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APPLICATION OF IMPEDANCE TECHNIQUE FOR STUDY OF IONIC CONDUCTING PROPERTIES OF $Li_xLa_{1-x}TIO_3$ PEROVSKITE THIN FILMS

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Abstract. Impedance spectroscopy (IS) technique has been analyzed and applied to measure the ionic conductivity of the films. For a superionic conductor, like a thin-film electrolyte, it is necessary to characterize IS by using a two-electrodes cell, where the thin film is deposited between two metallic electrodes. In a very thin film, the Helmholtz layer strongly affects to the conductivity during the measurement. So that, an equivalent scheme should be chosen with a separation of three frequency zones to fit the theoretical curves to experimental data. The best curve fitted with two to three circles is taken and elaborated to determine all the parameters of the scheme, and R4 – a parameter of the ionic conductivity – in particular.

Electron-beam-deposited $Li_xLa_{1-x}TiO_3$ crystalline thin films were used for IS measurements. Using the fitting method, the experimental data were fitted with the circles obtained by the chosen equivalent scheme. From these circles, the ionic conductivity at room temperature of a 350-nm thick $Li_{0.12}La_{0.88}TiO_3$ film was found to be of σ = 6,52 x10^{-6} S.cm^{-1}.

1. Introduction

It is known that for analyzing an ac current, Y-conductivity has been used, where Y = 1/Z. If Z is $Z = |Z|\ e^{i\phi}$, $Y = 1/|Z|\ e^{-i\phi}$. Thus Y is a vector with a value of $1/|Z|$ and an opposit phase to the phase of Z. Z is dependent on the frequence of the ac current. The common and suitable range used for study is of 10 mHz to 10 MHz. In the electrolytes, in solide state in particular the ionic mobility is much smaller than the electron mobility, so that to respond to the change of the electrical field, it is neccessary to measure in the range of low frequencies. From the experimatal data obtained in the impedance spectra (IS) one can determine the ionic conductivity and other parameters such as the charge transport, diffusion coefficient in solids. However, it is sometimes very difficult to analyze the results for thin films, because for very thin films all above mentioned parameters are strongly affected by the

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thickness and contacts in the measurement cells. Thus, the choice of the equivalent schemes consisting with subschemes of resistance, capacity, etc. plays an important role to find out real values of the parameters. One of the most important principles to design the equivalent schemes is that the total current value as well as the phase shift must have the same values as the measured sample do.

Recently, multicompound superionic conductors with a perovskite structure such as $Li_xLa_{1-x}TiO_3$ have increasingly been studied. This is because these materials have a high Li-ion conductivity, even at not very high temperature. Especially, the thin-film formed $Li_xLa_{1-x}TiO_3$ can be used in many scopes like all-sold-state ionic batteries, electrochromic display, elctrochemical sensors, etc. [1].

However, in the experimental researches, to determine the ionic conductivity of the thin and/or very thin films of $Li_xLa_{1-x}TiO_3$ by the IS technique is always to face many difficulties, that obtained results often have a large error. So that, the aim of this work is to utilize this technique with analysing a series of equivalent schemes applied to fit with the obtained experimental data from IS measurements on the thin films.

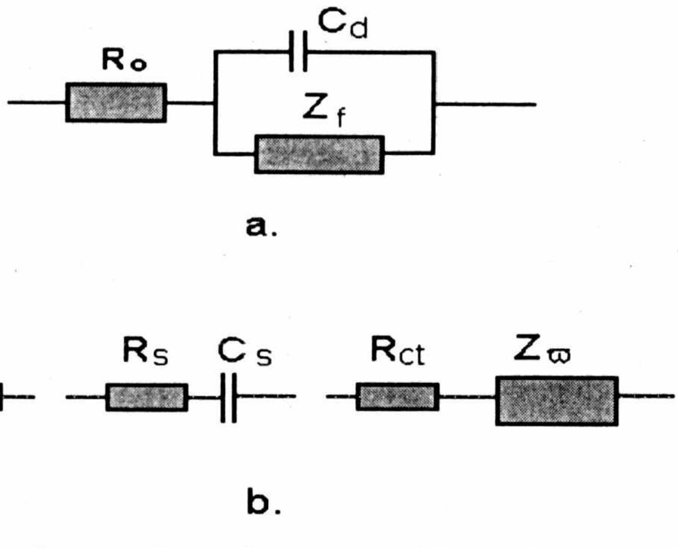

Fig. 1. *Equivalent schemes of samples measured in an electrochemical cell (a) and the corresponding elements of* Z_f *part*

