{OH} = 6.8 × 10^{-10} cm^2/s) an interesting and new question emerges.

7. The nature of the supporting electrolyte: the role of adsorbed anions

The influence of the nature of the supporting electrolyte, e.g., non-adsorbing anions such as $HClO_4$ or strongly adsorbed anions (H_2SO_4) appear to play a role in the observation of multiple peaks in the CO stripping voltammetry. Although the role of the adsorbing anions is of paramount importance in the mechanistic aspects of the CO oxidation, the discussion here will be limited only to their effect on the peak multiplicity. As a clear illustration of the influence of the electrolyte, Fig. 13 shows CO stripping voltammetry carried out on a sample of unsupported Pt black in 0.5 mol L^{-1} H_2SO_4 (Fig. 13a), and in 0.1 mol L^{-1} $HClO_4$ (Fig. 13b). Both electrolytes (and concentrations) were chosen given they are the most used in the literature. It is evident from the figure that the current-potential profile is altered in the presence of adsorbing anions as (bi)sulfate from the electrolyte. Whether adsorbed anions influence other phenomena (e.g. CO surface diffusion, adsorption geometries, surface coverage, amount of available defect sites for the adsorption of OH, etc.) is still to be determined, but the effect is clearly present and has to be considered when analyzing the data. Moreover, little is known regarding the effect of the size of Pt (nano)structures on the adsorption of (bi)sulfate on Pt nanoparticles; rather, the majority of the published papers refer to macroscopic Pt surfaces, such as polycrystals and single crystals. The latter indicates that the adsorption strength of (bi)sulfate on Pt (111) is higher than on (100) and (110) planes, as reviewed by Markovic and Ross Jr. [5]. An indication of a size effect on the adsorbed (bi)sulfate on Pt nanoparticles during the oxidation of CO was provided by Maillard et al. [31]. By comparing CO stripping voltammetry on a sample of carbon-supported Pt nanoparticle with a bimodal size distribution obtained in 0.1 mol L^{-1} $HClO_4$ and 0.1 mol L^{-1} H_2SO_4 it was observed a change in the position of the voltammetric peaks towards more positive potential, shifting ~20 mV for large particles and ~ 80 mV for small ones [31].

8. The role of the experimental protocol

When CO stripping experiments are carried out using potentiodynamic sweeps (linear sweep voltammetry and cyclic voltammetry) the scan rate is a very important parameter to observe or not peak splitting, as shown in our previous publication [17]. As explained in prior sections, at a given scan rate the position of the peaks found in the CO stripping voltammetry could provide some insights to the factors involved, such as particle size, for instance. Thus, data acquisition and analysis of the current-potential profile should be done with additional care. First, ohmic drop has to be properly accounted for; otherwise the position of the peak would be a function of the uncompensated solution resistance [56]. Most of the studies deals with diluted acids or bases in the range of 0.05 to 1 mol L^{-1} and uses thin films of the electrocatalysts deposited onto appropriate substrates (glassy carbon, pyrolitic carbon, gold, among others with a typical loading of about 14 to 80 μg of Pt cm^{-2}) [57,58]. Thus, depending on the geometry and design of electrochemical cell used, the resistance can be higher than 10 Ω, for which the peak potential can be displaced by more than 10 mV under a current of, say, 1 mA. Obviously, not only the electrochemical cell's resistance but the amount of catalyst (the electrochemical active area, more specifically) can be responsible for ohmic losses, since it determines the magnitude of the current of the CO stripping on a given electrode. For potentiostatic experiments, the choice of the potential to be applied to the electrode to oxidize CO is also of importance: if the potential is too positive, only one peak may be observed (ref. [17]), whereas for low potentials multiple peaks would be visualized.

Second, the history of the electrode has to be taken into account for the reason explained in the following. It should be born in mind that CO stripping at Pt nanoparticles is an extremely complex reaction. Thus, the type and number of experiments carried out before CO stripping may modify the microstructure of the electrode and, consequently, the CO stripping profile (see Section 3.2). Previous works from Arenz et al. [59] showed that depending on the pre-treatment performed on carbon-supported Pt electrode the current-potential curve for CO stripping will appear differently, i.e., distinct peak shapes and positions, shown in Fig. 14. They found that for a given particle size, the peak potential in the CO stripping conducted at 1 mV s^{-1} is shifted towards more positive

