

Calculation of the platinum's active surface

I- Introduction

The state of surface of an electrode can be very important depending on the experiment carried out. It should always be as neat as possible to avoid parasite reactions. It should also be, according to the electrode's geometry, as smooth as possible. For example, in the case of a planar electrode, the surface should be as plane as possible on a microscopic scale. In the proper conditions, characteristic values can be determined such as the number of adsorption sites per surface unit for a given material.

The aim of this tutorial is to show the user how to determine the active surface of an electrode from a voltammetric curve giving I vs. E_{we} .

II - Experimental conditions

- Working electrode: RDE (Rotating Disk Electrode) of platinum, working area: 0.0314 cm^2 ,
- Counter electrode: Platinum wire,
- Reference electrode: Saturated Calomel Electrode,
- Solution: H_2SO_4 (0.25 M).

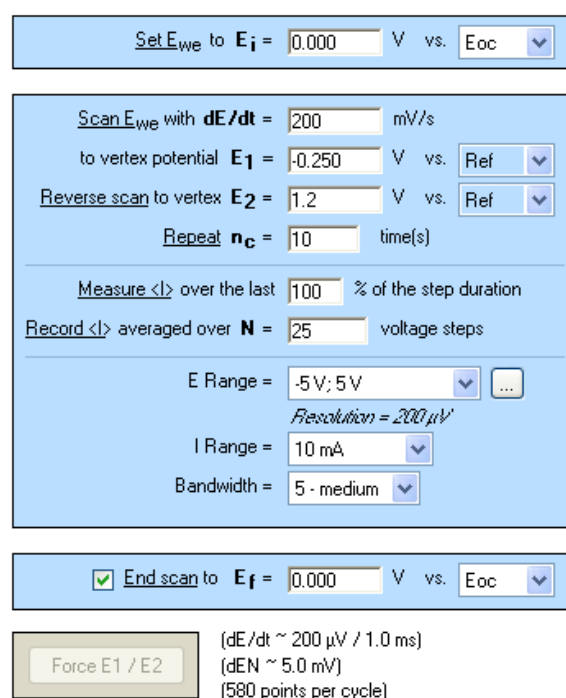
III - Protocol description

The working electrode was polished with alumina and then rinsed with methanol and distilled water.

The solution was degassed with argon and agitated ($\Omega = 4000 \text{ rpm}$) for 15 minutes before launching the experiment. During the measurement, the electrode rotation was stopped.

The technique used under EC-Lab[®] was Cyclic Voltammetry. The parameters settings are described in Fig. 1.

Note: adjustment of E Range and then increase of the potential control resolution (span) can be important. For this experiment, E Range was adjusted between [-5; 5] V and then the minimum potential step height from 300 to 200 μV [1].



Set E_{we} to E_i = 0.000 V vs. Eoc

Scan E_{we} with dE/dt = 200 mV/s
 to vertex potential E_1 = -0.250 V vs. Ref
 Reverse scan to vertex E_2 = 1.2 V vs. Ref
 Repeat n_c = 10 time(s)

Measure $\langle I \rangle$ over the last 100 % of the step duration
 Record $\langle I \rangle$ averaged over N = 25 voltage steps

E Range = -5 V; 5 V
 Resolution = 200 μV

I Range = 10 mA
 Bandwidth = 5 - medium

☒ End scan to E_f = 0.000 V vs. Eoc

Force E_1 / E_2 (dE/dt ~ 200 μV / 1.0 ms)
 (dEN ~ 5.0 mV)
 (580 points per cycle)

Fig. 1: Cyclic Voltammetry "Parameters Settings" window.

The curve obtained is displayed in Fig. 2, and its shape is comparable to those found in literature [2]. The related data file was processed to separate the different cycles of the curve.

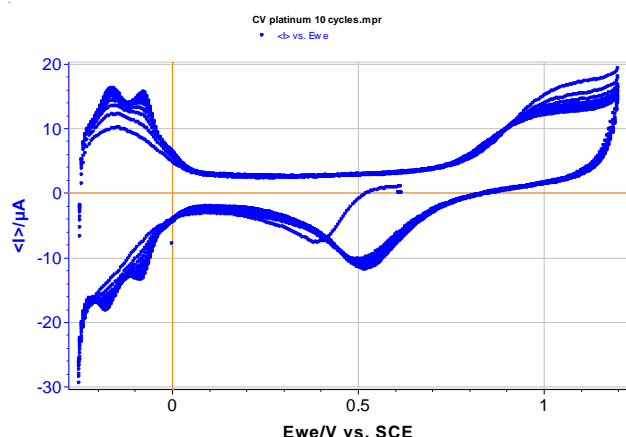


Fig. 2: Voltammetric curve I vs. E_{WE} obtained by cyclic voltammetry (10 full cycles) for platinum in an acid solution.

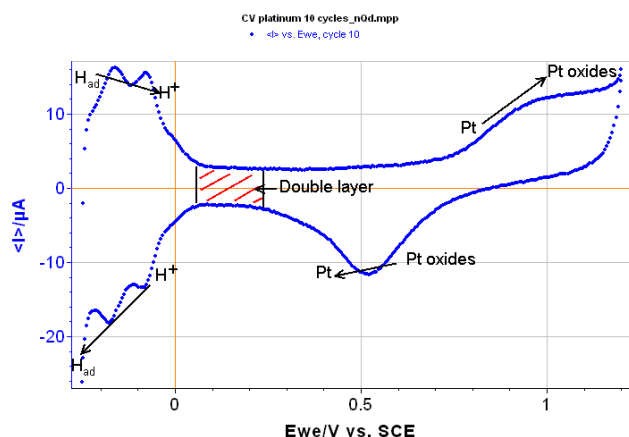
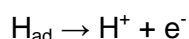


Fig. 3: 10th cycle isolated from the curve with oxido-reduction specificities for platinum.

