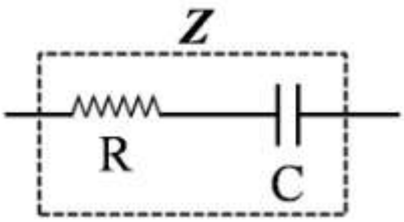
Electrochemical Impedance Spectroscopy

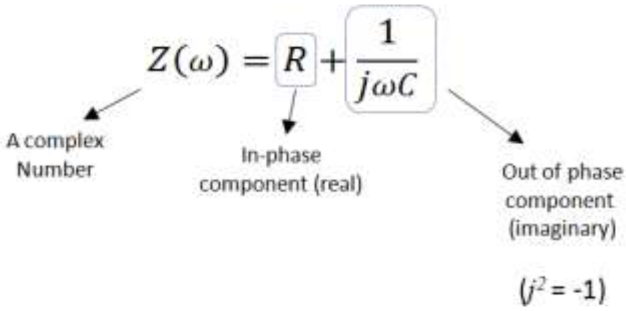
Working Questions

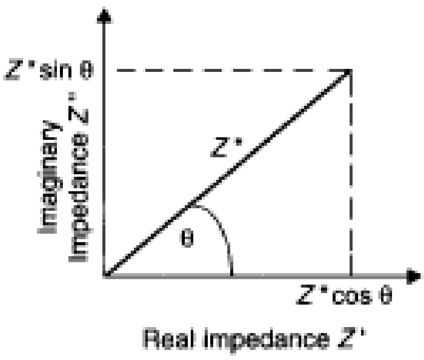
1)What actually happens during the impedance experiment? 1)What actually happens during the impedance experiment? How do you construct a nyquist plot for an equivalent circuit consist a Resistor and a Capacitor in <u>Series?</u>

1) Answer

an equivalent circuit consist a Resistor and a Capacitor in Series is following







A Nyquist plot of the imaginary impedance Z” against the real impedance Z‘, showing how **Z*** and Ɵ are defined.

The frequency-dependent resistance **Z*** of a cell or sample is measured over as wide a frequency range as possible (typically 10^6 -10^{-2} Hz**).** The apparatus measuring the impedance is known as a **frequency analyser.**

The analyser applies a tiny voltage **V(t)** across the sample (perhaps superimposed on a pre-set or **off.set** voltage). The magnitude of **V(t)** varies with time since it is sinusoidally modulated. The analyser measures the respective time-dependent currents **I(t)**, and hence calculates **Z*** and the **time lag** ϕ experienced between the current and voltage.
The frequency analyser then alters the frequency at which the voltage oscillates and **Z*** is determined once more, with this procedure being performed for as many as 50 different frequencies. (It is the usual practice to start at the upper frequencies and progress down to the lower frequencies.)
From these values of **Z*** and ϕ **,** the components Z' and Z'' are obtained, and so a Nyquist plot can be generated.

2**) a) What is Electrochemical impedance?what is the Response signal in a linear system and AC resistance?**
b)Why does the concentration not change if a non-equilibrium potential is applied?
2a) Answer

a)

Applying a constant voltage V across a resistance **R** induces a constant current **I** according to Ohm's law In a similar way, application of a sinusoidally varying potential) across an electrochemical cell induces an alternating current (AC). The AC analogue of Ohm's law is given by the following:

V(t)= I (t). Z

Z= V(t) / I (t)

where Z is the impedance, and the V(t) /I (t) imply that these quantities are time-dependent. At its simplest, impedance is a resistance that varies in a cyclical manner, and therefore, Z has the units of ohms **(Ω),** just like any other type of resistance determined with a direct current **(DC)**

In a linear system, the response signal, the current *I(t)*, is shifted in phase *(ϕ)* and has a different amplitude, I_0:

$$I(t) = I_0 \cos(\omega t - \phi)$$

An expression analogous to Ohm's Law allows us to calculate the **impedance Z (=the AC resistance)** of the system :

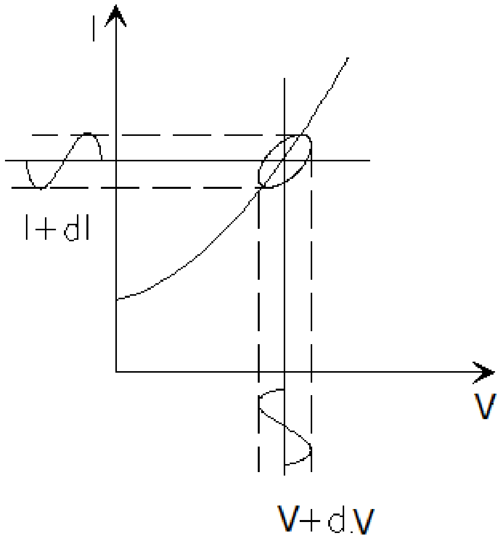
$$Z(t) = \frac{V(t)}{I(t)} = \frac{V_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$

