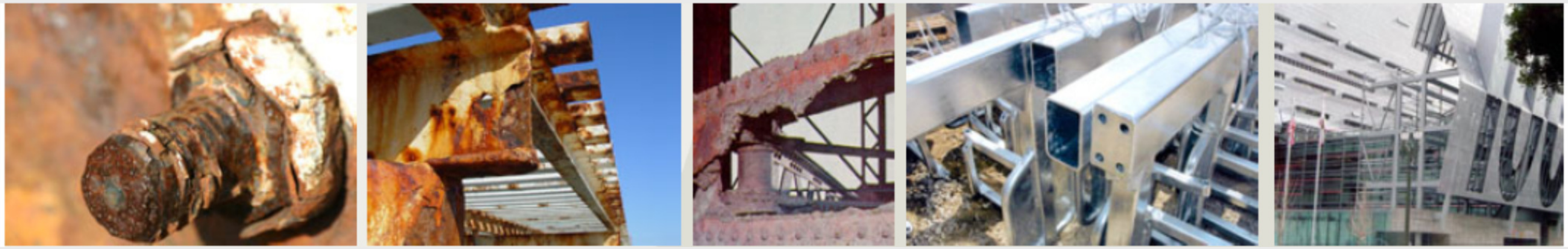

EIS 2014

Electrochemical Impedance Spectroscopy

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- Overview of the technique
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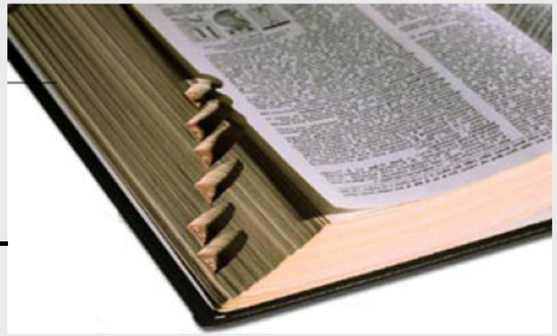
EIS

Electrochemical impedance spectroscopy is a tool in corrosion and solid state laboratories that is slowly making its way into the service environment as units are decreased in size and become portable.

Impedance Spectroscopy is also called AC Impedance or just Impedance Spectroscopy.



Bigger unit

Smaller unit

Portable EIS

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Principle

- Impedance is determined by applying an alternative potential of widely varying frequency
- The corresponding current response is recorded
- Alternating voltage;

$$V(t) = V_o \sin \omega t$$

- Current response at phase difference, ϕ;

$$I(t) = I_o \sin(\omega t + \phi)$$

Principle

According to Ohm law, the ratio between the potential, V(t) and current, I(t) is called the impedance, Z(ω), at the chosen angular frequency, ω.

$$Z(\omega) = \frac{V(t)}{I(t)} = \frac{V_o \sin(\omega)}{I_o \sin\left(\omega t + \phi\right)} = Z'(\omega) + jZ''(\omega)$$

Impedance, Z is given in term of real, Z' (ω) and imaginary, jZ''(ω)

The angle, ω accounts for the shift of the peak current value with respect to that of the potential.

Overview of Technique

- Uses small periodic signal to perturb electrode surface
- Measure an electrochemical response
- Response to be analyzed to gain information on corrosion mechanism and corrosion kinetic
- Common to apply 10-50 mV sinusoidal voltage signal to a corroding electrode interface and measure the resulting current signal occurring at the same excitation frequency

Overview of Technique

- Z(ω)→complex impedance: account for the relationship between amplitudes and current signal/phase shift

- The measurement is spectroscopic → complex impedance measure over range of frequencies (0.0001-100kHz)

- Example bare metal (5-20kHz) anodized coating (50 to 100kHz) → Lower frequency (<0.001kHz) seldom used as it takes longer time (>24h) and owing the instability of corroding metal surfaces

Overview of Technique

- **EIS measurement on corroding surfaces normally use 3 cell electrode.**

- **The working electrode (WE) is your sample you are studying, the reference electrode (RE) sets the potential of the solution, and the counter electrode (CE) is a current source.**

- **A potentiostat is used to control the potential between the WE and RE and measure the current flow between the CE and WE.**

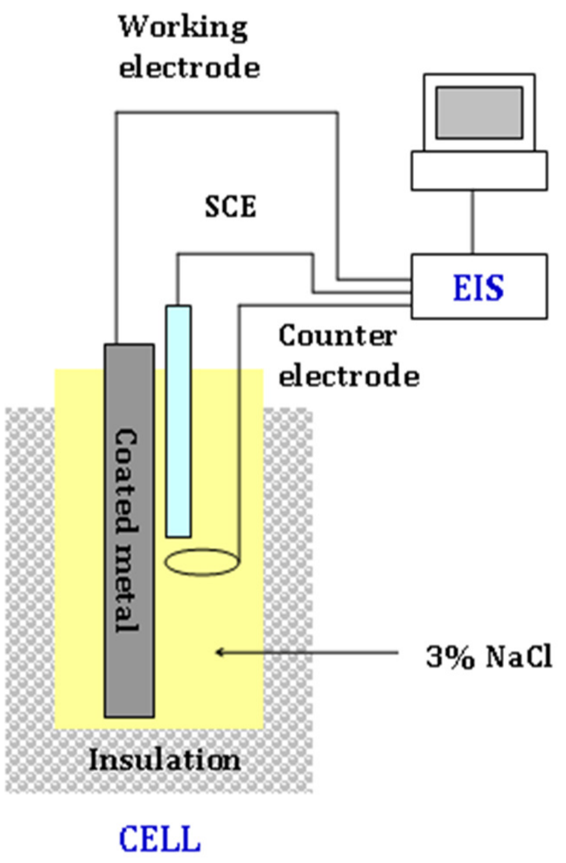
- **An impedance analyzer (usually already built in the potentiostat or can be added) is needed to measure the complex impedance.**

$$Z(\omega) = \frac{V(t)}{I(t)} = \frac{V_o \sin(\omega)}{I_o \sin(\omega t + \phi)} = Z'(\omega) + jZ''(\omega)$$

Overview of Technique

A three-electrode cell consist of coated metal as the working electrode, platinised titanium/graphite rod as the counter electrode, saturated calomel electrode, SCE as the reference electrode.

