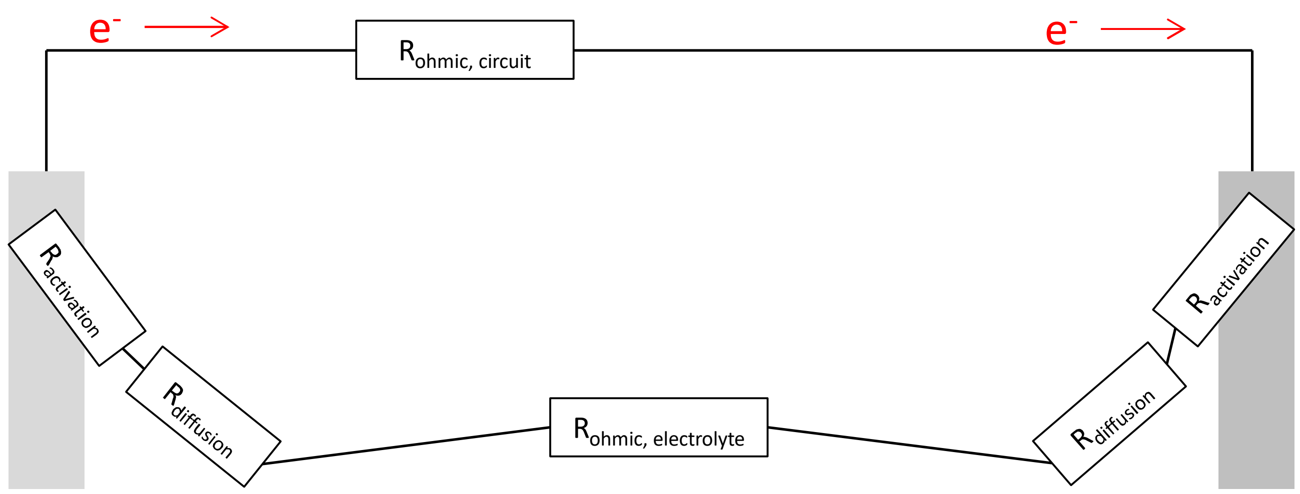
Microbial electrochemical technologies – fundamental aspects and methods of analysis

Week 7 – Methods and analysis 3

- Electrochemical impedance spectroscopy
  - The method
  - Equivalent circuit modelling
  - Applications in studies of METs

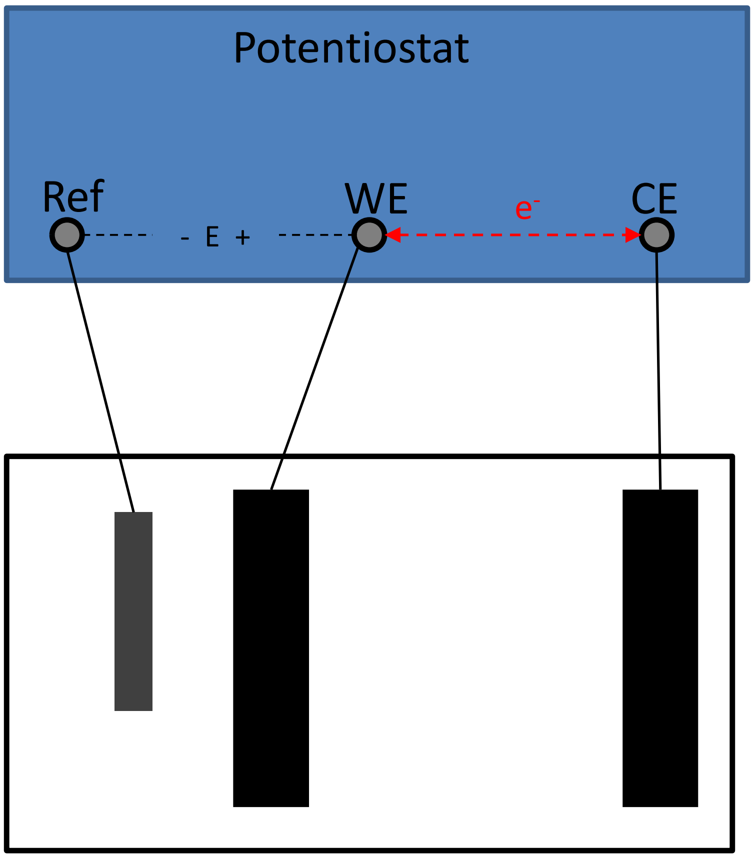
Before we start 1…

- Remember, the figure below is a simplified model. Capacitors at the electrode surfaces could be added to explain non-faradaic currents during potential steps. Observed resistances also depend on e.g. mass transfer limitations.

