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Complex impedance analysis and relationships with electrical conductivity, and dielectric constants

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Introduction

AC impedance spectroscopy is a valuable tool for studying both the bulk transport properties of a material and the ac conductivity and the dielectric properties.The principle of the impedance analysis method is based on measurements of the sample impedance taken over a wide range of frequencies and then analysed in the complex impedance plane . The mathod was firstly applied to solid electrolytes problems by Bauerle[(19)]and then used by many workers for various superionic conductors. The impedance analysis method requires the determination from the measurements two parts of the complex impedance of the sample Z* = Z' + J Z". The main parameters Rand C are deduced from the analysis of impedance method

Theoretical background:

The impedance is defined as the Z is the complex ratio of the applied (ac) voltage V (ω) to the resultant current I(ω) at frequency ω

$$Z = \frac{V(\omega)}{I(\omega)} \qquad (1)$$

The impedance is most directly interpreted when written in polar form, can be expressed in terms of the the modulus $|Z|$ and the phase angle φ

$$Z^* = \mathbf{V^*}/\,\mathbf{I^*} = |Z|\, e^{\varphi} \qquad (2)$$

Where the magnitude $|Z|$ represents the ratio of the voltage difference amplitude to the current amplitude, while the argument φ gives the phase difference between voltage and current and j is the imaginary unit.

Using Euler's relationship:

$$Z^* = |Z|\ \cos\varphi + j|Z|\ \sin\varphi \qquad (3)$$

The impedance is then expressed as

$$Z^* = Z' + J\,Z'' \qquad (4)$$

$$\boxed{Z' = |Z|\ \cos\varphi} \qquad (5)$$

$$\boxed{Z'' = |Z|\sin\varphi} \qquad (6)$$

The ~~main parameters deduced from the analysis of impedance method are~~ Rand C

In Cartesian form Z* is defined as

$$Z^* = \mathbf{V^*}/\,\mathbf{I^*} = R + J\,X \qquad (7)$$

where the real part of impedance is the resistance R and the imaginary part is the reactance X . In case of a capacitor Zc =1/jωC i,e. $X=X_C$ = (-1/ωc). The capacitor is a result of the sample's geometry, while the resistor represents the resistivity of the bulk This impedance depends on the frequency and is entirely capacitive.

$$Z^* = R + j(-1/\omega C) \qquad (8)$$

From above relations we obtain :

$$\boxed{R = Z'} \qquad (9)$$

$$-1/\omega C = Z''$$

$$\boxed{C = -1/\,\omega\, Z''}$$

(10)

$$\tan\varphi = Z''/\,Z' \qquad \text{Or} \qquad \mathbf{Tan}\delta = Z'/Z'' \qquad (11)$$

Table

F (Hz)	Z (Ohm)	Q	Z' =**|Z|cosφ**	Z" **=|Z|sinφ**	C **=1/ωZ"**	R =z'	tan δ =z'/z''
-	-	--					

Data Presentation

<u>Complex Impedance Plot</u>

If the real part *Z'* is plotted on the x-axis and the imaginary part Z''
on the y-axis of a chart, a so called "Nyquist plot," or complex plane impedance diagram, is revealed. As shown

in Figure , this plot has the shape of a semicircle. Notice that in this plot the y-axis was chosen as negative notation and that each

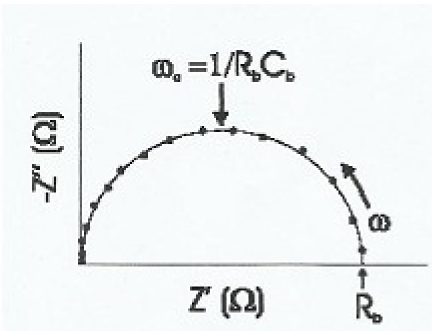

Figure 1. Nyquist Plot with Impedance Vector

point on the Nyquist plot is the impedance at one frequency [1]. On the Nyquist plot the impedance can be represented as a vector of length| Z |. The angle between this vector and the x-axis is φ, or "phase angle"which also has a negative notation, as (from Eq. 1-11):

