EIS: Corrosion & Coatings

GAMRY INSTRUMENTS

Electrochemical Corrosion Measurements

- Corrosion is an electrochemical (redox*) process.

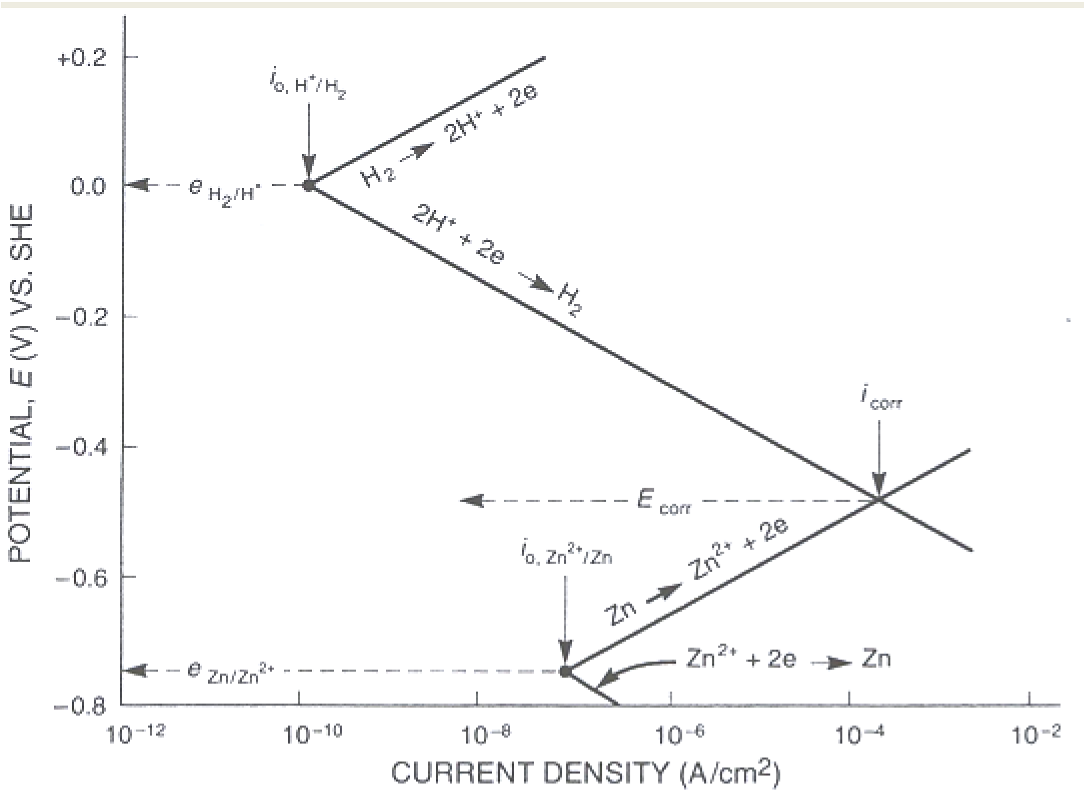
$$Fe \longrightarrow Fe^{2+} + 2e^{-}$$

- Electrochemical techniques have been developed to measure the corrosion rate
- The starting point for all these measurements is the open circuit potential

The Open Circuit Potential

- The Open Circuit Potential, E_{oc}, is the potential difference between the Working and the Reference Electrodes with no (net) current flowing.
- E_{oc} is a “mixed potential” whose value is determined by the potentials of the half-reactions of the electrochemical system, *not* by the instrument!
- A stable E_{oc} is taken to indicate that the corroding system has reach a “steady state” and the experiment may begin.
- An applied voltage positive of E_{oc} will accelerate an oxidation (corrosion) reaction. An applied voltage negative of E_{oc} will accelerate a reduction reaction.
- The terms “E_{oc}” and “Ecorr” (corrosion potential) are often used interchangeably.
- The value of the E_{oc} is not particularly useful as a predictive tool.

Mixed Potential Theory

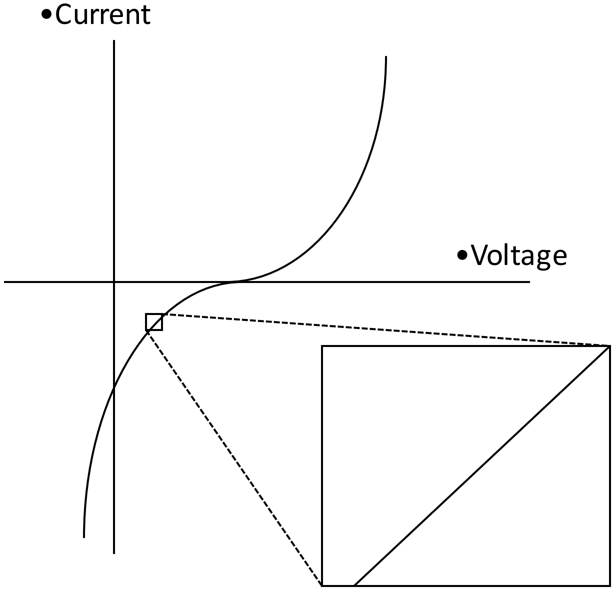


- Anodic current equals cathodic current at Icorr
- Both reactions must occur on the same surface, so their potentials must change to a common value, which is Ecorr
- Ecorr is called a “mixed potential”.

Electrochemistry: A Linear System?

Circuit theory is simplified when the system is "linear".

Z in a linear system is independent of excitation amplitude. The response of a linear system is always at the excitation frequency (no harmonics are generated).



Look at a small enough region of a current versus voltage curve and it becomes linear.

If the excitation is too big, harmonics are generated and EIS modeling does not work.

The non-linear region can be utilized.

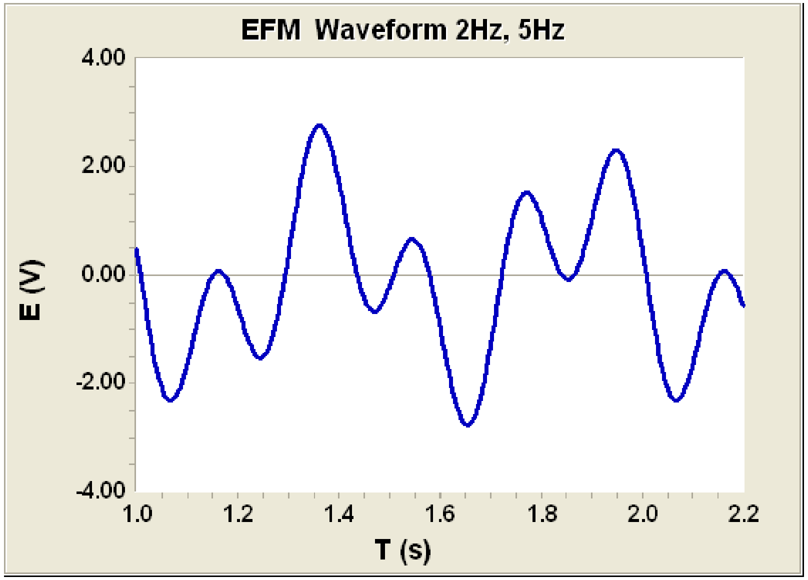
EFM: Electrochemical Frequency Modulation

- Pushes into the non-linear response region
- Utilizes harmonics
- Validation from “causality factors”
- Results include beta values and Rp

- Non-destructive Tafel

EFM: Electrochemical Frequency Modulation

- Apply two sine waves simultaneously.
  - Equal amplitudes
  - Centered on E_{CORR}
  - Frequencies ‘relatively prime’
    - Do not share any common factors
    - Additional restriction
    - e.g. 2 Hz, 5 Hz
  - Slow enough so minimum charging current!
- 5-10 mV amplitude
  - Non-destructive
- Measure current response vs. time



