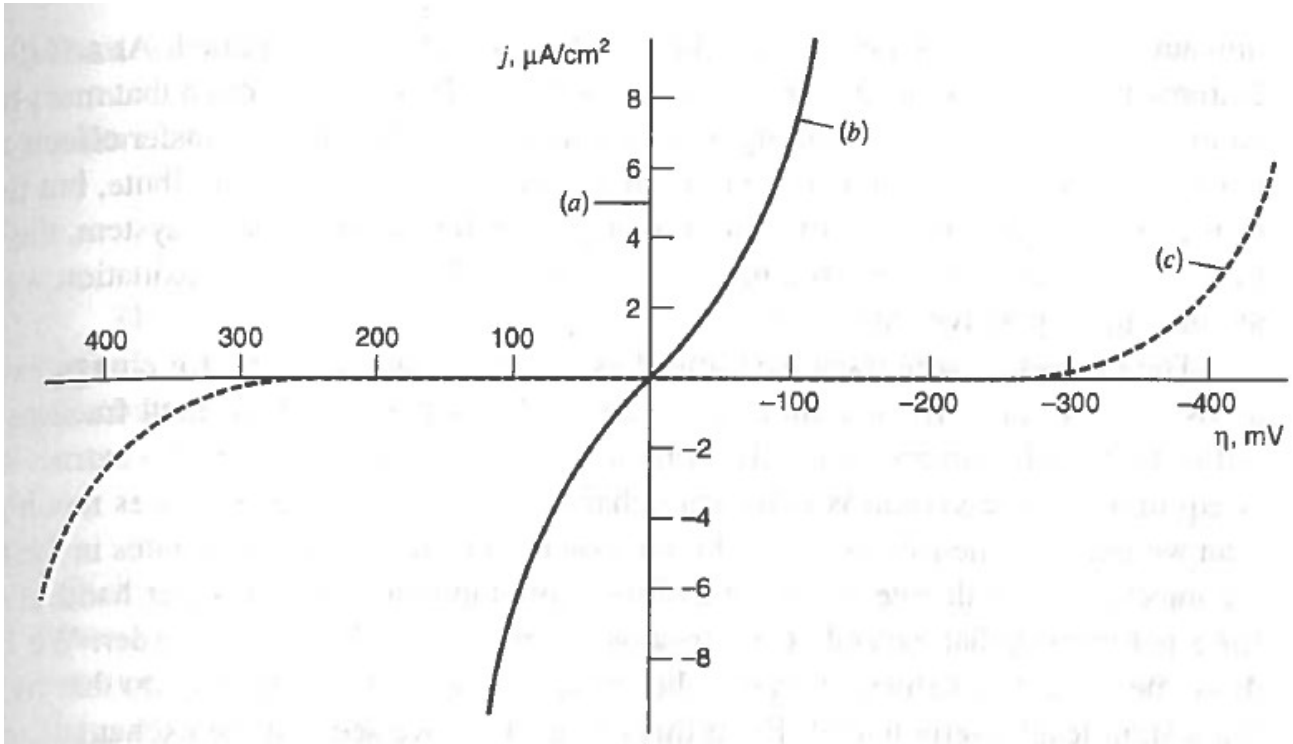
Microbial electrochemical technologies – fundamental aspects and methods of analysis

Week 6 – Methods and analysis 2

- More advanced analysis of electrochemical systems
- The potentiostat
- A range of methods
  - Potential or current step
  - Potential sweep (linear-, cyclic voltammetry, differential pulse)

