

CHEM-E6185 Applied Electrochemistry and Corrosion  
LABORATORY EXERCISES SPRING 2023

## ELECTROCHEMICAL MEASUREMENTS OF REACTION RATES, EFFECT OF OXIDANTS AND INHIBITION

### General

Completion of the course includes three laboratory exercises. The measurements in the laboratory will be done in max. 2 person groups, and each group will return one report. Each report is credited with maximum 15 points of the total course maximum 100 points.

The laboratory works are:

1. Measurement of oxygen evolution rate on permanent anodes using polarization curves.
2. Effect of oxidant on the corrosion of copper.
3. Measurement of inhibitor efficiency using electrochemical impedance spectroscopy.

Each laboratory exercise is estimated to take 3 hours work in the laboratory.

**Remember to bring your lab. coats and glasses!**

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## EXERCISE 1, Oxygen evolution in sulfuric acid

### Background

The purpose of anodes is to supply current to the electrochemical cell. A vast number of materials and their combinations are electrical conductors and may be used as anode materials. Most of the hydrometallurgical processes use sulphuric acid solutions. The main anodic reaction is oxygen evolution by decomposition of water. In these solutions, the traditional anode materials have been lead alloys, mainly due to their low cost. The oxygen overpotential of lead dioxide layer is high, and therefore mixed metal oxide anodes based on for example Ru or Ir as active component have been developed. When evaluating the electrochemical activity of a permanent anode, there are several ways to quantify it. The intrinsic electrocatalytic properties of an anode material towards oxygen evolution can be simplified to exchange current density and Tafel slope. High exchange current density, low starting potential and low Tafel slope are beneficial. The ultimate aim is to have high current density at low operating potential. The task is to compare anodes and estimate their effect on cell voltage.

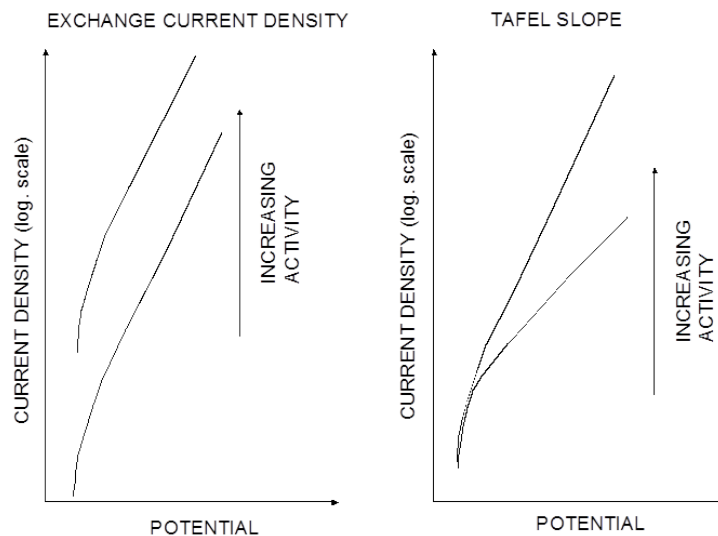


Fig. 1. Anode properties affecting its efficiency.

### Experimental

The task is to measure anodic polarization curve for three different anode materials:

- Traditional PbCa1 alloy
- Experimental activated Pb anode (alloying elements include Sn and Ir)
- Mixed metal oxide (MMO) electrode with Ir-Ta oxide active coating.

Tests are done in 150 g/l sulphuric acid at room temperature. Test consists of preoxidation of the anode at 5 mA/cm<sup>2</sup> for 10 minutes followed by anodic polarization curve at scan rate 100 mV/min. Automatic IR-compensation can be used. The test can be interrupted at 40-50 mA/cm<sup>2</sup>.

The test cell is a normal three-electrode cell with Pt counter electrode and saturated sulphate reference electrode.

### Result analysis

The parameters describing anode activity can be put into equation (1)

$$E_{op} = E_{eq} + \log\left(\frac{i}{i_0}\right) \cdot b_a \quad (1)$$

where  $E_{op}$  is operating potential,  $E_{eq}$  is equilibrium potential,  $i$  is operating current density,  $i_0$  is exchange current density and  $b_a$  is Tafel slope. As equilibrium potential and exchange current density apparent values as shown in Fig. 2 can be used. The anode-dependent parameters in equation (1) are Tafel slope, equilibrium potential and exchange current density.