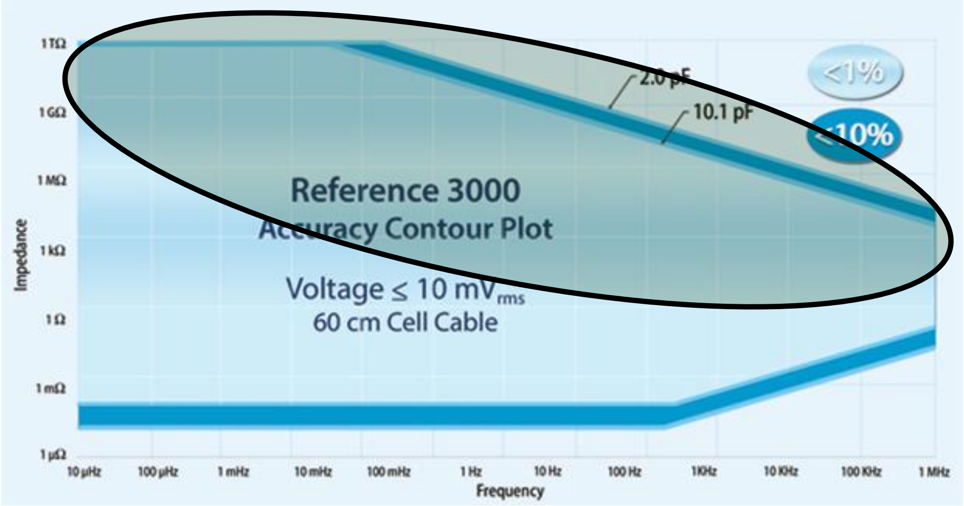
EIS of Corrosion and Coatings

- Impedance from a tens of Ω to over several GΩ

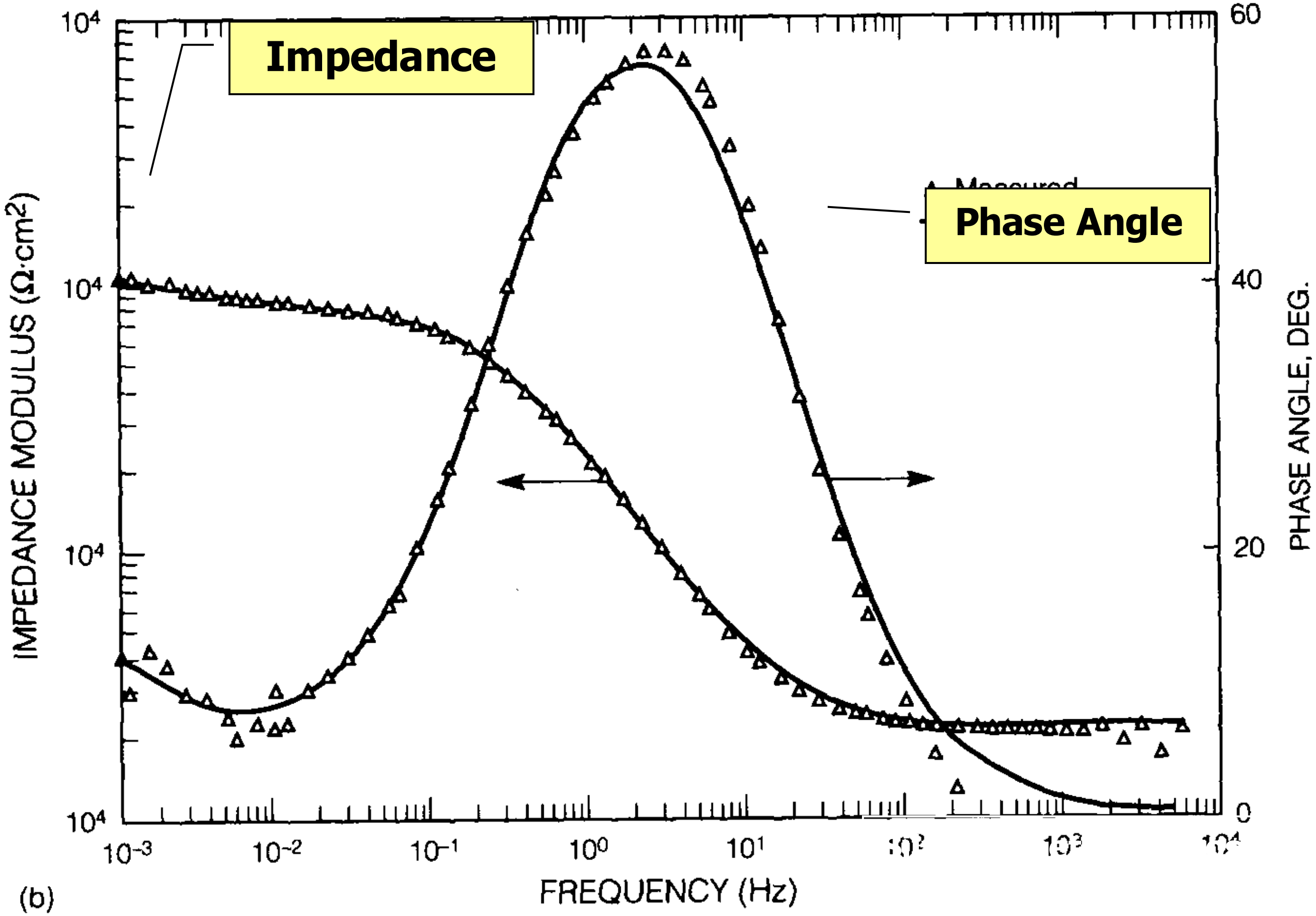
- EIS of general corrosion looks to measure Rp
- Corrosion events like pitting/passivation can be identified with EIS, but complicate analysis

- Insulating coatings model as (very) small capacitors
- EIS is often used in conjunction with stress to measure how coatings/ surfaces change/breakdown

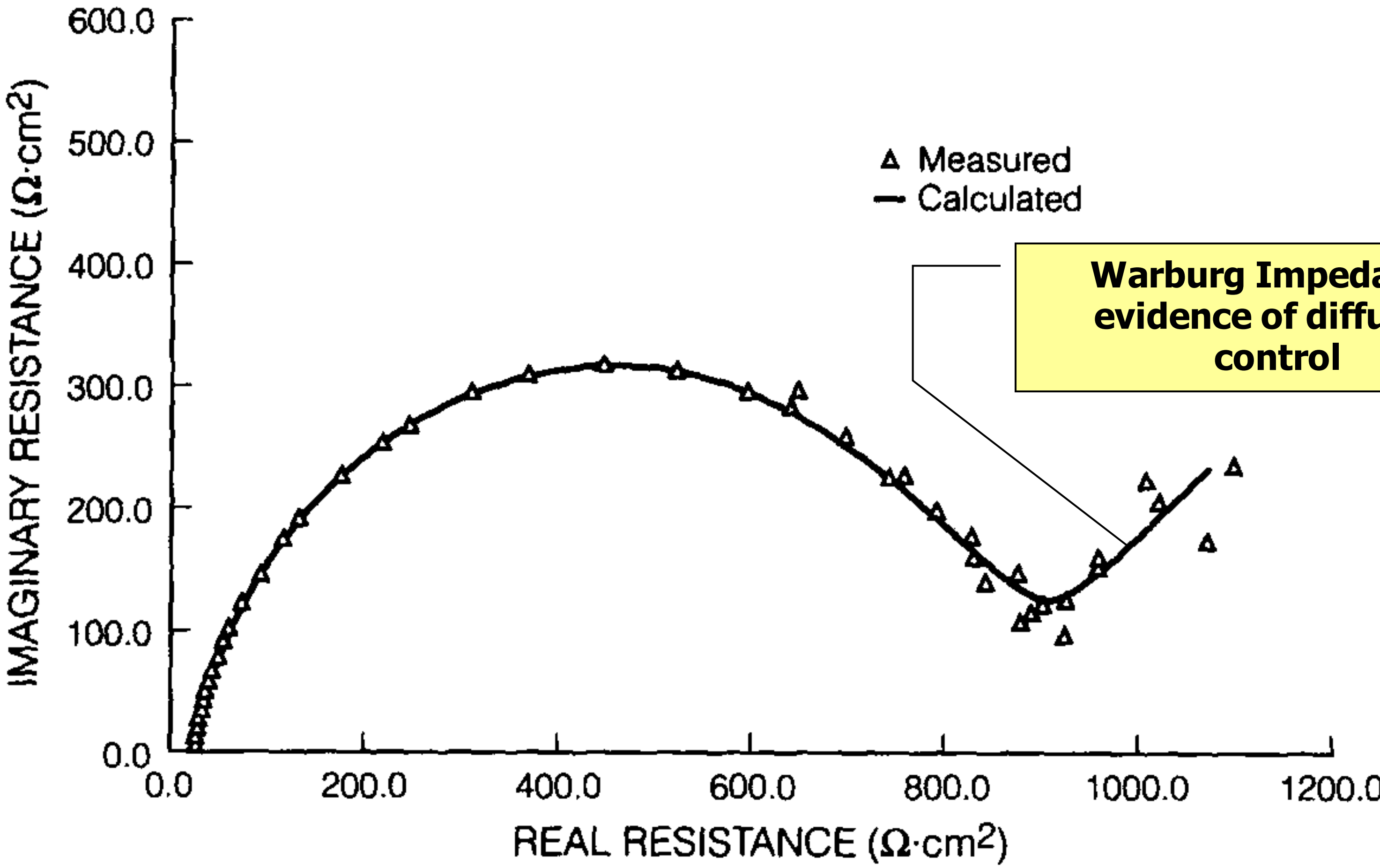
- Systems can exhibit drift
- Diffusion related events may occur



Bode Plot of Carbon Steel in Aerated Water with 1000 ppm Cl^-



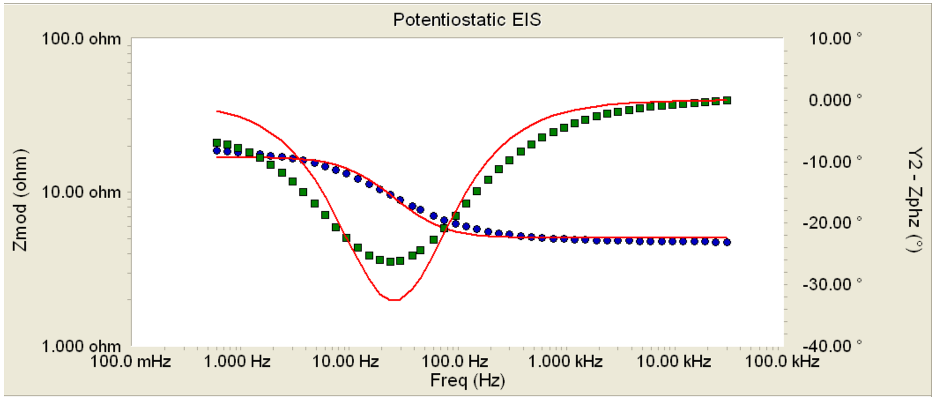
Complex Plane Plot of Carbon Steel in Aerated Water with 1000 ppm Cl^-



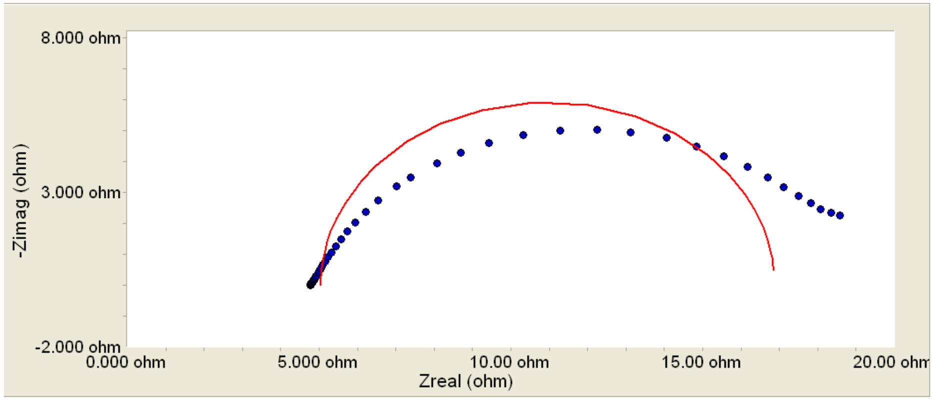
430 SS in H2SO4, Randles Model

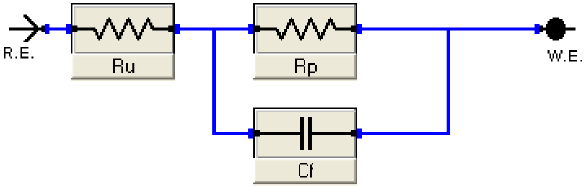
- Data from a 430 Stainless Steel sample