2. Analysis of the impedance theory

2.1. Equivalent schems for a three-electrodes cell and IS characteristics

It is well-known that an equivalent scheme for the sample measured in the three-electrodes cell has a Randle scheme as presented in Fig. 1. In this scheme C_d is the capacity of the double layer, Z_f characterizes the electrochemical proccess. For simplicity, Z_f is splitted into two parts connected in serial R_s and C_s or R_{ct} and Z_w, where R_s and C_s, respectively is a real and an image part of the impedance, R_{ct} is the resistance of the charge transport, Z_w is the Warburg impedance characterizing a mass transport, R_o is the resistance of the liquid electrolyte.

Among these parameters, only C_d and R_o are not depent onto the frequency. By calculation as shown in [2], the expression for the frequency relationship of R_s and C_s, respectively is:

$$R_s = R_{ct} + \sigma/\omega^{1/2} \quad \text{and} \quad Cs = 1/(\sigma\omega^{1/2}) \tag{1}$$

where σ is determined as follows:

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{D_O^{1/2}C_O^*} + \frac{1}{D_R^{1/2}C_R^*}\right) \tag{2}$$

Where R is the ideal gas constant, T is the absolute temperature, n is the ion valence, F – Faraday constant, A – electrode area, DO, DR – diffusion coefficents, respectively of oxidation and reduction reactions, C_O^*, C_R^* - corresponding ion concentrations.

One can express the frequency dependences of the real and image parts of the equivalent schem as follows:

$$Z_{Re} = R_o + \frac{R_{ct} + \sigma\omega^{-1/2}}{\left(C_d\sigma\omega^{1/2} + 1\right)^2 + \omega^2C_d^2\left(R_{ct} + \sigma\omega^{-1/2}\right)^2} \tag{3}$$

$$Z_{im} = \frac{\omega C_d\left(R_{ct} + \sigma\omega^{-1/2}\right)^{-1/2} + \sigma\omega^{-1/2}\left(\omega^{1/2}C_d\sigma + 1\right)}{\left(C_d\sigma\omega^{1/2} + 1\right)^2 + \omega^2C_d^2\left(R_{ct} + \sigma\omega^{-1/2}\right)^2} \tag{4}$$

At the low frequencies, ω→ 0, the equations (1) and (2) can be expressed as:

$$Z_{Re} = R_0 + R_{ct} + \sigma\omega^{-1/2} \tag{5}$$

$$Z_{im} = \sigma\omega^{-1/2} + 2\sigma^2C_d \tag{6}$$

By combining two above equations, one can eliminate ω and obtain:

$$Z_{im} = Z_{Re} - R_o - R_{ct} + 2\sigma^2C_d \tag{7}$$

That is meaning, the image-vs-real part dependence is a linnear one, when ω→ 0 the image part also approaches to zero, then the real part has a value equals to:

$$(R_o + R_{ct} - 2\sigma^2C_d).$$

In the range of high AC frequency, the expressions (3) and (4), respectively transform into:

$$Z_{Re} = R_o + \frac{R_{ct}}{1 + \omega^2C_d^2R_{ct}^2} \tag{8}$$

$$Z_{im} = \frac{\omega C_d R_{ct}^2}{1 + \omega^2 C_d^2 R_{ct}^2} \tag{9}$$

From these equations one can combine in one expression of the other kind relationship between the real and image parts, as folows:

$$\left(Z_{Re} - R_o - \frac{R_{ct}}{2} \right)^2 + Z_{im}^2 = \left(\frac{R_{ct}}{2} \right)^2 \tag{10}$$

