An Introduction to Electrochemical Impedance Spectroscopy (EIS)

C. Reece

Excellent references:

"Identification of Electrochemical Processes by Frequency Response Analysis"
http://www.solartronanalytical.com/technicalsupport/technicalnotes/technote04.htm

"Basics of Electrochemical Impedance Spectroscopy"
http://www.gamry.com/App_Notes/EIS_Primer/EIS_Primer_2007.pdf

Impedance Spectroscopy: Theory, Experiment, and Applications
E. Barsoukov and J. R. Macdonald, Eds., Wiley-Interscience, 2005.

Basics

- **We are interested in what happens at the interface between an SRF surface and a reactive media.**
  - Chemical etching may occur spontaneously without electrical potential.
  - Addition of an externally-defined potential changes the dynamics of chemical reactions at the surface.
  - Such changes in the electrochemical dynamics at an interface are extremely nonlinear.
  - We need appropriate process characterization tools.

Why Electrochemical Impedance Spectroscopy?

- For diagnostic purposes, we want to characterize changes at a surface under specific system parameters.
- For application purposes, we want to tailor system parameters in order to obtain a desirable effect on a surface.
- EIS is a tool that bridges both purposes.
- **EIS is a perturbative characterization of the dynamics of an electrochemical process.**
  - A tool for unraveling complex non-linear processes.

What is Electrochemical Impedance Spectroscopy?

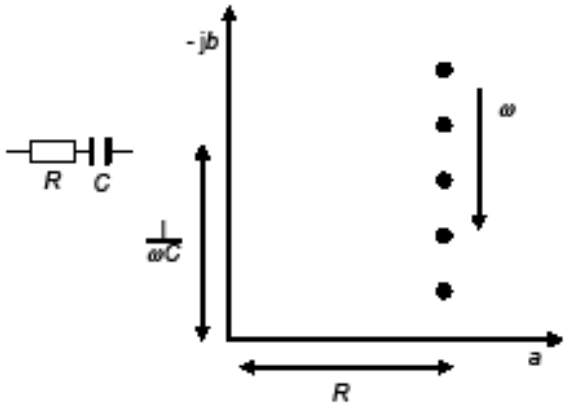
- **Exploit Faraday's Law to characterize a chemical process in terms of electrical measurements.**

- **Electrochemical impedance** is the response of an electrochemical system (cell) to an applied potential.
  - The frequency dependence of this impedance can reveal underlying chemical processes.

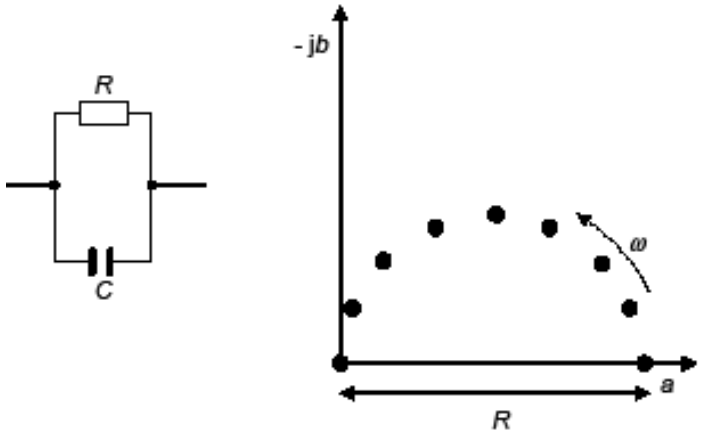
What is Electrochemical Impedance Spectroscopy?

- The response of electrochemical systems is very nonlinear.
- We interrogate the impedance in a perturbative manner:
  - Small amplitude (~10 mV) AC ripple on top of the controlled DC polarization potential.
- The complex response of the system is usually displayed in Nyquist format, with the reactance inverted (since such systems are inherently capacitive).

What is Electrochemical Impedance Spectroscopy?

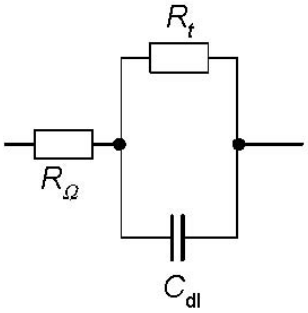


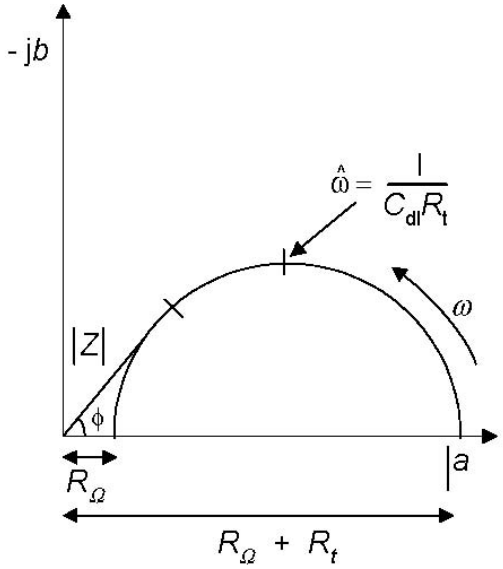
Complex plane impedance spectrum - series resistance, capacitance



- Complex plane impedance spectrum - parallel resistance, capacitance

- The response of the system as a function of the perturbation frequency can reveal internal dynamics.
- The capacitance at the metal/electrolyte interface always plays an important role.