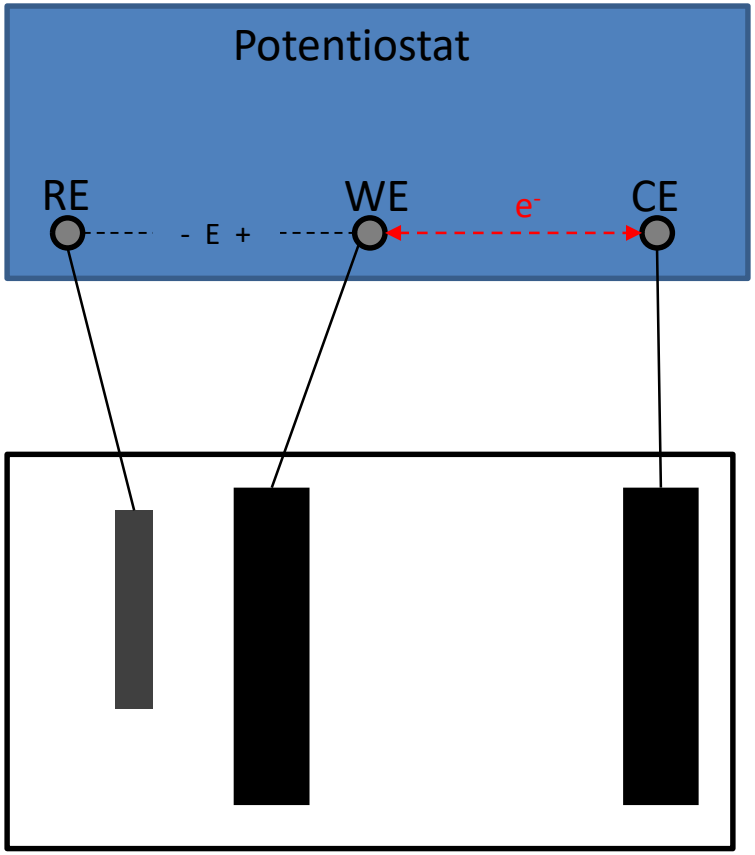
Before we start...

- **How do we generate current vs potential curves, and how can we analyze them?**



Potentiostat

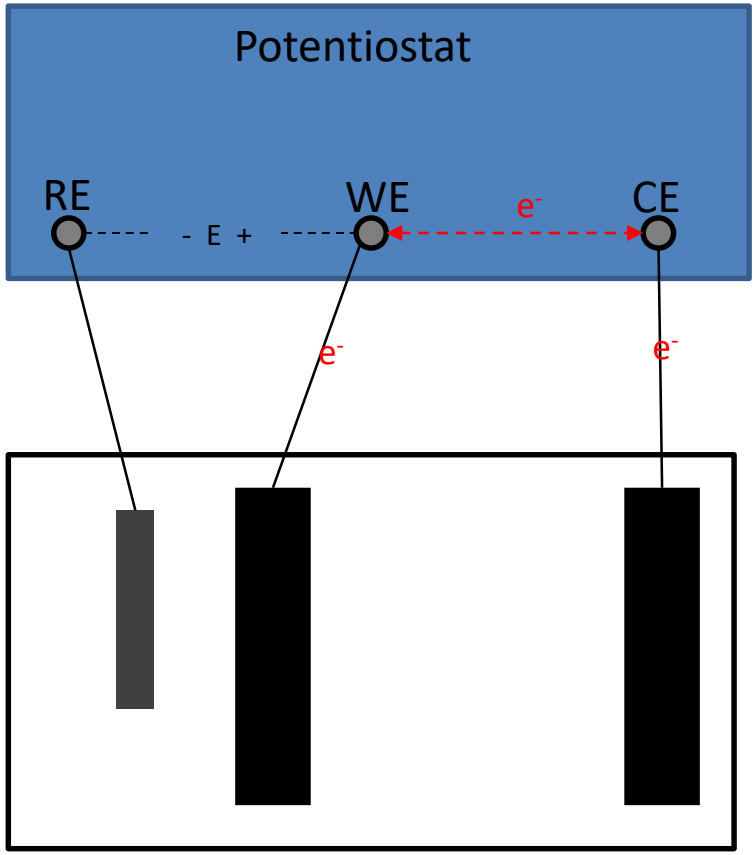
A good description about how a potentiostat works can be found here:
http://www.bank-ic.de/encms/downloads/potstae2.pdf



