

# Practical 2P7- Corrosion

## Safety

All electrical equipment must be treated with respect; under no circumstances should students open or interfere with electrical apparatus.

Chemicals must be handled with care (for instance by protecting eyes with safety spectacles when handling acids); you will need to check with the demonstrator whether any special precautions are needed for the solutions you are asked to use. If acid is spilled, clear it up promptly wearing rubber gloves to protect your hands. Safety specs and gloves should be worn at all times.

When you have finished the practical, you **must**:

- Exit from Windows and switch off the computer
- Turn off the potentiostat
- Dispose of the test solution
- Rinse out the cell and then rinse and dry the electrodes



# Practical 2P7- Corrosion

## Aims

To introduce students to using a computer controlled potentiostat for electrochemical measurements and familiarise them with fundamental concepts of corrosion.

You will study corrosion of iron in acid and investigate how pH influences the anodic and cathodic reactions. You will also plot polarisation curves for stainless steel to see different passivation behaviours.

## Materials

- Fe wire
- Stainless steel wire

## Electrolytes

Two different concentrations of sulphuric acid (ideally with sulphate ion concentration maintained constant) with different pH,

e.g.:

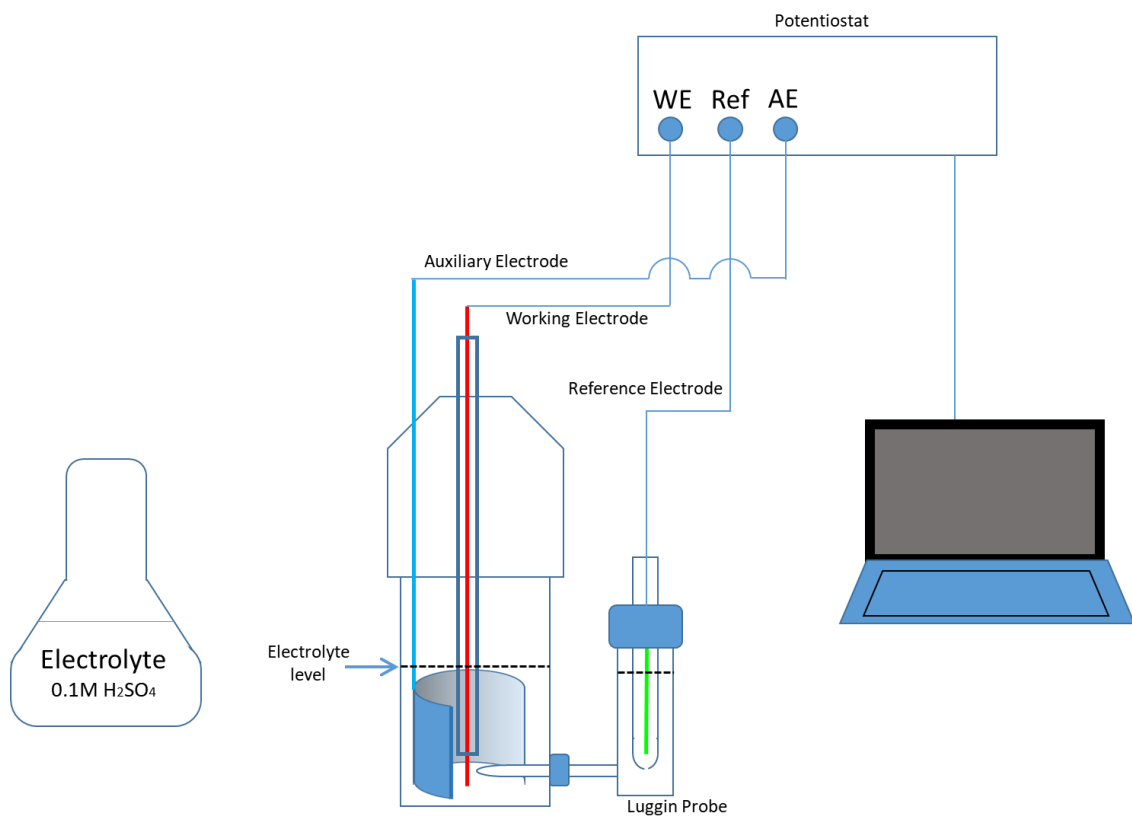
- 0.1M  $\text{H}_2\text{SO}_4$
- 0.01M  $\text{H}_2\text{SO}_4$  + 0.09M  $\text{Na}_2\text{SO}_4$

If time allows:

- 3% NaCl solution (optional, only to be used with the stainless steel sample)

## Apparatus

1. Laptop and potentiostat.
2. Cell containing the specimen, a counter electrode and side arm (Luggin capillary) holding a saturated calomel reference electrode - all are immersed in the test solution.