There is a parameter $\tau=RC$ called "time constant," which is associated with this circuit, and a corresponding "characteristic circular" frequency $\omega_c= 1/\tau$ and "characteristic" or "critical relaxation" frequency. At very high frequencies the impedance is completely capacitive, while at low frequencies it becomes completely resistive and approaches the value of *R,* which equals the diameter of the Nyquist plot semicircle. The phase angle φ tends towards -90° at high frequency and towards 0°at low frequency, and critical frequency f_c corresponds to a midpoint transition where the phase angle is -45° and $Z' = Z'' = R/2$.*The diameter of the semicircle is taken as the bulk resistance.Then*

$$\sigma_b = \frac{1}{R_b}.\frac{t}{a}$$

The Nyquist Plot in Figure 1 results from the electrical circuit of Figure 2. The semicircle is characteristic of a single "time constant". Impedance plots often contain several semicircles. Often only a portion of a semicircle is seen.

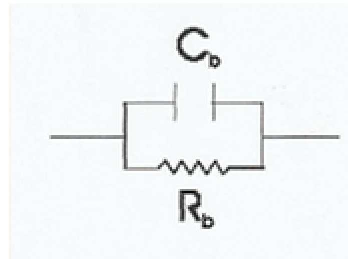

Figure 2. Simple Equivalent Circuit with One Time Constant

Another popular presentation method is the Bode Plot. The impedance is plotted with log frequency on the X-axis and both the absolute values of the impedance ($|Z|=Z_0$) and the phase-shift on the Y-axis.Unlike the Nyquist Plot, the Bode Plot does show frequency information.

Ac conductivity σ(ω) is calculated by using the relation,

$$\sigma(\omega) = \frac{1}{R} \times \frac{t}{a}$$

where R is the resistance , (t) and (a) are the thickness and the area

Dielectri constant ε' is calculated using the following relation:

$$\varepsilon' = \frac{C}{\varepsilon_o} \times \frac{t}{a}$$

where C is the capacitance $\varepsilon_o = 8.85 \times 10^{-12}\ F/m$, t and a are the thickness and the area.

Dielectric Loss ε" is calculated using the following relation:

$$\varepsilon'' = \underline{\varepsilon'} \tan \delta$$

where δ = (90- φ) , φ is the phase angle.

Conclusions

The impedance measurements of the sample is taken in terms of the the modulus $|Z|$ and the phase angle φ taken over a wide range of frequencies. The values of Z' and Z'' can be found ,R and C are deduced._Ac conductivity σ(ω), dielectri constant ε' and dielectric Loss ε'' are determined.

References

The following sources were used in preparing this application note

Bauerle J E 1069 *J Phys. Chem. Solids* **30** 2657.

Mackdonald J R (ed) 1987. Impedance spectroscopy emphasizing solid state materials and systems (New York Wiley).

The Equivalent Circuit of Impedance

The simplest model for an electrode – sample system under an applied voltage is a capacitor and resistor in parall. Figure a. The capacitor is a result of the sample's geometry, while the resistor represents the resistivity of the bulk. The impedance of such circuit at frequency ω consists of the real part R and **the imaginary part 1/□c and is written as :**

$$\frac{1}{Z} = \frac{1}{R} + j\omega c$$

The value Z can put in the form ;

$$Z = R\left[\frac{1 - j\omega\tau}{1 + \omega^2\tau^2}\right] \quad ;$$

Which can be separated into the real part $Z^{`}$ and the imaginary part $Z^{``}$ as :

$$Z` = \frac{R\omega\tau}{1 + \omega^2\tau^2}$$

$$Z`` = \frac{R}{1 + \omega^2\tau^2}$$

By ellimainating ω□ these two equations (1.10) and (1.11) can be combined and written in the form of a circle :

$$Z^{`2} - Z^{`} R + Z^{``2} = o$$

Adding $R^2/4$ to both sides of equation (1.12) one obtains

$$(Z^{`} - ½ R)^2 + Z^{``2} = (½ R)^2$$

Comparing this equation with the standard form of the equation of a circle , one can see that the Z-plane plot is a semicircle in the first quadrant with center at (½ R,0) and with a radius ½ R fig 3.1.b. It can be shown also that at the maxium of the semicircle ω□ = 1 where □ = RC is the time constant or the relaxation time of the circuit .