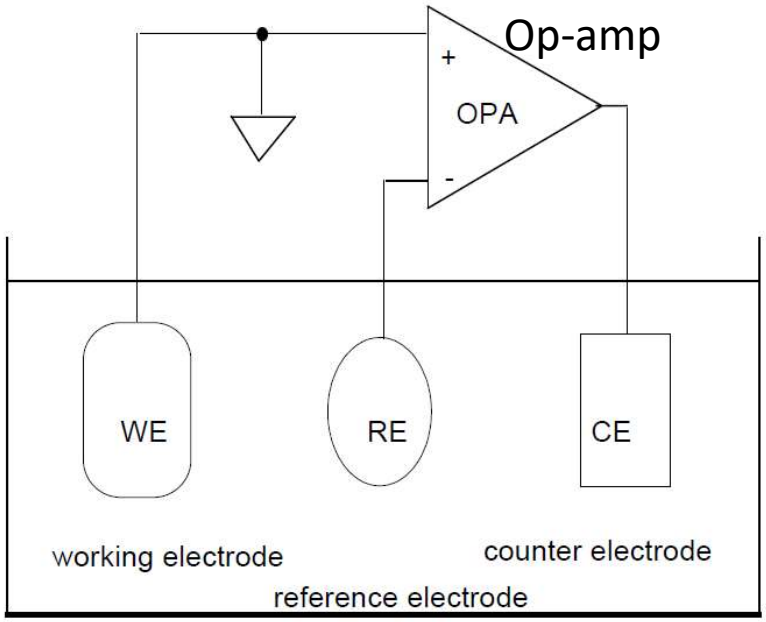
A potentiostat controls the potential between the working electrode (WE) and the reference electrode (RE) by passing a current between WE and the counter electrode (CE)

Terminology

- **Working electrode (WE):** This is the electrode we control.
- **Reference electrode (RE):** This is an electrode with constant potential that we control the WE against.
- **Counter electrode (CE):** This elecotrode supplies (or draws) the needed current to the WE.



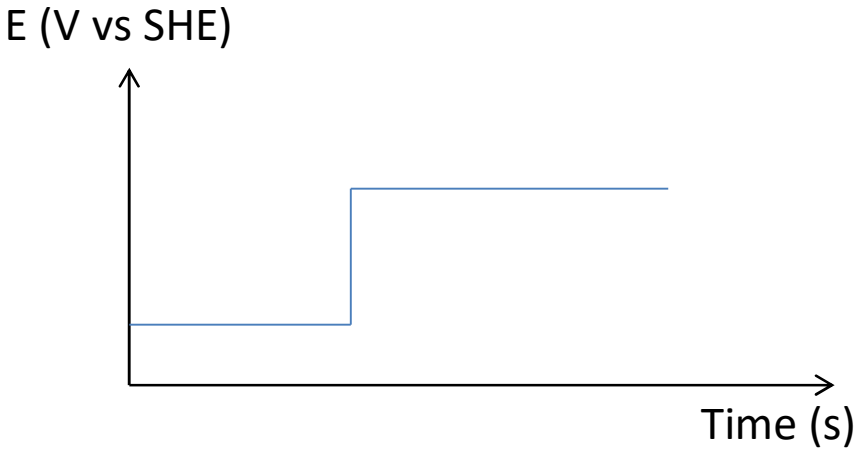
Basic potentiostat circuit

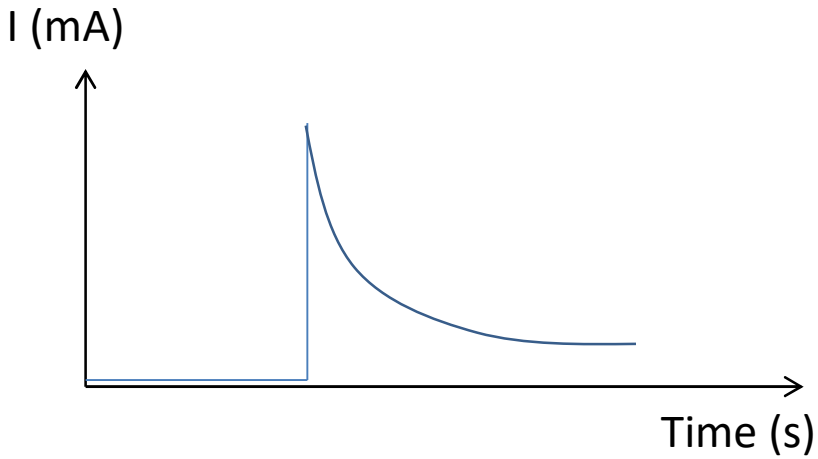


Potential step methods

- Do a step change in the potential of the WE.
- Monitor the current.