## Experimental Aims

### 1) Determine the Tafel constants and the polarisation resistance

- a) Compare the behaviour of iron and steel
- b) Compare the effects of PH for iron

For this, two polarisation curves have to be plotted for each electrolyte:

- A. For a wide range of overpotentials relative to the rest potential (say, -150mV to +120mV). This allows the Tafel slopes ( $b_a$  and  $b_c$  to be determined and the corrosion current estimated, by extrapolating the linear Tafel regions to the corrosion potential.
- B. For a narrow range of overpotentials: +20mV to -20mV and back (using a slower scan rate). This will allow the linear polarisation resistance to be determined and the corrosion current to be calculated from the Stern-Geary equation using the values of  $b_a$  and  $b_c$  determined from (A).

**Compare the value** from B) with the value estimated from extrapolation of the Tafel lines in A).

**Use two concentrations** of sulphuric acid to make these measurements for the iron sample, ideally with sulphate ion concentration maintained constant). Use the same iron sample. We expect that an increase in hydrogen ion concentration will increase the cathodic exchange current, but you should also see a decrease in the anodic current because iron dissolution is catalysed by hydroxyl ions.

**Calculate the pH** of the two electrolytes used assuming that the  $H_2SO_4$  behaves as a strong acid. Include your calculations in the report.

## 2) Compare the anodic behaviour of Fe and stainless steel

NOTE: The stainless steel sample will only be tested in the 0.1M  $\text{H}_2\text{SO}_4$  solution.

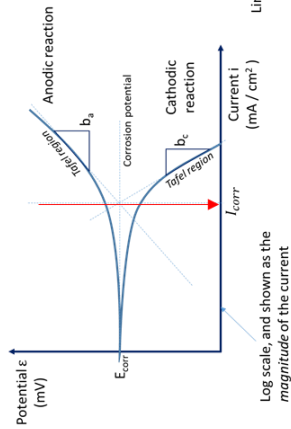
**Compare/discuss the passivation behaviour** of Fe and steel in the 0.1M  $\text{H}_2\text{SO}_4$  solution. For this you will have to use a much higher Stop potential (typically >1500mV). This time, you might want to run a full polarization cycle to better study the passivation behaviour while the potential is decreased after transpassivation has been reached. See the “Anodic behaviour of metals” for more details.

**Describe/discuss potential sources of error** in your measurements.

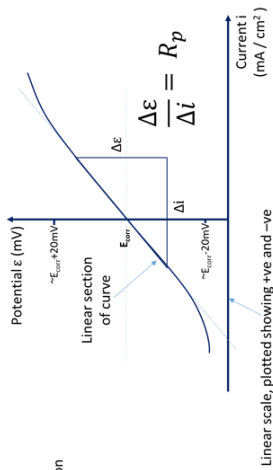
3) **Optional:** If time allows, acquire a polarization curve for the stainless steel sample in the NaCl solution. Describe/discuss the results.

## Data to collect

### Tafel plots



### Linear polarisation curve



Electrolyte 1: Iron, Stainless Steel

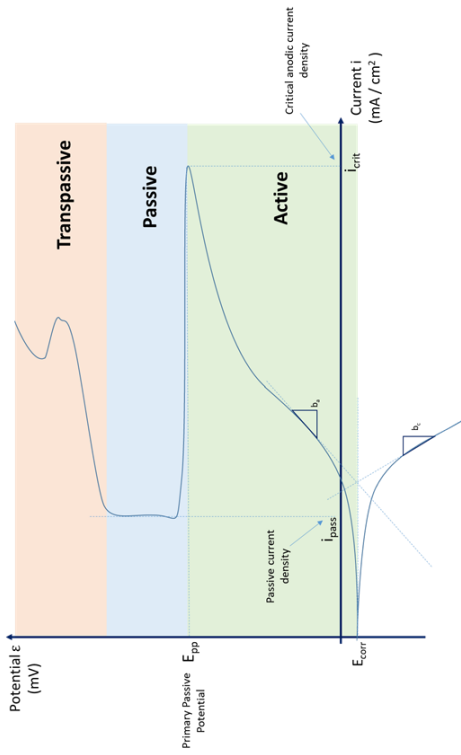
Electrolyte 2: Iron

$$I_{corr} = B / R_p \quad \text{where } B = \frac{b_a b_c}{2.3(b_a + b_c)}$$

Determine  $I_{corr}$  by extrapolating the Tafel regions of your Tafel plot. Compare this to a calculation of  $I_{corr}$  from the Stern-Geary equation, using the values of  $b_a$  and  $b_c$  from the Tafel plot, and  $R_p$  from the linear polarisation curve.

What are the differences between iron and stainless steel? What is the effect of PH?

### Anodic behaviour



Capture the anodic behaviour of the materials by studying the polarisation curve over a larger potential range. We are looking to capture the active, passive and transpassive zones of the polarisation curve, noting  $I_{crit}$ ,  $E_{pp}$  and  $I_{pass}$ .

When does iron passivate compared to stainless steel?  
How does the curve change when we change the PH?