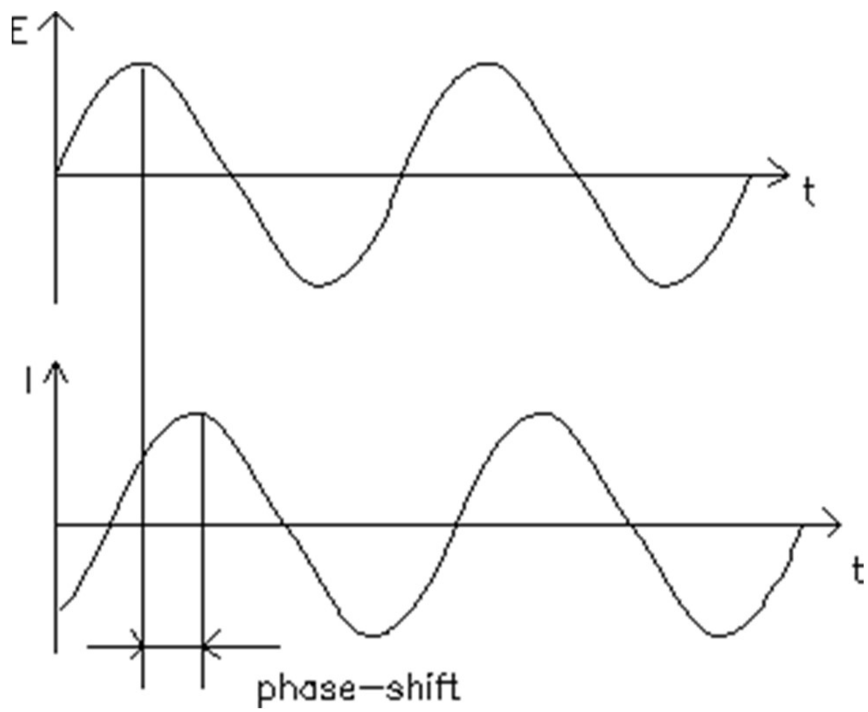


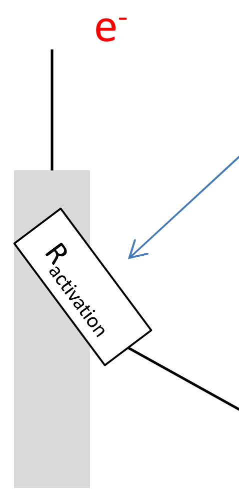
Before we start 2…

- **Remember how the potentiostat functions**

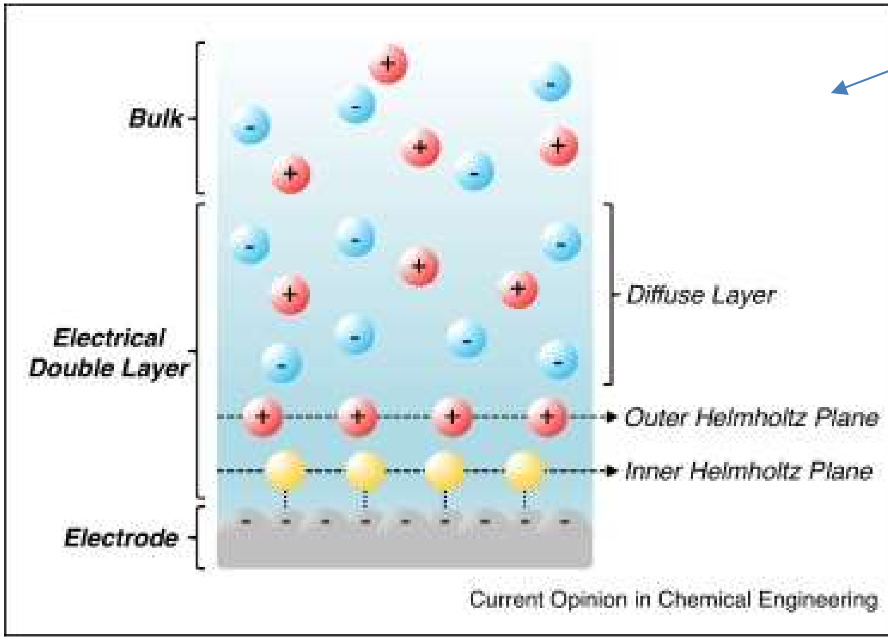


The method

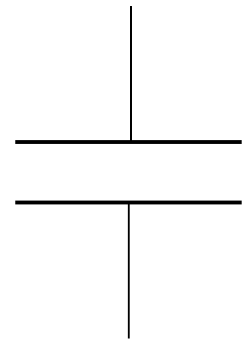


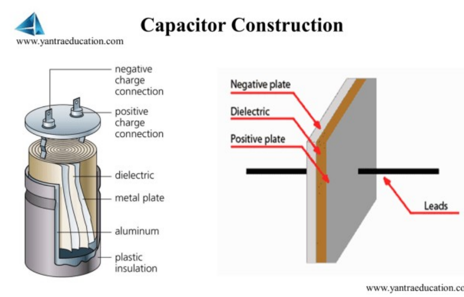


In reality, this not an ideal resistor, it is an impedance.



Similar to a capacitor





Dunwell et al. (2018). Current opinion in Chemical Engineering, 20, 151-158.