1. AC Impedance

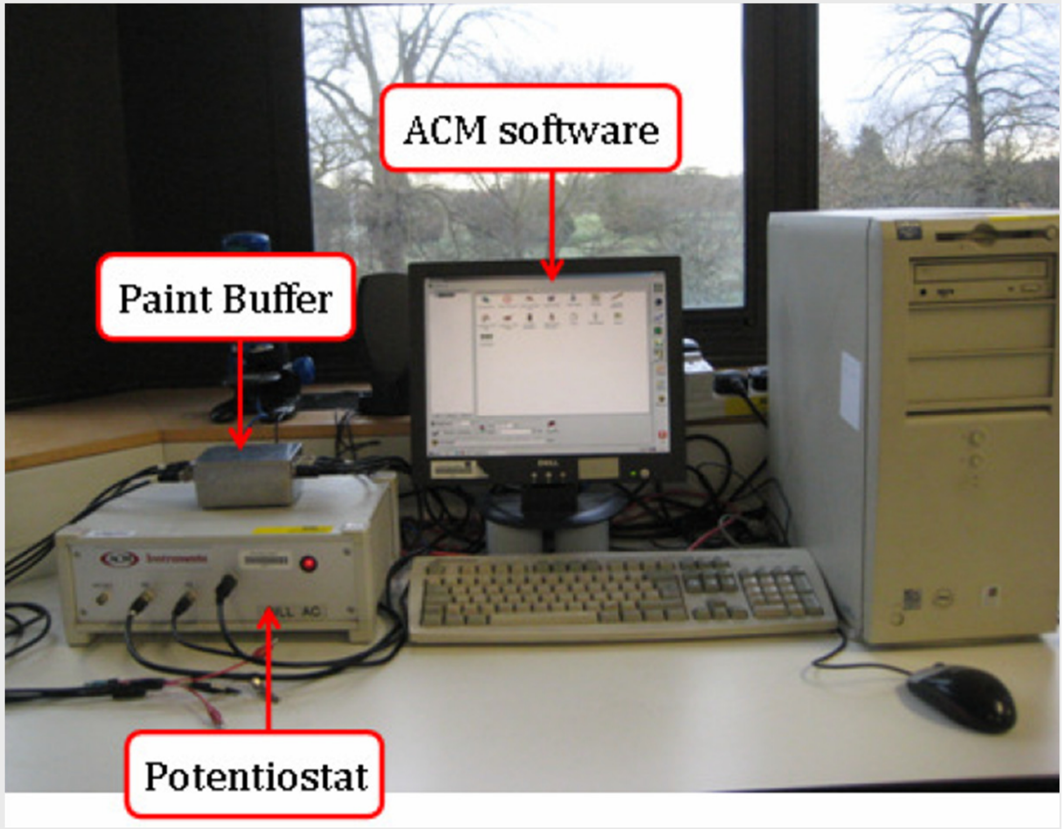


Coating	Thickness (μm)
Epoxy-phenolic	150

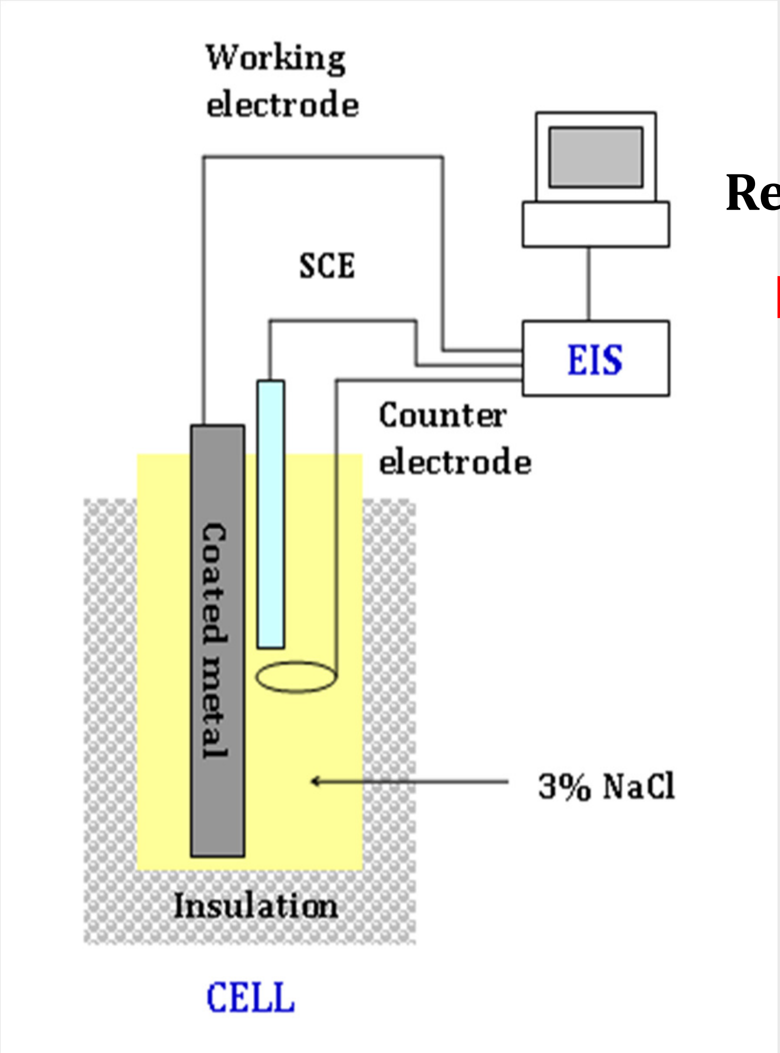
Amplitude	20 mV
Frequency	0.1 Hz~30 kHz

Overview of Technique

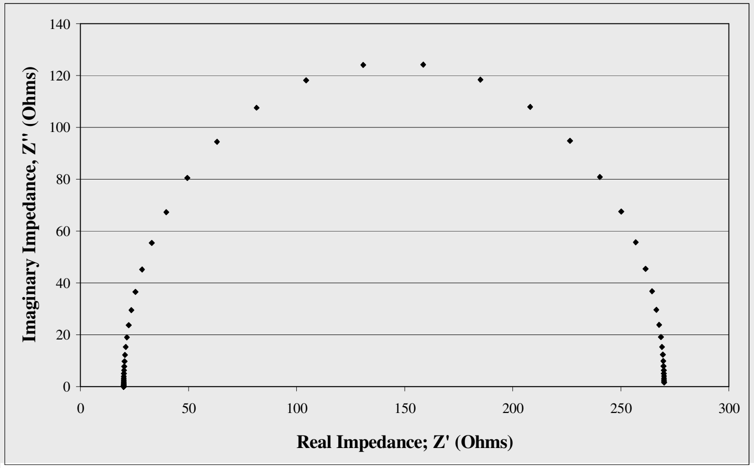
The measurement hardware is controlled by the personal computer, which run software that will coordinate the execution of the experiment and logs the data and provide graphical and numerical analysis of the EIS spectra



Overview of Technique



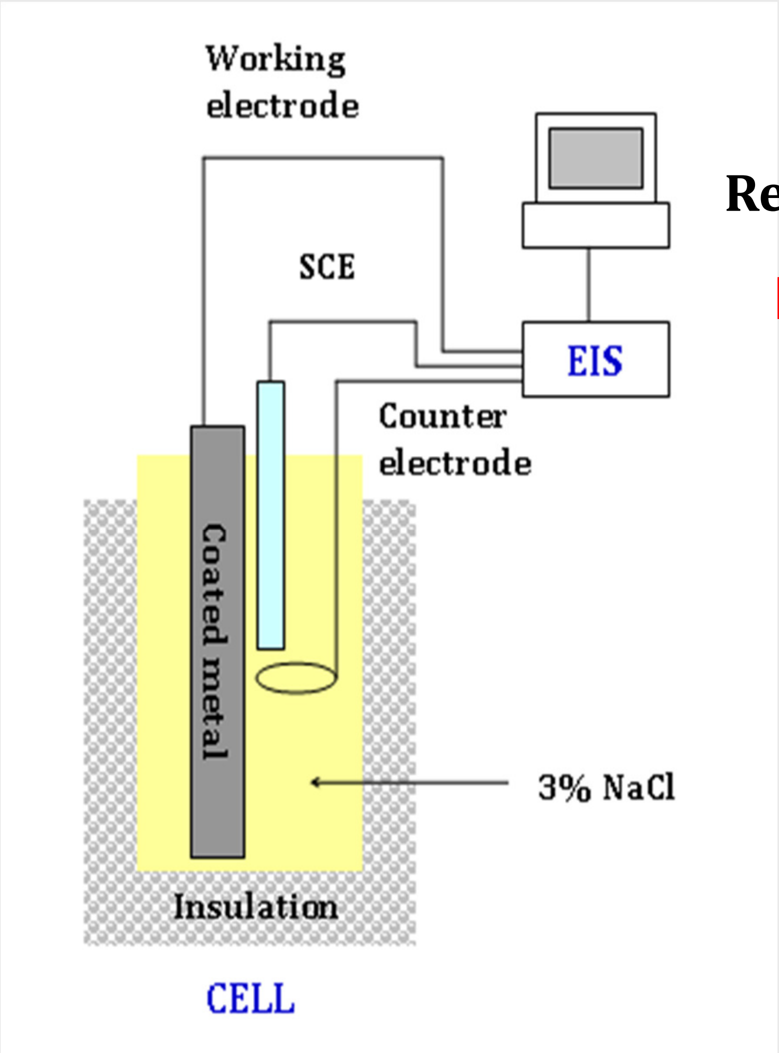
Response



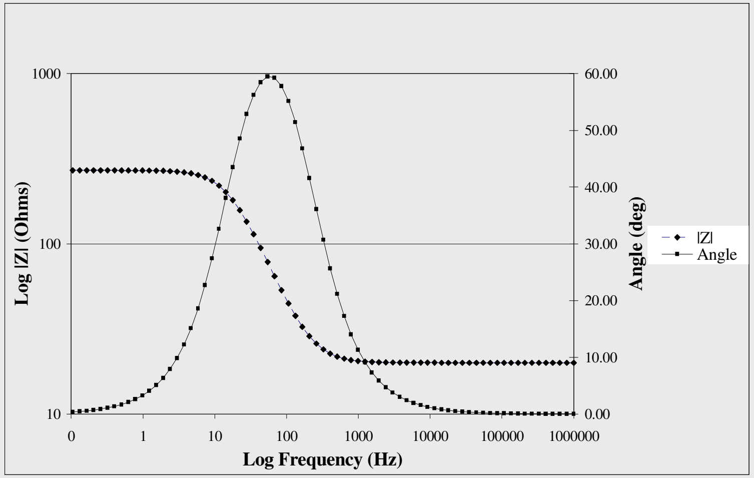
Nyquist/complex plane plot

Complex impedance at each frequency is located at its real and imaginary component

Overview of Technique



Response



Bode Plot:

→Impedance plot

→Phase angle plot

Log of impedance magnitude and phase angle are plotted against log of applied frequency

Overview of Technique

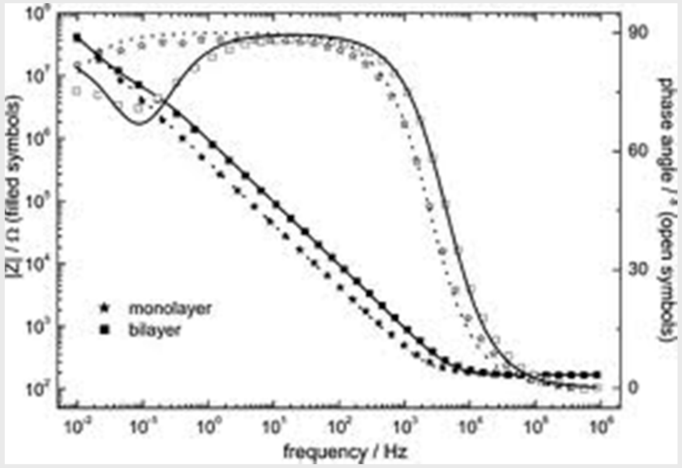
Advantages.