What is Electrochemical Impedance Spectroscopy?

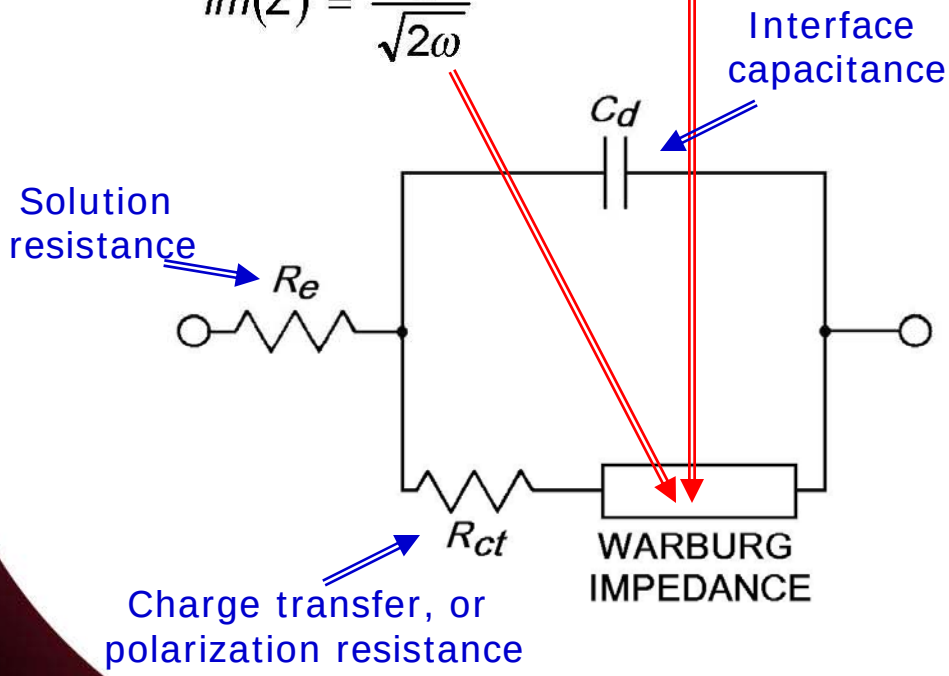
A process that depends on diffusion of reactants toward or away from the surface has a particular low-frequency character. ("Warburg" impedance)

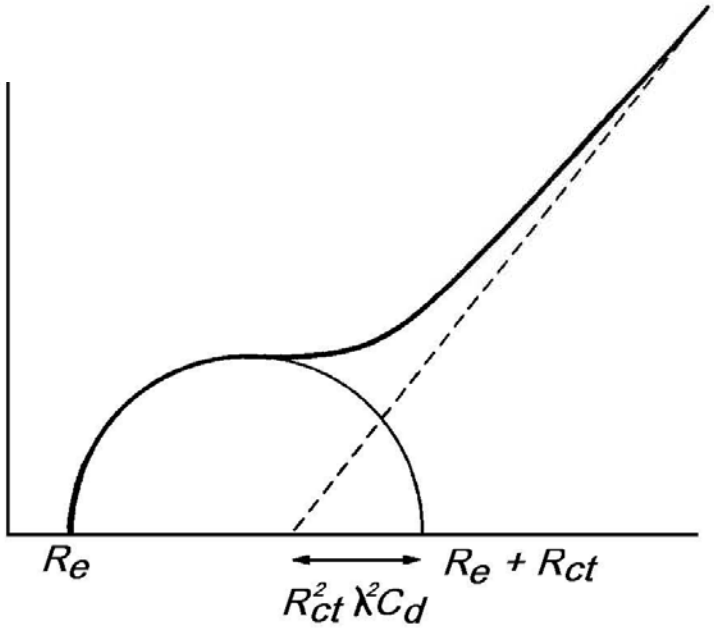
$$Re(Z) = R_e + R_{ct}\left(1 + \frac{\lambda}{\sqrt{2\omega}}\right)$$

$$Im(Z) = \frac{R_{ct}\lambda}{\sqrt{2\omega}}$$

$$\lambda = \frac{k}{\sqrt{D}}$$

k = chem reaction rate
D = diffusion coeff.