The impedance is therefore expressed in terms of a magnitude, Z_0, and a phase shift, ϕ

The admittance(Y) may also be written as complex function

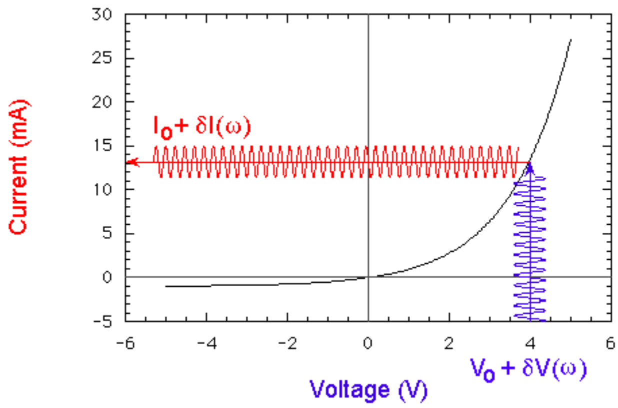
2b)

First, the potential is tiny - by a 'small' potential referred to above, we meant about **5 -10** mV or so. However, more importantly, the perturbing voltage changes in a cyclic sinusoidal manner, **so** we can say that the time-averaged overpotential is zero. In fact, we set up a type of steadystate situation. Accordingly, we have some of the advantages of a dynamic technique, although the actual changes do not occur on the macroscopic level.



we have an electrical element to which we apply an electric field **V*(t)*** and get the response ***I(t),*** then we can disturb this system at a certain field **V** with a small perturbation ***dV*** and we will get at the current ***I*** a small response perturbation ***dI***. In the first approximation, as the perturbation ***V*** is small, the response ***dI*** will be a linear response as well

The result will be **$Z(\omega,V_o) = \delta V(\omega) / \delta I(\omega)$**



3) Calculate the Impedance of a Capacitor formed by a semiconductive polymeric thin film ,presume the capacitance is 30 μFarads, and the frequency is 400 Hertz.

And presume the capacitor is ideal and has a phase shift of -90 degrees.

3)Answer

Simply stated, the impedance of the capacitor (Xc) is equal to 1 divided by the angular frequency multiplied by the capacitance. Put into the equation, where The impedance of the capacitor is inversely related to the frequency. This means the greater the frequency, the smaller the impedance.

$$X_c = 1/\omega c$$

Calculate the Angular Frequency (The lowercase omega sign, or 'w' in the equation) which is 2 multiplied by π multiplied by the frequency. In our example, this would be

$\omega = 2\pi f =$ 2 x π x 400 Hertz, which comes to 2,512 rad/s

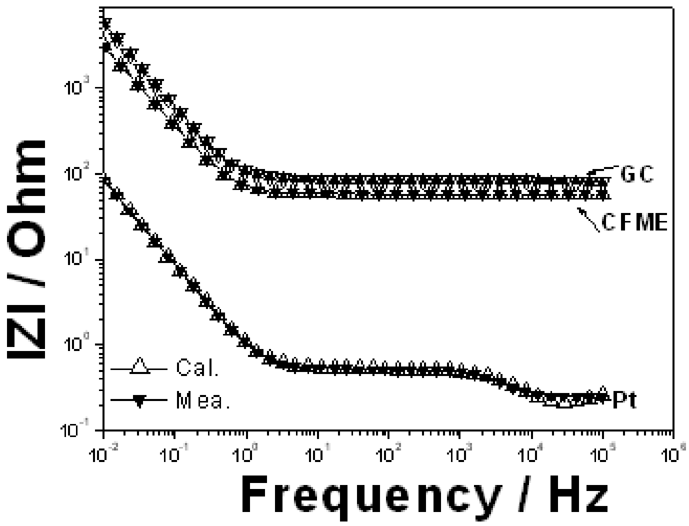
Write out the equation with the known values. In our example, we now have the impedance of the capacitor

(Xc) = 1 / (0.000030 farads x 2512 rad/s).