Bode Plot



Nyquist Plot

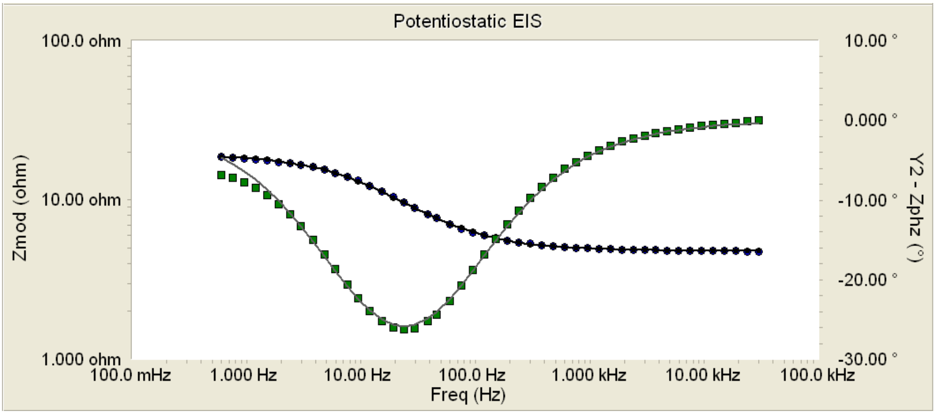




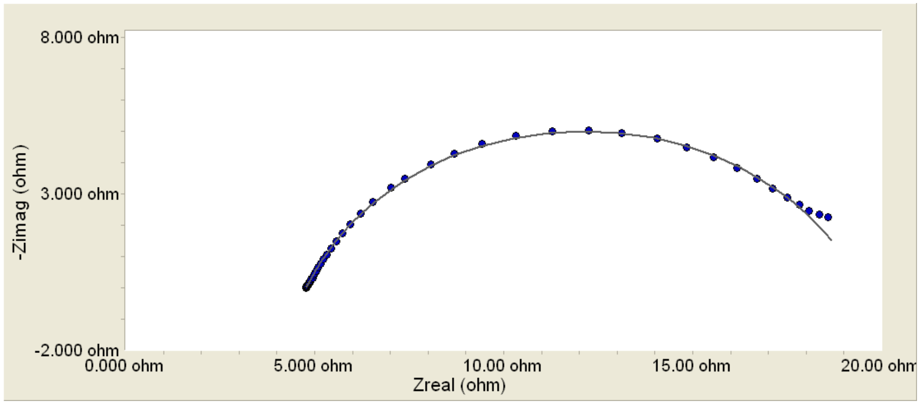
430 Stainless Steel, CPE Model

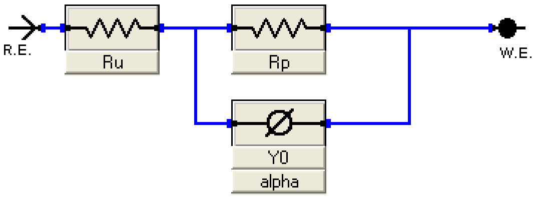
- Same Data Fit to CPE model

Bode Plot



Nyquist Plot

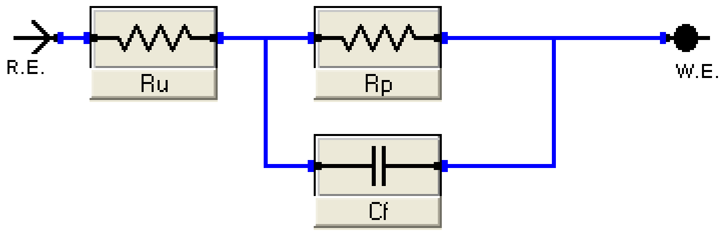


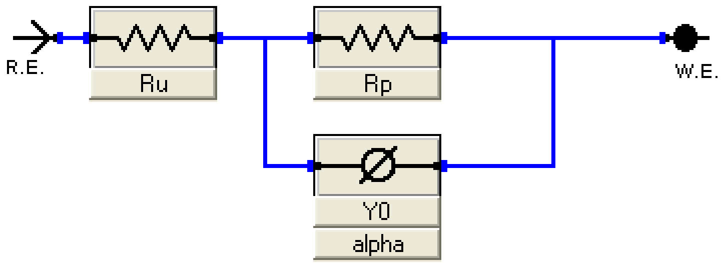


Randles versus CPE model

	Parameter	Value	± Error	Units
	Rp	11.83	115.8e-3	ohms
	Ru	5.048	23.90e-3	ohms
	Cf	945.5e-6	14.76e-6	F
	Goodness of Fit	7.068e-3		
	430 Polished in office_4.dta			

	Parameter	Value	± Error	Units
	Rp	14.66	246.5e-3	ohms
	Ru	4.786	31.91e-3	ohms
	Y0	3.025e-3	172.9e-6	S*s^a
	alpha	762.4e-3	10.90e-3	
	Goodness of Fit	109.0e-6		
	430 Polished in office_4.dta			





Experimental Issues with EIS of Insulating Coatings

- Because of the barrier properties of the coating, a painted metal substrate may initially exhibit a very high impedance ($>10^{10}\ \Omega$)
- A high impedance sample will exhibit low cell currents which are experimentally difficult to measure with confidence!
- Use a potentiostat designed for low-current applications
- Use a Faraday Cage
- You may have to increase the AC amplitude to 30-50 mV to see a measurable current
- You may have to use larger sample areas

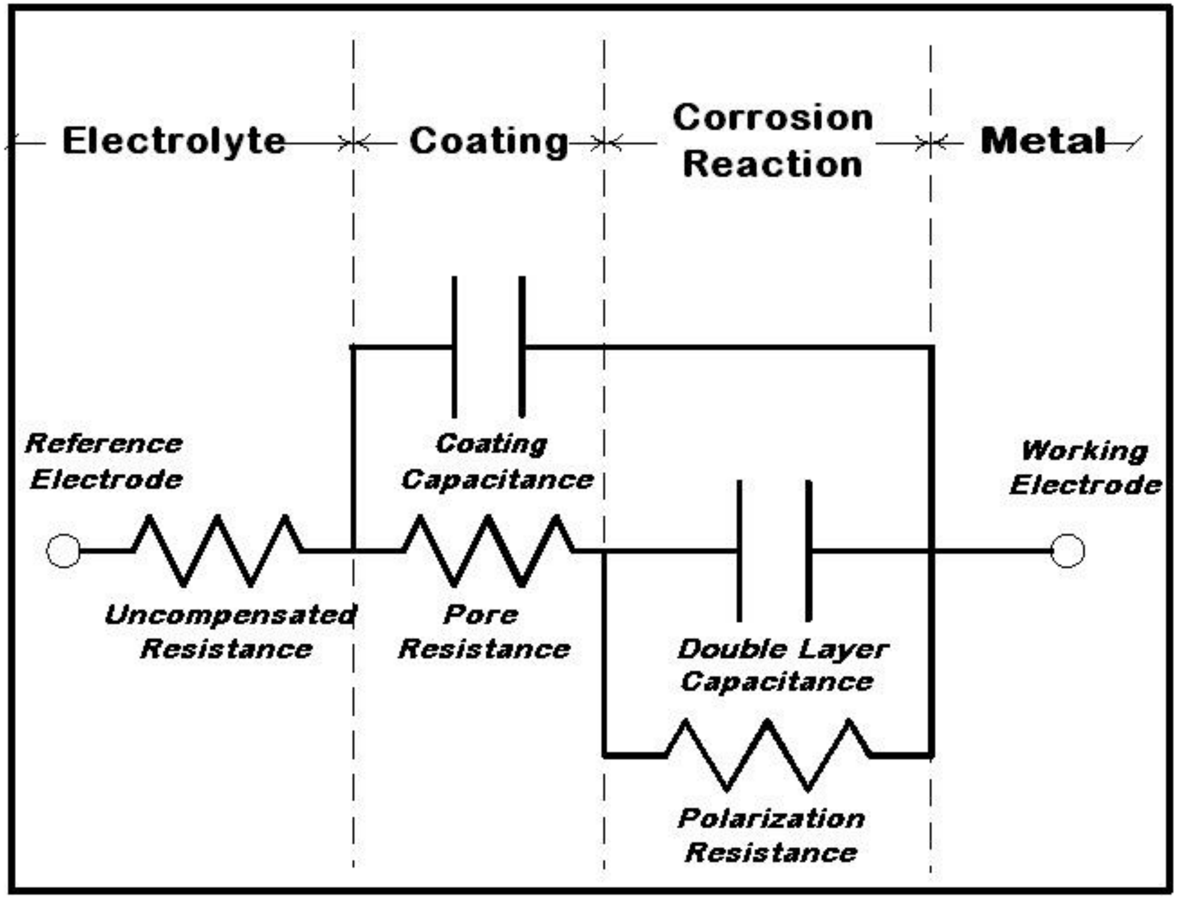
Capacitive Drift (Challenges of Very Good Barrier Coatings)

- An undamaged intact coating behaves like a capacitor
- The bias current from the electrometer of the potentiostat slowly charges this capacitor, causing what appears to be a drift in E_{OC}. It's actually caused by the charging of the "capacitor" by the bias current.
- Unless checked, the E_{OC} will continue to increase to values as high as 5 volts!
- To obtain the "first" EIS measurement, use an applied DC voltage that is equal to the E_{OC} of the metal substrate.
- As the coating deteriorates, a stable E_{OC} will be observed.

Experimental Procedure

- EIS is a very sensitive detector of coating condition
- Only look at relative changes
- Need a stress mechanism to induce failure
- As EIS is non destructive, failure can be tracked with time

