COMPLEX IMPEDANCE SPECTROSCOPY FOR MONITORING FREQUENCY RESPONSE TO THE ELECTRICAL PROPERTIES OF POLYCRYSTALLINE MATERIALS

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Abstract: Complex Impedance Spectroscopy (CIS) is a powerful experimental tool used for physical interpretation of the frequency response of the electrical properties of a wide range of materials at various temperatures. With the help of this technique the contribution of electrode- electrolyte interface, grains and grain boundaries on the overall electrical behavior of the material under study can be identified and isolated in the different frequency domains.

Keywords: CIS, CPE, z_{CPE}

1. Introduction

The fabrication of material and their characterization are the pre-requisites to determine the suitability of the material for its device application. In recent years, many advanced, economical fabrication and characterization methods have been developed to fabricate the technologically desired high-purity materials in different forms (i.e., bulk, thin film, single crystal, etc.,). Complex Impedance Spectroscopy (CIS) is a powerful experimental tool used for physical interpretation of the frequency response of the electrical properties of a wide range of materials [1].

The Complex Impedance Spectroscopy (CIS) is a non-destructive method to analyze the micro-structural and electrical properties of polycrystalline oxides [2]. With the help of this technique, it is possible to identify the resistive and capacitive effects of different regions of a polycrystalline ceramic sample [3, 4]. The technique is useful to correlate the structural changes brought by temperature and frequency variation and its consequences on dielectric and electrical properties of the polycrystalline oxides in a wide frequency and temperature range [5]. Generally, the impedance properties of a material are developed due to intra-grain, inter-grain and electrode effects. The transportation of charges could occur in various manners, i.e. (i) orientation of existing or induced dipoles (ii) space charge separation (iii) relative displacements of charge centers and (iv) free charge transportation. The complex impedance formalism is suitable to interpret this charge transportation in bulk, grain boundary and at the electrodes.

The impedance spectroscopy is used to measure complex impedance (Z^*), complex admittance (Y^*), complex electric modulus (M^*), complex dielectric permittivity (ε^*) of the materials [6-9].

2. Components of cis

Impedance of a solid electrolyte cell exposed to an ac supply is a vector which magnitude represents the resultant of resistance and capacitive reactance of the cell, and the phase angle represents the phase difference between the applied voltage and measured output current through the cell. The complex impedance Z^* can be defined as the ratio of voltage $V(t)$ to current $I(t)$ in the time domain when a sinusoidal signal of low amplitude is applied across a solid electrolyte. If the instantaneous values of voltage & current are defined as $V(t) = V_o exp(i\omega t)$ and $I(t) = I_o exp\,(i\omega t - \theta)$ (1)

Where (φ) is the phase angle at which current leads the applied voltage, then complex impedance of the sample can be expressed as;

$$Z^* = |Z|e^{-i\theta} \quad \text{(Cartesian form)}$$
$$= |Z|cos\theta - i\,|Z|sin\theta \quad \text{(polar form)}$$

$$= Z' - iZ'' \qquad (2)$$

Where $i = \sqrt{-1}$, $Z' = |Z|cos\theta$ and $Z'' = |Z|sin\theta$ are the real and imaginary parts of the complex impedance Z^*respectively.

The complex admittance, complex impedance and complex permittivity of the polycrystalline sample can respectively be expressed as;

$$Y^* = \frac{1}{Z^*} = Y' + iY'' \qquad (3)$$
$$M^* = i\omega C_o Z^* = M' + iM'' \qquad (4)$$
$$\varepsilon^* = \frac{1}{i\omega C_o Z^*} = \varepsilon' - i\varepsilon'' \qquad (5)$$

Where $C_o =$ capacitance when air/vacuum is the dielectric medium between the two electrodes and ω is the angular frequency of applied ac voltage.