Xc = 13.27 Ohms & Phase Change = -90 degrees

For the simplicity of this example, we have presumed that the capacitor is ideal, and the phase change was -90 degrees,
In our example, the capacitor will provide a resistance of 13.27 Ohms, and it will change the phase of the alternating current by -90 degrees

4)Electrochemical Impedance Spectroscopic Study of Polyaniline on Platinum, and Glassy Carbon (GC) electrodes were studied(Sarac et al *Int. J. Electrochem. Sci.,* 3 (2008) 777 – 786] The electrode area keeps up constant (Pt plate ~ 1.5 cm^2, GC ~0.07 cm^2, and CFME ~ 0.022 cm^2) The low frequency capacitance (C_{sp}) values of Polyaniline (PANI) film (at 0.01 Hz) were calculated by the following equation, $Csp=(2\pi f.Z_{im})^{-1}$ where C_{sp} is the specific capacitance; (Zim) is the slope of a plot of the imaginary component of impedance versus the inverse of the frequency (f)



From above bode magnitude graph for he 10 mHz frequency impedance value was found to be ~89 Ω for Pt and 6 kΩ for GC and 3kΩ for the CFME calculate the C_{sp} values

4) Answer

$Csp=(2\pi f.zim)^{-1}$
C_{sp} = 1/ (2 πf.Z im) = 1 / (2x3.14x 0.01 Hz .89 Ω) = 0.179 F / 1.5 cm^2 = 0.120 F/cm^2 for the Pt

For GC **C_{sp} = 1/ (2 πf.Z im)** = 1 / (2x3.14x 0.01 Hz .6000 Ω) = 0.0026 F / 1.5 cm^2 = 0.038 F/cm^2 for the GC

For Carbon Fiber microelectrode **C_{sp} = 1/ (2 πf.Z im)** = 1 / (2x3.14x 0.01 Hz .3000 Ω) = 0.0053 F / 0.0022 cm^2 = 2.41 F/cm^2 for the CFME

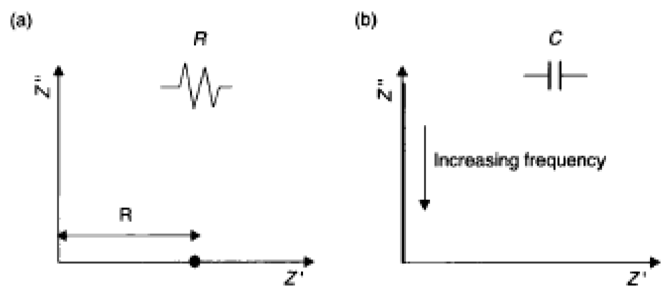
5 a) What is the impedance of a pure polymeric resistor having a resistance R of 1.2 x 10^5 Ω.
Draw the Sample Nyquist plots of 'pure' electrical components, shown for a resistor R and a capacitor C.
b)What is the impedance of a pure polymeric capacitor with a capacitance of 10^{-12} F at a frequency of 5 x 10^5 Hz?

5)Answer

(5a) The **resistance (R)** may be defined as an impediment to the flow of electronic charge. Consider **a** 'pure' resistor (that is, one having no capacitance whatsoever): its resistance when determined with a continuous currentt is **R,** and its impedance is frequency-independent. We can say that:

Z*(R) = **Z'** = **R**

Note that **R** is not described by **ω** at all, so a resistor **is** represented on a Nyquist plot by a single point on the x-axis (see Figure (a)).



Sample Nyquist plots of 'pure' electrical components, shown for **(a**) a resistor R and

(5b) a capacitor C.
From equation , the resistance and impedance of **apure** resistor are the same,

So $Z^*=Z'= 1.2x\ l0^5$ Ω.

b) We first convert from linear to angular frequency by saying **ω**= 2πf , which gives:
ω = 2 x 3.142 x **5** x 10^5 $\mathbf{s^{-1}}$ = 3.14 x $\mathbf{l0^6}$ rad $\mathbf{s^{-1}}$
Next, we insert the appropriate values into equation as follows:

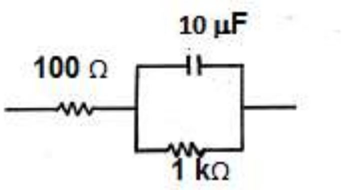
$Z^*_{(c)} = Z'' = 1/ j\omega C$

$Z^*_{(c)}$ =(**1/** j x 3.142 x **l0**^{6} x **10**$^{-l2}$) **ω**

= 3.18 **x 10^{5}j Ω**

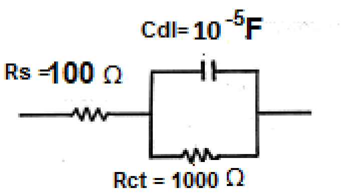
Notice that if we are strict with ourselves, we should really include the ' j ' term, although we should note that most workers don't do this. If we had written Z", then the ' j ' term would not have been needed since an imaginary impedance presupposes the inclusion of this term.