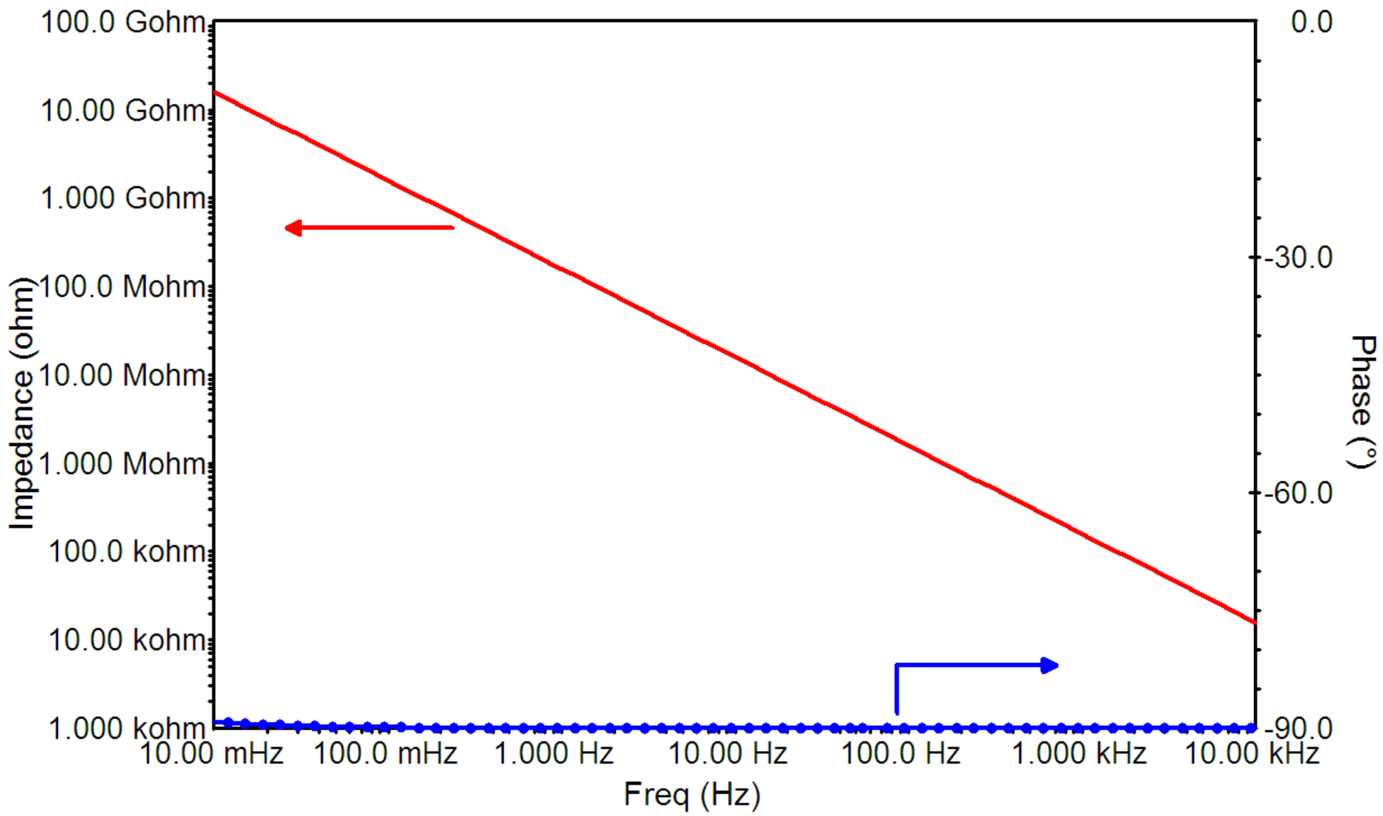
Description of Coated Surface



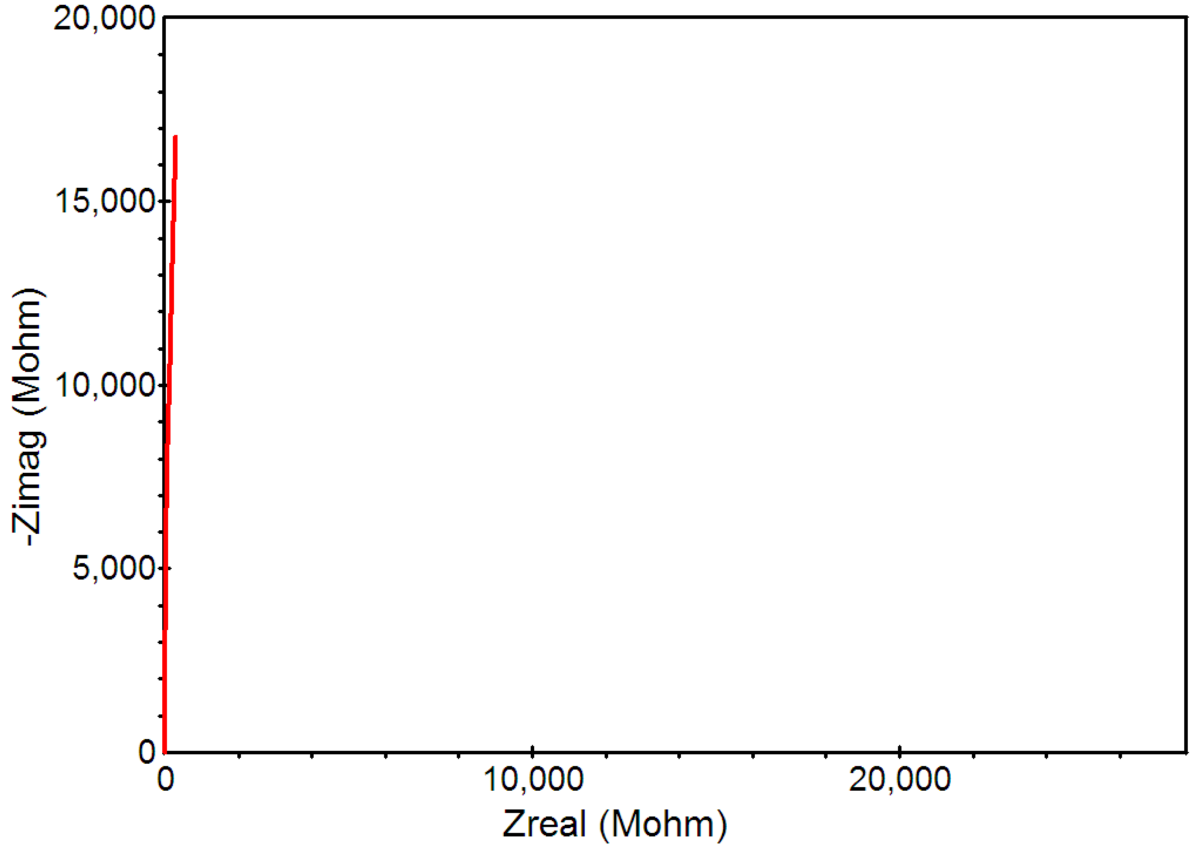
Data Analysis of Coated samples

- Degradation can be described in 5 stages
- Just a general case
- Helpful for visualization