Potential step - *chronoamperometry*



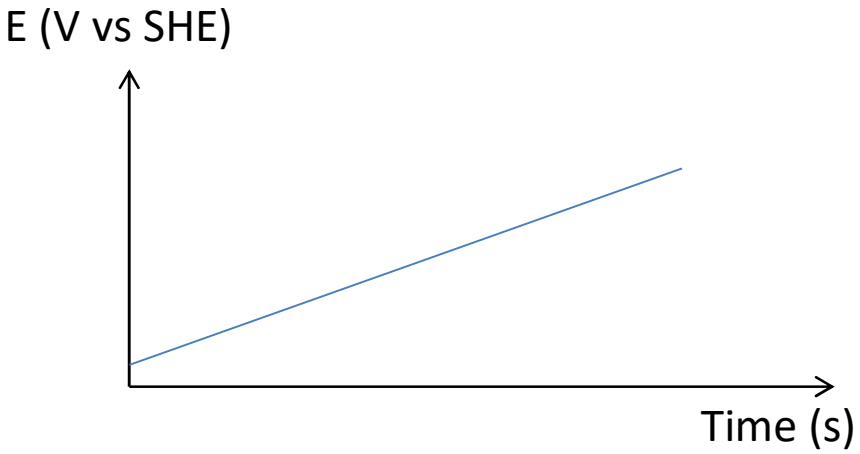


Cottrell equation (derived for a planar electrode)

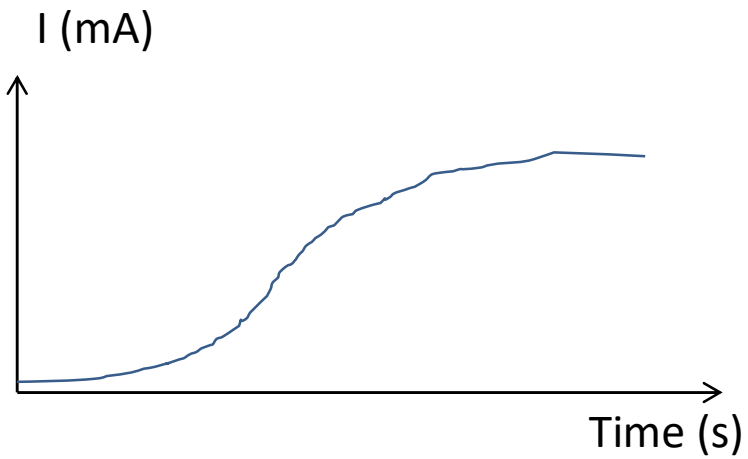
$$I(t) = \frac{n \cdot F \cdot A \cdot D^{0.5} \cdot C^*}{\pi^{0.5} \cdot t^{0.5}}$$

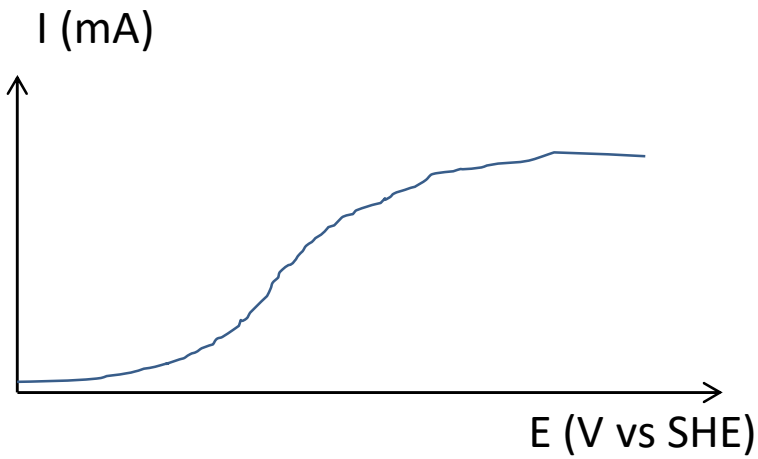
- If we know D, we could use it to find the electrochemically active area of an electrode.
- If we know A, we could use it to find D
- I is correlated with C*

Potential sweep – *linear sweep voltammetry*



Can be used to obtain polarization curves.