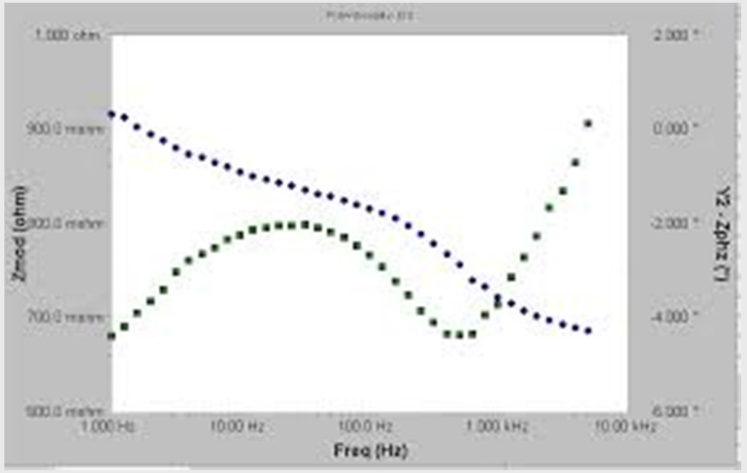
1. It uses very small excitation amplitudes→ cause only minimal pertubation to the electrochemical testing system
2. It is possible to take measurements as a function of frequency and the analysis of the response can provide important information regarding the corrosion process occurring

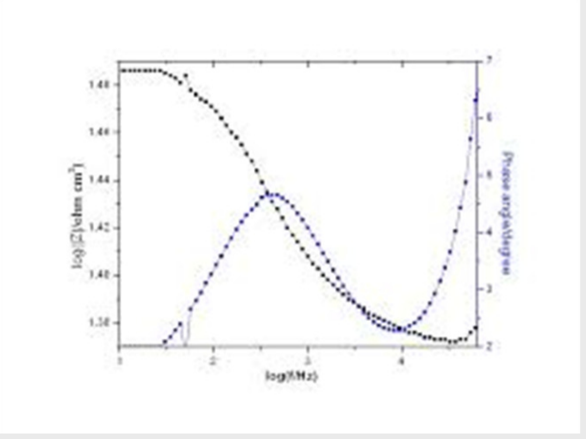
Disadvantages.

1. Expensive.
2. Massive complex data analysis for quantification.

EIS spectrum (Bode plot)







EIS spectrum (Bode plot)

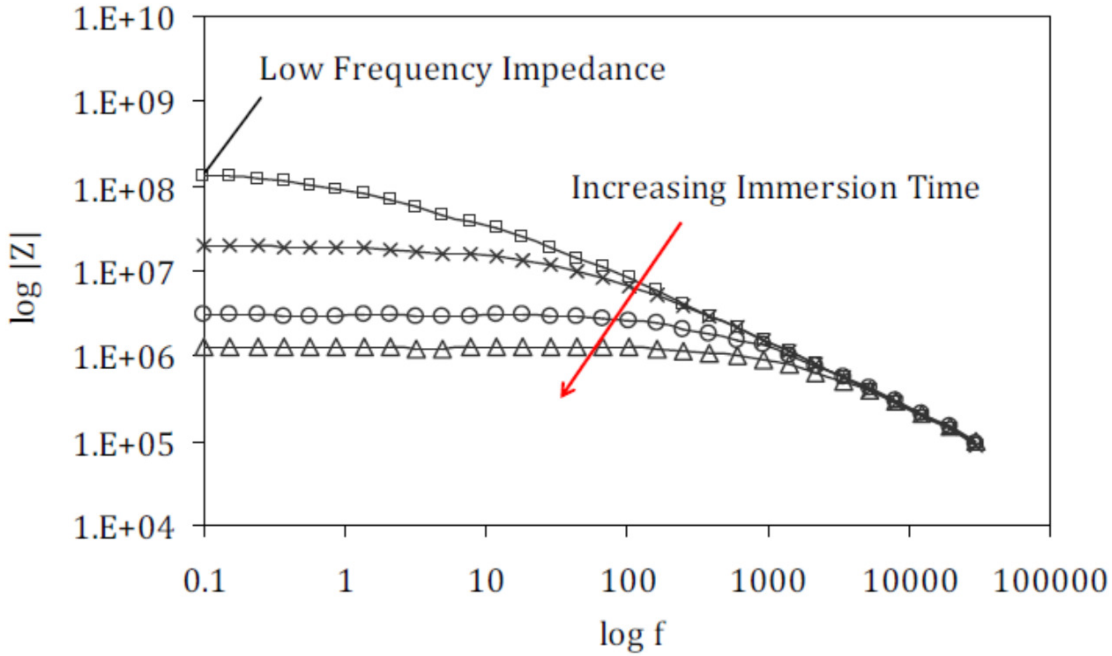


Figure 3.7 - Impedance modulus versus frequency for coated metal

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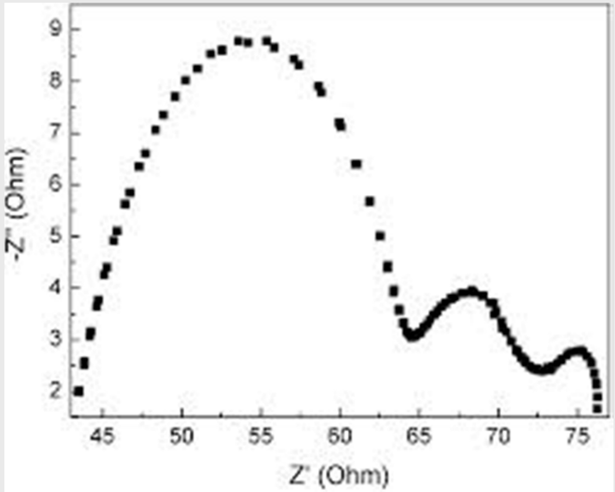
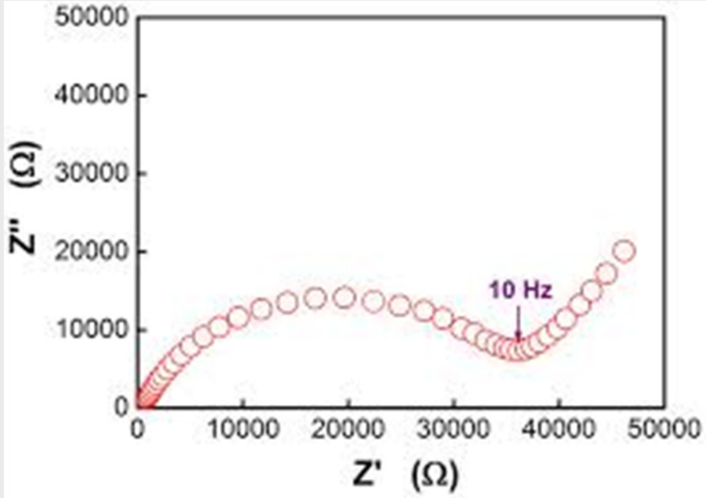
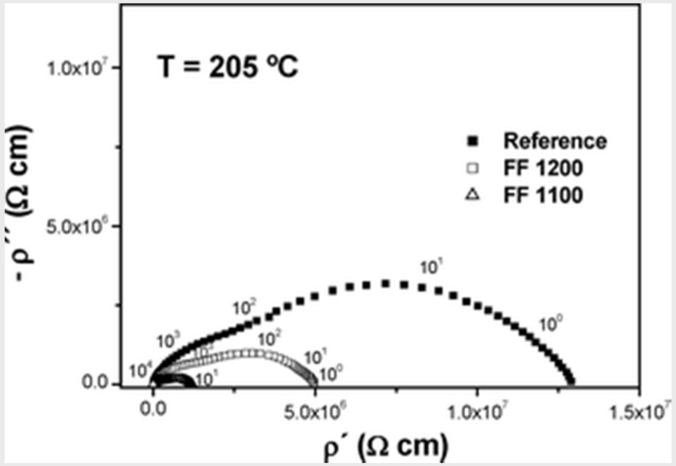
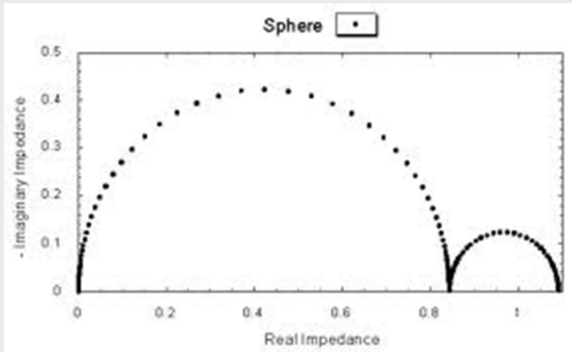
EIS spectrum (Nyquist plot)