This clearly demonstrates that in the graphic presentation, Z_{im}- Z_{Re} plot is a half of a round. This round crosses the horizontal axis at two points, the first one is at R_o corresponding to $\omega \rightarrow \infty$ and the second one is at $(R_o + R_{ct})$ – when $\omega \rightarrow 0$. The ionic conductivity (σ) can be found from experimental data obtained for R_{ct}, it is determined as follows:

$$\sigma = \frac{d}{SR_{ct}} \tag{11}$$

where d and S, respectively is the thickness and area of the working electrode.

2.2. Equivalent schem for a two-electrodes cell and its impedance spectrum

The theory of the IS measured on a two-flat-electrodes cell has been developed by MacDonall. Using this, the authors of [3,4] have studied ionic conductance of solid state electrolyte (or superionic materials). Basing on the MacDonall's argument, in general, the impedance is an AC frequency function with three characteristic ranges of high, middle and low frequencies. Depending on both the composition and structure of the ionic materials, the IS may have one, two or three circles in the Z_{Im}-Z_{Re} plots (Fig. 2). One can analyze the IS characteristics as follows:

- High frequency range: In this range there is no charge transport at the interface boundaries between the electrodes and electrolyte. The equivalent scheme is presented in Fig. 2a, where C_g is the geometrical capacity of the two parallel electrodes in the solid electrolyte, R_b is the resistance of the electrolyte. The IS has one circle (Arc3).

- Middle frequency range: In this range, the affect of the geometrical capacity can be neglected. The impedance is determined mainly by the capicity of the double layer formed at the contacts between the solid electrolyte and electrodes. Thus, the charge transport at this interface is dependent on the reactions at the contacting boundaries. The equivalent scheme is presented in Fig. 2b, where R_{ct} is the resistance of the charge transport, C_{dl} is the capicity of the double layer (Helmholtz layer). The corresponding IS is Acr2 circle.

- Low frequency range: in the first half circle the action of the AC current on ions enables to form a concentration gradient of the ions with the impedance Z_d. The impedance plot has linear form with a slop equals to unit. When $\omega \rightarrow 0$, the AC current acts like a quazy-DC one. Thus the $Z_{Im} \rightarrow 0$ and Z_{Re} then has the corresponding value of R_{ct} in the horizontal axis. The impedance spectrum has the form of Arc1 in Fig. 2.

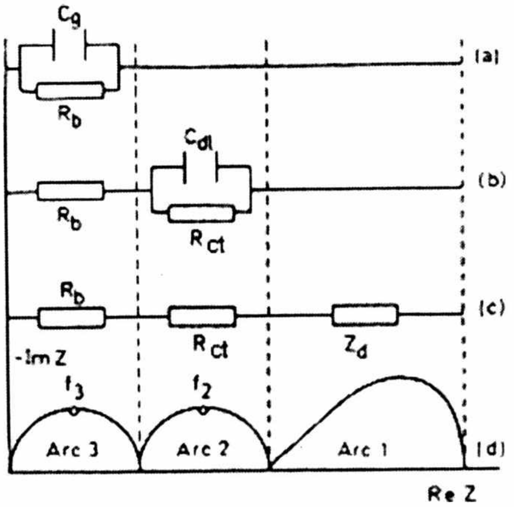

Fig. 2. Equivalent schemes at different friquencies ranges and corresponding impedance spectra of the samples measured by a two-electrodes cell.