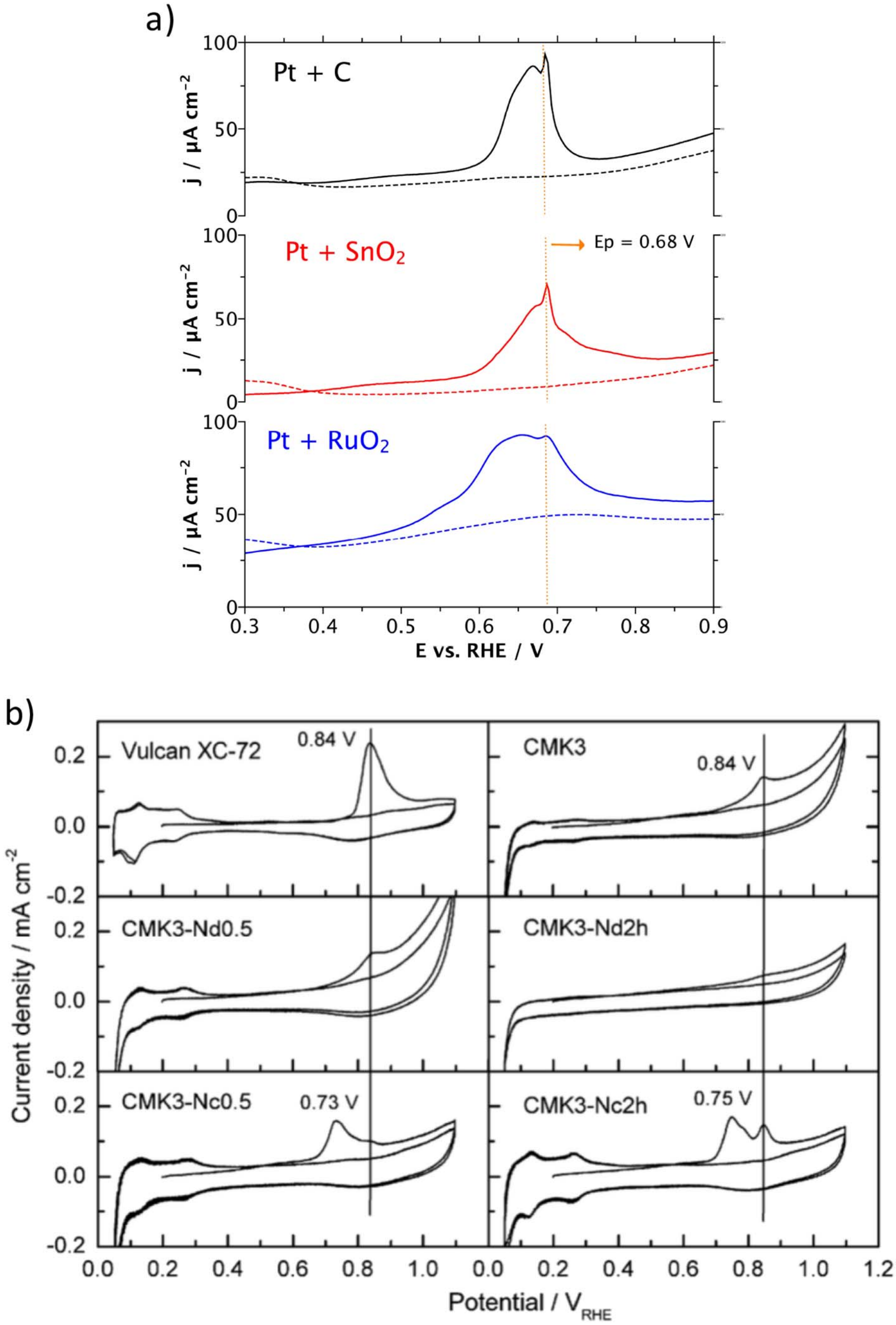

Fig. 11. a) CO stripping voltammetry carried out at Pt black (sample 2, prepared by chemical reduction) supported onto Carbon, SnO_2, and RuO_2 (20% wt Pt for all cases). Experimental conditions: sweep rate = 20 mV s^{-1}, electrolyte: 0.1 mol L^{-1} $HClO_4$. Adapted from Ciapina et al. (ref. [37]). Reproduced with permission. b) CO stripping voltammetry carried out in Pt nanoparticles anchored on chemically modified ordered mesoporous carbon. Results from Pastor et al. [47] Experimental conditions: 0.5 mol L^{-1} H_2SO_4; sweep rate 20 mV s^{-1}; Pt particle sizes ranging from 2.8 to 3.2 nm. Reproduced with permission.

values for "CO–annealed surfaces" (pretreatment in which the electrode is cycled with CO dissolved in solution) if compared to the electrode pretreated with the "oxide–annealing" method (pretreatment in which the electrode is cycled in the base electrolyte only). They explained the differences based on the fact that CO–annealed surfaces contained fewer irregularities (defects) than the surfaces subjected to potential cycling in the base electrolyte. Later, Shao-Horn et al. [60] showed by TEM that the pre-treatment with CO-annealing remove defects (high index *hkl* planes) from the nanoparticles through rearrangements of atoms from the first layers. The effect can be understood on the basis of the high energy of adsorption of CO on Pt that results in an expansion of the surface layer (of ≈ 4% at 0.05 V) [5] followed by the subsequent contraction due to the removal of the CO by oxidation. Other studies carried out with Pt single crystal also indicate that a CO-treated surfaces present fewer defects than those obtained by other methods [23,61].