## Theory

### Determination of the Tafel constants, the corrosion current and the linear polarisation resistance from polarization curves

In corrosion, metal is able to dissolve because the anodic current required to oxidise the metal comes from cathodic reduction of another species, often oxygen. At the corrosion potential the rates of the anodic and cathodic reactions are equal (i.e.  $I_a = I_c = I_{\text{corr}}$ ). In corrosion experiments, we usually control the potential of a metal sample with a potentiostat and measure changes in current. The measured E/I characteristic is called a polarisation curve. Under activation control, both anodic and cathodic currents increase exponentially with overpotential, so that if  $\log I$  is plotted against E (a Tafel plot), linear regions are seen on both anodic and cathodic curves. The linear regions correspond to potentials where either anodic or cathodic reaction dominates. Near the corrosion potential the current is the difference between the anodic and cathodic current, which is non-linear on this plot. Extrapolation of the straight lines to the corrosion potential should indicate the corrosion current (anodic and cathodic current being equal). The slopes of the lines can provide mechanistic information, but we will use them here as another method of finding corrosion current.

For large currents the presence of concentration polarisation (arising from diffusion effects) or resistance polarisation (from potential drops in solution between the sample and the reference electrode) can lead to non-linear Tafel plots. The potentiostat is equipped to correct resistance polarisation ( $iR$  drop) if  $R$  is known.



A commonly used method to monitor corrosion in industry is the "polarisation resistance" method. If a small current is passed between two identical probes corroding in an installation, the potential of one is raised, that of the other is lowered. If the potential shift is less than about 30mV, the magnitude of the shift  $\Delta E$  at each of the electrodes (half the total) is proportional to the impressed current  $\Delta i$ . The ratio  $\Delta E/\Delta i$  is known as the polarisation resistance,  $R_p$ , and is related to the corrosion current at the corrosion potential by the Stern-Geary equation:

$$I_{corr} = B / R_p$$

The proportionality constant,  $B$ , for a particular system can be determined empirically (calibrated from separate weight loss measurements) or, as shown by Stern and Geary, can be calculated from  $b_a$  and  $b_c$ , the slopes of the anodic and cathodic curves in a Tafel plot. The relationship is:

$$B = \frac{b_a b_c}{2.3(b_a + b_c)}$$

In this practical, the polarisation curves will be plotted, for iron in 0.1M  $H_2SO_4$  and 0.01M  $H_2SO_4$  + 0.09M  $Na_2SO_4$ , using the ACM software and potentiostat and the results analysed on computer to determine the Tafel constants, the linear polarisation resistance and to compare the corrosion current obtained by linear extrapolation of Tafel lines and using the Stern-Geary equation.

## **Experimental Method** (*lab instructions*)

Fit the reference electrode into the side compartment via the screw cap and insert the Luggin probe into the cell. Tighten the caps. Support the cell in a retort stand and fit the counter electrode. Fill the cell (~ half-way so it covers the auxillary electrode) with test solution – loosen the screw cap on the side arm to allow air to escape and the side compartment to fill with solution. Bubbles in the capillary will break the electrical circuit and prevent correct operation of the potentiostat. The cap can now be fitted over the counter electrode lead. Clean the sample and use SiC paper to remove the surface oxide layer, taking care not to pull the wire out of the glued end. Before insertion, use the calipers to measure the dimensions of the exposed sample, and calculate the surface area. Insert the sample such that it sits centrally surrounded by the counter electrode with the tip of the Luggin probe 1-2 mm away. (Loosen screw caps to adjust, then retighten).

### **Determination of the Tafel constants and estimation of the corrosion current**

*Note: these instructions are written for the ACM-Gill AC potentiostat. A different set of instructions will be provided for those using the newer Biologic potentiostat.*

- 1) Switch on the PC and potentiostat; assemble and connect the cell, ensuring that the electrodes are connected correctly (as indicated by the labels on the wires).
- 2) Click “start” button, select “programs”, find “Gill AC Serial No.### sequencer” and click to open.
- 3) Select “Sequencer” by double clicking – this gives overall control of experiments and can set up a lengthy sequence of operations, but you will only need to run one at a time.
- 4) In sequencer, select “cyclic sweep” by clicking once, which will then appear in the sequence list on the left hand side. Subsequent operations can all be conducted by clicking on this icon in your list. Don’t select

“cyclic sweep” again or you’ll get two in your sequence.

- 5) Click on “cyclic sweep” in sequence list.
- 6) Verify that "Offset sweep to rest potential" box has been checked - this will ensure that the potential is controlled with respect to the rest potential.
- 7) Make sure that “Autoranging during test” is checked – this will ensure that currents can be measured accurately across a wide range of values and protect the instrument from damage.
- 8) Set “cycles” to 0.5 initially by clicking the up/down buttons– this gives half a cycle (just upwards; later you may want to set 1 cycle, to see up and then down).
- 9) It will be useful to check and set a “cell settle time” (a short pause at the start potential, say 20s) to give the electrode a moment to adjust to the initial polarisation.
- 10) To set up the polarisation curve select the following sweep parameters:

**Start Potential = -250mV**

**Stop Potential = +250mV**

**Sweep Rate = 100 mV/min**

To set the start potential and the stop potential etc, click the mouse with the pointer on the appropriate box and enter the above values. The demonstrator can show you other ways to set up this window. Trial runs can be carried out at a faster rate; good results may require a slower one. You may need to carry out repeat tests on the same sample - varying control parameters as required - but  $I_{\text{corr}}$  will change over time. That’s OK. It’s up to you to find experimental conditions that give good

results. The demonstrators will help.

