



## Determination of the real surface area of powdered materials in cavity microelectrodes by electrochemical impedance spectroscopy

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### ABSTRACT

The electrochemical impedance spectroscopy (EIS) technique has been used to determine the electrochemically active (real) surface of electrode materials via the measurement of the double layer capacitance. The real surface is of utmost importance in electrocatalysis, allowing determination and comparison of the intrinsic activities of different catalysts. EIS is a fast, *in situ* and a non-destructive method that allows the determination of the surface area of mono and multielement catalysts. In this study, Pt, Ru, and PtRu unsupported powders prepared by high energy ball milling (BM) were used as electroactive materials. They were inserted into cavity microelectrodes (CMEs) and studied in sulfuric acid solution. In addition, impedance method applied to porous materials allows for the determination of the porosity of the cavities.

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### 1. Introduction

Electrocatalysts are generally characterized by high electrocatalytic activity that may arise as a result of high real surface area and/or high intrinsic activity [1,2]. From a fundamental viewpoint, it is imperative to differentiate between both contributions. This implies that fast and simple methods must be devised for the *in situ* determination of the real surface area. Moreover, since most of the catalysts are in the powdered form, these methods must be applicable to such samples.

Platinum is a metal for which it is relatively easy to determine the real surface area. It is often used as a reference catalyst, and its surface is measurable using different electrochemical methods [3] including the charge of the hydrogen underpotential deposition peaks (H UPD) in cyclic voltammetry [2], and stripping charges of adsorbed CO [4–6], or Cu UPD [7]. However, these are not absolute methods, all of them have their advantages and disadvantages. Since they are based on purely experimental values of charges, none of them is viewed as being more reliable than the others.

For Pt-based electrocatalysts, the measurement of H UPD charge includes contributions from bisulfate adsorption, vary for different crystallographic planes [8] and the total charge is sensitive to sur-

face defects [9] and impurities [10]. In most practical cases, the methods that are the most interesting for the preparation of electrocatalysts (ball milling, chemical reduction, etc.) produce highly dispersed or high surface area Pt catalysts composed of small porous particles with numerous defects that could also include impurities (from the ball milling process) and/or mechanical strain [11,12], all of which may interfere with the H UPD process. In the particular case of Pt particles supported on carbon materials, hydrogen spillover may also induce an additional error in the measured H UPD charge [3]. In the case of CO adsorption, surface coverage does not reach unity and different modes of adsorption on Pt were found that influence the measured charge. As for Cu UPD measurements the method assumes that one Cu atom is adsorbed at one Pt atom despite some differences in their sizes.

The difficulties related to the determination of the real surface area are even greater when bi or multi metallic catalysts are studied like PtRu, PtSn or PtRuSn, which are the most often studied materials for applications in direct alcohol fuel cells. In the case of PtRu catalysts, the H UPD region on the cyclic voltammogram overlaps with Ru oxidation. Consequently, the H UPD integration method cannot be used with confidence for PtRu. Moreover, this method is not suited for alloys containing elements such as Sn, Ni, and other non-noble metals, as there is no H UPD on these elements. CO stripping is also used to evaluate PtRu surface area [2,13–15]. However, this method is not unanimously recognized because the CO stripping behavior changes with the electrocatalytic activity of the catalysts [2,16] and, therefore, with the Ru content [13]. Copper

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UPD is an alternative method to evaluate PtRu surface area [2,16,17] although several problems were also raised [2].

Cavity microelectrodes (CMEs) [18–27] allow electrochemical analysis to be carried out on unsupported catalysts without using binders like Nafion. However, it is difficult to determine the amount of powder contained in the cavity because it is too small to be weighted using a conventional laboratory balance. Microscopic determination of the surface area is impossible due to a very large particle size distribution typical of BM electrocatalysts. Also BET surface area determined by gas–solid interactions is not reliable since it is usually larger than the electrochemically accessible area. In addition, our reproducibility tests performed with the same catalyst in identical CMEs pointed out that the surface accessible to electrochemical processes varies from one sample to another. In fact, the real surface area of each filled CME is found to be influenced by parameters like the BET surface of the material, the packing density achieved during filling (manual), and the cavity size. While some groups reported directly measured currents regardless of the electroactive surface in CMEs [21,22], other estimated the active surface using the specific surface area by assuming that the amount of powder in the cavity does not vary from one sample to another [28]. Another approach to evaluate the amount of catalyst in a CME consisted in dissolving the cavity content and quantifying it using ICP spectroscopy [18].

The present paper proposes a non-destructive and *in situ* method based on electrochemical impedance spectroscopy (EIS) to quantify the electrochemically active surface area of a filled CME from its double layer capacitance. The method is fast and does not require the solution or the cell to be changed (Cu UPD) or purged with reactive gas (CO stripping). Unsupported Pt, Ru, and PtRu prepared by high energy ball milling (BM) were used as catalysts. This method allows the intrinsic activity of catalysts having different granulometry and composition to be rigorously compared between them. The EIS based approach also gives information about the powder packing density and the average pore size.