6 a)For the following circuit Calculate the Z(w) and Z' and Z'' for the f= 1.6 Hz ,16.0 Hz etc and show the shape of the Nyquist ,bode magnitude plots



6a)Answer

$$Z(\omega) = R_s + \underbrace{\frac{R_{CT}}{1+\omega^2 {C_{dl}}^2 {R_{CT}}^2}}_{Z'} - j\underbrace{\left(\frac{\omega C_{dl} {R_{CT}}^2}{1+\omega^2 {C_{dl}}^2 {R_{CT}}^2}\right)}_{Z''}$$



For the $\omega = 2\pi f$, $\omega = 2 \times 3.142 \times \mathbf{1.6}\ \mathbf{s^{-1}} = 10$ rad $\mathbf{s^{-1}}$

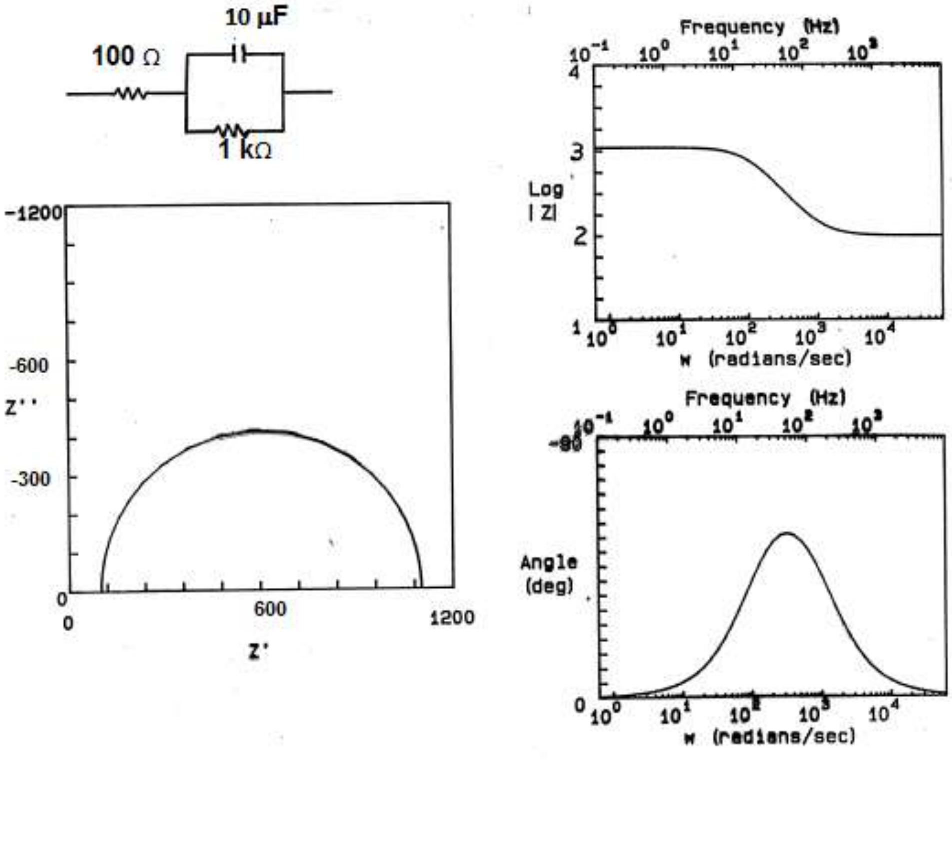
$Z' = 100 + 1000/[1+10^2 .(10^{-5})^2.1000^2] = 100 + 1000/(1+0.01) = 1090\ \Omega$

$Z'' = 10.10^{-5}.1000^2/[1+10^2 .(10^{-5})^2.1000^2] = 100/(1+0.01) = 99\ \Omega$

For the f =16 Hz , $\omega = 2 \times 3.142 \times \mathbf{16}\ \mathbf{s^{-1}} = 100$ rad $\mathbf{s^{-1}}$

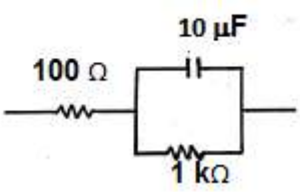
$Z' = 100 + 1000/[1+100^2 .(10^{-5})^2.1000^2] = 100 + 1000/(1+1) = 600\ \Omega$

$Z'' = 100.10^{-5}.1000^2/[1+100^2 .(10^{-5})^2.1000^2] = 1000/(1+1) = 500\ \Omega$