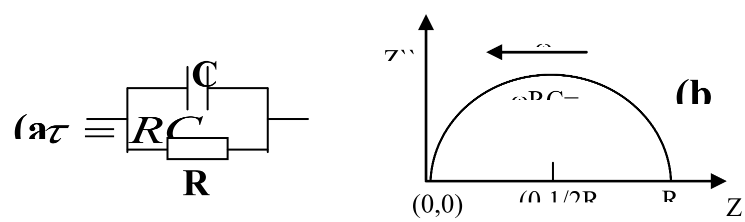

Figure (1) : Complex impedence plot for the parallel circuit RC .

So, when from the complex impedance measurements when only one semicircle obtained and this semicircle originates in the (0,0) point ,it means that only one resistance R and one capacity c both parallel combined , can be described to the sample in such a case, these should be the bulk resistance and capacity of the sample .

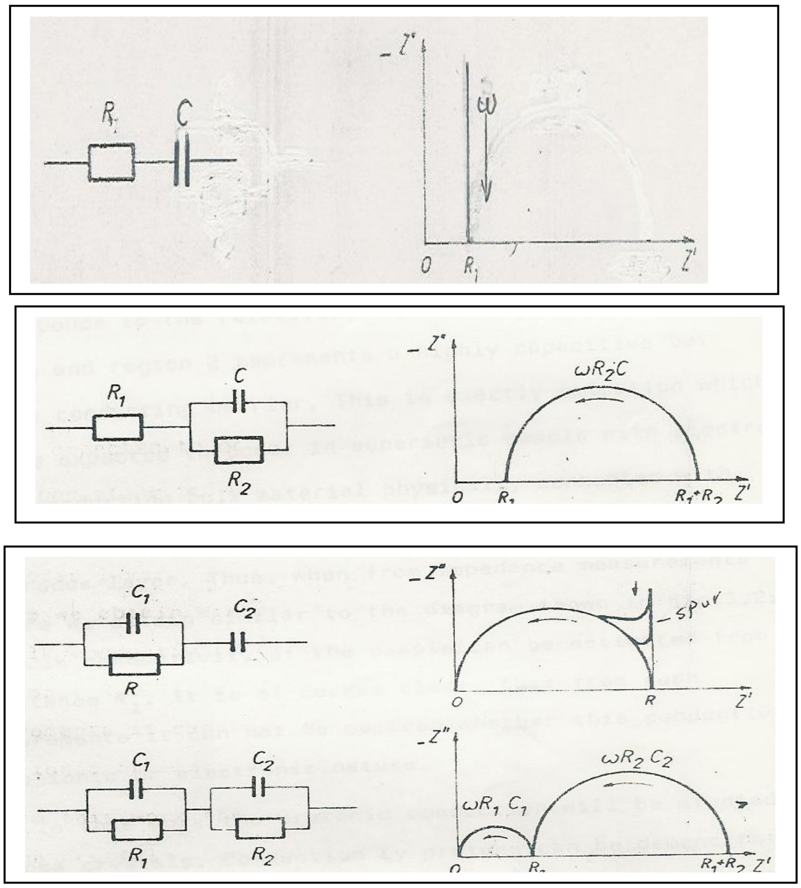

Figure (2,3.4&5) : Complex impedence plots for simple circuits RC of different combinations a, b c, d, e, f and g respectivley.

Nyquist and Bode representation of complex impedance data for ideal electrical circuits

<u>(Nyquist Plot)</u>

The impedance analysis method requires the determination from the measurements at each frequency f two parts of the impedance: the real part Z' and the imaginary part Z". The real