Part 2: How do we measure electrochemical reactions?

Potentiostat

A typical tool which scientists use for measuring electrochemical reactions is called a potentiostat. This tool allows you to change the voltage of your experiment while measuring the current, and thus letting you understand the reactions taking place. A potentiostat is an electronic instrument as shown in figure 1 and is basically a box with wires, called electrodes coming out of the instrument. The potentiostat is also connected to the computer so that you can see the graphs it produces which we will talk about later.

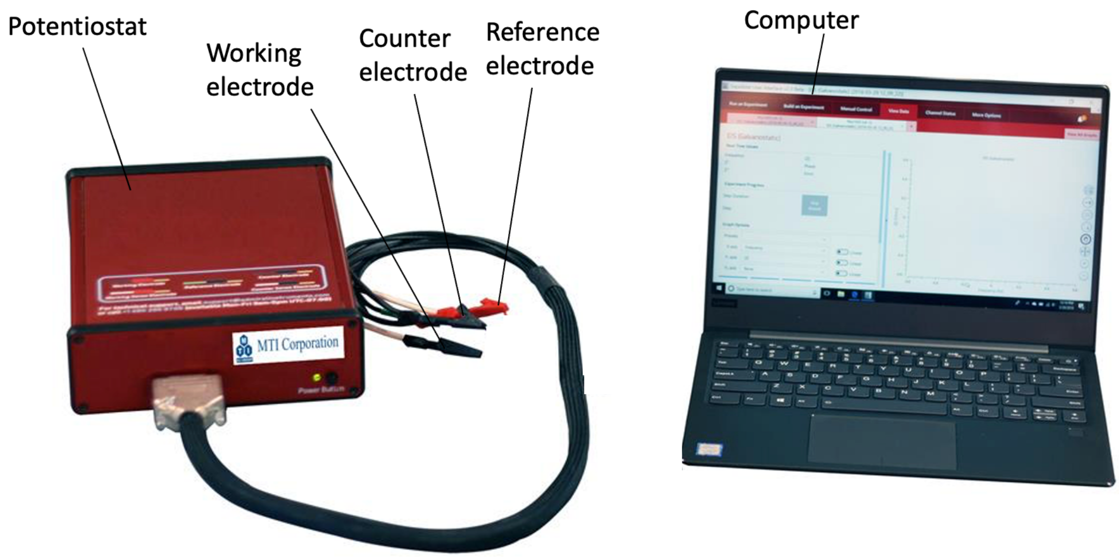

Figure 1. A potentiostat with three electrodes and a computer.

The potentiostat has three wires coming out of it and these are known as: the working electrode, counter electrode and reference electrode.

- Working electrode: This is the electrode which we are interested in. We change the voltage through this electrode using the potentiostat and measure its current.
- Counter electrode. This electrode completes the circuit of the experiment and makes sure that the current is constant in the experiment.
- Reference electrode. This electrode is used so that we can know the voltage passing through the working electrode is correct.

The electrodes are used to build your experiment. Let's look at an example, say you want to know how your cathode in your battery works. You would take your cathode and attach this to the working electrode as you are interested in seeing what happens to the current in the cathode as you change its voltage. Then you would take your anode and attach this to the counter electrode to complete the electrical circuit. Then you would use a special probe and attach this to the reference electrode. Special probes which are sensitive called "Standard calomel electrode" (SCE) are used as the reference electrode because they are good at measuring small amounts of current.

Once you have attached your electrodes you then put these in a beaker of solution known as electrolyte. If you remember back to part 1 this is the liquid inside your battery. We do this so that the ions in the electrolyte can go into and out of the cathode (working electrode) when you change the voltage in it. Figure 2 shows this setup.