Impedance

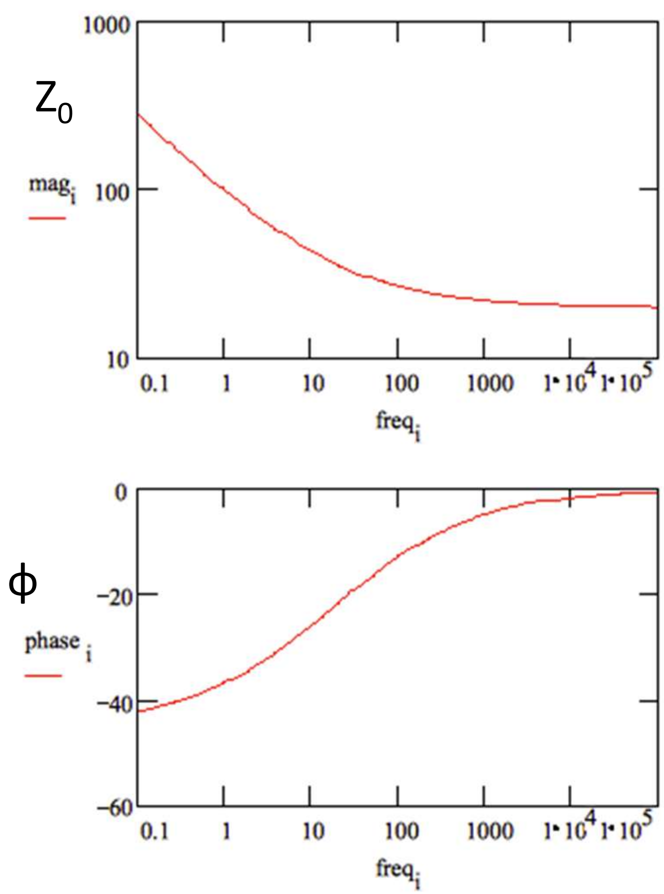
- $E_t = E_0 \sin(\omega t)$
- $I_t = I_0 \sin(\omega t+\phi)$
- $Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t+\phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t+\phi)}$
- The impedance is a function of a magnitude (Z_0) and a phase shift (ϕ)
- It can also be represented as a complex number:
- $Z(\omega)=Z_0 (\cos(\phi)+j \sin(\phi))$