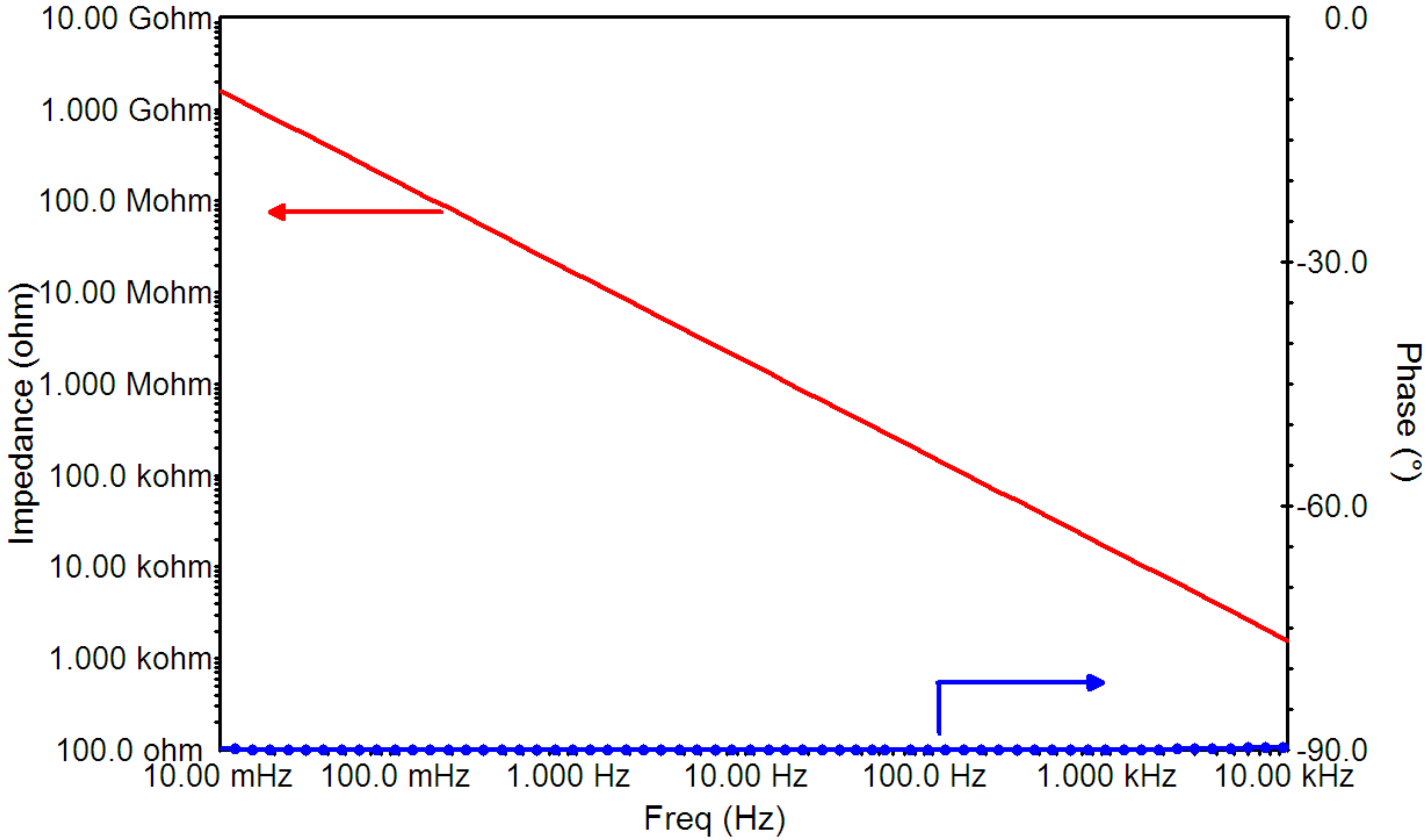
Stage One:Capacitative



Stage One:Capacitative



Stage Two: Water Uptake



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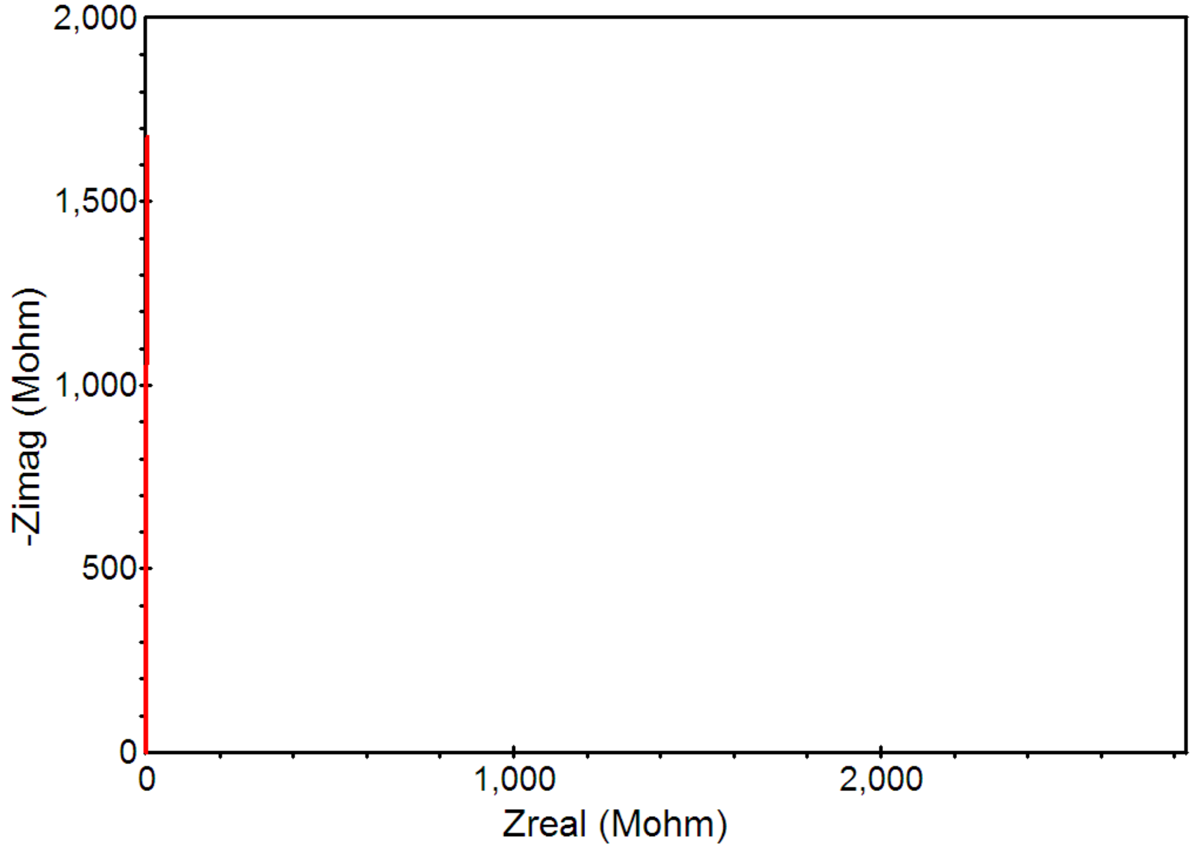
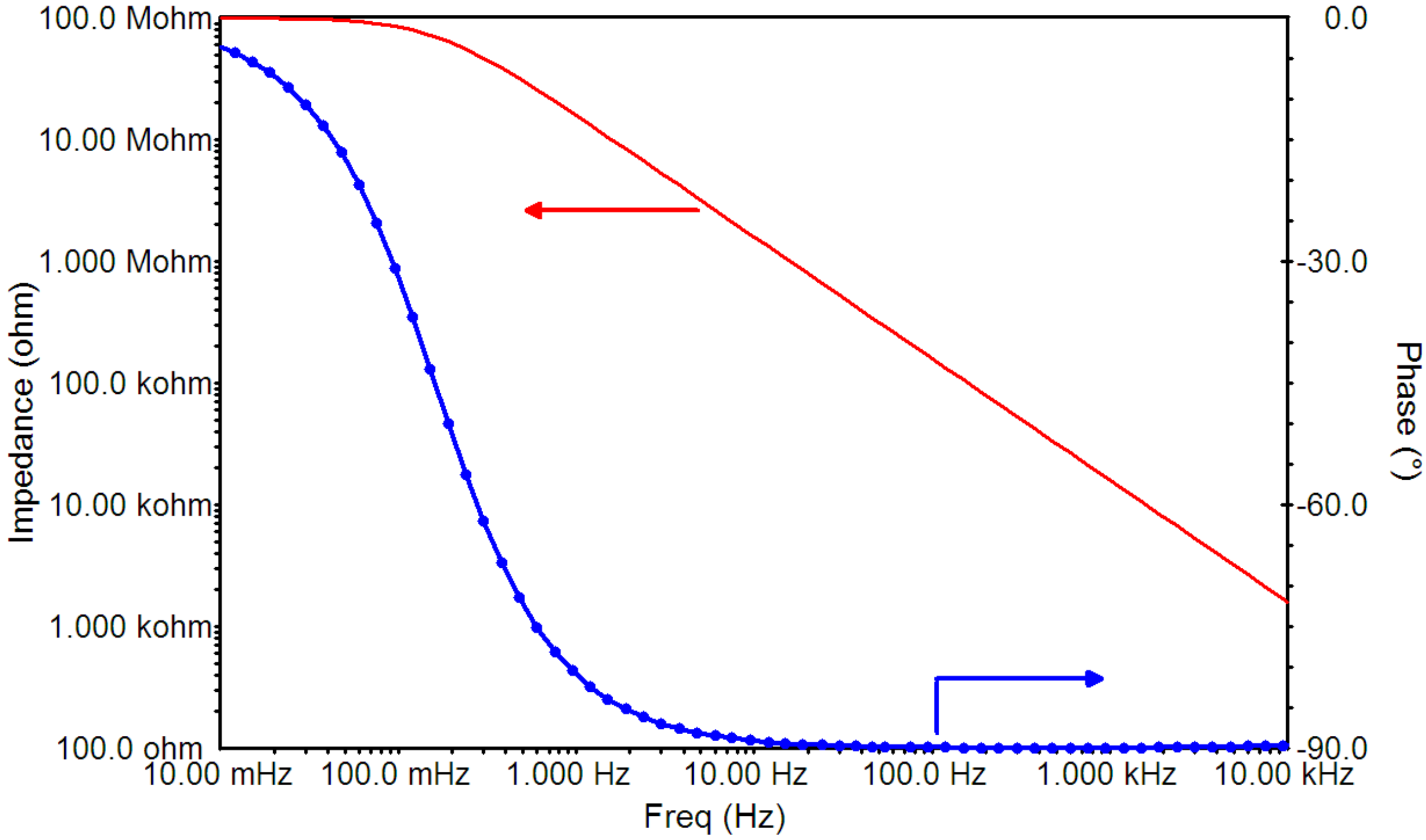
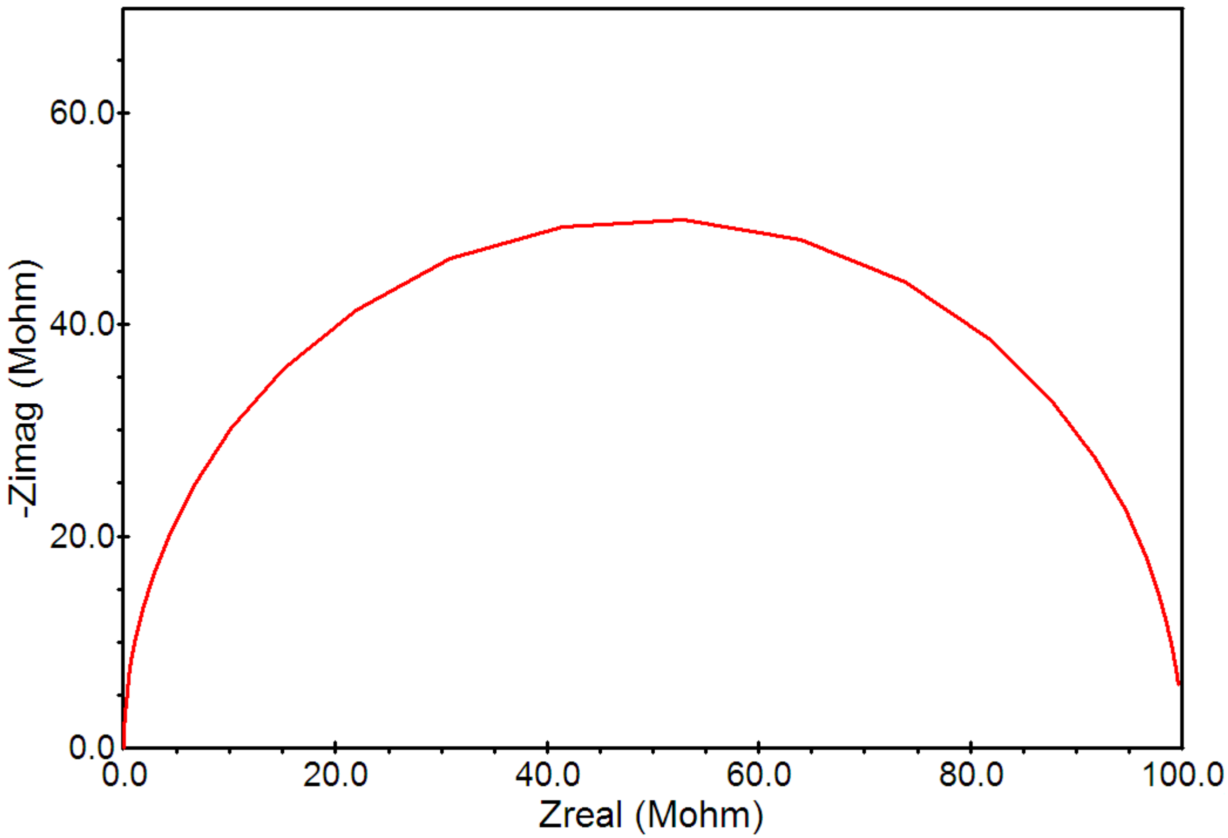