- 11) Before you start each run, you will need to enter a file name for the data in the data storage box (at bottom). Make sure you change the name each time you run, or you will overwrite existing results (OK if you don't want to keep – but you may want to discuss strange results with me). It is also useful to enter the surface area of your sample (measure and calculate), so you can obtain current densities.
- 12) Double click on the "Run now" button to begin the run. The program will then plot the polarisation curve automatically on E-log(I) axes. If you fail to achieve good results, it is sometimes better (but more troublesome) to do two scans away from the corrosion potential rather than a single sweep in one direction.

There is a display of various useful information below the toolbar in the “core running” window that you can check while the experiment runs:

- “Int CR” is the value of the counting resistor (used to convert current to a voltage for the computer to measure) – it should change in steps as current rises or falls.
- “Reading” – is the number of the measurement in progress. Potential and current tell you the latest measurement.
- “Rp” (would you believe!) displays the initial rest potential, not polarisation resistance.

Note: If you don't see this window when a run is in progress, then click on “core-running”.

When a run is finished you can click on “sequencer”, select “cyclic sweep” in the left-hand list (not main bicycle icon), reset parameters and click “run now” to do a new experiment.

### **Analysing the Data**

Once the graph has been drawn, you can select the analysis icon to analyse your result. You can leave all analysis until the experiments are finished, but it is useful (always) to check how successful your measurements are before proceeding further.

- 1) When the Analysis window appears all your graphs will be in view as icons; double click the new graph and its file name will appear in the list at the bottom. To plot this graph, you need to check “yes” against the file (default) and “no” against other files. By selecting several files, you can plot the results all together in one graph.
- 2) Click on the "Draw Graph" button to see your graph. Note that the current scale is logarithmic, so that anodic and cathodic currents plot in the same direction. Identify where the currents trend towards zero ( $E_{corr}$ ). You can switch to a “potential-current” plot in the main graph window (click for menu) if you are confused. Here, sign of the current is apparent. Select Tafel plot to return.
- 3) To determine Tafel slope and corrosion current, select "Tafel Rulers" on the toolbar at the top of the display. You will now see a set of three lines on your graph: a Horizontal Rest Potential (HRP) line and two diagonal rulers - one above the HRP line and one below. These lines can all be moved using the mouse as follows:

- i) Move the mouse pointer until it is on the HRP line (  $\updownarrow$  will appear)

and then, with a mouse button pressed, drag the line up or down until it intersects the "point" at the left-hand side of the plot.

- ii) The two diagonal lines can be fitted to linear parts of the curve by moving the mouse into either box (when you see  $\updownarrow$ ), then hold a mouse button (LH end with L button, RH end with right) to drag either end of the line horizontally till you are happy with the fit.
- 4) Ideally, these two lines will intercept the HRP line at the same point. This point represents the corrosion current.
  - 5) The values of the Tafel slopes and both intercepts can now be read off at the top of the screen.
  - 6) To print a copy of your graph, click the printer icon as usual. The demonstrator can tell you which network printer to use. You can add labels to your graph first if you wish. If you want colour graphs, you will need to save your files and print later in the computer room.

### **Determination of the linear polarisation resistance**

This part of the experiment is carried out on the same sample in the same solution, but the cyclic sweep is set up over a small potential range

- 1) Create another file in which to store your data as outlined previously.
- 2) Select the following sweep parameters:
  - Start Potential = - 50 mV;**
  - Stop Potential = 50 mV;**
  - Sweep Rate = 20 mV/min**
- 3) Set at least one cycle (two?).
- 4) Click on the "Run now" button.
- 5) When the run is complete, select "Analysis" again and follow the same procedure as before to recall your data. When the graph has been drawn, select "potential current" from the graph menu. You should see

a straight line plot of  $E$  vs  $I$ .

- 6) Select a section of the curve to determine the slope at the corrosion potential, when  $I=0$  (this might not necessarily be the straight portion of the graph!). Click on the cursor icon in the toolbar, move the arrow to a point on the trace and place cursor 1 by pressing the left button. Place cursor 2 with the right button. Now LPR should show top right. Make sure you know whether this is for your whole sample, or unit area (depends on settings). If the line is not straight, a tangent drawn at zero current gives a perfectly valid result.
- 7) Print a copy of the graph. You can measure LPR from any trace by selecting a potential-current plot on linear axes and zooming in onto the region around the corrosion potential (done by clicking “zoom”, moving the cursor to the top corner of your chosen area, then clicking a mouse button and dragging a rectangle). This area will then plot. Fit a section with the cursors.