ω = radial frequency (rad/s), $\omega=2\pi f$

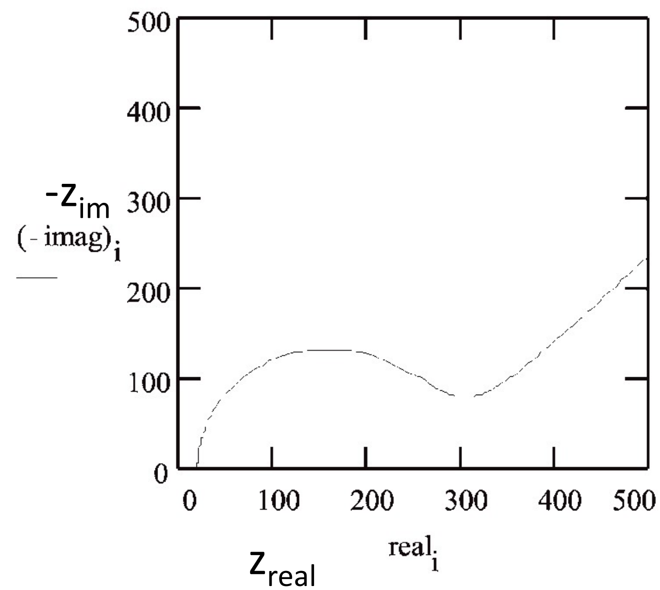
Obtaining data

- Determine Z_0 and ϕ for different frequencies

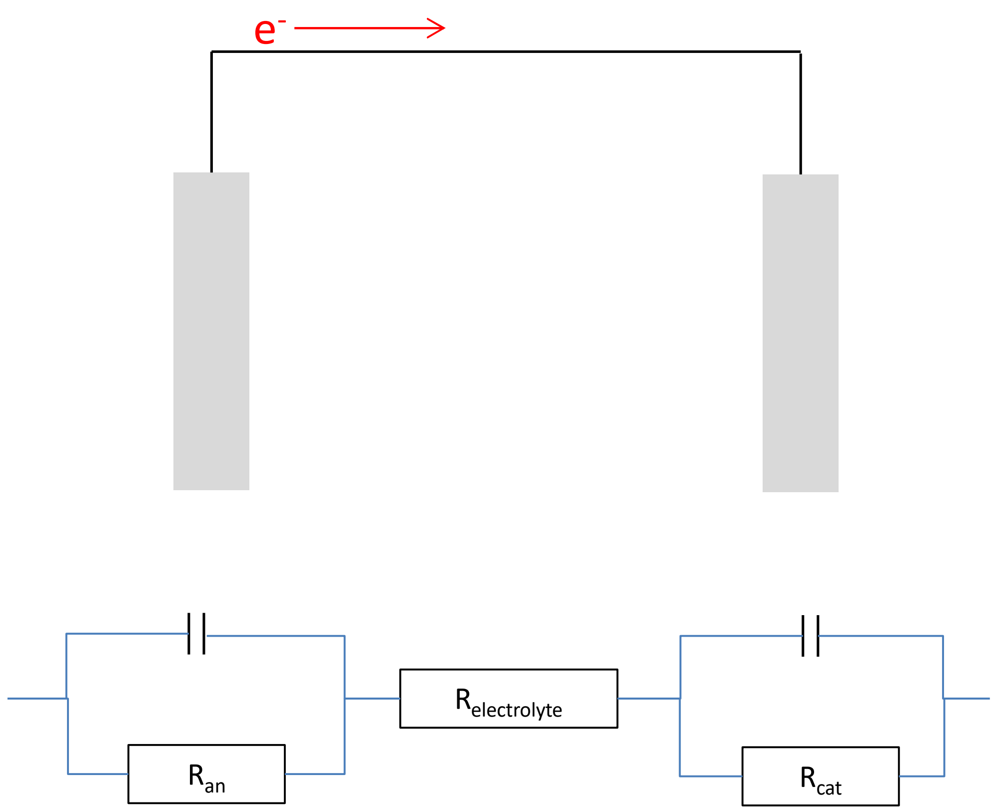
Bode plot



Nyquist plot



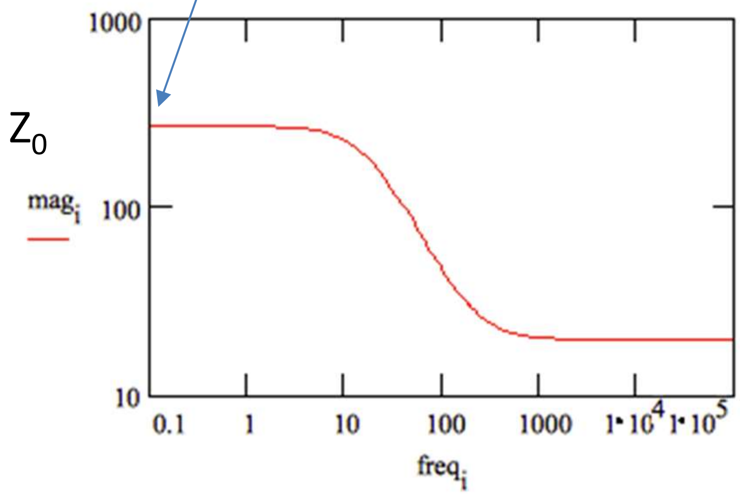
Equivalent circuit modelling