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Electrical Circuit Elements

EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors.

To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most models contain a resistor that models the cell's solution resistance.

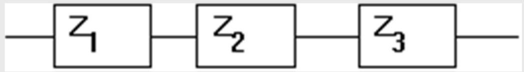
Basic Circuit Element

Component	**Current Vs.Voltage**	**Impedance**
resistor	$E = IR$	$Z = R$
inductor	$E = L\, di/dt$	$Z = j\omega L$
capacitor	$I = C\, dE/dt$	$Z = 1/j\omega C$

Serial and Parallel Combinations of Circuit Elements

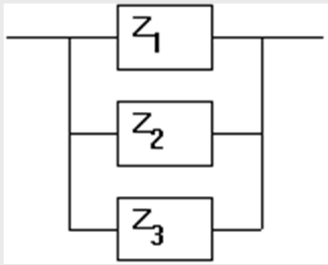
Very few electrochemical cells can be modeled using a single equivalent circuit element. Instead, EIS models usually consist of a number of elements in a network. Both serial and parallel combinations of elements occur.

Impedances in Series:



$$Z_{eq} = Z_1 + Z_2 + Z_3$$

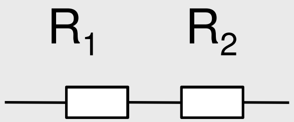
Impedances in Parallel



$$\frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3}$$

Serial and Parallel Combinations of Circuit Elements

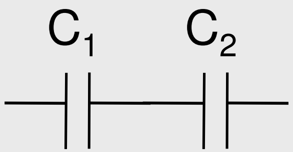
Suppose we have a 1Ω and a 4 Ω resistor is series. The impedance of a resistor is the same as its resistance (see Table 2-1). We thus calculate the total impedance Z_{eq}:



$$Z_{eq} = Z_1 + Z_2 = R_1 + R\ _2 = 1\Omega + 4\Omega = 5\Omega$$

Resistance and impedance both go up when resistors are combined in series.

Now suppose that we connect two 2 μF capacitors in series. The total capacitance of the combined capacitors is 1 μF



$$\frac{1}{Z_{eq}} = Z_1 + Z_2 = \frac{1}{i\omega C_1} + \frac{1}{i\omega C_2}$$

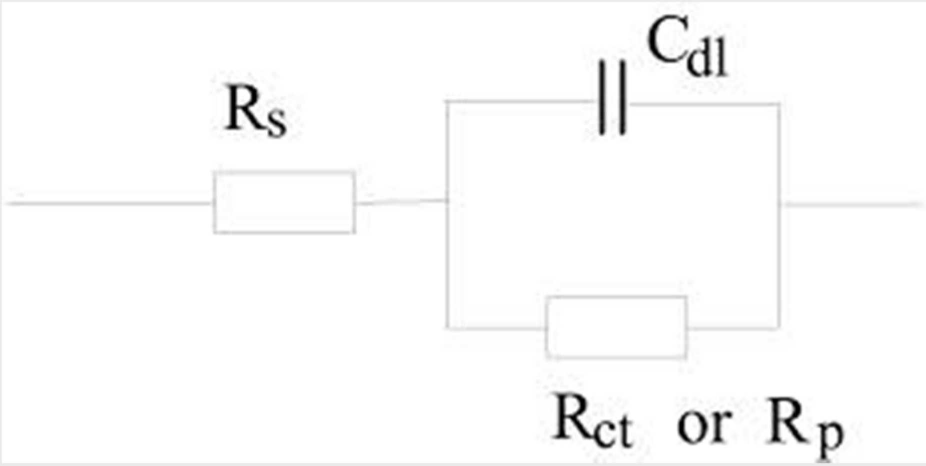
$$= \frac{1}{i\omega(2e^{-6})} + \frac{1}{i\omega(2e^{-6})} = \frac{1}{i\omega(1^{e-6})} = 1\ \mu\text{F}$$

Impedance goes up, but capacitance goes down when capacitors are connected in series. This is a consequence of the inverse relationship between capacitance and impedance.

Equivalent

Circuit

Randles Circuit

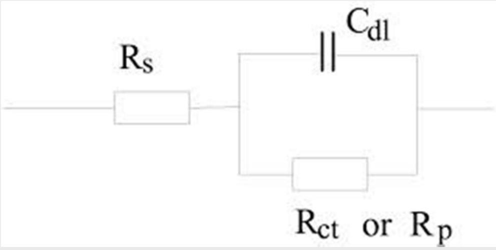


R_s : Electrolyte Resistance

R_p or R_{ct} : Charge Transfer Resistance

C_{dl} : Double Layer Capacitance

Randles Circuit



R_s: normally very small so negligible

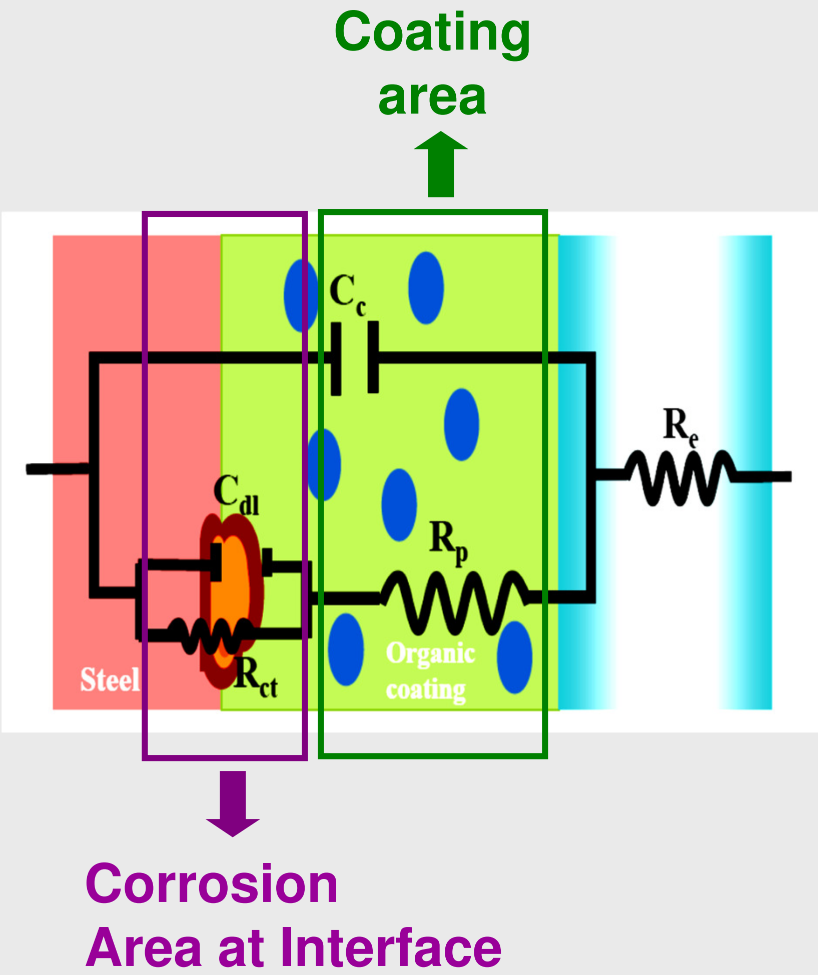
C_{dl}:thin film on substrate form due to contact with solution and form double layer capacitor