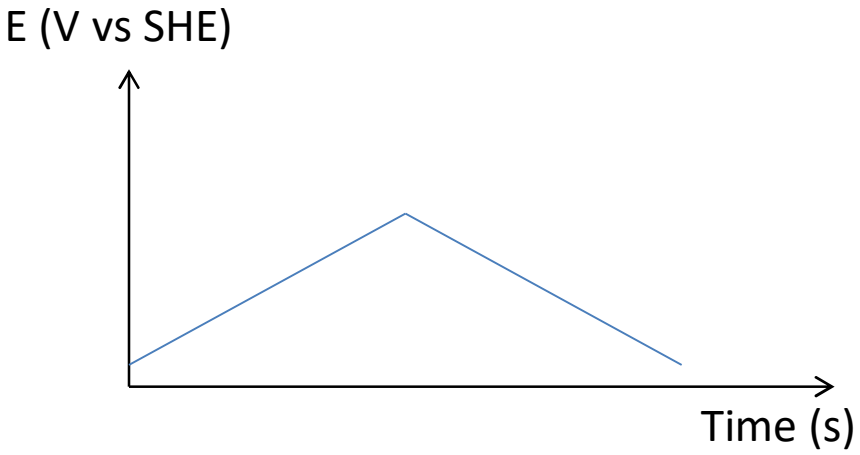


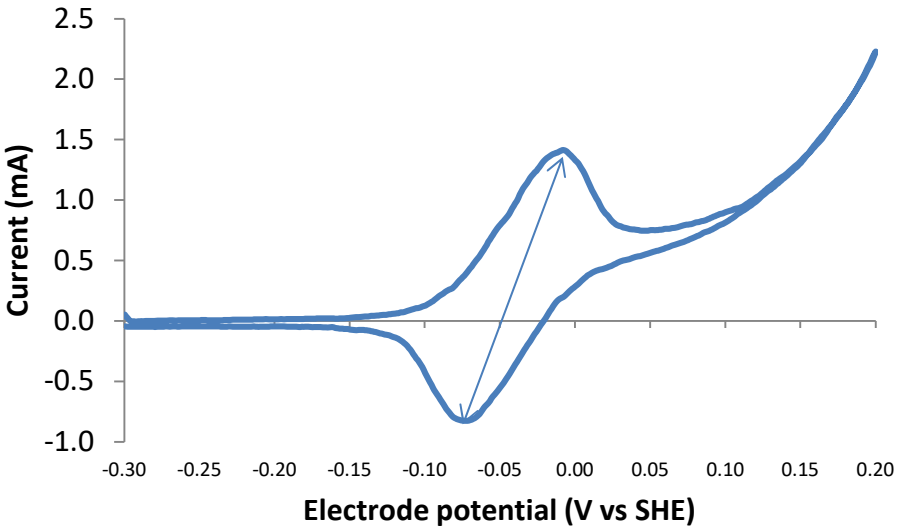


Potential sweep

- Change the potential of the WE continuously.
- Monitor the current.

Potential sweep – *cyclic voltammetry*





Recommended reading:
Elgrishi (2018). J Chem. Educ. 95, 197-206.

Important parameters:

- Scan rate (mV/s)
- Scan limits (V vs SHE)

Recommended reading:

Harnisch and Freguia 2012, A basic tutorial on cyclic voltammetry for the investigation of electroactive microbial biofilms. Chem Asian J. 7, 466-475.

Some relationships

Randles-Cevik equation for freely diffusing redox species. Linear relationship between the peak current and the square root of the scan rate.

$$i_p = 0.446nFAC^0\left(\frac{nF\upsilon D_o}{RT}\right)^{1/2}$$

For surface-bound redox species there is a linear relationship between the peak current and the scan rate.

$$i_p = \frac{n^2F^2}{4RT}\upsilon A\,\Gamma^*$$

Elgrishi (2018). J Chem. Educ. 95, 197-206.

Two types of current

- Non-faradaic current = capacitive current = double layer current
  - When we change the potential of an electrode, electrons will flow to or from the electrode. This current is not associated with electron transfer between the electrode and compounds in the electrolyte.

- Faradaic current
  - This is the current associated with electrons transfer across the electrode/electrolyte interface. This is usually the current we are interested in.