From the practical point-of-view, while CO stripping is generally used to assess the electrochemical active surface area of the electrocatalysts, and considering that CO annealing could be considered as a defect removal tool, its use prior the "main" electrochemical study (oxidation of methanol, ethanol, formic acid, oxygen reduction, etc.) might alter the initial state of the electrode. Whether or not the a single CO stripping voltammetry carried out on an electrode before the main reaction under investigation alters significantly the response of the surface for any particular study, this is to be determined for each case.

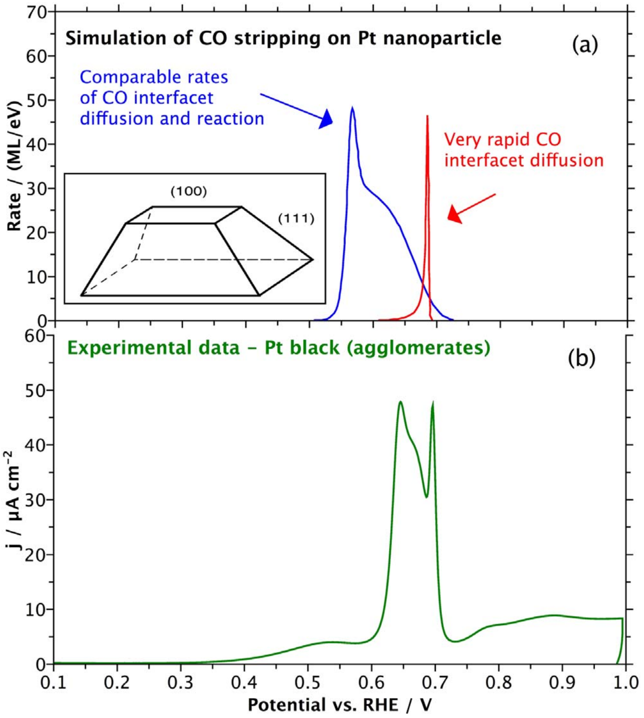

Fig. 12. a) Simulations of CO stripping voltammetry on nanosized Pt particles by Zhdanov and Kasemo [16] in two distinct situations (as depicted in the Figure); b) Experimental CO stripping voltammetry carried out at 10 mV s^{-1} in unsupported Pt black (Johnsom Matthey Co.) in 0.1 mol L^{-1} $HClO_4$ as reported in ref. [17]. Reproduced with permission.

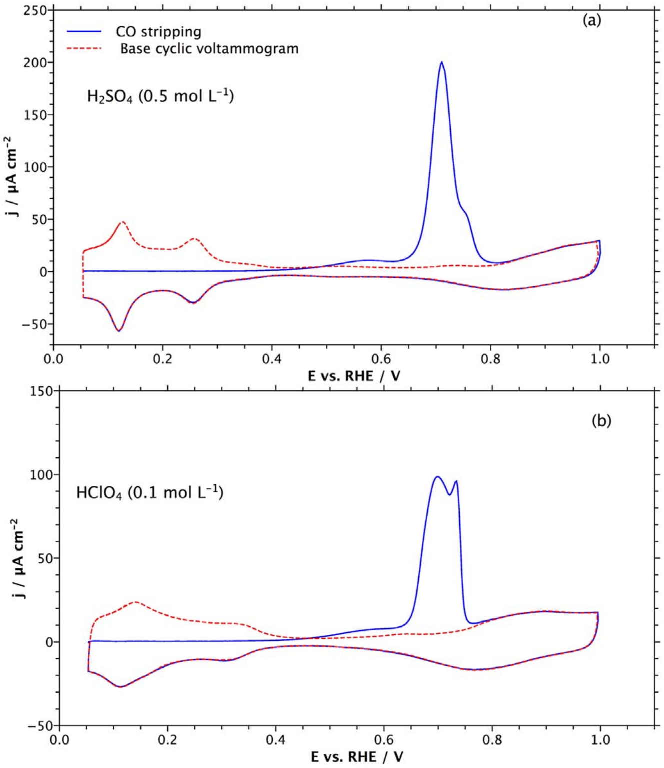

Fig. 13. CO stripping voltammetry and the subsequent CVs at 20 mV s^{-1} obtained for a commercial unsupported Pt black (Johnson Mattey Co) recorded in different supporting electrolytes: a) 0.5 mol L^{-1} H_2SO_4; and b) 0.1 mol L^{-1} $HClO_4$. Currents normalized to the active surface area of the electrodes determined from the charge of CO stripping.