3. The impedance spectra of $Li_xLa_{1-x}TiO_3$ thin films

3.1. Experimental evidence. The thin films of $Li_xLa_{1-x}TiO_3$ with x = 0.12 has been prepared by electron beam deposition. The experimental impedance spectra obtained for two-electrodes cells vs. the film thickness are shown in Fig. 3. For the films thicker 350 nm, the IS becomes narrower with the decrease of the film thickness. This is consistent with the MacDonall's theory for the two-electrodes cells. From the thickness of 350 nm down, instead, the conductivity is increased, the IS is not only condensed but also expanded into 2 times of the circle radius (see d3 plot). This shows that the MacDonall's theory can be applied only for the films with some critical thickness. In present samples it is around 350 nm. This may probably be attributed to the films thickness effect. So that, the choice of equivalent schemes similar to the schemes from Fig. 1 is not suitable more for such a thin film. It is necessary to take the influence of both the capacity of Helmholtz layer and the charge of the concentration gradient into the equivalent schemes.

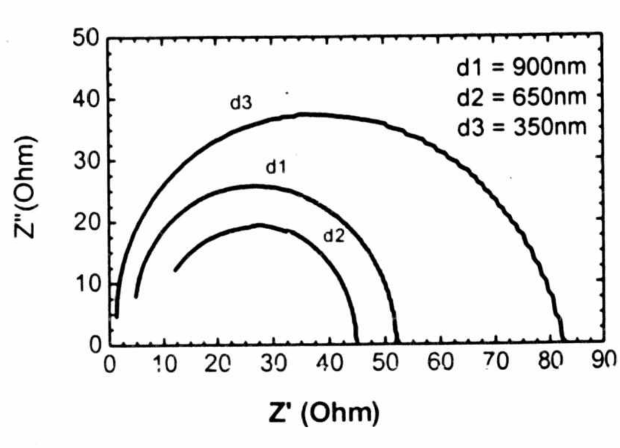

Fig. 3. *Impedance spectra of $Li_xLa_{1-x}TiO_3$ thin films with different thickness: d = 900 nm (d1), 650 nm (d2) and 350 nm (d3)*

3.2. Analysis and estimation of ionic conductivity. Figure 4 presents the IS data (dark points) of a 350 nm - thick $Li_xLa_{1-x}TiO_3$ film. In the frequency range from 10 mHz to 10 MHz, the IS splits on two clear circles. Moreover, the second circle starts at the frequency when the first circle is not finished yet. This shows that all the processes occuring in the middle and low frequencies have strongly affected to the samples. Indeed, the appearance of large circle concernning to the low frequency range proves a much considerably large influence of the electrochemical processes in the interface between the solid electrolyte and electrodes. Thus, for fitting the theoretical IS with the experimental data it is neccessary to design a series of equivalent schemes where above mentioned processes must be taken in considering. Using software available in the Auto.Lab-Potentiostat-PGS-30, one can choose different parallel and serial parts of the schemes to design an equivalent scheme that is most fitted with experimental circles. By this method we have obtained a scheme as presented in Fig. 5. The result of this fitting is shown by the solid circles in Fig. 4.

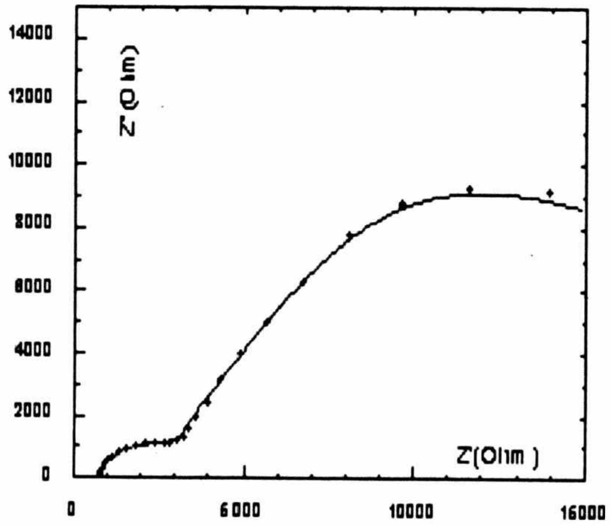

Fig. 4. Impedance spectra data (dark points) of a 350-nm thick $Li_xLa_{1-x}TiO_3$, measured in frequency range from 10 mHz to 10 MHz. The solid circles are the fitted IS obtained from the equivalent scheme of Fig. 5

The equivalent scheme in Fig. 5 consists of three parts corresponding to three ranges of AC frequencies, as follows:

- The part I has only R1, the resistance of contact and lead wires does not depend on the frequency. So the impedance has only real part.