R_p or R_{ct}: defined as the slope of the potential vs current density (dE/di) curve at the free corrosion potential. Related to reaction under activation control to the corrosion current by Stern-Geary equation

$$R_p = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c) I_{corr}}$$

β_a, β_c from anodic and cathodic Tafel slope

Model Circuit Representing Coated Metal and Corrosion at Interface



R_e : Electrolyte Resistance

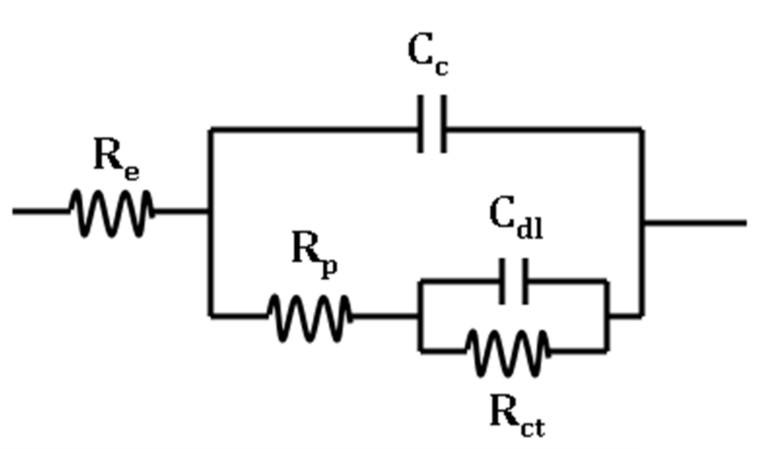
R_p : Coating Resistance

C_c : Coating Capacitance

R_{ct} : Charge Transfer Resistance

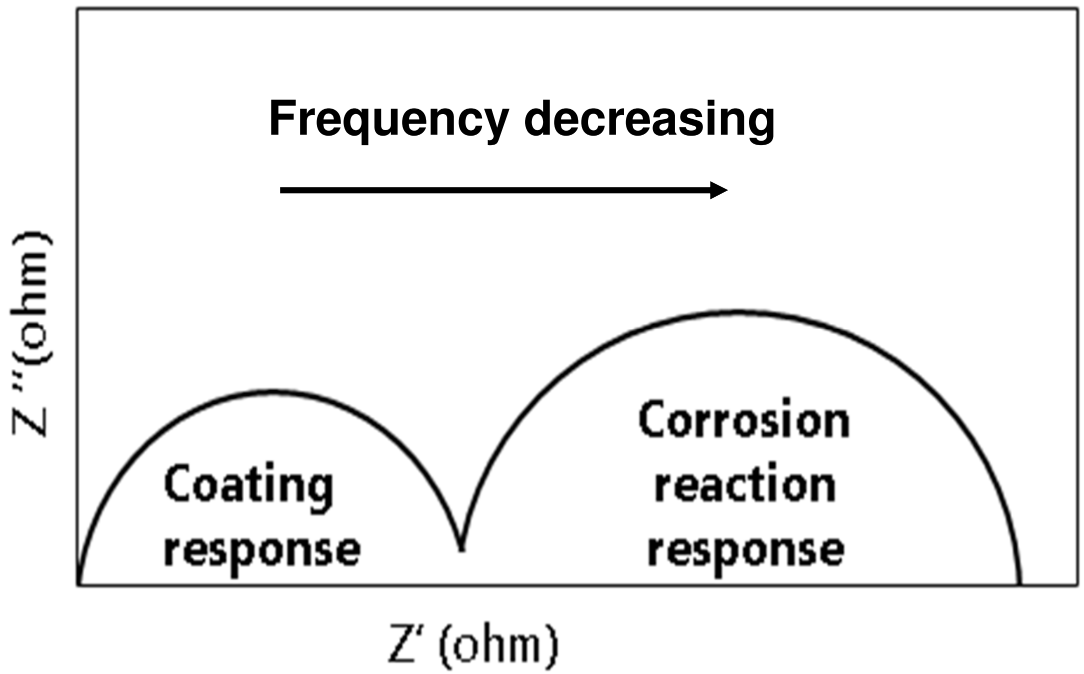
C_{dl} : Double Layer Capacitance

Model Circuit and Nyquist Plot