### Anodic Behaviour of Metals

In this part of the experiment you will use the same equipment to plot qualitative curves, so you can see for yourselves various different features of the anodic behaviour of metals. All you need to do is obtain and plot out polarisation curves. Samples of stainless steel and iron will be provided.

To capture the various features of anodic behaviour, you will need to use a much higher stop potential ( $\sim 2V$ ). If your sweep rate is too high, you might not see the formation of a passive layer (try 200mV and adjust if need be).

Make sure your write up explains the form of the curves and explains how the plot arises from separate anodic and cathodic reactions. Remember that some alloys will passivate spontaneously, so that  $E_{\text{corr}}$  lies above the active peak and only passive currents are seen. Pay attention to the **size** of the

measured current densities in deciding what they mean.

The main features you are likely to see are active dissolution, passivation (where growth of an oxide film by anodic oxidation brings an end to active dissolution), transpassivity (where a passive film is oxidised to soluble ions and anodic current increases) or pitting (Above a critical "pitting potential" you will see an erratic breakdown of passivity and a sudden increase of current when pits begin to grow). In this case, if the potential is scanned downwards again (by using a full polarization cycle), behaviour is not reversed, but repassivation does eventually occur.

In acid, the cathodic curve will show Tafel behaviour, but in the neutral solution a limiting current for oxygen reduction should be observed. For iron in sulphuric acid, the onset of passivation is preceded by deposition of a salt film (iron(II) sulphate, that leads to diffusion controlled dissolution.

Try to vary the samples and test solutions for this part of the experiment: ask the junior demonstrator how best to test the ones you have been provided with. You need only report your own results, but it may be of interest to compare notes with others.

#### **Assessment:**

Log book only.

#### **References**

"Electrodeposition and Corrosion Processes"

J.M. West



"The Fundamentals of Corrosion"

J.C. Scully

"Principles and Prevention of Corrosion"

D.A. Jones

### **Analysing the data using excel**

*This part is only relevant if you are following the experiment online and do not have access to the potentiostat software.*

The data from this practical is provided as comma separated variable (csv) files, in txt format.

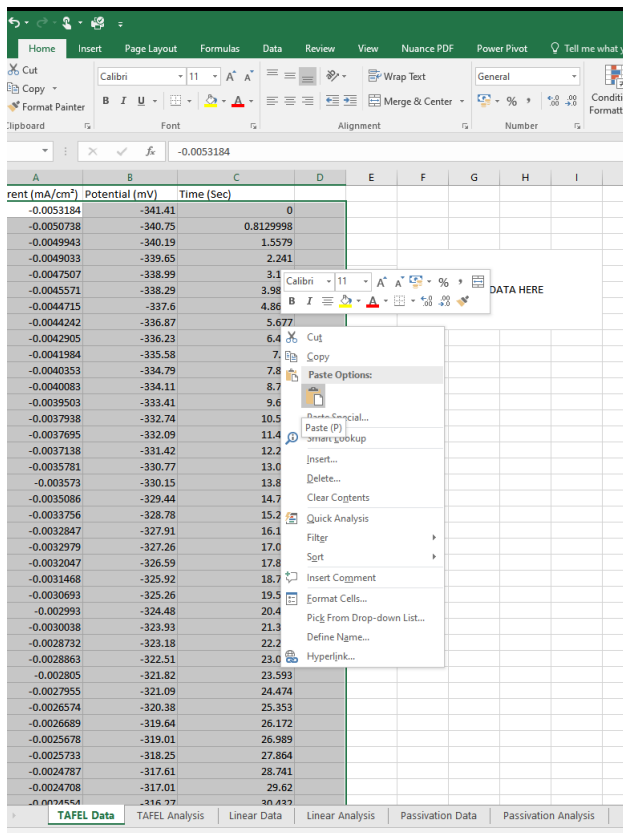
Name	Date modified	Type	Size
iron linear 0.01M h2so4.txt	26/11/2020 17:18	Text Document	24 KB
iron passivation 0.01M h2so4.txt	26/11/2020 17:19	Text Document	34 KB
iron passivation 0.1M h2so4.txt	26/11/2020 14:39	Text Document	32 KB
iron tafel 0.01M h2so4 2.txt	26/11/2020 17:17	Text Document	15 KB
iron tafel 0.1M h2so4 2.txt	26/11/2020 14:52	Text Document	14 KB
SS linear 0.1M h2so4.txt	26/11/2020 17:23	Text Document	25 KB
SS passivation 0.1M h2so4.txt	26/11/2020 17:23	Text Document	33 KB
SS passivation 3% NaCl.txt	26/11/2020 17:25	Text Document	34 KB
SS tafel 0.1M h2so4 2.txt	26/11/2020 17:21	Text Document	15 KB

We can import this data into excel in various ways. The easiest is to simply open the file in Notepad (or TextEdit in Mac) and copy and paste into excel. You can ignore most of the header text, though you might want to make note of the area, as indicated.