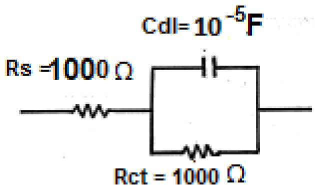


Etc

6b)For the following circuit Calculate the Z(w) and Z' and Z'' for f= 1.6 Hz ,16.0 Hz etc and show the shape of the Nyquist ,bode magnitude plots



6b) Answer



For the f=1.6 Hz , **ω** = 2 x 3.142 x **1.6 s**$^{-1}$ = 10 rad **s**$^{-1}$

$$Z(\omega) = R_s + \frac{R_{CT}}{1+\omega^2 {C_{dl}}^2 {R_{CT}}^2} - j\left(\frac{\omega C_{dl} {R_{CT}}^2}{1+\omega^2 {C_{dl}}^2 {R_{CT}}^2}\right)$$

Z' **Z''**

For the ***ω*****=** 10 Hz

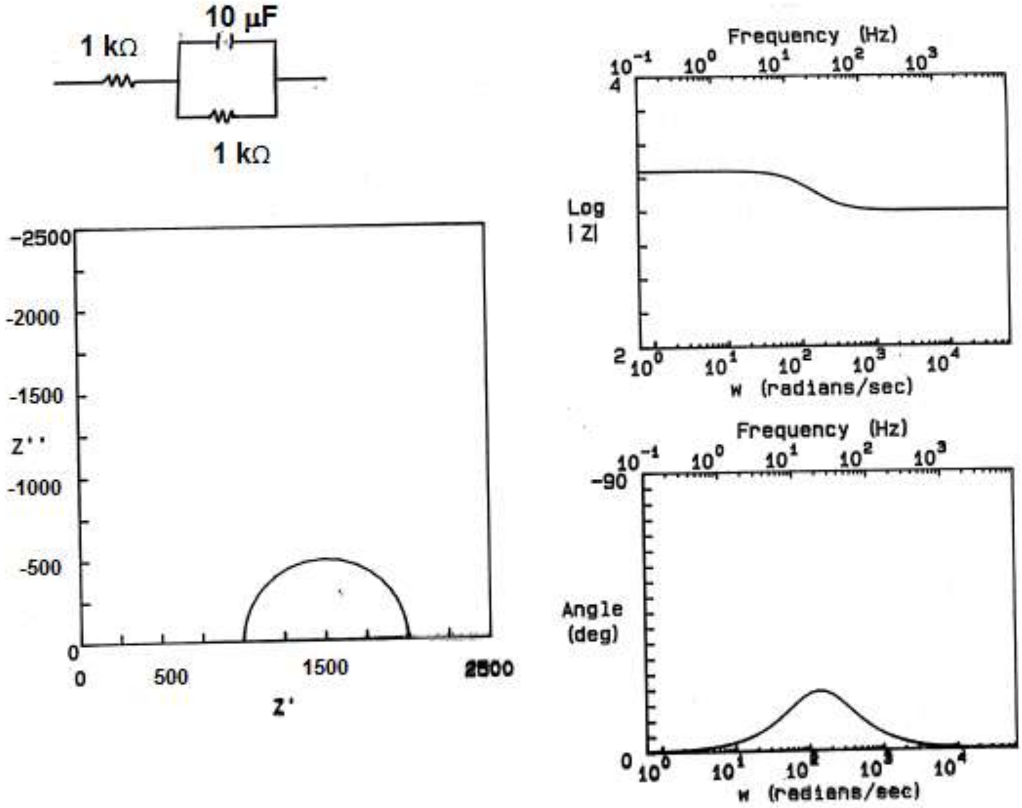
Z' = 1000+ 1000/[1+10^2 .(10^{-5})^2.1000^2] = 1000+ 1000/ (1+ 0.01) = 1990 Ω

Z'' = 10.10^{-5} .1000^2/[1+10^2 .(10^{-5})^2.1000^2] = 100/ (1+0.0 1) = 99 Ω

Etc

For the f =16 Hz , **ω** = 2 x 3.142 x **16 s**$^{-1}$ = 100 rad **s**$^{-1}$
Z' = 1000+ 1000/[1+100^2 .(10^{-5})^2.1000^2] = 1000+ 1000/ (1+ 1) = 1500 Ω

Z'' = 100.10^{-5} .1000^2/[1+100^2 .(10^{-5})^2.1000^2] = 1000/ (1+1) = 500 Ω


10 μF
1 kΩ
1 kΩ
-2500
-2000
-1500
Z''
-1000
-500
0
0
500
1500
2500
Z'
Frequency (Hz)
Log
|Z|
w (radians/sec)
Angle
(deg)
-90