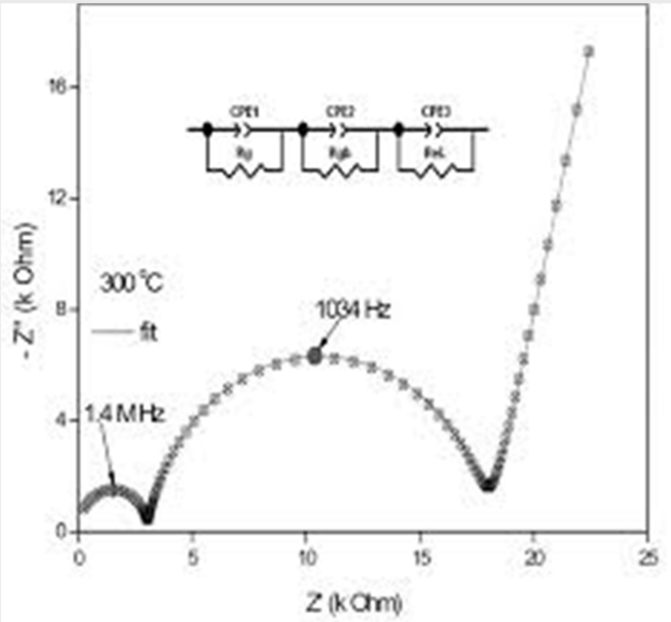


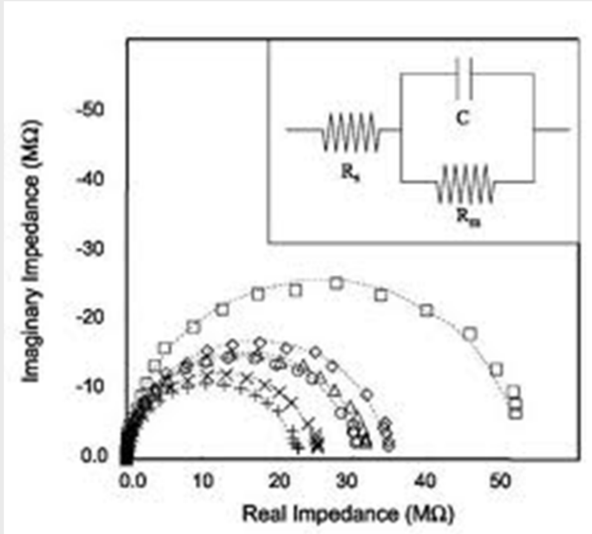
Model Circuit

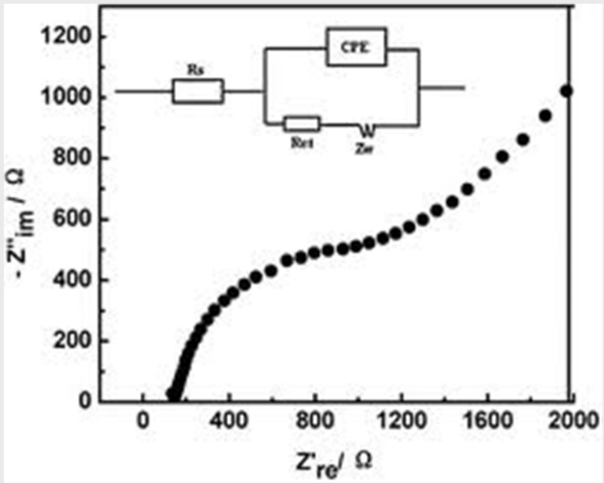
Nyquist Plot

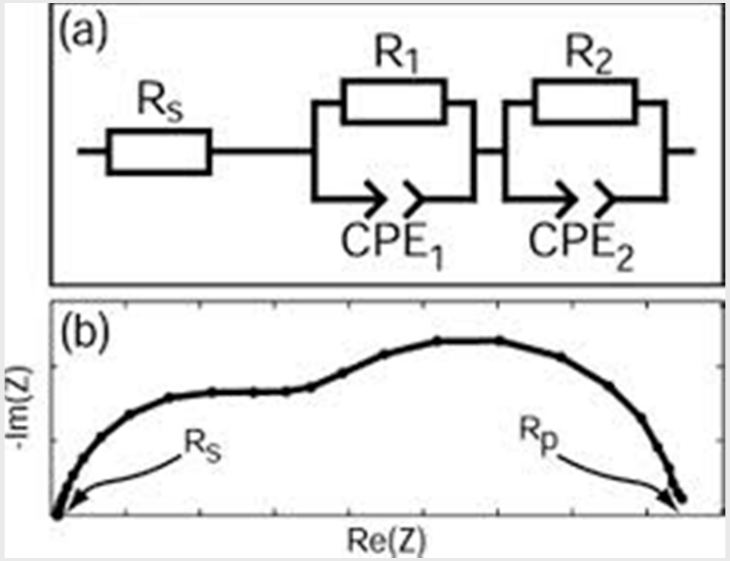


Model Circuit and Nyquist Plot









Model Circuit and Nyquist Plot

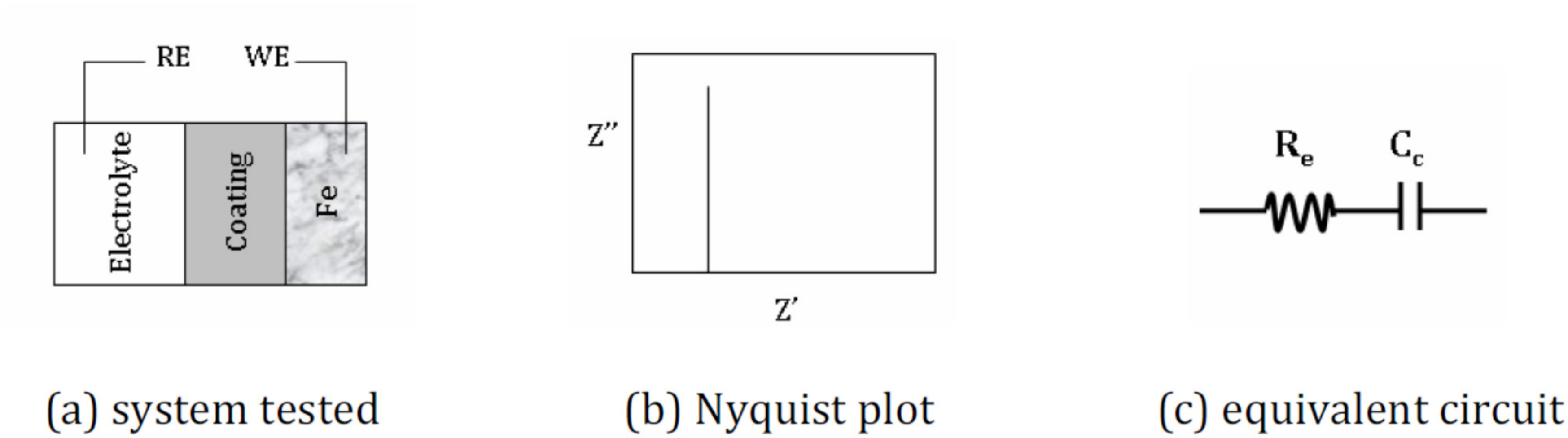
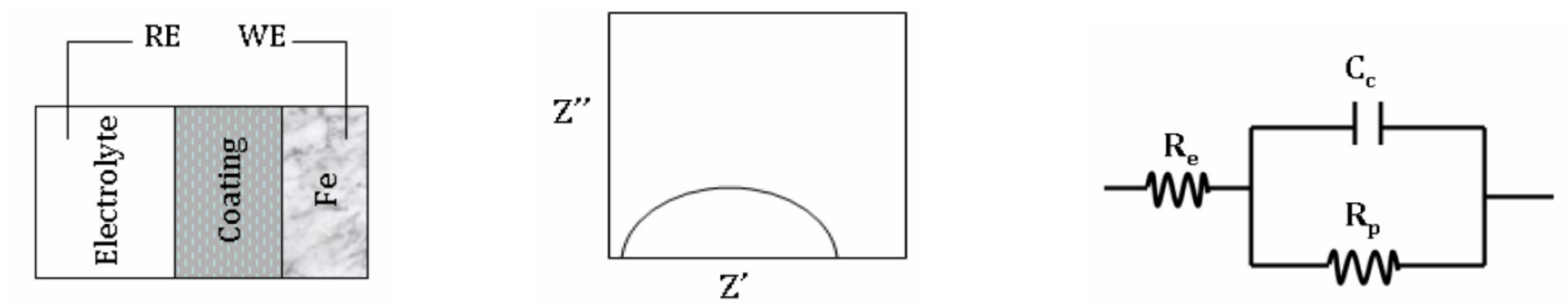


Figure 3.4-Schematic electrochemical characteristics of defect-free coating [113]

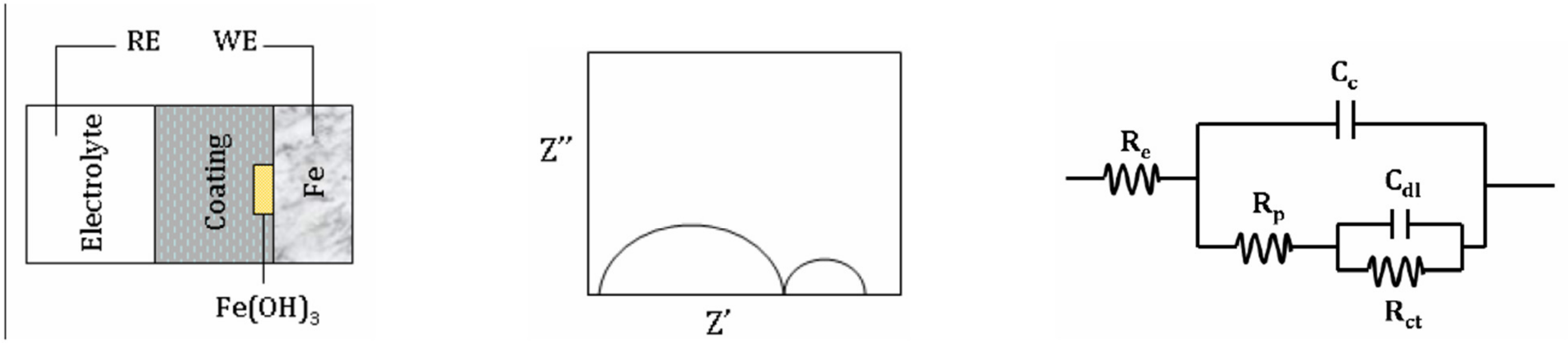
Model Circuit and Nyquist Plot



(a) system tested (b) Nyquist plot (c) equivalent circuit

Figure 3.5-Schematic electrochemical characteristics of a permeable coating [113]