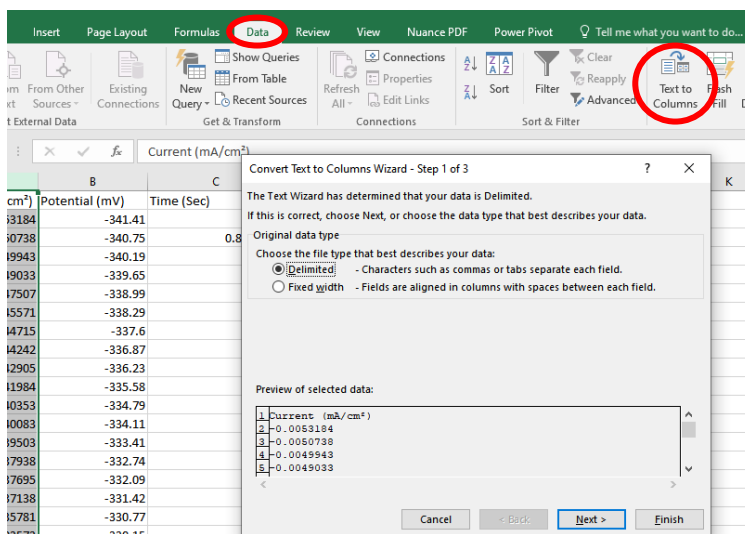
SS tafel 0.1M h2so4 2.txt - Notepad
File Edit Format View Help
ACM Instruments v4 analysis (26/Nov/2020 17:21)
File name,C:\Users\jackc\Documents\2 - POST DOC\teaching\corrosion data\data\
Test type,Cyclic sweep,
Instrument serial number,1085,
Physical channel,1,
Sequence number,1,
ZRA Number,n/a,
Time and Date,09:58:12 17/Nov/2020,
Data points,526,
Area (cm²),0.449,
Rest Potential (mV),-161.23,
Metal,Stainless Steel (13Cr),
Metal factor,1123,
LPR (Ohm.cm²),76657,
Ba (mV),120,
Bc (mV),120,
Icorr (mA/cm²),0.0003403,
Corrosion Rate (mm/year),0.0038216,
Corrosion rate (mils/yr),0.1504585,
Intercept (mA/cm²),0,
Intercept corrosion rate (mm/year),0,
Intercept corrosion rate (mils/yr),0,
IR Compensation value (Ohm.cm²),N/A,
Current (mA/cm²),Potential (mV),Time (Sec),
-0.0053184,-341.41,0,
-0.0050738,-340.75,0.8129998,
-0.0049943,-340.19,1.5579,
-0.0049033,-339.65,2.241,
-0.0047507,-338.99,3.115,
-0.0045571,-338.29,3.9899,
-0.0044715,-337.6,4.8639,
-0.0044242,-336.87,5.677,
-0.0042905,-336.23,6.487,

SS tafel 0.1M h2so4 2.txt - Notepad
File Edit Format View Help
0.0023847,-3.6556,405.29,
0.002474,-2.9986,406.16,
0.0024845,-2.2879,406.97,
0.0023939,-1.6694,407.78,
0.0024699,-1.0212,408.65,
0.0024311,-0.2949569,409.52,
0.0024542,0.398942,410.08,
0.0025159,1.215,411.02,
0.002456,1.9505,411.89,
0.0025381,2.6097,412.83,
0.002462,3.3406,413.7,
0.0024387,3.9963,414.57,
0.0024752,4.6991,415.38,
0.0025159,5.3873,416.19,
0.0024777,6.0682,417,
0.0024738,6.6426,417.82,
0.0025314,7.3339,418.38,
0.0025094,8.0634,419.25,
0.0025271,8.7821,420.13,
0.002581,9.4679,421,
0.0025782,10.202,421.89,
0.00251,10.875,422.76,
0.0025879,11.546,423.63,
0.002586,12.214,424.44,
0.0025667,12.867,425.31,
0.0025666,13.574,426.19,
0.0026193,14.322,426.75,
0.0025674,15.033,427.62,
0.0026107,15.79,428.49,
0.002655,16.48,429.36,
0.0026363,17.141,430.24,
0.0025785,17.888,431.12,
,431.68,

Open the provided excel file and, starting with the Tafel data, copy and paste the data into the sheet labelled “Tafel Data”.