## 2. Theory

The objective of the impedance measurements presented in this study is to determine the electrical double layer capacitance in a pure supporting electrolyte and in the absence of electrochemical reactions. Consequently, the electrodes were tested in the potential range where they display an ideally (or close to ideally) polarized behavior. In such a case, the total impedance is described as  $Z_t = R_s + 1/j\omega C_{dl}$ , where  $R_s$  is the solution resistance in  $\Omega$ ,  $C_{dl}$  the double layer capacitance of the electrode in F,  $\omega$  is the angular frequency of the ac signal and  $j = \sqrt{-1}$ . The complex plane plots display in such a case a vertical capacitive straight line intersecting the real axis at  $Z' = R_s$  [29]. Such a behavior is observed for polycrystalline platinum between 0.4 and 0.7 V [30]. In practice, the double layer capacitance must be replaced by the constant phase element (CPE) [29,31] and the total impedance is described as:

$$Z_t = R_s + \frac{1}{(j\omega)^\phi} T_t \quad (1)$$

where  $T_t$  is the capacitance parameter in  $F s^{\phi-1}$  and  $\phi$  is the CPE exponent. The average double layer capacitance,  $\bar{C}_{dl}$  (in F), might be estimated using equation proposed by Brug et al. [31]:

$$\bar{C}_{dl} = \frac{T_t^{1/\phi}}{R_s^{1-(1/\phi)}} \quad (2)$$

Since the electrodes studied in the present paper were made of packed powders enclosed in a cavity, the expected impedance results show typical features of porous electrodes at high frequencies, in addition to the low-frequency capacitive line [29,32–35]. In

that case, the complex plane impedance plots exhibits a 45° line at high frequencies that is a consequence of the coupling of the solution resistance and double layer impedance for the ac signal penetration depth which is smaller than the pore length. A rigorous treatment of the model used for a porous electrode can be found in references [29,32,36]. A porous model was used earlier to determine the surface area of larger electrodes [32,34,35] and it will be adopted here for cavity microelectrodes.

The impedance of porous electrodes is represented by the equivalent circuit consisting in a solution resistance in series with the impedance of the porous electrode,  $Z_p$ . Therefore, the total impedance of a porous electrode with  $n$  cylindrical pores is:

$$Z_t = R_s + Z_p \quad (3)$$

where:

$$Z_p = \left( \frac{R_{\Omega,p}}{\Lambda^{1/2}} \right) \coth(\Lambda^{1/2}) \quad (4)$$

and  $R_{\Omega,p}$ , the total resistance of the solution in  $n$  pores in parallel (in  $\Omega$ ), is

$$R_{\Omega,p} = \frac{\rho l}{n\pi r_p^2} \quad (5)$$

where  $\rho$  is the electrolyte specific resistivity ( $\Omega \text{ cm}$ ),  $l$  the pores length (cm),  $r_p$  the pores radius (cm) and  $n$  the number of pores.  $\Lambda$  is the non-dimensional admittance of the porous electrode

$$\Lambda = \frac{j\omega C_{dl}^0}{a} \quad (6)$$

where  $C_{dl}^0$  is the specific capacitance of the double layer of the pores walls ( $F \text{ cm}^{-2}$ ) and  $a = r_p/2\rho l^2$  in  $\Omega^{-1} \text{ cm}^{-2}$ .

Taking into account that, for real electrodes, the double layer capacitance is replaced by the constant phase element (CPE), Eq. (6) is replaced by  $\Lambda = (j\omega)^\phi T^0/a$  where the specific double layer capacitance  $C_{dl}^0$  was replaced by the specific capacitance parameter  $T^0$  in  $F \text{ cm}^{-2} s^{\phi-1}$ . Thus, Eq. (4) can be written as:

$$\begin{aligned} Z_p &= \frac{R_{\Omega,p}}{[(j\omega)^\phi (T^0/a)]^{1/2}} \coth \left[ (j\omega)^\phi \frac{T^0}{a} \right]^{1/2} \\ &= \frac{R_{\Omega,p}}{[(j\omega)^\phi B_p]^{1/2}} \coth \left[ (j\omega)^\phi B_p \right]^{1/2} \end{aligned} \quad (7)$$

where  $B_p = T^0/a$ . At low frequencies, Eq. (7) reduces to a connection of the resistance and the CPE element in series:

$$Z_p = \frac{R_{\Omega,p}}{3} + \frac{1}{(j\omega)^\phi T_t} \quad (8)$$

where  $T_t = B_p/R_{\Omega,p} = T^0 S$  is the total capacitance parameter in  $F s^{\phi-1}$  and  $S$  is the total surface area of the porous electrode [37]. Approximations with this model using the complex nonlinear least square method (CNLS) permitted for the determination of four experimental parameters:  $R_s$ ,  $R_{\Omega,p}$ ,  $B_p$  and  $\phi$ , from which  $T_t$  and the average double layer capacitance,  $\bar{C}_{dl}$ , was obtained using Eq. (2).

## 3. Experimental

### 3.1. Preparation and filling of the cavity microelectrodes

CMEs were made by inserting a gold wire (127  $\mu\text{m}$  diameter, 2–3 cm long, Alfa Aesar, 99.99%) inside a glass capillary tube (o.d. 1.5 mm, i.d. 0.75 mm, 9 cm long). The gold wire was connected to a copper wire by spot welding. One end of the capillary was

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