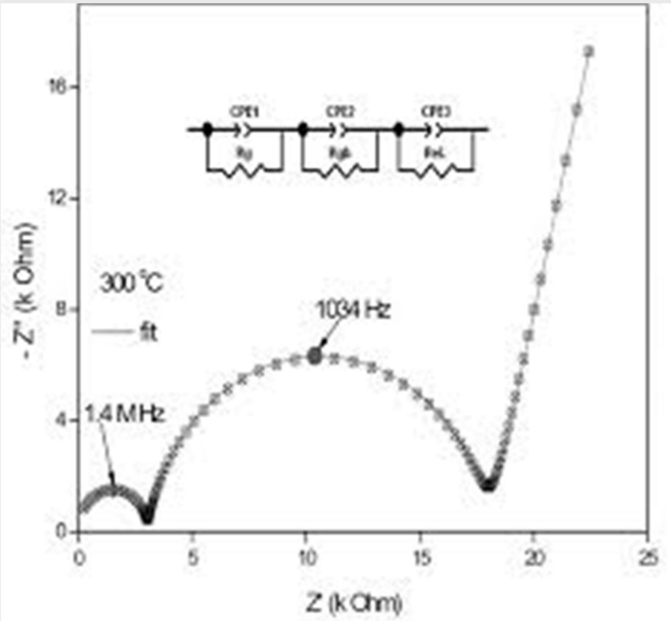
Model Circuit and Nyquist Plot

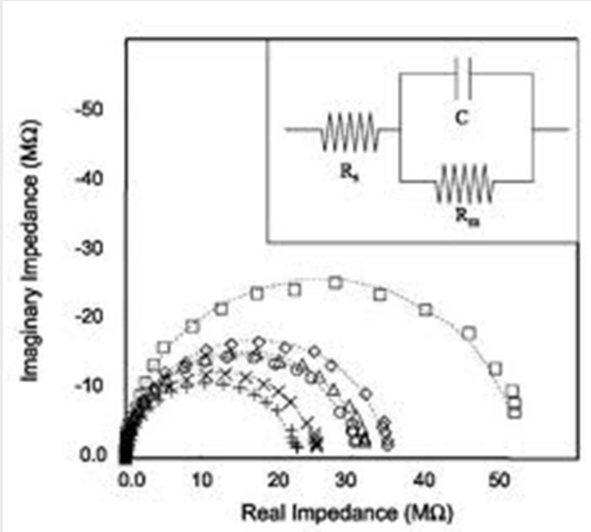


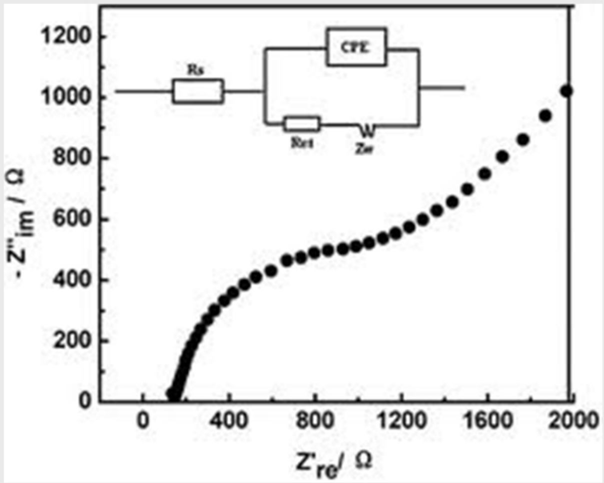
(a) system tested (b) Nyquist plot (c) equivalent circuit

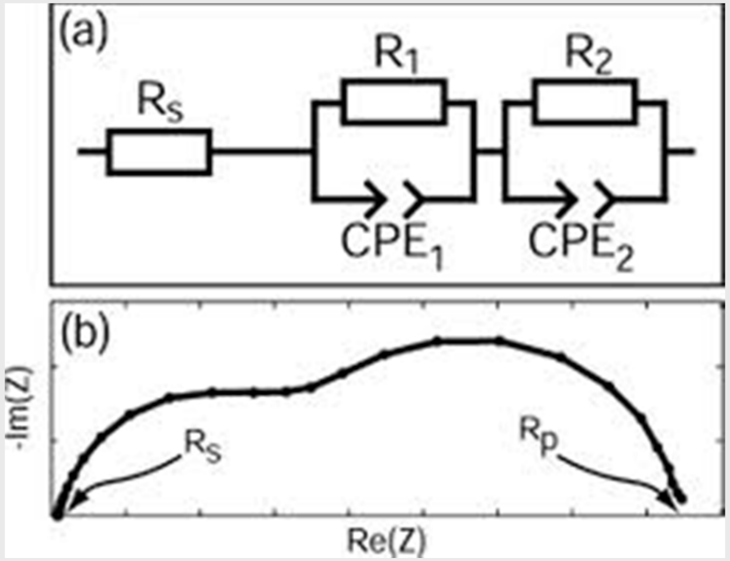
Figure 3.6-Schematic electrochemical characteristics of coating systems with corrosion processes at the interface [113]

Model Circuit and Nyquist Plot



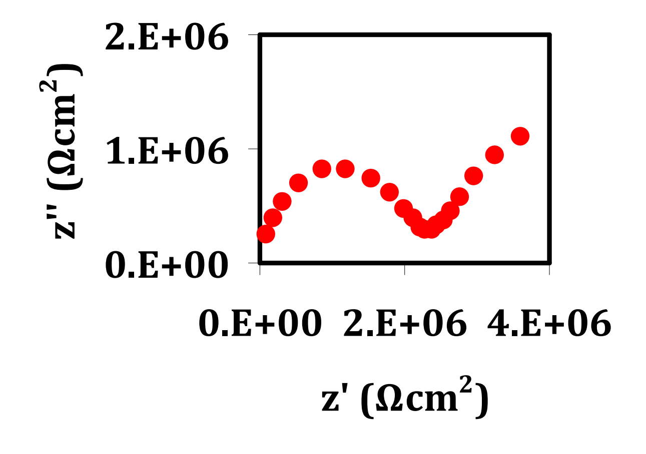


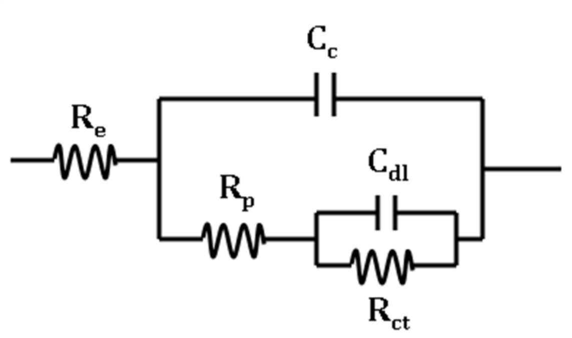




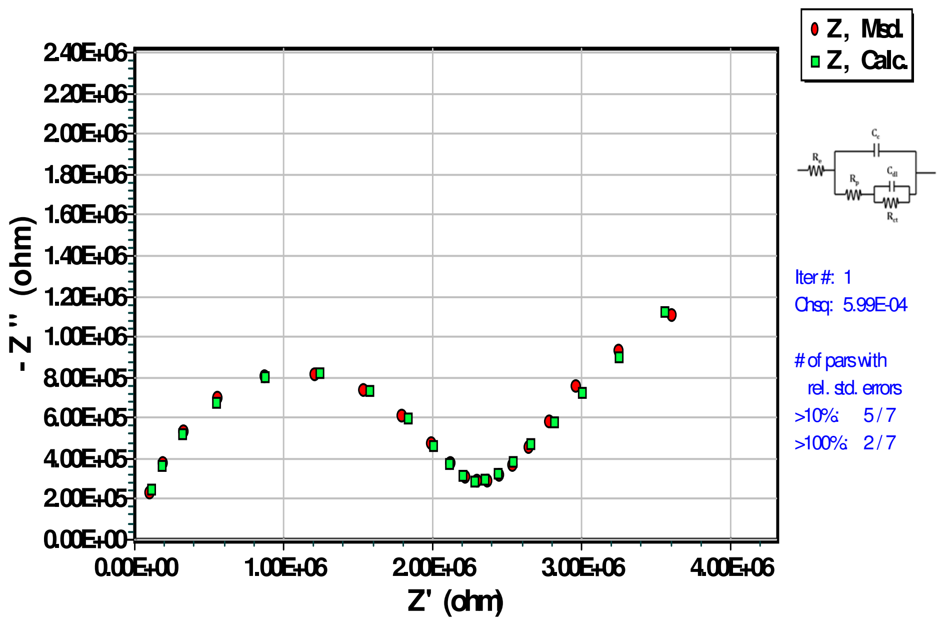
Fitting of Impedance Spectra

EIS result → Model circuit





ZSimpWin fitting software



Coating Parameters

R_p	2.14×10^6 Ωcm²
C_c	1.05×10^{-9} F/cm²
R_{ct}	5.55×10^6 Ωcm²
C_{dl}	6.44×10^{-7} F/cm²

Table A

EIS can be used to characterise an intact coating on steel substrate

It can measure

1. **The deterioration of the organic coating caused by exposure to an electrolyte, shown by a decrease in resistance, R_p**

2. **The increase in corrosion rate of the metallic substrate due to the degradation of the coating and subsequent attack by the electrolyte shown by falling of the charge transfer resistance, R_{ct}**

Case study

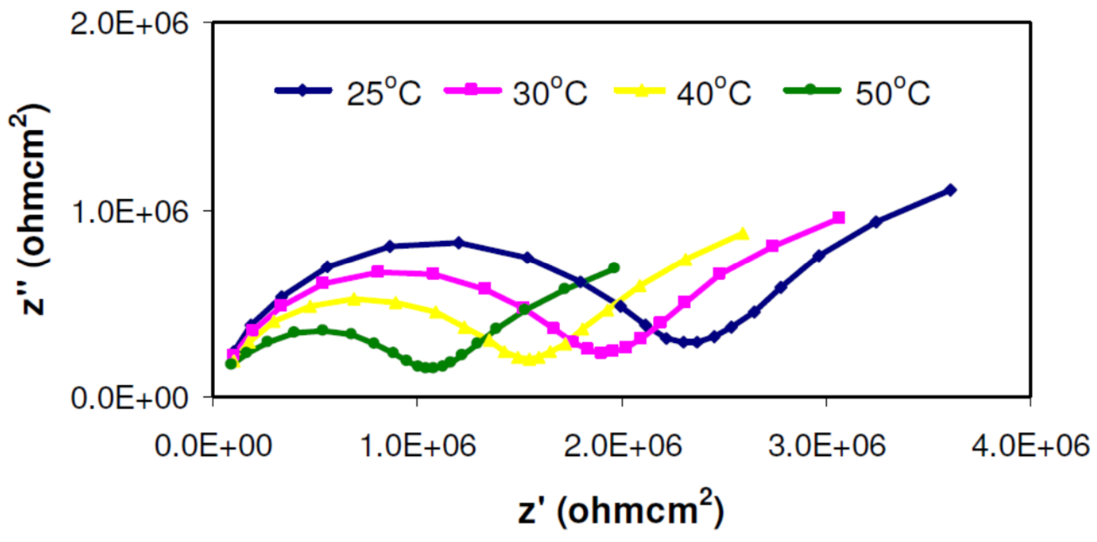
Effect of Temperature on the Impedance Behaviour of Coated Metals in 3% Sodium Chloride Solution

The aim of the study was to assess the effect of temperature on the protective properties of several epoxy coatings.