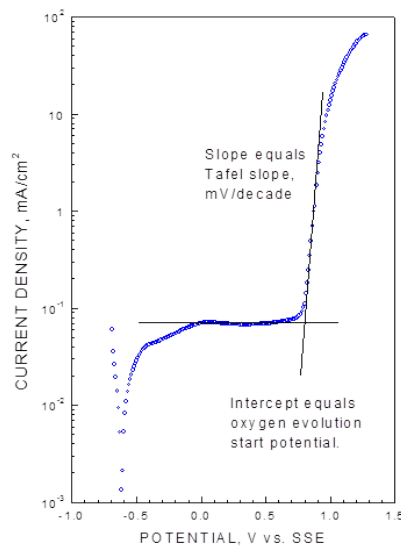


Figure 2. Analysis of the polarization curve.

Make plots of the anodic polarization curves. Determine the starting potential and current density of oxygen evolution and Tafel slope for all anodes. Tabulate these values. Write the equations in the form of eq. (1) describing the operating potential for the three anodes and using these equations calculate the potential at current densities 100 and 300 A/m<sup>2</sup>.

Find out the typical cell voltages in Cu, Ni and Zn electrowinning. Make an estimate how much energy could be saved if the PbAg-alloy is replaced either by the experimental lead anode or the MMO anode.

## Report

- Short introduction that includes the background. Find out few references about base metal electrowinning and energy consumption, especially the drawbacks of lead anodes.
- Short description of the test equipment, test environment and data analysis methods.
- Results and discussion showing examples of measured data, data analysis example and tabulated values describing the anode performance. Discuss the energy savings.
- Conclusions shall include ranking of the anodes and decision whether the energy savings are significant (for example energy costs vs. metal price).
- Literature references well documented.

## EXERCISE 2, THE EFFECT OF OXIDANT ON CORROSION OF COPPER

### Background

Copper canisters are used in the disposal of nuclear waste. The corrosive environment in the bedrock will be saline water with varying levels of dissolved salts, pH and redox potential. The current view is that the environment will be oxic at the beginning but turn to anoxic when the remaining oxygen has been consumed. Another view is that corrosion can also happen in the anoxic environment because dissolved copper can act as oxidant. The task of this exercise is to measure corrosion rate of copper under air purging, nitrogen purging and nitrogen purging with cupric ions.

### Experimental

Copper corrosion is measured in saline water at room temperature in a three-electrode cell. The test solution is synthetic ground water on bentonite pore water. The copper material is Cu-OF rod. Three samples are needed. Counter electrode is Pt and reference saturated calomel SCE.

Measure the geometric surface area of the sample. Clean the sample surface by water grinding with 800 mesh paper and pickle the surface by immersing it three times for 3 minutes in 10% citric acid. Rinse with water between immersions and finally with water and ethanol.

Measure a volume of about 400 ml of water and record the volume.

Measure a polarization curve from -200 mV to +200 mV vs. OCP. Use scan rate 50 mV/min.

First test is in air purged solution. The water will be purged by air for 30 minutes. Measure the oxygen concentration with a Hanna DO meter. Record the potential of the Pt counter electrode. Second test is nitrogen purged solution. After the first measurement purge the water with nitrogen for 30 minutes and measure DO level and Pt potential. In the third measurement continue with nitrogen purging but add few ml of 0.1 M  $\text{CuSO}_4$  solution. Measure the DO and Pt potential.

### Result analysis

Plot the polarization curves. Calculate the corrosion current density with Tafel method and then corrosion rate as  $\mu\text{m}/\text{year}$ .

### Report

- Short introduction that includes the background and typical factors that can affect copper corrosion in natural waters.
- Short description of the test equipment, test environment and data analysis methods.
- Results and discussion showing the Tafel plots and calculated corrosion rates.
- Conclusions of the corrosion rates, how much did the oxidants affect corrosion rate.
- Literature references well documented.