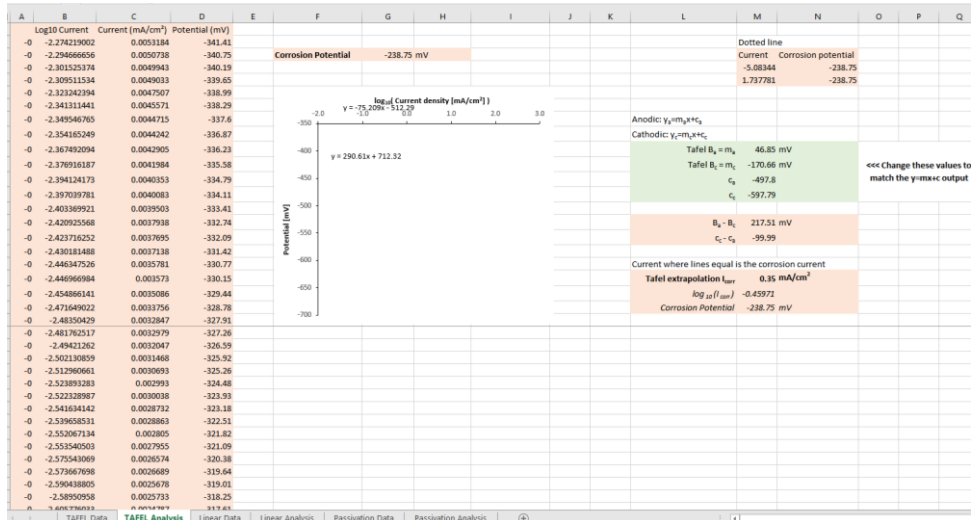


If the data doesn't automatically separate itself into distinct columns, then you'll need to do a Text to Data conversion:

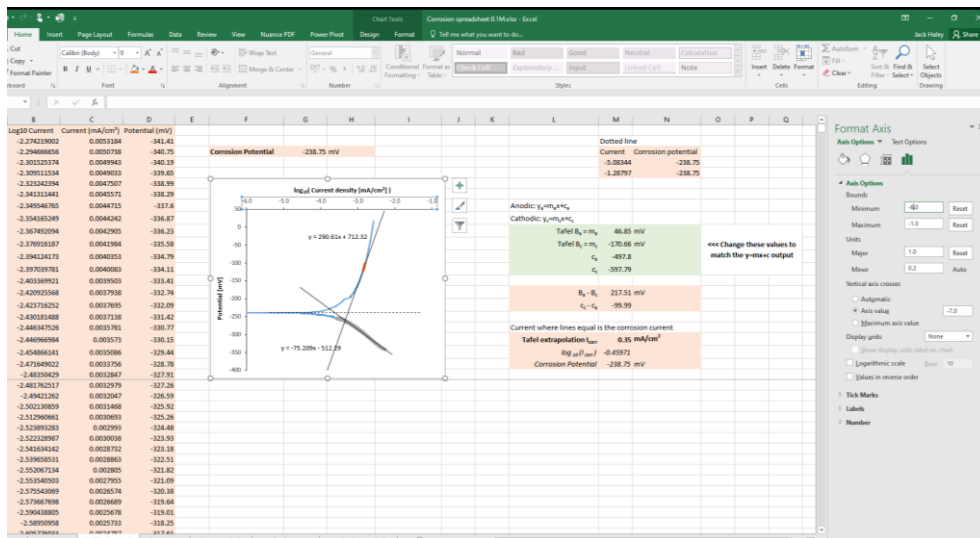


For the text to data conversion, select "Delimited", click next, then tick the checkbox next to "comma" and hit finish.

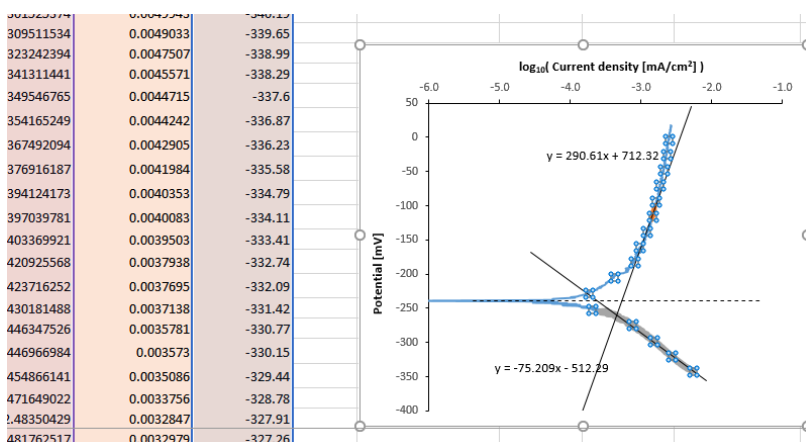
Now navigate to the “Tafel Analysis” sheet. You should see the data from the previous sheet on the left hand side, but this is now modified to the log of the magnitude of the current density. The data is plotted in the included figure, but you may need to adjust the axes to see the data.