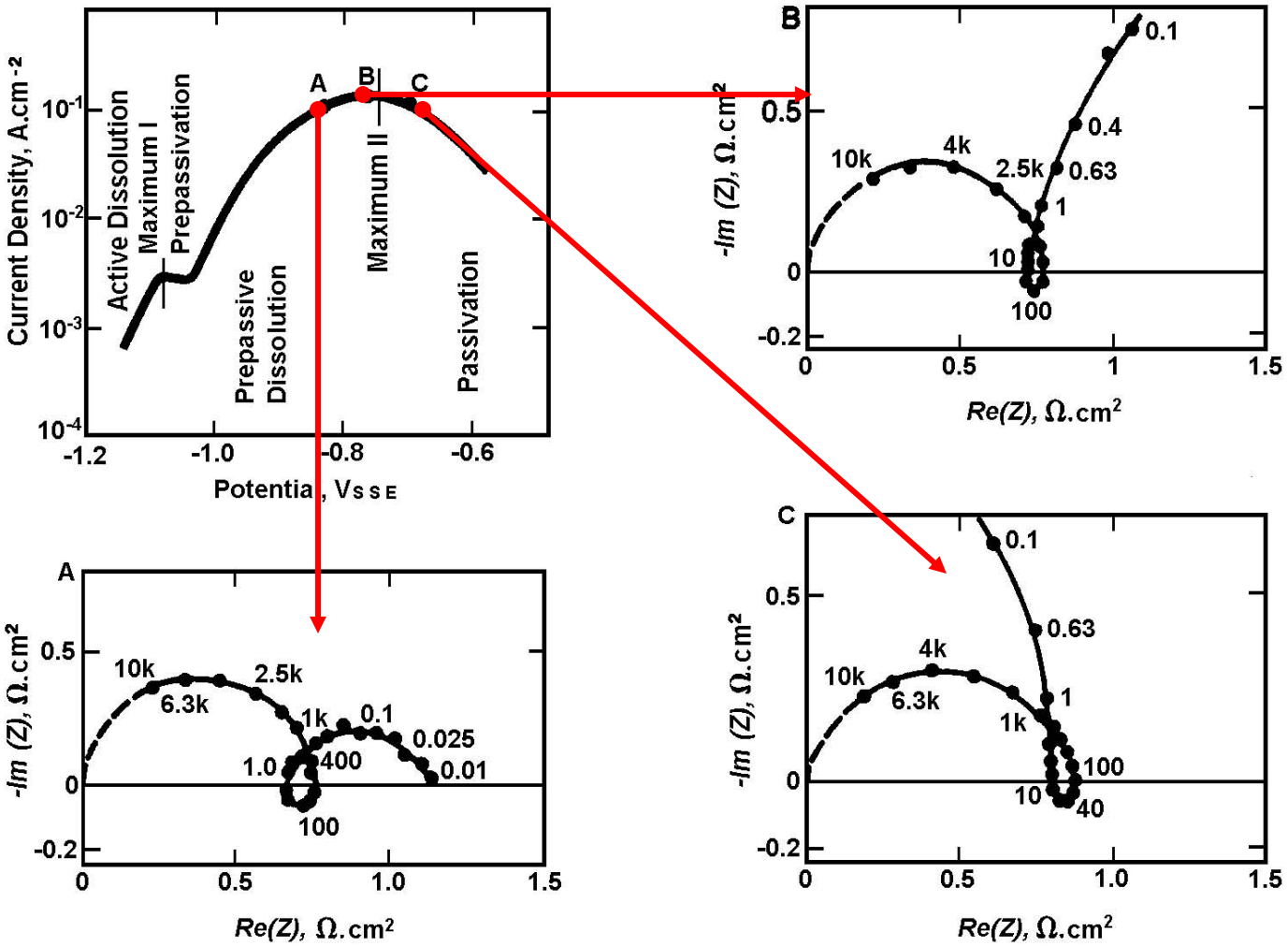




What is Electrochemical Impedance Spectroscopy?

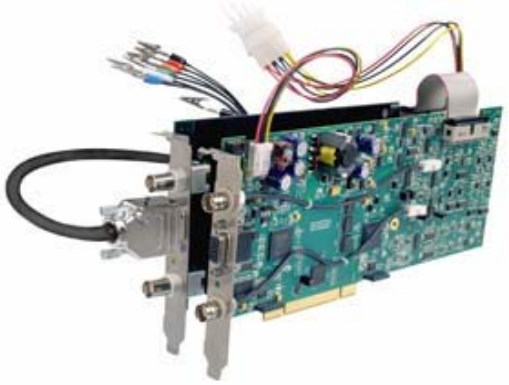
➢ **Example**: Anodic corrosion of iron in sulfuric acid

The impedance spectrum changes at different points on the polarization curve.