The impedance data was calculated from the experimentally observed parallel-equivalent valuesR_p, C_p(or series- equivalent valuesR_s, C_s) represents a complex network. A complex plane is used to represent the real and imaginary parts of electrical quantities likeZ^*, M^*,Y^*, ε^*. Though all the possible complex plane plots are derived from the same measured data, each type of representation has its own advantages in different circumstances. In the high frequency region the information can be highlighted by the permittivity and admittance plots. Where as in the low frequency range the impedance and electric modulus plots provides better information.
For an ideal series combination of resistance (R_s) & capacitance (C_s) the complex impedance is given by;

$$Z^* = Z' - Z'' = R_s - \frac{i}{\omega C_s} \qquad (6)$$

Where $ReZ^* = R_s$ and $ImZ^* = \frac{1}{\omega C_s}$ (7)

Figure 1(a) shows that when R_s & C_s are connected in series the resultant impedance can be represented by a straight line parallel to the imaginary (Z'') axis and intersects the real (Z') axis at R_s. The corresponding admittance plot is a semicircle [shown in Figure 1(b)] intersecting the real axis at the origin and at another point $\frac{1}{R_s}$.

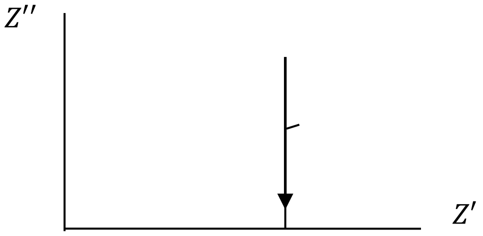

Figure 1(a) impedance plot for series RC

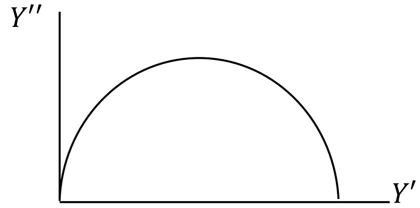

Figure 1(b) admittance plot for series RC

For an ideal parallel combination of R_p and C_p the complex impedance is given by;

$$\frac{1}{Z^*} = \frac{1}{R_p} + i\omega C_p \qquad (8)$$

Hence,
$$Z^* = \frac{R_p}{\left[1+(\omega R_p C_p)^2\right]} - i\frac{\omega C_p R_p^2}{\left[1+(\omega R_p C_p)^2\right]} \qquad (9)$$
$$= \frac{R_p}{1+\omega^2\tau^2} - i\frac{\omega C_p R_p^2}{1+\omega^2\tau^2} \qquad (10)$$
$$= Z' - iZ'' \qquad (11)$$

Here $\tau = R_p C_p$ represents the relaxation time.

As shown in Figure 2(a) the complex impedance plot for a parallel combination of R_p and C_p represents a semicircle, which intersects real Z' axis at the origin and at another pointR_p. The difference between the two intercept values on the real Z' axis is equal to the bulk resistance (R_b) of the material. The corresponding complex admittance plot (shown in Figure 2(b)) is a straight line parallel to imaginary Z'' axis, intersecting the real axis at $\frac{1}{R_p}$

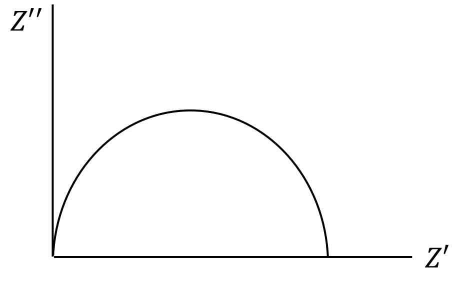

Figure 2(a) impedance plot for parallel RC

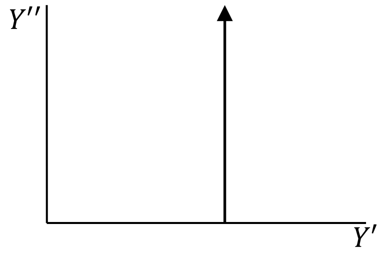

Figure 2(b) admittance plot for parallel RC

For an ideal solid electrolyte (theoretical), the impedance plot is a perfect semicircle (for parallel combination of R& C) or a vertical straight line parallel to Z'' axis (for series combination of R & C) as shown in Figure 3