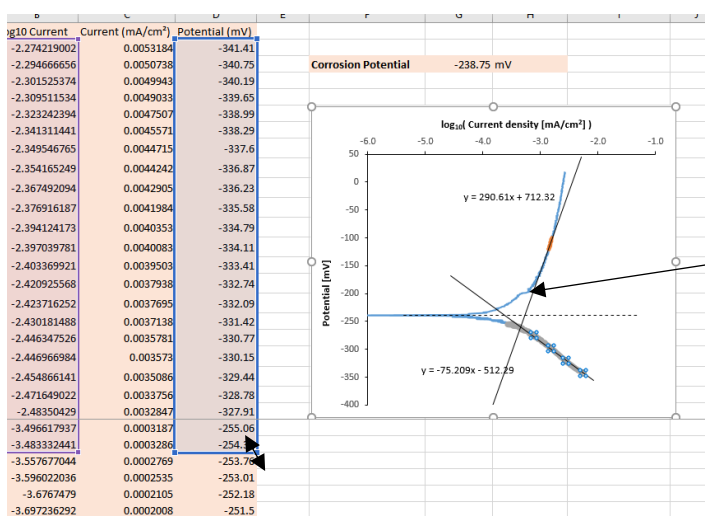
To adjust the axes, simply double click on an axis to access the “Format Axis” panel on the right hand side, and select the tab that looks like a mini bar graph to view the axis options. Reset the minimum and maximum limits and adjust them to get the data shown to your liking, plus any other tweaks to the graph display you might want.



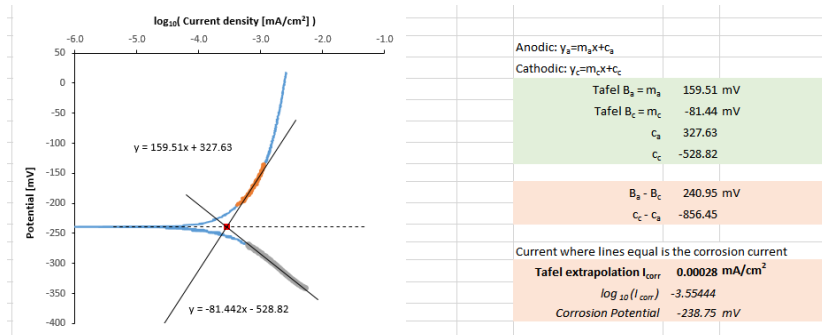
Now we need to adjust the fitting parameters. On the graph you'll see a blue line indicating the full set of data, a grey line and an orange line. The grey and orange lines are the portion of the data that straight lines are being fitted to in the cathodic and anodic regions, respectively. If you click on either the blue, grey or orange lines, the data should be highlighted in the excel columns.



You will need to adjust the range of data being plotted for the cathodic and anodic regions so that the straight lines follow the Tafel behaviours of the curve, ensuring they intersect at the corrosion potential (indicated by the dashed line). Select, e.g., the grey line to highlight the cathodic portion of the data being plotted, then click and drag the corners of purple/blue boxes around the data to adjust the range to your liking.



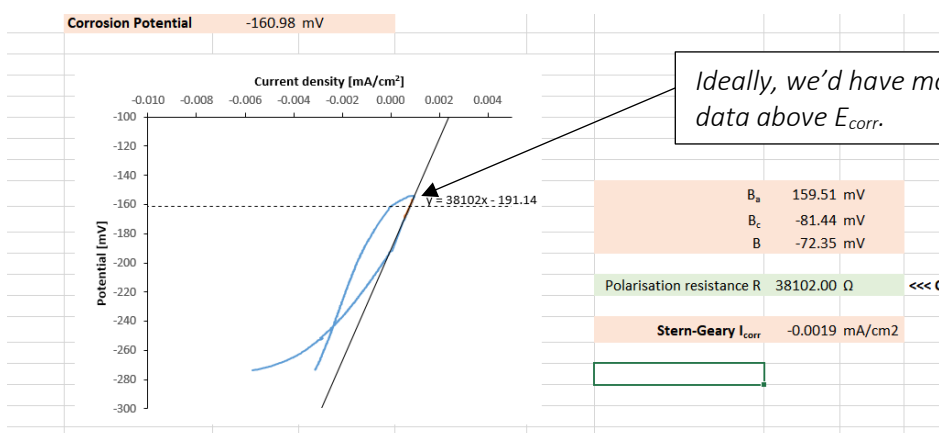
Once you're happy with the fitting of the Tafel regions, copy over the fitting parameters into the cells marked in green (these are not updated automatically unfortunately). If all works well, a red data point should appear where the lines intersect.



### Linear polarisation data analysis

This is pretty similar as for the Tafel curves, only you are showing the plot on linear axes and you only need to fit one line, best fitted through the curve where  $I=0$ . The Tafel constants are fetched from the previous sheet, and used to compute the factor B, and then this applied within the Stern-Geary equation with the gradient you extract from the curve.

For the stainless steel, you may need to adjust the "Forward" and "Backwards" parameters for the trendline in order to display the graph properly ( $\pm 0.01$  seems to work ok).



### Passivation curve analysis

Import the data again for the passivation analysis and annotate your graph to indicate active, passive and transpassive regions. Also note the critical current, the passivation current, and primary passive potential, and lastly comment on any other interesting features in the data.