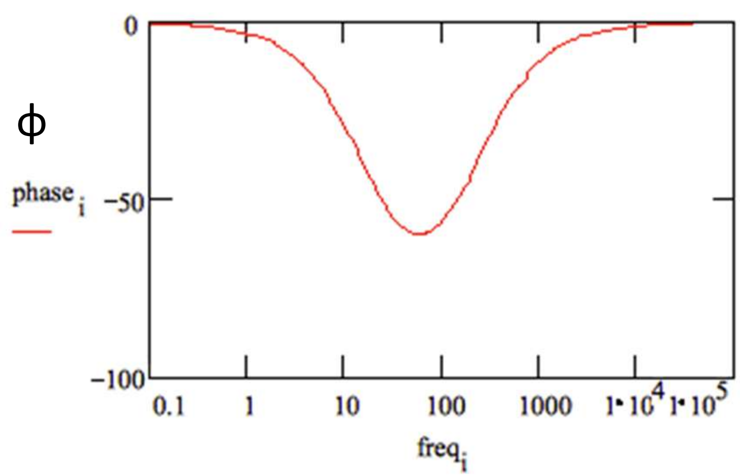


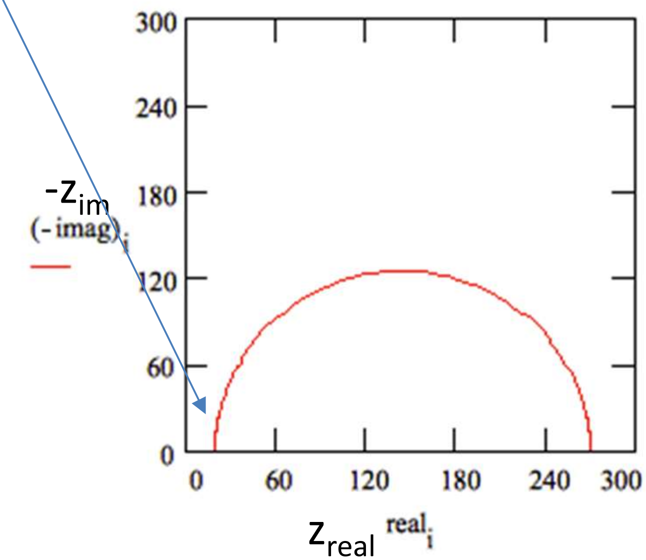
http://www.gamry.com/application-notes/basics-of-electrochemical-impedance-spectroscopy/

Low freq = capacitor impedance infinite. Thus $Z_0 \approx R_{an} + R_{cat} + R_{electrolyte}$