Electrochemical Impedance Spectroscopy

- EIS is widely used as a standard characterization technique for many material systems and applications (corrosion, plating, batteries, fuel cells, etc.)
- PC-based modern DSP electronics+software packages now replace lock-in amplifier techniques for implementing EIS.

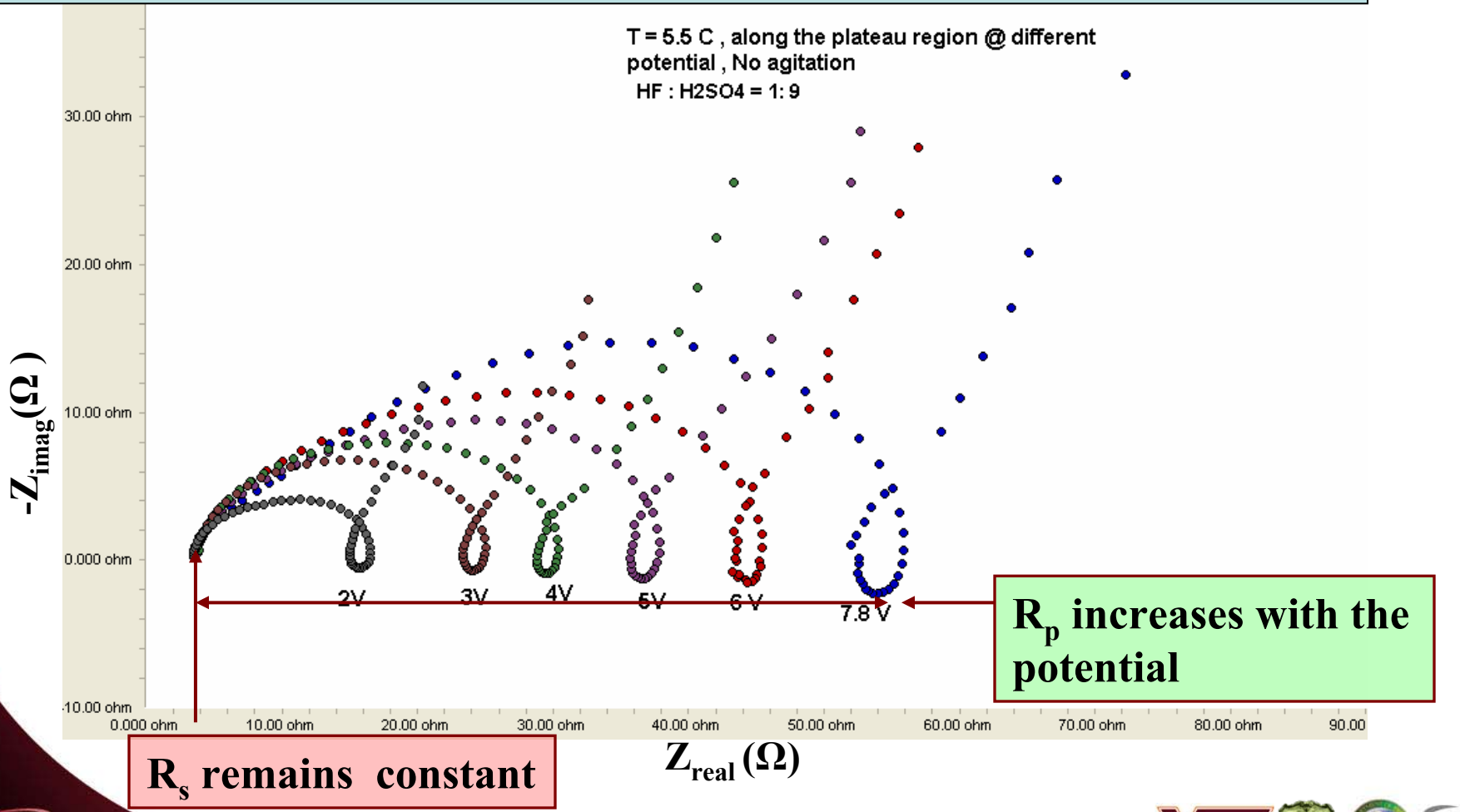


Gamry Instr. G 300

What is Electrochemical Impedance Spectroscopy?

Example of EIS of niobium electropolishing with a particular parameter set.

See H. Tian's talk for more data and interpretation



Using Electrochemical Impedance Spectroscopy

- EIS has been helpful for discerning the mechanism involved with electropolishing niobium.

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The Mechanism of Electropolishing of Niobium in Hydrofluoric–Sulfuric Acid Electrolyte

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- EIS may also be useful as an EP process characterization tool that aids in surface optimization and quality control.
  - Protocol development for engineered surface topography
  - On-line process feedback