

# Non-Faradaic Processes and Tafel Plots

## Chemicals and Instruments

Aqueous solution of sulfuric acid (1 M) purged with N<sub>2</sub>

Potentiostat

Pt wire counter electrode

Pt black electrode

Ag/AgCl/KCl(sat'd) reference electrode

Electrochemical cell or 3-necked flask

Thermometer

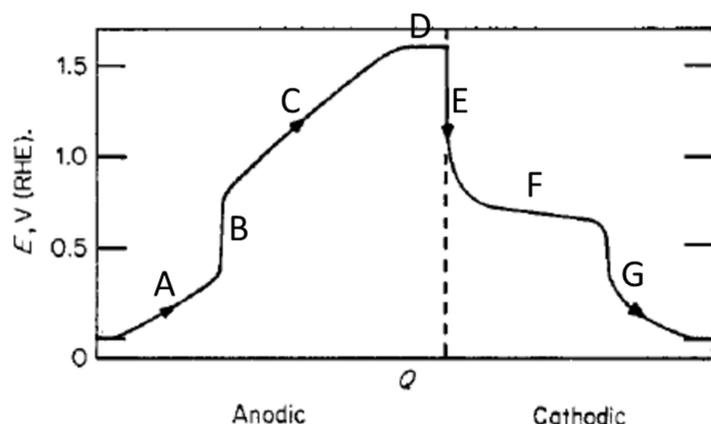
## Non-Faradaic Processes (B&F Chapter 1.2.4)

### Task

Estimate the surface area of a platinum black electrode from the charging curve. Measure the double-layer capacitance of the electrode from 1) the potential response to a current step and from 2) the current response to a linear potential sweep.

### Fundamentals

The active surface area of Pt black electrodes, as opposed to the apparent surface area, is usually measured by electrochemical deposition of hydrogen atoms on the surface. In this method, the electrode is electrochemically "cleaned". First the electrode is anodized to form oxide on the surface, and then a cathodic pulse is applied to reduce the oxide and to evolve H<sub>2</sub> from an aqueous electrolyte. Just prior to H<sub>2</sub> evolution, the electrode acts as a capacitor, accumulating charge corresponding to the deposition of a monolayer of H atoms on the surface. If a current step is used for this process, the charging curve looks like:



Charging curve for a platinized platinum electrode in an aqueous electrolyte.<sup>1</sup> A) Ionization of adsorbed hydrogen. B) Double-layer charging. C) Formation of a layer of adsorbed oxygen. D) O<sub>2</sub> evolution. E) Removal of adsorbed oxygen. F) Hydrogen adsorption (hydrogen arrest). G) H<sub>2</sub> evolution.

The charge passed during the hydrogen arrest is used to estimate the surface area of the electrode.

For a current step of magnitude  $i$ , the behavior of the potential,  $E$ , with time,  $t$ , is:

$$E = i \left( R_s + t / C_d \right)$$

For a potential sweep at a rate  $v$ , the behavior is:

$$i = v C_d \left[ 1 - e^{\frac{-t}{R_s C_d}} \right]$$

Where, in both equations,  $R_s$  is the solution resistance and  $C_d$  is the capacitance of the double layer.

## Procedure

Fill the cell or flask with the nitrogen-purged sulfuric acid solution.

Connect the Pt black electrode to the working electrode connection of the potentiostat. Connect the Pt wire electrode to the counter electrode connection of the potentiostat. Connect a Ag/AgCl/KCl(sat'd) reference electrode to the reference electrode connection of the potentiostat. Step the current from 0 A to 0.1 mA for about 20 s and then to -0.1 mA for another 20 s. Collect potential versus time data.

Connect a Ag/AgCl/KCl(sat'd) reference electrode to the counter electrode and reference electrode connections of the potentiostat. Connect the Pt black electrode to the working electrode connection of the potentiostat.