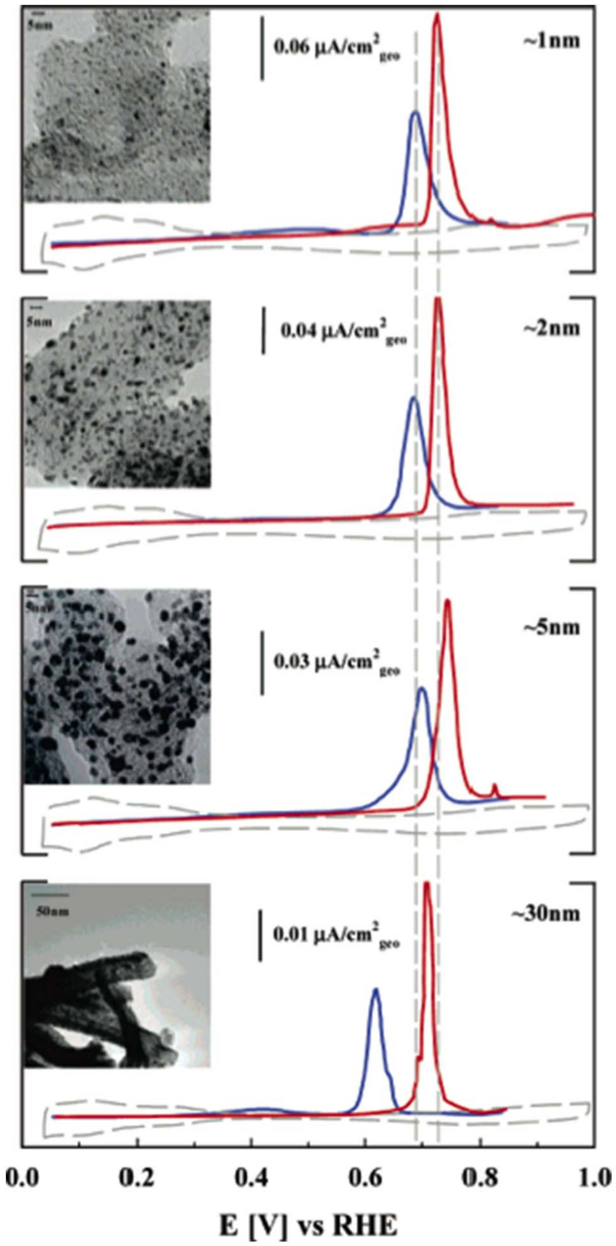

Fig. 14. The effect of the pre-treatment of the electrode on the current-potential profile during CO stripping voltammetry: potentiodynamic CO stripping voltammetries obtained for carbon-supported Pt nanoparticles (Pt/C) with distinct sizes with distinct pre-treatments: oxide-annealing (blue curve) and CO-annealing (red curves). Conditions: 0.1 mol L^{-1} $HClO_4$; T ~ 20 °C, scan rate 1 mV s^{-1}. Figures from Arenz et al. [59]. Reprinted with permission from The Journal of the American Chemical Society. Copyright (2017) American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As an example, CO-annealing in PtCo/C nanoparticles drastically alters the electrocatalytic activity for the electrochemical reduction of oxygen in both alkaline and acidic media [62,63].

9. Conclusions

The electrochemical oxidation of CO is extremely sensitive to the structure and to the experimental protocol used, i.e., pre-treatments of the electrode (potential cycling in base electrolyte, defect removal by cycling in CO-saturated solution, etc.), the nature of the supporting electrolyte (the presence or not of strongly adsorbing anions). Whereas the scenario is quite intriguing when studying single crystals, the situation becomes much more complex on nanoparticle systems, where a variety of additional factors may come into play (particle size, (hkl) domain size, CO surface diffusion, crystallography of the surface planes, particle agglomeration, support, etc.). On such systems, the separation of each effect may be extremely difficult mainly because some of these effects are originated from interdependent features of the electro-catalysts. On the other hand, the separation of these effects throughout the manuscript allows us to explain the state of the art concerning the role played by each effect on CO stripping in peak multiplicity. Moreover, in situ spectroscopic data is highly needed for providing information regarding adsorption geometries of CO on electrode surfaces and how they are related to the CO stripping. We expect this article can give an overview on the variety of the phenomena related to the question of peak multiplicity on CO stripping on Pt surfaces, in the hope that by gaining further knowledge of the fundamental processes of the CO oxidation, new and more active electrocatalyst for real fuel cells can be found.

Conflicts of interest

None.

Acknowledgements

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