Measuring Adsorption Processes on Platinum Electrodes using the Solartron ModuLab Potentiostat.

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Application Guide: ANML01

Introduction

The determination of the active surface area of Platinum is of great interest to electrochemists. For example fuel cell scientists wish to calculate the utilization of catalyst to improve performance and reduce costs. This is traditionally achieved using cyclic voltammetry as the diagnostic technique. Furthermore, the principles presented in this guide can be applied to the analysis of any cyclic voltammogram. This demonstration guide explains how such calculations are performed using the ModuLab software package.

Experimental

i) Chemicals and Electrodes

- WE: 2 mm Platinum Disk (Goodfellows >99.9 %) (working area = 0.0314 cm^2), CE: Platinum mesh, RE: Hg / Hg_2SO_4
- 0.5 M H_2SO_4

ii) Hardware Required

- 1 M sample s^{-1} ModuLab Potentiostat

iii) Software Settings

- 1st Vertex Potential = 1.2 V vs. Ref, 2nd Vertex Potential = -0.35 V vs. Ref
- Scan rate = 100 mV s^{-1}
- Measurement Mode: E change (amount of change = 5 mV)

Results and Discussion

A sample voltammogram is presented in Figure 1 with the oxygen and hydrogen regions identified. The shaded area represents the region associated with the desorption of hydrogen including double layer charging. The total charge is calculated using the following expression;

$$Q = \frac{1}{\upsilon} \int_{E1}^{E2} I.dE \qquad (1)$$

where Q = charge (C), υ = scan rate (V s^{-1}), E_1 = lower potential limit, E_2 = upper potential limit, I = current (amps)

To perform this calculation in ModuLab, follow these steps;

i)   Select the region of the curve to integrate. The software requires two markers to define this region; marker A defines E_1 and B defines E_2 (see Figure 1).
ii) (See Figure 2) change graph 1 to Q *vs.* t in the axes control panel and click *'Refresh'*. Note that the cursors are at the same point with respect to time as those in Figure 1.
iii) To calculate the total charge, subtract the value of the charge at point A from that at point B.

(Note: These values will appear on the screen when you hover over the green text boxes).

This is the total charge associated with this region of the I-V curve. One must now subtract the double layer charge.
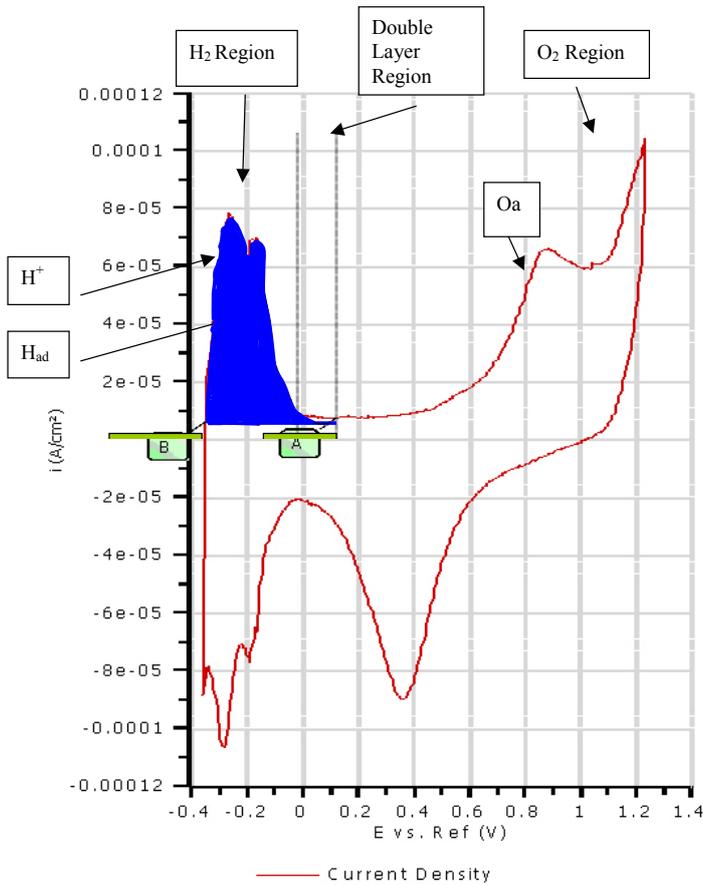

Figure 1: Cyclic Voltammogram of a Pt disk electrode in H_2SO_4. The hydrogen desorption region is highlighted in the shaded region.

Figure 3 shows the expanded I-V curve of the region of interest. The dashed regions (Cdl (a) and Cdl (b)) represent the double layer charging whilst the region H is charge associated with the desorption of hydrogen. To calculate Cdl (a) and Cdl (b);

i)   first define the baseline. Using the line fit tool in the fitting options, place two cursors on a linear section of the curve and click 'run'. The results of the regression analysis will be presented in the dialogue box together with the line fit in the graph.