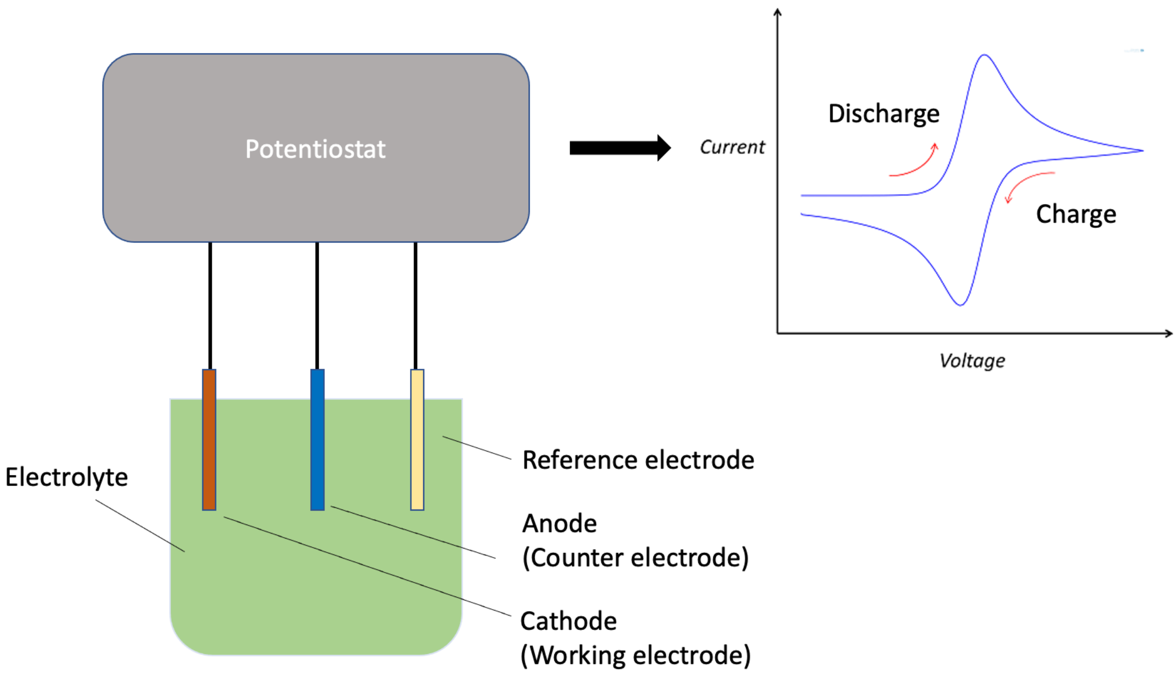

Figure 2. Potentiostat setup measuring the cathode of a battery.

Cyclic Voltammetry

The potentiostat and setup in figure 2 will produce current measurements and plot these on a graph on the right hand side of figure 2. These graphs are called cyclic voltammetry graphs or CV abbreviated and can be used to understand how your electrochemical reaction works. In the example of the cathode, we are interested to see how the ions in the electrolyte in the beaker are going into and out of the cathode when we change the voltage.

To understand how to interpret CV graphs we will take the example of our experiment and explain why we see this particular shape in figure 3.

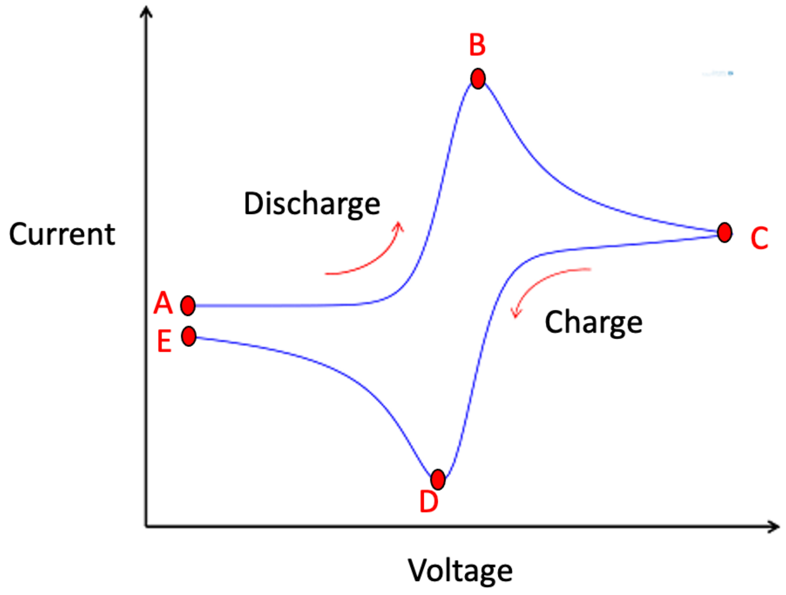

Figure 3. Typical CV graph for an electrode as the voltage is increased and then decreased again.

The 5 key points (A➞B➞C➞D➞E) of the CV graph in figure 3 can be explained as such:

A) This is the starting point. The voltage begins at this low point and increases. As the voltage is increased from A to B, the ions which are currently in the cathode are not given enough of a push to leave the cathode and so there is no electron movement as there is no ion movement and the current remains constant. This is why in the beginning the graph is flat lined. When the voltage gets big enough to move the ions out of the cathode, the current then starts to increase as the ions are moving out.

B) At this point the ions are moving out of the cathode at a maximum rate which is why we are getting a maximum current. But the ions cannot keep leaving the cathode forever as there only a limited number of ions in the cathode to begin with. This is why the current starts falling after B because the number of ions is decreasing, and the fewer ions moving, the smaller the current.

C) When all the ions have left the cathode there is no longer any ion movement and so the current stops changing. As the voltage has reached a maximum we change the voltage to decrease now so the ions can start to return to the cathode. This reverses the ion movement and so reverses the electron movement giving a negative current on the way back. Similar to A, the ions need a certain voltage to be pushed enough to go back to the cathode and until that happens the current will be constant, giving a flat line just after C.

D) Once the ions are given enough of a push they start going back into the cathode and when the maximum number of ions are moving into the cathode we reach the maximum negative current at D. Similar to B, this cannot be sustained as there is only a finite number of ions and so the current gets smaller again after D.

E) Once all the ions have gone back into the cathode there is again no ion movement which means no electron movement and thus no current change giving a flat line once again at E.