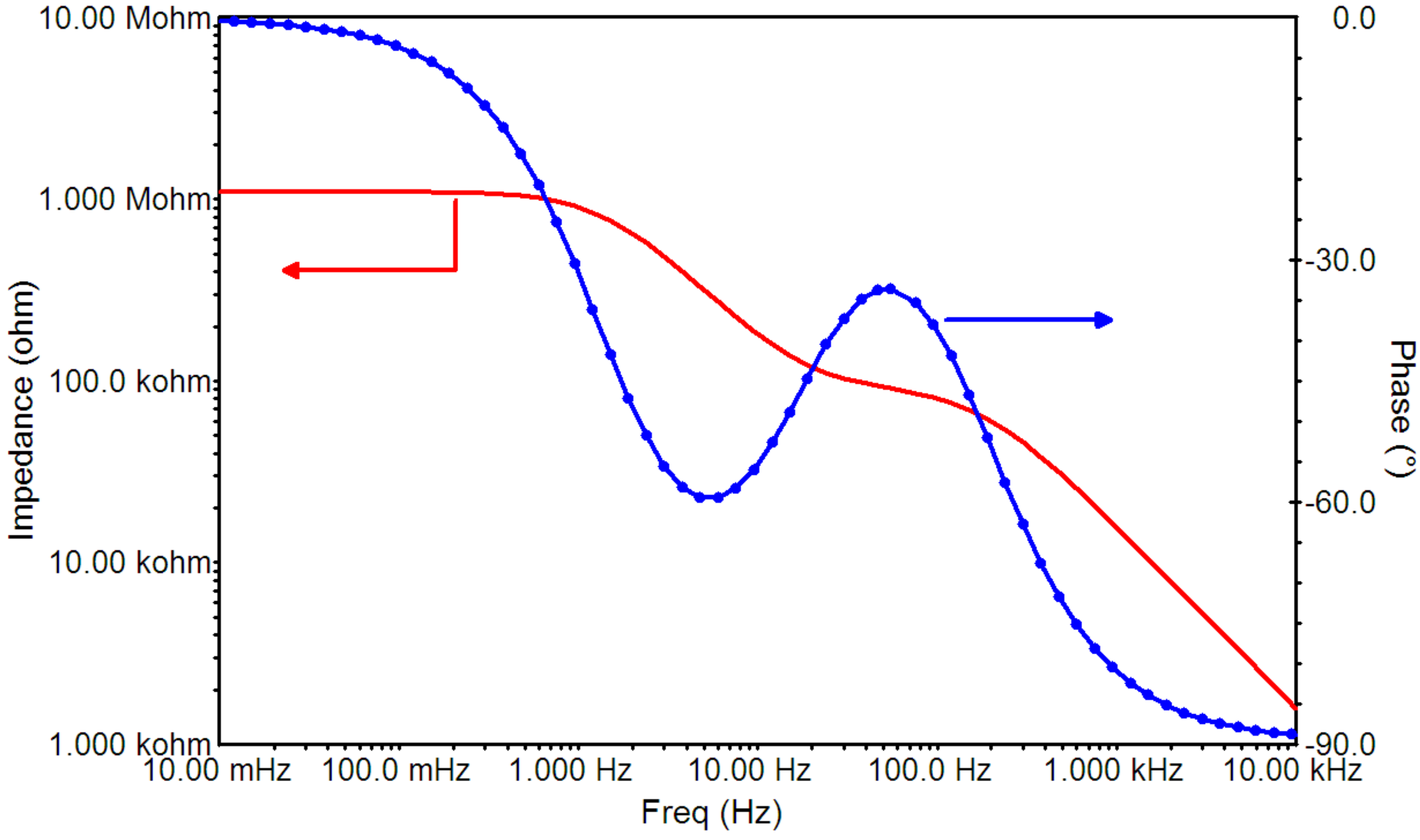
Stage Three:Pore Resistance



Stage Three:Pore Resistance



Stage Four: Corrosion Initiation



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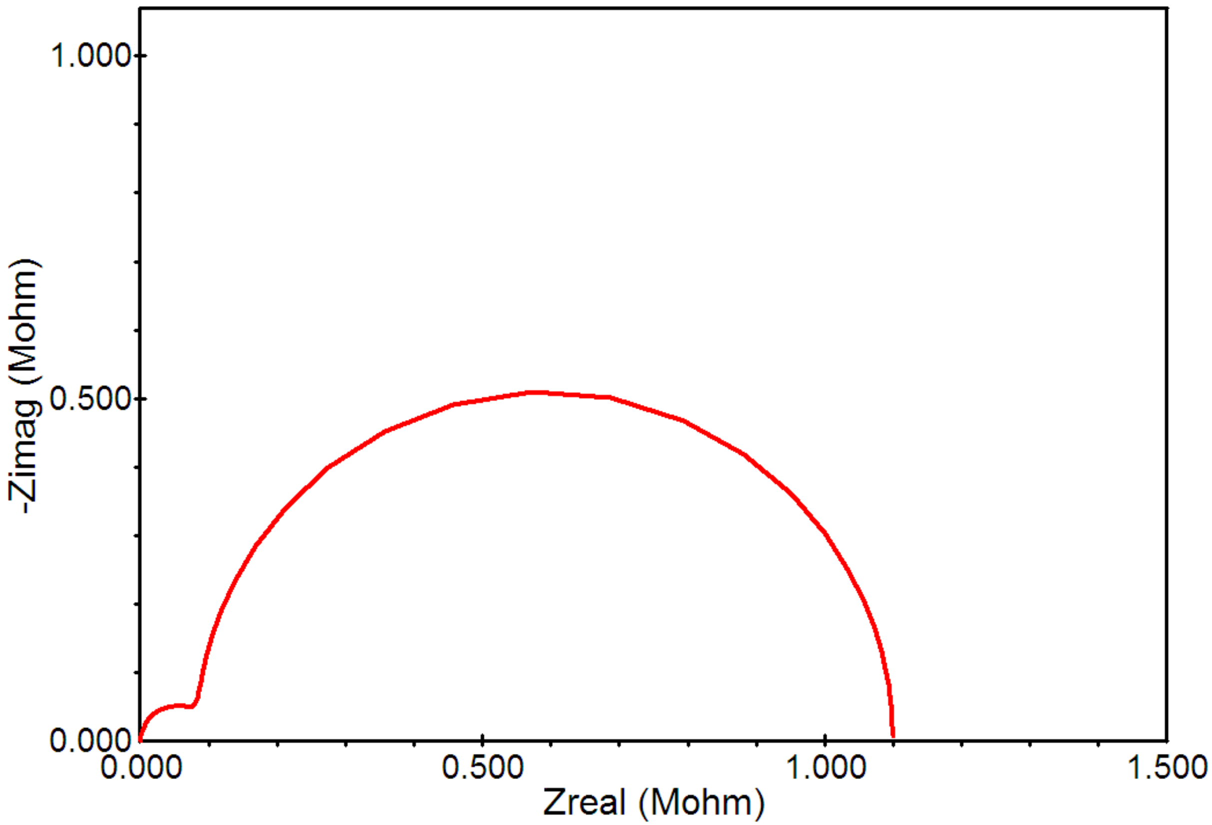
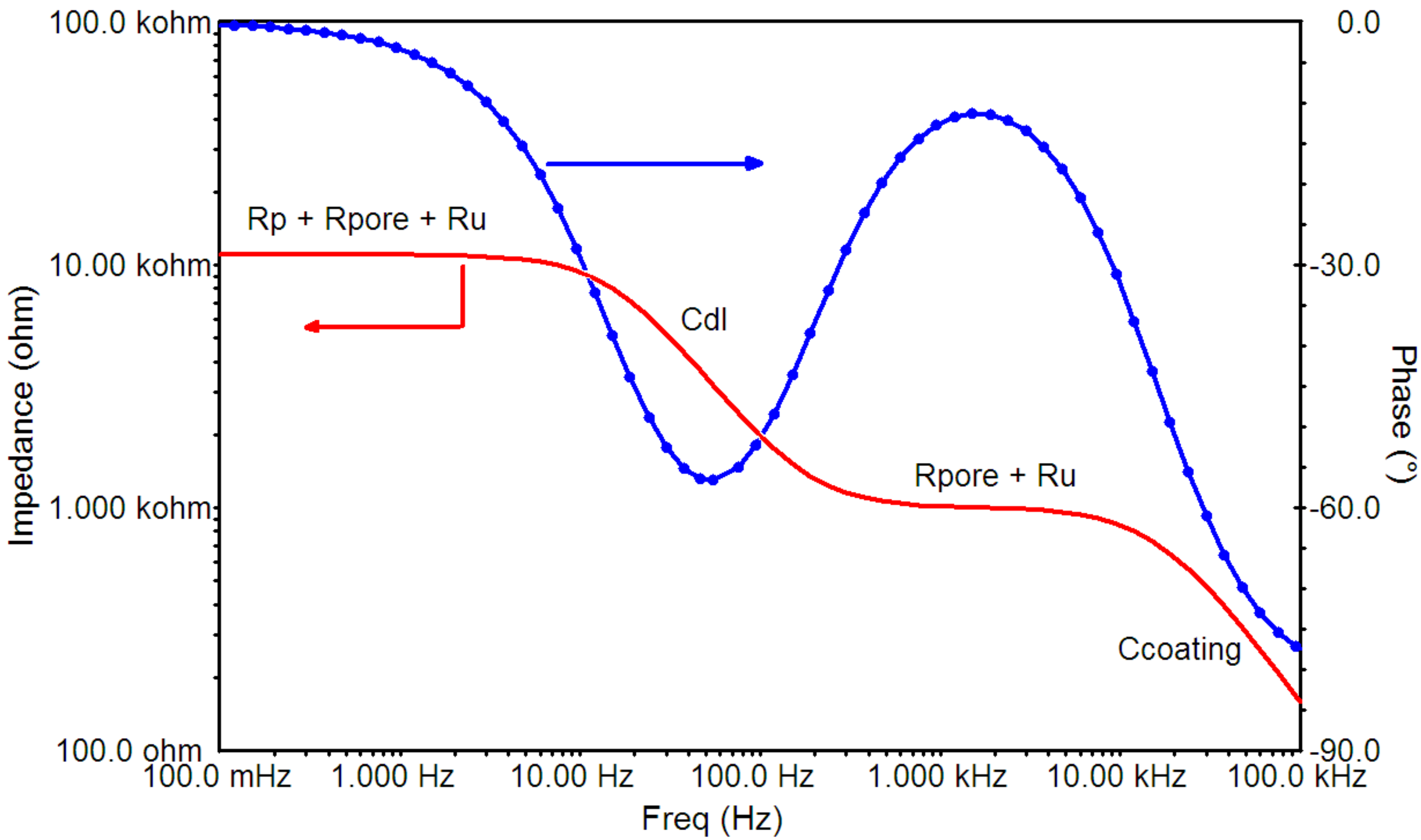
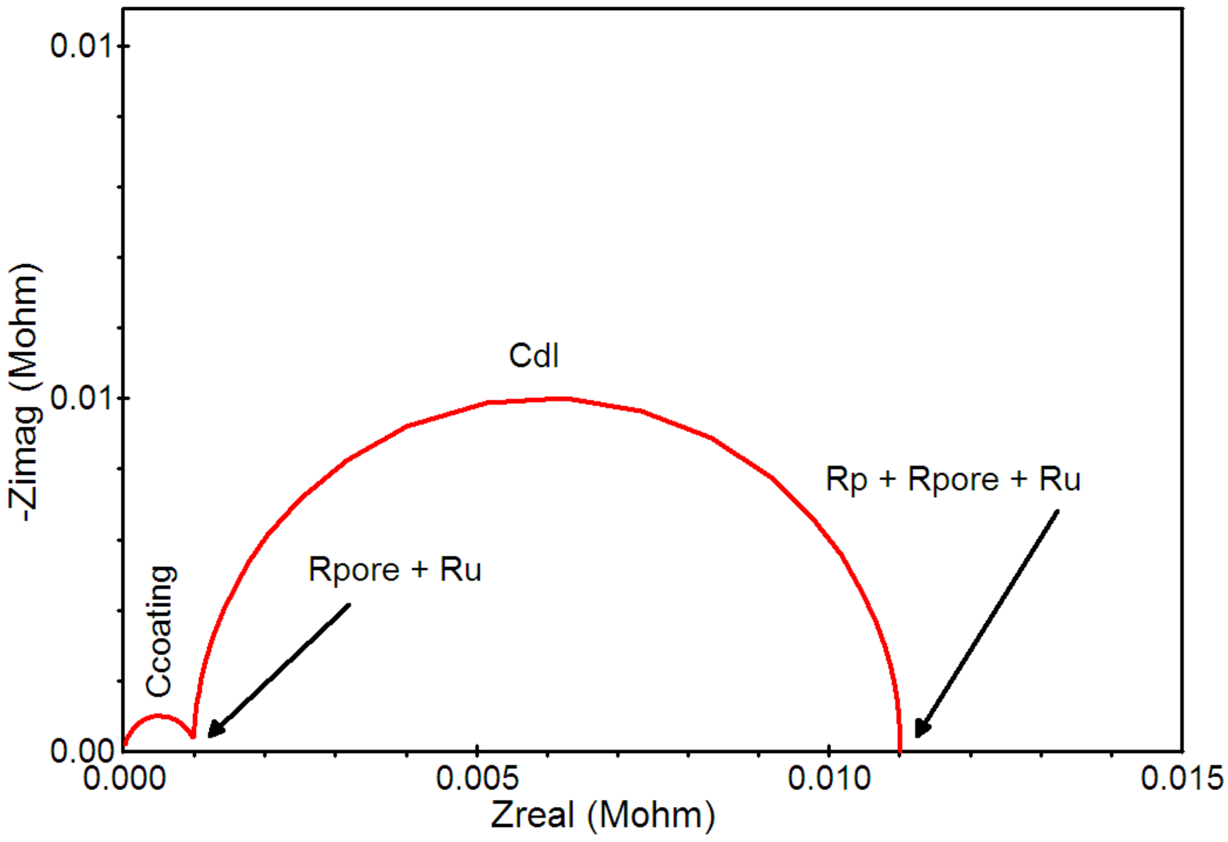


Stage Five: Major Damage



Stage Five: Major Damage



Experimental Methods Of Coating Evaluation

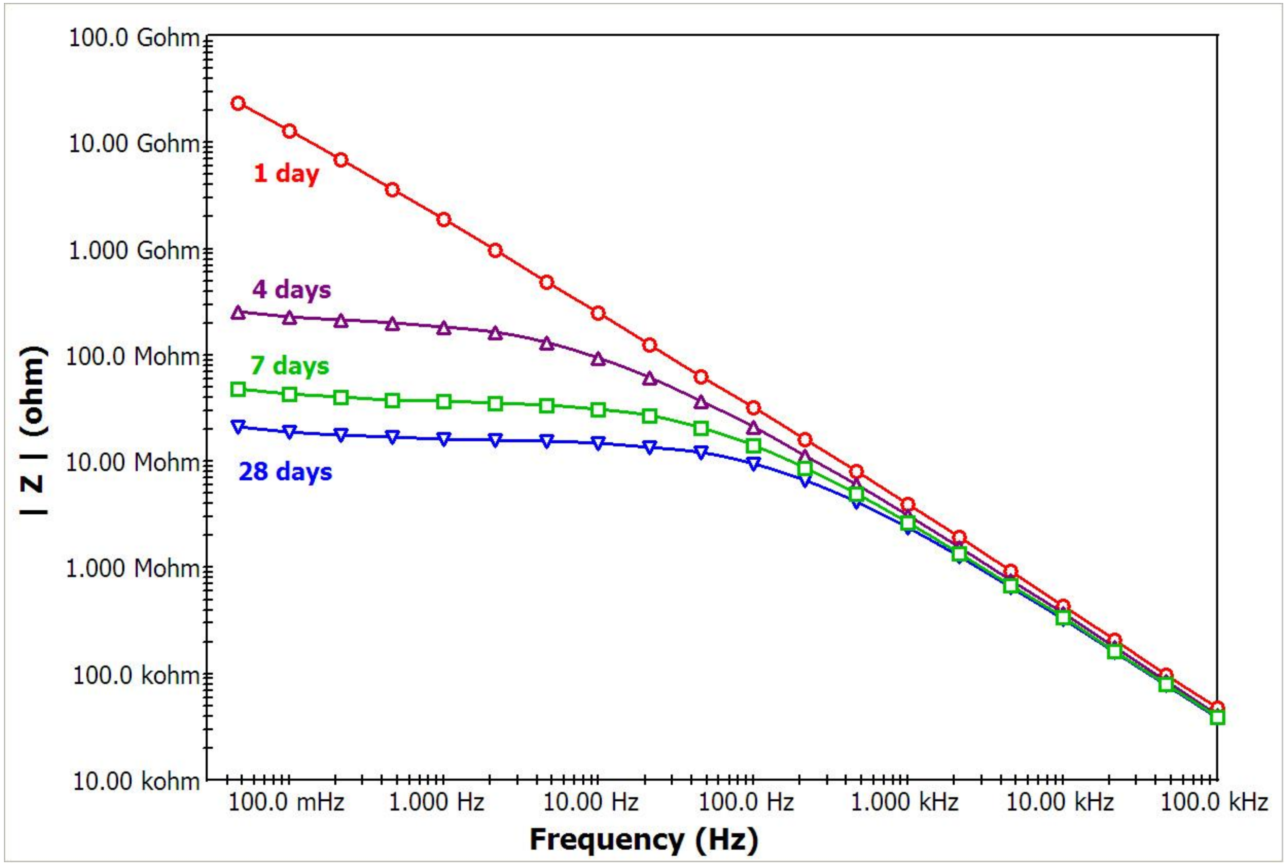
- Measurement at 0.1 Hz
- EIS and Cabinet Tests
- Thermal Cycling
- Rapid Electrochemical Assessment of Paint (REAP)
- AC-DC-AC
- Free standing films