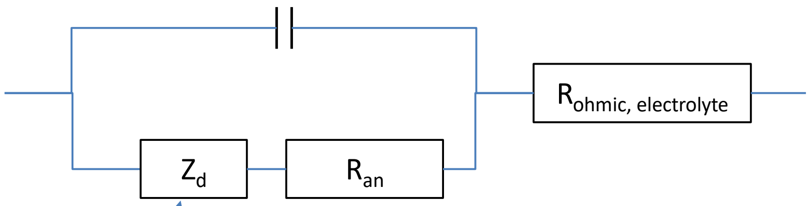
High freq = almost no impedance associated with capacitor. Thus $Z_0 \approx R_{electrolyte}$



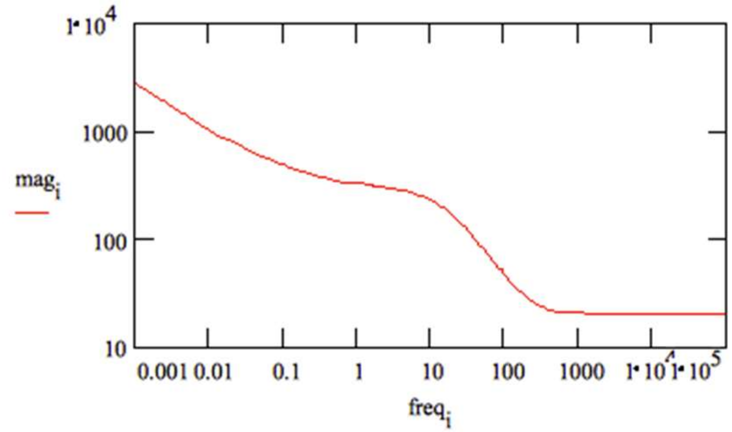


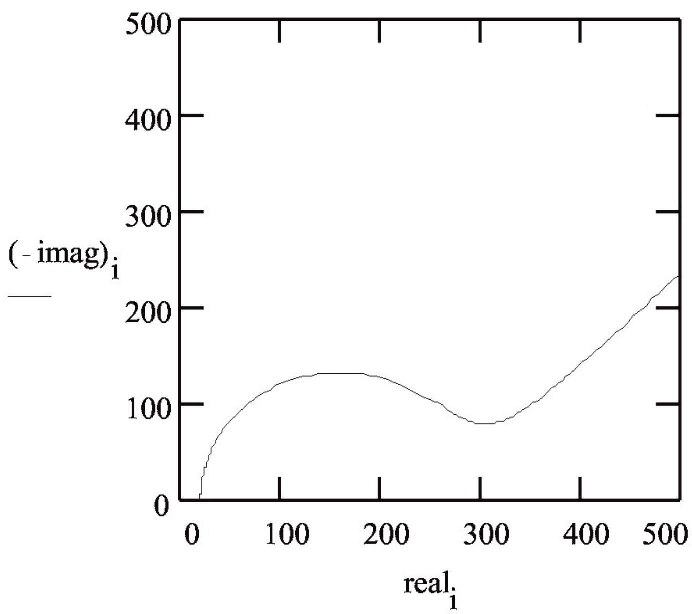


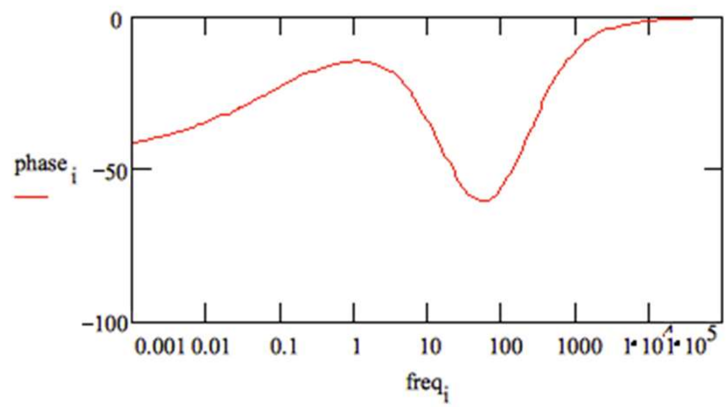
Circuit model including diffusion



Impedance associated with diffusion = Warburg impedance







Some examples

Aaron et al. Energies, 3, 592-606, 2010

Ter Heijne et al. 2011, Energy & Environmental Science 11(4), 5035-5043.