- The part II characterizes the contribution of the electrochemical processes in the interface between the thin film and electrodes. Here R2 is the resistance of metal/solid electrolyte contact; C1 and R3, respectively are the capacity and the resistance caused by the concentration of ions in the electrolyte; C2 is the capacity of the Helmholtz layer (that strongly affect to the sample when the last is thin enough). Besides, Q characterizes the grain and boundaries size effect. Its corresponding impedance is $Z(Q) = A^*(j\omega)^{-n}$, where n = 0, Q is intrinsic resistance, n = 0.55, Q is the Warburg impedance, and n = 1, Q is the capacity.

- The part III characterizes ionic conductivity of the thin films in the low frequency range. Here C3 is the capacity formed between the two parallel electrodes and R4 is the resistance of the ionic conductance.

Table 1. Presented all the values of the parameters obtained from the calculation by this equivalent scheme.

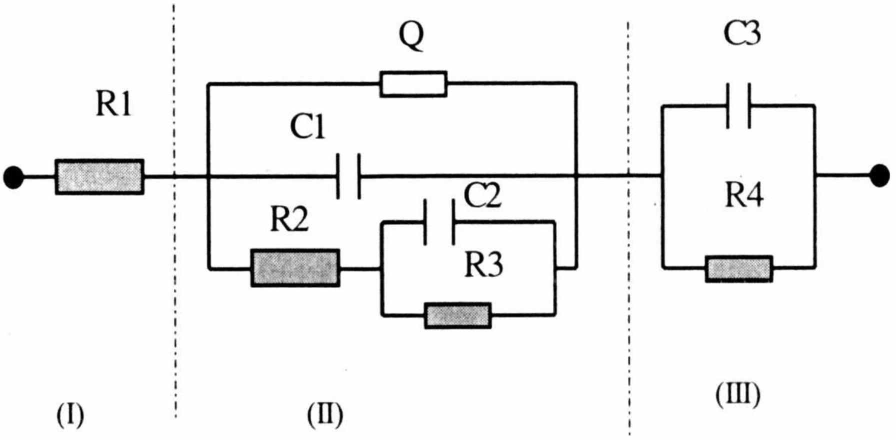

Fig. 5. *Equivalent schemes for a 350 nm - thick film of* $Li_xLa_{1-x}TiO_3$

Table 1. Physical parameters determined from the equivalent scheme in Fig. 5 for the $Li_{0.12}La_{0.88}TiO_3$ thin film

(I)	(II)						(III)	
R1(Ω)	R2(Ω)	R3(Ω)	C1(μF)	C2(μF)	Q		R4(Ω)	C3(μF)
					A(Ω)	n		
794	-2,5	37	10^{-5}	0,61	$0,2x10^{-6}$	0,52	5,37	0,12

Taking the value of R4 = 5.37 Ω from the table, for the $Li_{0.12}La_{0.88}TiO_3$ sample with a thickness of 350 nm and an electrode area of 1 cm^2, using formula (11), one can determine the Li-ion conductivity, it equals to $\sigma = 6,52 \text{ x}10^{-6}$ $S.cm^{-1}$ that is much higher than that of the thicker sample. This value is quite close to the result that was reported in [5].

4. Conclusion

The ionic conducting properties of thin fimls of perovskite structures has been studied by analysing and application of the impedance technique for the two-electrodes cells. The result has shown how to fit the theoretical IS with the experimental data for very thin film samples. The ionic conductivity of the $Li_xLa_{1-x}TiO_3$ thin films deposited by electron beam was determined with a high accuracy due to the application of the fitting method. For a 350 nm-thick film of $Li_{0.12}La_{0.88}TiO_3$, the Li-ion conductivity was found to be $\sigma \approx 6,52 \text{ x}10^{-6}$ $S.cm^{-1}$.

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