Immersion and Measurement at 0.1Hz

- Straightforward
- Measure EIS Spectrum (5% NaCl (aq))
- Place in oven at 65°C
- Remeasure at different time intervals
- Plot log (|Z|) vs. time
- log (|Z|) > 7, adequate corrosion protection

Gray, L and Appleman, B,J. Prot. Coat. Linings, p66, Feb 2003

Immersion and Measurement at 0.1Hz

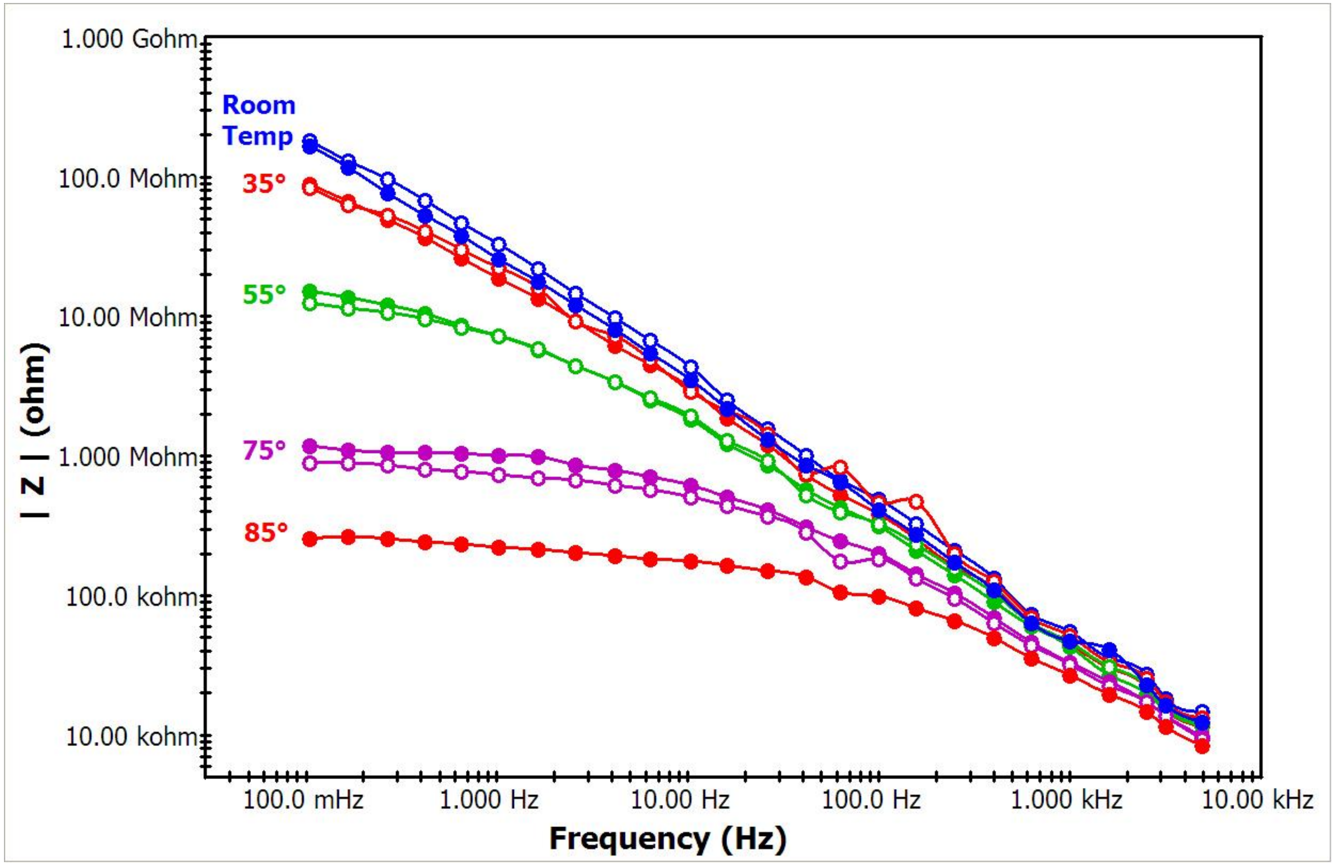


Thermal Cycling

- Accelerate failure by using increased temperature
- Cycle temp. and measure at 35°C,55°C, 75°C, 85°C
- Same sequence back to room temp.

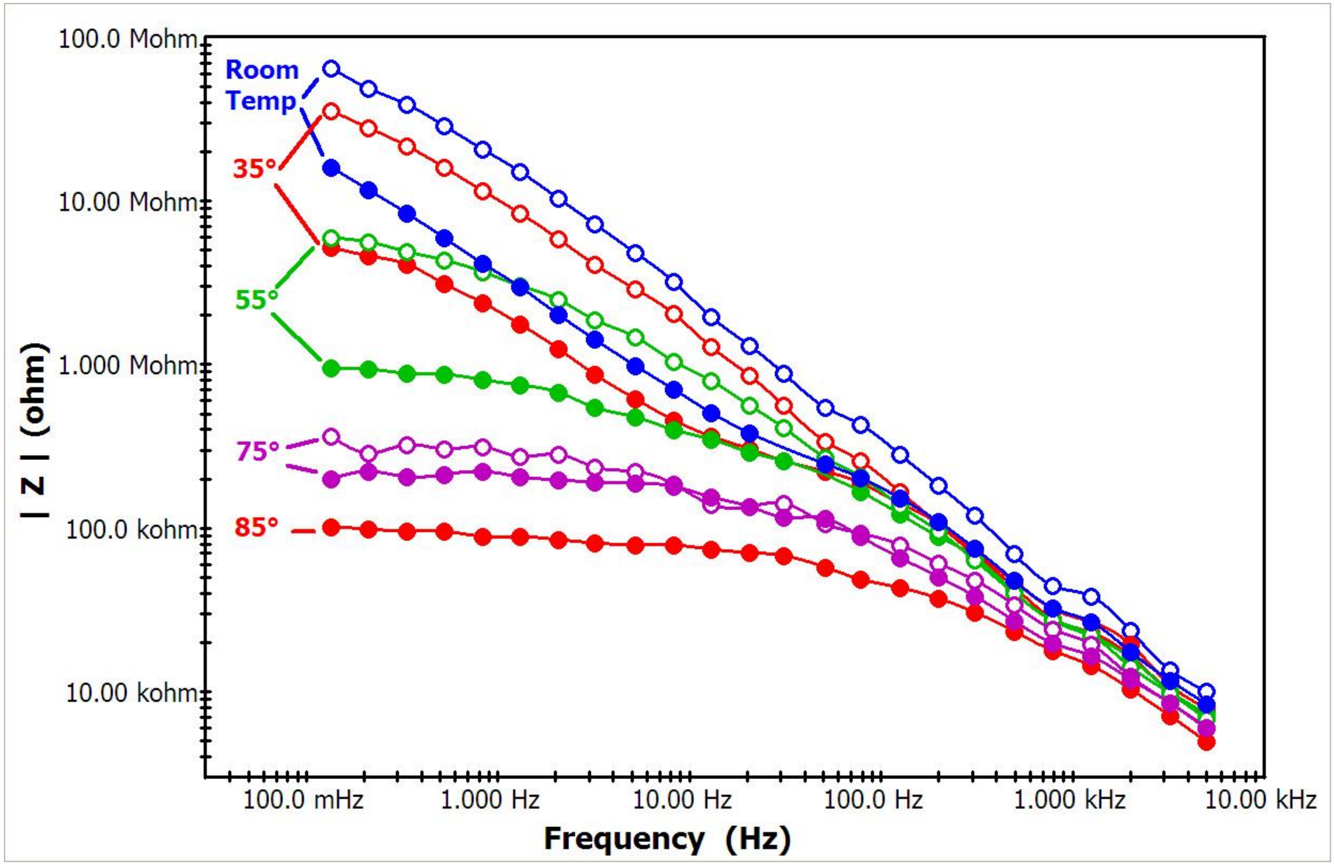
Bierwagen, G.P., He, L., Li, J., Prog. Org. Coat., 39, 67, (2000)

Thermal Cycling



- Reversible Behavior

Thermal Cycling



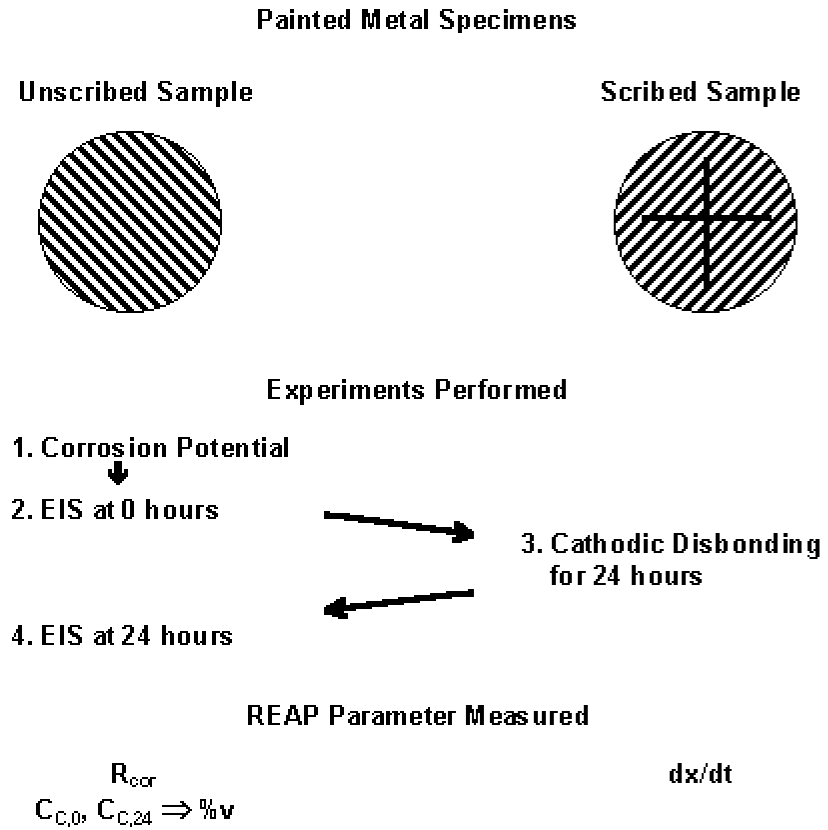
- Irreversible behavior

REAP

- EIS measurement and Cathodic Disbonding
- Only method to combine EIS and physical test
- EIS data modeled according to previous model
- CD sample measured for disbondment
- Rcor, % water uptake, and pullback (dx/dt) used to estimate time to failure (TTF)