Note: It is possible to load the different CV_platinum files with EC-Lab[®] software in the following folder: C:\EcLab\data\samples.

IV– Calculation of the active surface

During the reduction of platinum, protons from the acid are adsorbed at the surface of the electrode. During the oxidation, these atoms of hydrogen are desorbed according to the following electrochemical reaction:



The measure of the number of electrons liberated during the oxidation of platinum for low potentials gives the number of hydrogen atoms desorbed and thus the number of adsorption sites present on the electrode's

surface. This defines the active surface of the electrode.

The total charge corresponding to the hydrogen desorption can be related to the integral of the curve for a certain interval of potentials where the atoms are being desorbed. This part of the curve is presented in Fig. 4.

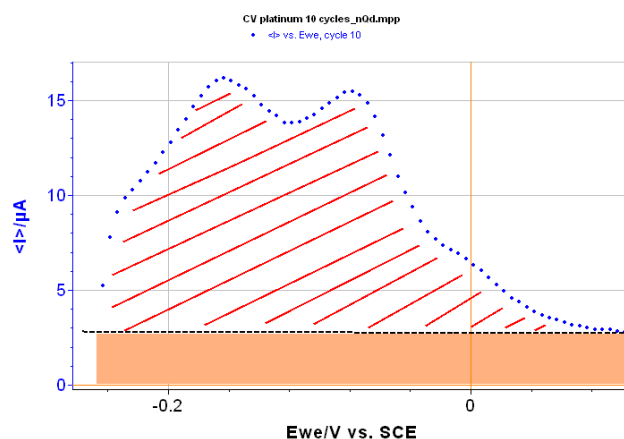


Fig. 4: Zoom of the curve presented in Fig. 3 for low potentials in oxidation. The red area corresponds to the desorption of hydrogen. The orange area corresponds to the capacitive current due to the double layer capacitance.

The expression of the total charge of desorption can be written as follows:

$$Q = \int_{E_1}^{E_2} I \cdot d\tau = \frac{1}{v_b} \int_{E_1}^{E_2} I \cdot dE$$

where v_b is the scan rate. This integral can be calculated with EC-Lab[®]'s Integral graph tool. However, the capacitive current due to the double layer capacitance is not to be taken into account, and the corresponding area must be subtracted from the integral calculated by EC-Lab[®].

EC-Lab[®]'s Integral graph tool gives the following result:

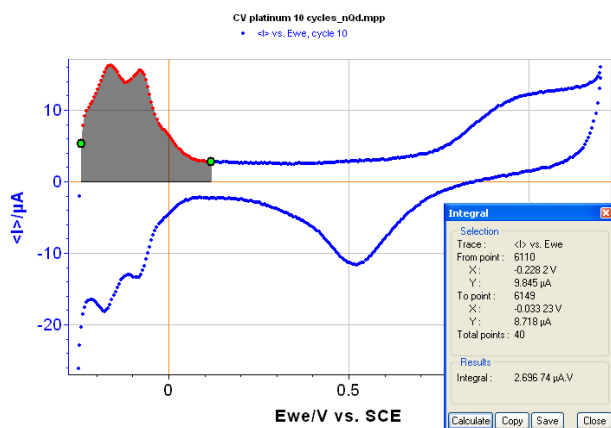


Figure 5

Fig. 5: EC-Lab®'s Integral analysis tool.

$$\int_{\text{red-zone}} I \cdot dE = 2.69 \cdot 10^{-3} \text{ mA.V}$$

The area, due to the double layer, must be calculated manually. If the capacitive current is constant for all potentials, it simply needs to be multiplied by the length of the potential interval used for the integral.

In this experiment, the capacitive current value is 2 μA and stays constant for the potential interval considered (340 mV).

The area corresponding to the **double layer** equals:

$$2 \cdot 10^{-3} \times 0.34 = 6.8 \cdot 10^{-4} \text{ mA.V.}$$

Therefore the area corresponding to the **desorption** equals:

$$(2.69 - 0.68) \cdot 10^{-3} = 2.01 \cdot 10^{-3} \text{ mA.V.}$$

To have the **charge value for the desorption of hydrogen**, the previous result needs to be divided by the scan rate v_b , and to get the **charge value per surface unit**, the new result needs to be divided by the electrode surface.

$$2.01/0.2 = 10.05 \mu\text{C}$$

$$Q = 10.05/0.0314 = 320 \mu\text{C.cm}^{-2}$$

In literature, the electrical charge generally associated with monolayer adsorption of hydrogen is **210 $\mu\text{C.cm}^{-2}$** [3]. The result found previously is a bit higher, but it can be explained. The theoretical value is for a plane surface of the electrode. Although the working electrode was polished for this experiment, a good microscope would show that the surface is not totally plane and consequently that the surface area is bigger than in theory. This means there would be more adsorption sites for the hydrogen atoms, which can partly explain the experimental results obtained.

Note: the number of protons absorbed and thus the number of adsorption sites can be determined by dividing the final result with the charge of a proton ($1.6 \cdot 10^{-19} \text{ C}$).

References:

- [1] Bio-Logic Technical Note #8 (<http://www.bio-logic.info>)
- [2] M. Chatenet, M. Aurousseau, R. Durand, and F. Andolfatto, *J. Electrochem. Soc.*, 2003, **150** (3), D47-D55.
- [3] S.-A. Sheppard, S.A. Campbell, J.R. Smith, G.W. Lloyd, T.R. Ralph, and F.C. Walsh, *Analyst*, 1998, **123**, 1923-1929.