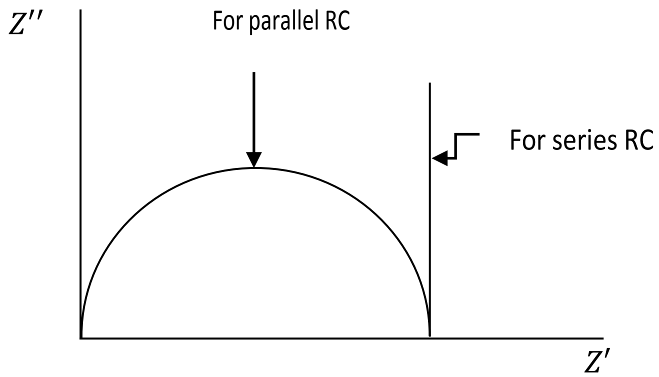

Figure 3: Impedance plots for ideal solid electrolyte for parallel combination of R and C and for series combination of R and C

But for a real solid electrolyte, the impedance plot is an inclined straight line (for series combination) and a depressed semicircle (for parallel combination) due to the presence of electrode-electrolyte capacitance (shown in Figure 4). The angle of inclination of the straight line and extent of depression of the semicircle depends on the microscopic material properties, called constant phase element (CPE) [10].

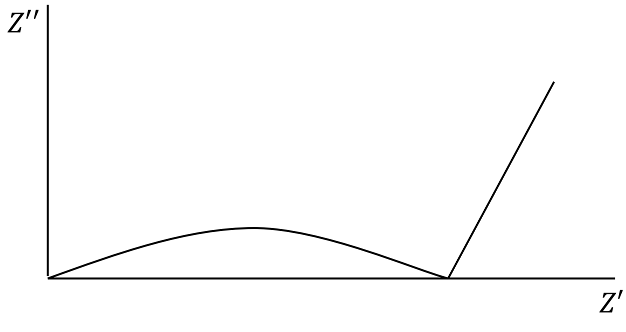

Figure 4: impedance plot for real solid electrolyte

It is a well known fact that the conduction of electrical signal through a series/parallel R&C branched transmission line can be well described by the differential equation which describes the diffusion process of charge carriers. It was noted that a branched transmission line exhibit constant phase behavior and hence is an electrical equivalent of a constant phase element (CPE).
The CPE impedance is defined as;

$$Z_{CPE} = Z_o\,(i\omega)^{-\alpha} \qquad (12)$$

Where Z_o & α are frequency independent but temperature dependent real parameters, such that Z_o determines the magnitude of dispersion and the value of α lies between 0 to 1 i.e $0 \leq \alpha \leq 1$. For a pure resistive circuit $\alpha = 0$ i.e $Z_{CPE} = R$, where as for a pure capacitive circuit $\alpha = 1$ i.e $Z_{CPE} = C$ [11, 12]. The fractional value of α represents the non Debye type capacitor or the existence of a constant phase angle element [13].

When an ac signal is applied as input perturbation to the polycrystalline solid electrolyte, the complex plot is represented by three depressed semicircles (Figure 5), one corresponds to resistance inside grains of the material, the second one corresponds to grain boundary resistance (resulted due to the complete or partial blocking of charge carriers at the boundary) and the third one is due to electrode-material (electrolyte) interface phenomenon [14]. Thus the equivalent circuit for a polycrystalline sample is represented by the parallel grouping of (Z_{CPE}) with bulk resistance(R_b) connected in series with another parallel combination of (Z_{CPE}) with grain boundary resistance(R_{gb}) and then in series with Z_{CPE} of the interface. (as shown in Figure 6)