Effect of Temperature on the Impedance Behaviour of Coated Metals in 3% Sodium Chloride Solution

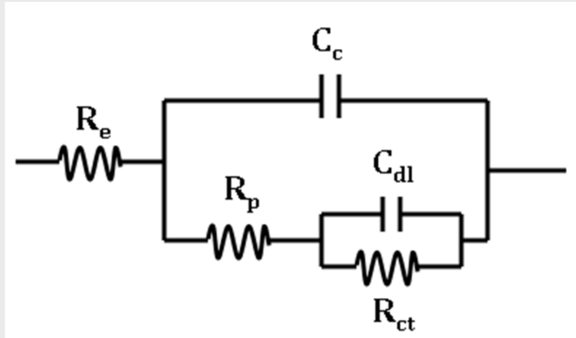
EIS impedance measurements were taken across a range of temperatures and used to determine the activation energies for ion conduction and the corrosion process.

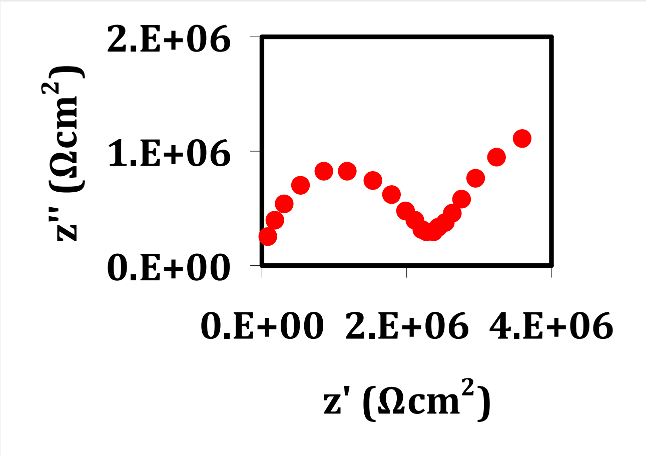
The temperature dependence test is conducted to explore the correlation between the coating resistances with the corrosion rate underneath the coating.



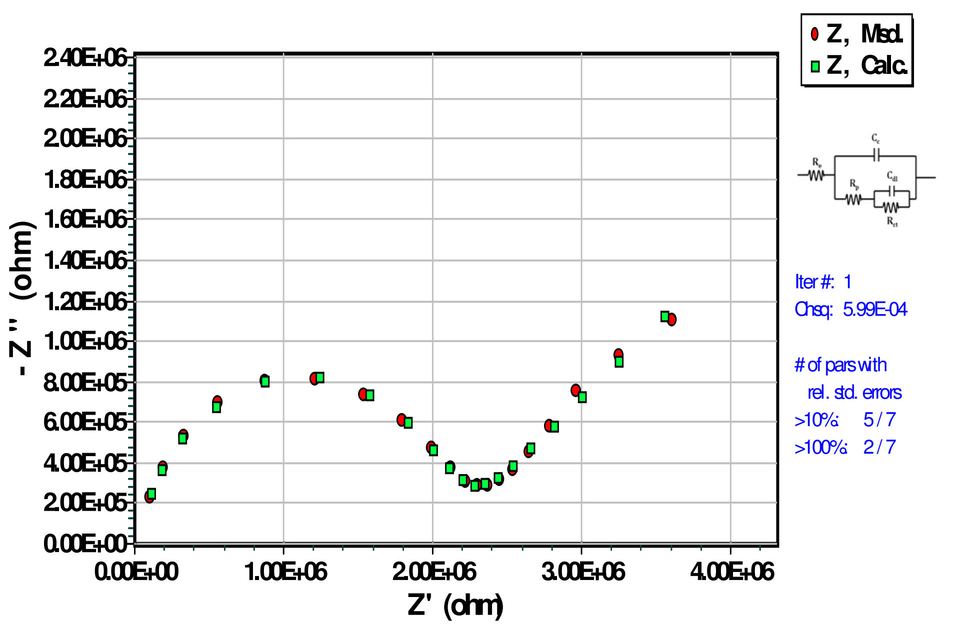
Fitting of Impedance Spectra

EIS result → **Model circuit**





ZSimpWin fitting software

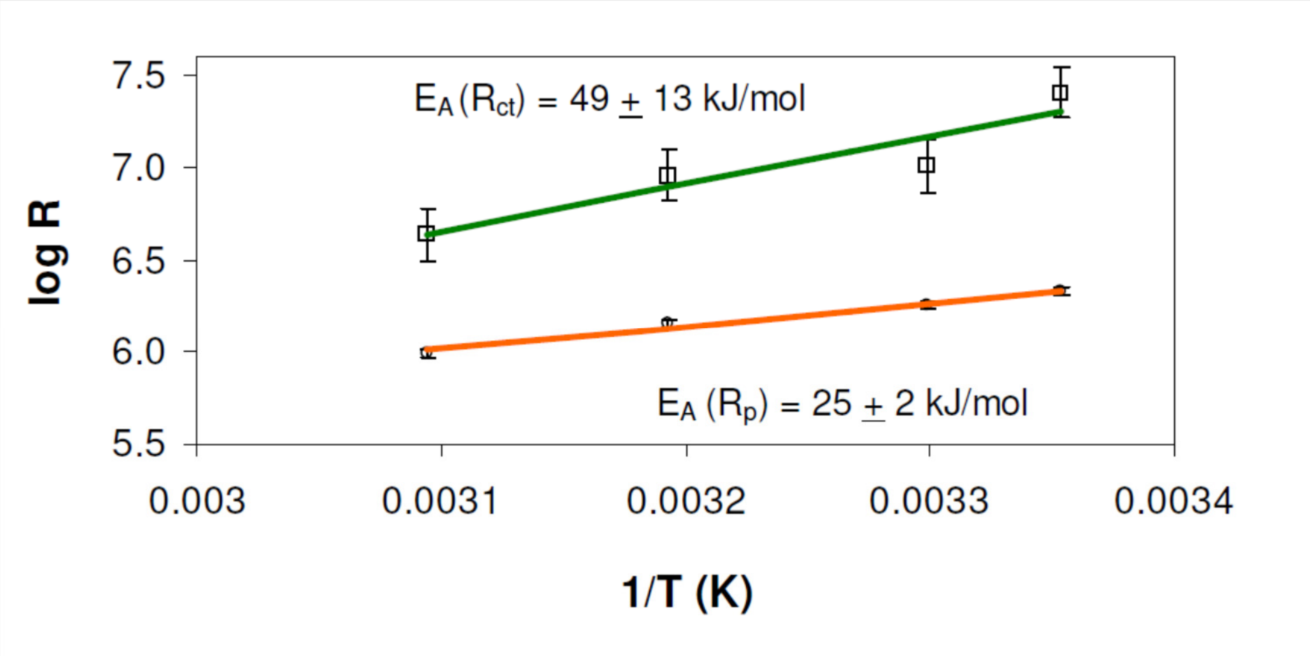


Coating Parameters

R_p	$2.14 \times 10^6\ \Omega cm^2$
C_c	1.05×10^{-9} F/cm^2
R_{ct}	$5.55 \times 10^6\ \Omega cm^2$
C_{dl}	6.44×10^{-7} F/cm^2

Table A

Effect of Temperature on the Impedance Behaviour of Coated Metals in 3% Sodium Chloride Solution



The calculated activation energy for coating resistance is significantly lower than the activation energy for the charge transfer resistance. This suggest the ion conduction in the coating, cannot be controlling the corrosion rate

Question?

The End

Thank You for the Attention!

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