Step the current from 0 A to +50  $\mu$ A. Hold the step for tens of seconds. View the potential versus time data. The data should look linear (with a slope of  $i/C_d$  and an intercept on the E axis of  $iR_s$ ). Collect E versus t data for at least two more current steps of varied size. To observe only non-Faradaic properties (i.e., charging the double layer), the potential should not exceed  $\sim +0.8$  V.

Next, measure  $C_d$  by sweeping the potential from 0 V to +0.7 V, at a rate of +20 mV/s and collect current versus time data. Collect i versus t data for at least two more sweep rates.

## Work-Up and Questions

- 1) Plot the charging curve for the Pt black electrode. Estimate the surface area of the Pt black electrode assuming that charging the double layer of such an electrode in 1 M  $H_2SO_4$  requires  $\approx 210 \mu C \text{ cm}^{-2}$ .
- 2) Make plots of the E versus t data for the various current steps. For each data set, calculate  $R_s$  and  $C_d$ . Are the values consistent?
- 3) Make plots of the i versus t data for the various potential sweep rates. For each data set, calculate  $C_d$ . Are these values consistent?
- 4) Do the values of  $C_d$  measured by the two techniques agree?

## Tafel Plots (B&F 3.4.3)

### Task

Measure the exchange-current density and the slope of the Tafel plot for 1) H<sub>2</sub> evolution and 2) O<sub>2</sub> evolution from a platinum black electrode.

### Fundamentals

The Butler-Volmer equation describes the relationship between the current density,  $j$ , for a reaction and the overpotential,  $\eta$ , for that reaction. In the absence of mass-transfer effects:

$$i = i_0 [e^{-\alpha n f} - e^{(1-\alpha) n f \eta}]$$

Where  $f = F/RT$ ,  $n$  is the number of electrons transferred in the rate-limiting step, and  $\alpha$  is the transfer coefficient.

At large absolute overpotentials ( $|\eta| \gg 1/nf$ ), one of the exponential terms in the equation becomes negligible, and the equation can be simplified and rearranged:

$$i = i_0 e^{-\alpha n \eta}$$
$$\eta = \frac{RT}{\alpha n F} \ln(i_0) - \frac{RT}{\alpha n F} \ln(i)$$
$$\log(i) = \frac{-\alpha n F}{2.3 RT} \eta + \log(i_0)$$

Therefore, a plot of overpotential versus  $\log|i|$  is (mostly) linear with a slope diagnostic for  $\alpha$ , and an intercept of  $i_0$ .

### Procedure

Keep the Pt black electrode in the cell connected to the potentiostat as the working electrode and the Ag/AgCl/KCl electrode connected to the potentiostat as the reference electrode. Place the Pt wire electrode in the cell and connect it as the counter electrode.

For H<sub>2</sub> evolution, measure the potential of the electrode at  $i = 0$  mA. Increase the current stepwise to more negative values, taking at least 5 readings at different current values spanning at least 3 decades. For example,  $i = -0.001, -0.003, -0.010, -0.030, -0.100$  A. Observe the working and counter electrodes when the current is being passed.

Next set the working electrode to a positive potential sufficient to drive vigorous oxygen evolution ( $\approx 2.5$  V), and hold that potential for a few minutes (i.e., purge the solution with O<sub>2</sub>).

Repeat the experiment above using positive currents.

### Work-Up and Questions

- 1) Make a plot of overpotential versus  $\log(|j|)$  for H<sub>2</sub> evolution. What is the exchange-current density,  $j_0$ ? What is the slope of the Tafel plot?

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- 2) Make a plot of overpotential versus  $\log(|j|)$  for  $O_2$  evolution. What is the exchange-current density,  $j_0$ ? What is the slope of the Tafel plot?
- 3) Create a Tafel plot for  $H_2$  evolution and a Tafel plot for  $O_2$  evolution. What is the exchange current,  $i_0$ , in each case? What is the Tafel slope in each case?

## References

1. Feltham, A. M.; Spiro, M., Platinized platinum electrodes. *Chemical Reviews* **1971**, *71* (2), 177-193.