REAP

1. Scribe sample B
2. EIS on sample A at t = 0
   a. Get $C_{C,0}$
3. CD on sample B for 24 hrs
   a. Measure pullback
4. EIS on sample A at t = 24 hrs
   a. Get $C_{C,24}$
   b. Get Rcor
5. Calculate
   a. dx/dt = pullback/24/2
   b. %water = 100 log $(C_{C,0}/C_{C,24})$/log(80)
   c. TTF = -830.1 + 118 log Rcor – 169.2 log (dx/dt) – 48.03 (%water)



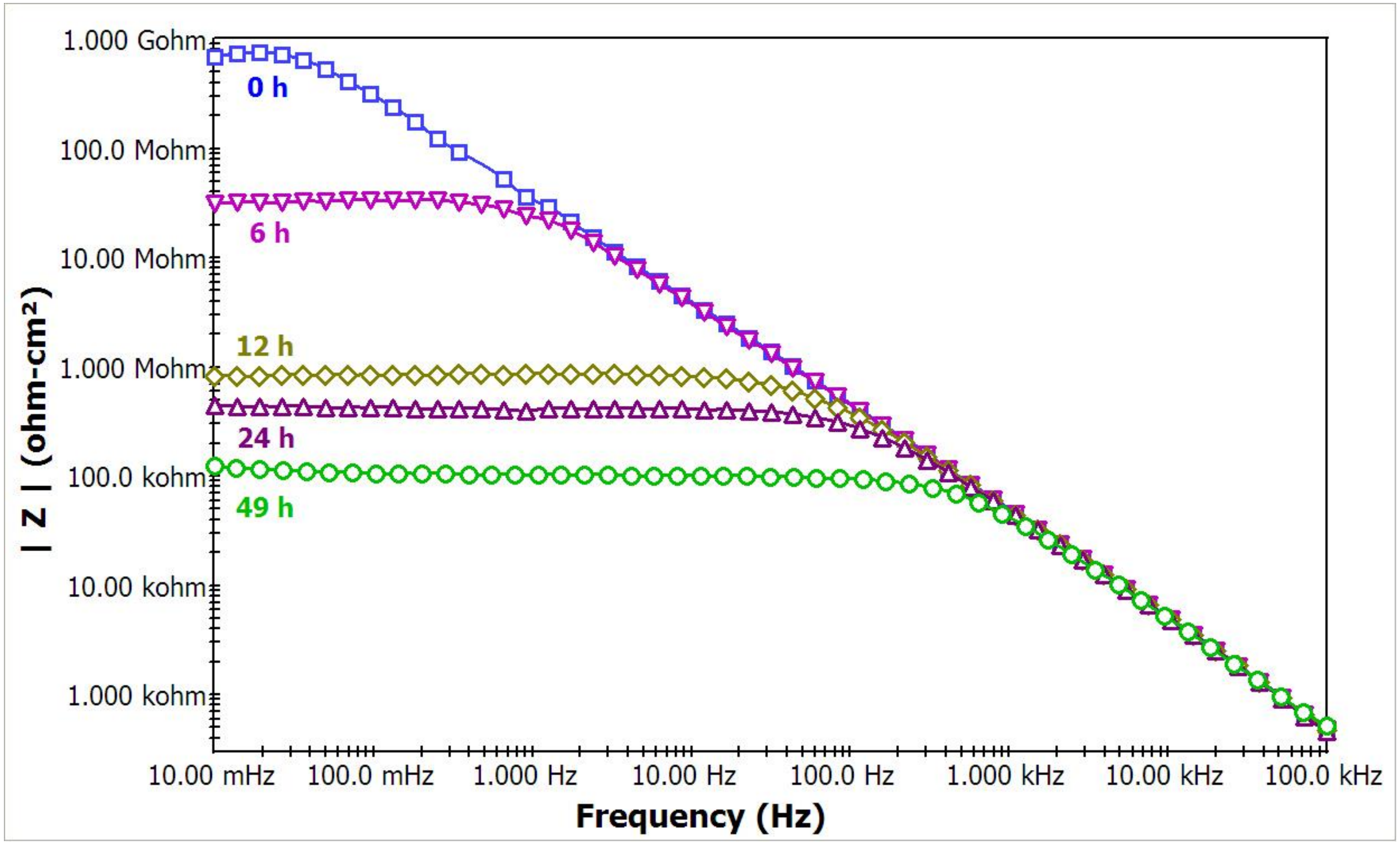
AC-DC-AC

- Measure condition of coating before and after electrochemical disbonding

- Measure EIS
- Cathodically polarize sample
- Remeasure EIS and Repeat

Suay, J.J., et a., J. Coatings Tech., 75, No. 946, 103 (2003)

AC-DC-AC



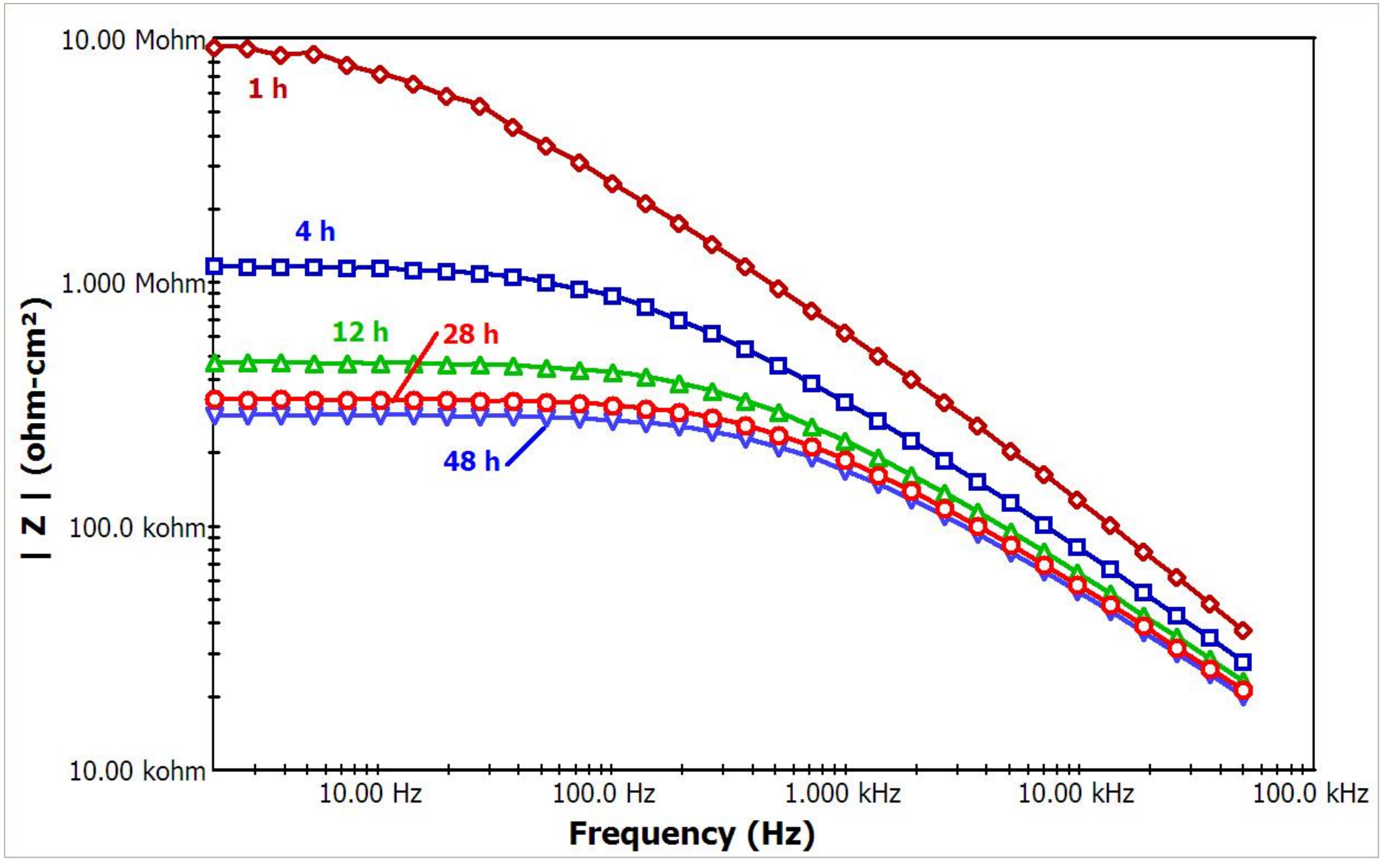
1.000 Gohm
100.0 Mohm
10.00 Mohm
1.000 Mohm
100.0 kohm
10.00 kohm
1.000 kohm
| Z | (ohm-cm²)
0 h
6 h
12 h
24 h
49 h
10.00 mHz
100.0 mHz
1.000 Hz
10.00 Hz
100.0 Hz
1.000 kHz
10.00 kHz
100.0 kHz
Frequency (Hz)

Free Standing Films

- Information just on paint film
- Membrane 4 terminal measurement
- Permeation of coating by ions and water can be precisely studied
- Changes occur faster

Mattos, O.R., Margarit, I.C.P., Electrochimica Acta, 44, 84 (2003)

Free standing Films



Conclusions

- EIS can be very useful for understanding coatings degradation
- Many different approaches, all with merit
- Only useful for metal coated samples (in general)

References for EIS

- For more information visit www.gamry.com to download 3 articles from JCT Coatings Tech on this subject
- Electrochemical Impedance and Noise, R. Cottis and S. Turgoose, NACE International, 1999. ISBN 1-57590-093-9.

  An excellent tutorial that is highly recommended.
- Electrochemical Techniques in Corrosion Engineering, 1986, NACE International

  Proceedings from a Symposium held in 1986. 36 papers. Covers the basics of the various electrochemical techniques and a wide variety of papers on the application of these techniques. Includes impedance spectroscopy.
- Electrochemical Impedance: Analysis and Interpretation, STP 1188, Edited by Scully, Silverman, and Kendig, ASTM, ISBN 0-8031-1861-9.

  26 papers covering modeling, corrosion, inhibitors, soil, concrete, and coatings.
- An Introduction to Electrochemical Corrosion Testing for Practicing Engineers and Scientists, 1994, W. Stephen Tait, PairODocs Publications, PO Box 45383, Madison, WI 53744-5383. E-mail: pairodocs@voyager.net.

  Very basic discussion of DC and AC electrochemical techniques.