### EXERCISE 3, Inhibitor efficiency in acid solution

#### Background

Inhibitors are chemicals that can decrease corrosion rate of metals at low concentrations. The inhibitors can be classified using their operating mechanisms: Anodic inhibitors decrease the rate of the anodic reaction, cathodic inhibitors that of the cathodic reaction and film-forming inhibitors cover the surface of metals and thereby decrease rate of both reactions. The efficiency of an inhibitor can be determined by comparing the corrosion rates at different inhibitor levels.

#### Experimental

The test solution is tap water with pH raised with 1 M NaOH to above 8 or lowered to below 4 with 1.5 M H<sub>2</sub>SO<sub>4</sub>. Test material is cast iron. The inhibitor is sodium nitrite in tap water as 100 g/l solution or tannic acid in tap water as 100 g/l solution. Sodium nitrite is used in alkaline water and tannic acid in acid water.

Test cell is a standard three electrode cell with Pt counter electrode and calomel reference electrode.

Measure a volume of tap water (about 400 ml) and record the volume. Measure the dissolved oxygen and pH of the solution

Measure first the EIS without inhibitor. Then add inhibitor solution in 1-2 ml steps and measure the EIS after each inhibitor addition. The inhibitors should provide 95% protection at some point, but if that is not reached then the inhibitor is considered as not effective.

#### Result analysis

Plot the impedance spectra as Bode plots, log (Z) and phase angle vs. log (f).

Determine the polarization resistance and double layer capacitance values.

Calculate the inhibitor efficiencies using the polarization resistance values using equation (1), where R<sub>p0</sub> is without inhibitor and R<sub>pi</sub> with inhibitor.

$$\eta = \frac{1/R_{p0} - 1/R_{pi}}{1/R_{p0}} \quad (1)$$

Using the mixed potential theory, analyze if the inhibitor is anodic, cathodic or film-forming. A film-forming inhibitor should show linear dependence between efficiency and surface coverage. The surface coverage can be calculated from capacitance values

$$\mu = 1 - C_{di}/C_{d0} \quad (2)$$

To determine the capacitance, you can use at least two methods. These are given for example in Robert G. Kelly, John R. Scully, David W. Shoesmith, Rudolph G. Buchheit, *Electrochemical Techniques in Corrosion Science and Engineering*. Marcel Dekker Inc, New York 2002, 426 p.

When using the Bode plot

$$C_{dl} = \frac{1}{\omega_{max,Bode} \cdot R_p} \cdot \left(1 + \frac{R_p}{R_\Omega}\right)^{1/2}$$

Select from the Bode plot the frequency that corresponds to phase angle maximum and calculate the angular velocity  $\omega_{max, Bode}$  and determine the polarization resistance  $R_p$  and solution resistance  $R_\Omega$  from the minimum and maximum impedance values of the Bode plot.

When using Nyquist plot

$$C_{dl} = \frac{1}{\omega_{max,Nyquist} \cdot R_p}$$

Select from the Nyquist plot the frequency at which the imaginary component of the impedance has its largest value.

A film-forming inhibitor should show linear dependence between efficiency and surface coverage. The surface coverage can be calculated from capacitance values

$$\mu = 1 - C_{di}/C_{d0}$$

Note that this assumes that the capacitance decreases with increasing inhibitor concentration. If the capacitance increases one method is to compare the system with inhibitor to systems with no inhibitor and full inhibitor coverage.

$$\mu = \frac{C_{d0} - C_{di}}{C_{d0} - C_{d\ max}}$$

In this analysis the  $C_{d\ max}$  is the highest capacitance value. It should describe the system with full surface coverage, but that is not always certain. The capacitance depends on all adsorbed species, not only on the inhibitor coverage.

## Report

- Short introduction that includes the background, hypotheses and description of the methods to verify hypotheses about inhibitor mechanism.
- Short description of the test equipment, test environment and data analysis methods.
- Results and discussion showing examples of measured data (2-3 plots), tabulate all  $R_\Omega$ ,  $R_p$  and  $C_{dl}$  values, and calculated inhibitor efficiencies and coverages.
- Plots of efficiency and coverage vs. inhibitor concentration.
- Conclusion about the inhibitor function, did it work using the test concentrations, what is the typical concentration based on literature and the inhibitor mechanism.
- Literature references well documented.