ii)   Using the equation of a straight line, y = mx + c, calculate the value of I_2 at x = E_2. Similarly, calculate I_1 at x = E_1

iii)   For the area Cdl (b),

$$Q = \frac{1}{2\upsilon} \int_{E1}^{E2} I.dE \quad \text{or} \quad [(I_2\text{-}I_1)*(E_2\text{-}E_1)]/2 * \upsilon$$

iv)   Similarly, the area Cdl (a) ,

$$Q = \frac{1}{\upsilon} \int_{E1}^{E2} I.dE \quad \textbf{or} \quad [(I_1)*(E_2\text{-}E_1)]/ \ \upsilon$$

v)   Subtract both of these values from the total charge to yield the charge associated with the desorption step.
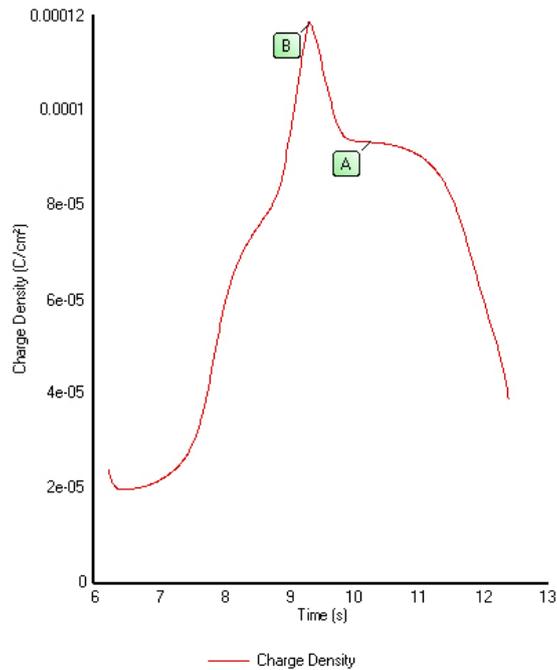
Figure 2: Plot of Q vs t (derived from Figure 1 in the software)

Worked Example

Using the data from the results in this note, the following calculation is intended to guide the user through the methodology presented in the previous sections.

i) Using Figure 2 to calculate the total charge: A = 9.32 x 10^{-5} C, B = 1.18 x 10^{-4} C.
    Therefore total charge (B - A) = 24.8 µC

ii) Using figure 3 to calculate double layer charging:

    Results of regression analysis, (y = mx + c)
    m = -1.58 x 10^{-6}, c = 1.134 x 10^{-6} .

    Therefore substituting for x, we can calculate the following
    I_2 = -1.58 x 10^{-6} x $E_{2|}$ (0.34 V) + 1.134 x 10^{-6} = 1.7 µA
    I_1 = 1.1 µA (at E_1 = 0V)

iii) Area Cdl (b) = [(I_2 - I_1) * | E_2 - E_1|] / 2
    =   [(1.7 µA) – (1.1 µA) * (0.34)] / 2 * 0.1
    =   1.02 µC

iv) Area Cdl (a) = [(I_1) * | E_2 - E_1|]
    =   (1.1 µA) * (0.34) / 0.1
    =   3.7 µC

Charge due to desorption = 24.8 μC – 4.7 μC = 20.1 μC for a 2 mm diameter electrode

*** or 639 μC cm^{-2}. ***

According to the literature, the charge associated with the monolayer adsorption of hydrogen = 210 μC cm^{-2}. The difference in results reflect the difference between the geometric and true surface area of the electrode under investigation.

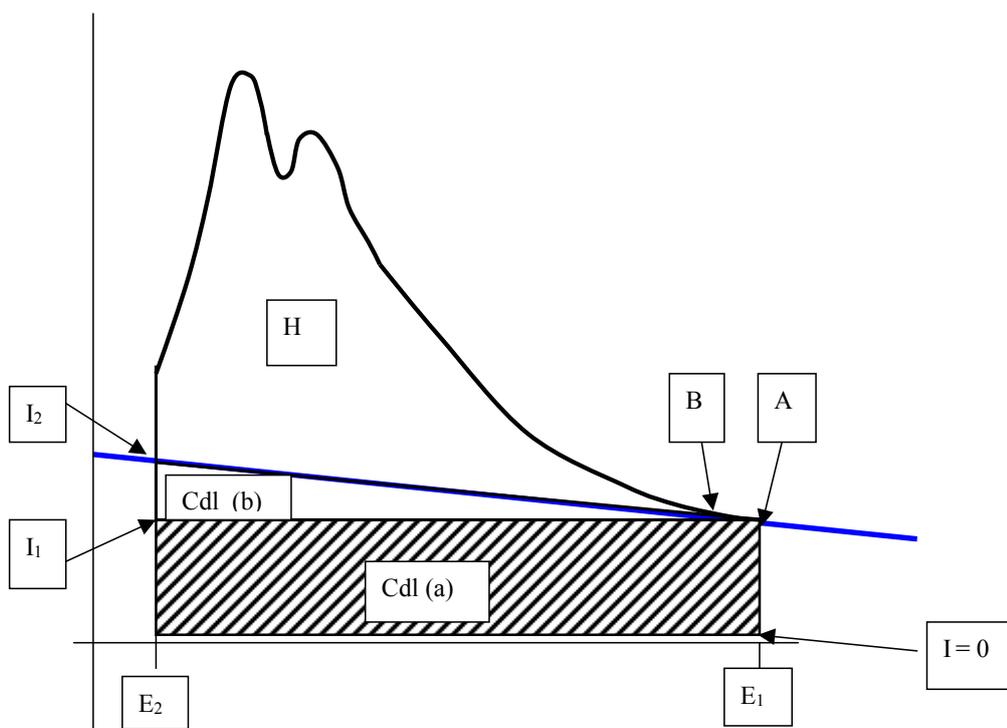Figure 3: Expanded I-V curve of hydrogen desorption region. (derived from Figure 1). The total charge, Q, comprises the charge associated with desorption (region H) and that of double layer charging (Cdl (a) and (b)).

Conclusions

The ModuLab software package allows the rapid and accurate determination of adsorption/desorption processes on electrode surfaces. This will be of great benefit to fundamental and applied electrochemical studies.

Application Note

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