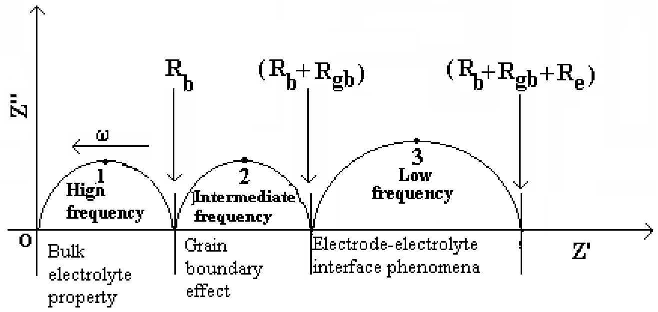

Figure 5: Complex impedance plot for a polycrystalline solid electrolyte

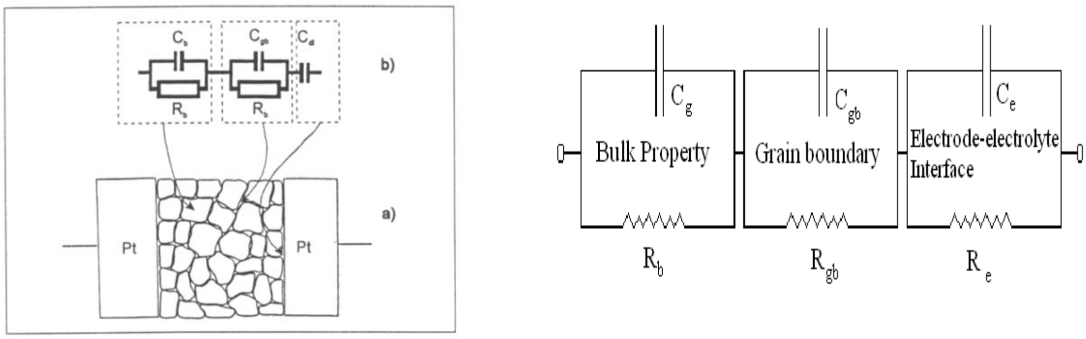

Figure 6: Proposed electrical equivalent circuit in complex impedance plane.

The $Z'' \sim Z'$ complex plane plots [cole-cole (1941)] and frequency explicit plots are very useful in separating the various contributions to the dielectric and electrical conductivity of a polycrystalline sample. (Putley,1970). As shown in Figure 2.8, the semicircles in the complex plane plot intersects the Z'axis at different points i.e., ideal Debye type behaviour. The intercept of the first semicircle on Z'axis in the high frequency region is due to the bulk effect of grains and represents the bulk resistance (R_b). The second semicircle at the middle frequency is due to grain boundary and gives the value of R_{gb} , whereas the third one in the low frequency region is due to the effect of electrode-electrolyte interface [15,16]. The value of the relaxation frequency (f_{max}) and relaxation time (τ) of the bulk material can be calculated by using the following relation (from the peak of semicircular arc corresponding to bulk effect at high frequency);

$$f_{max} = \frac{1}{2\pi R_b C_b} \qquad (13)$$

$$\text{and} \quad \tau = \frac{1}{2\pi f_{max}} \qquad (14)$$

Where R_b and C_b are the bulk resistance and bulk capacitance of the specimen respectively.

3. Conclusion

The complex impedance (Z^*) and complex modulus (M^*) analysis is quite reliable to investigate the electrical and relaxation behavior in the materials. The Z^* formalism was found suitable to analyze the resistive and capacitive effects of grain and grain boundary when long range conductivity is dominating while M^* formalism was found suitable when localized relaxation is dominating. The complex impedance spectra helps to predict the contribution of both bulk (grain) and grain boundary to the electrical conductivity at higher temperatures and also indicates whether the temperature dependent non- Debye type relaxation phenomena exist in the material or not. The effects of structural modification due to substitution, on the physical properties of studied compounds were explained by relevant electrical equivalent circuit models in CIS technology.

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Biographical Notes

Dr. Niranjan Panda completed his M.Sc. in Physics with specialization in electronics and earned his PhD. at the SOA University, Bhubaneswar. He is currently working as Professor and HOD in the Dept. of Engineering Physics at DRIEMS, Cuttack. His areas of interest include the properties of perovskite oxides and study of the small size effect on the phase transitions and functionality of thin films and nanocrystals.