

IMPEDANCE AND MODULUS SPECTROSCOPY OF POLYCRYSTALLINE SOLID ELECTROLYTES

I.M. HODGE *, M.D. INGRAM and A.R. WEST

Chemistry Department, University of Aberdeen, Meston Walk, Aberdeen AB9 2UE (Scotland)

(Received 17th January 1976; in revised form 21st February 1976)

ABSTRACT

A method of characterising the electrical properties of polycrystalline electrolytes is described which enables grain boundary (intergranular) and bulk (intragranular) impedances to be separated and identified, by reference to an equivalent circuit which contains a series array of parallel RC elements. In the simple case of the "ideal solid electrolyte", the equivalent circuit contains a single RC element. The impedance and modulus spectra, i.e. plots of Z'' and M'' versus $\log \omega$, are simple "Debye" peaks whose peak maxima coincide at an angular frequency $\omega_{\max} = (\tau_{\sigma})^{-1}$, where τ_{σ} is the "conductivity relaxation time" and the complex modulus is the inverse complex permittivity. For real solid electrolytes there is usually a distribution of relaxation times, in which case the maxima in the impedance and modulus spectra no longer coincide. An assignment of peaks in these more complex spectra is possible in principle, since the modulus spectrum effectively suppresses information concerning grain boundary (and electrode) effects. Experimental results are presented for cold-pressed lithium orthosilicate and germanate, and for sintered β -alumina. Some advantages of this new approach are demonstrated by comparison with conventional impedance and admittance plane methods of analysis.

INTRODUCTION

Solid electrolytes of practical importance are frequently polycrystalline, and as a consequence their study presents special problems. In the determination of conductivity by a.c. methods, it is usual to seek a frequency independent region or plateau in the conductivity, but with β -alumina it has been found impossible to locate this plateau using two or three terminal techniques at frequencies below 1 MHz [1]. Frequently it is suspected that grain boundary impedances are the main cause of this failure and alternative methods of analysis based on complex plane diagrams have been used to extract bulk conductivities from experimental data. Bauerle [2] has analysed data for doped zirconia in the complex admittance plane while Armstrong et al. [3] have favoured the complex impedance formalism for analysing data on β -alumina and $RbAg_4I_6$.

More recently, Powers and Mitoff [4] have achieved the experimental separation of electrode and grain boundary effects from bulk conductivities in β -alumina electrolyte by using 4-terminal a.c. methods.

The successful separation of intergranular from bulk phenomena depends ultimately on the choice of an appropriate equivalent circuit to represent the electrolyte properties. Armstrong et al. [3] have used model equivalent circuits to simulate, in the complex impedance plane, the effects of blocking electrodes, grain boundaries, etc., and have shown that this method of circuit analysis can be applied to practical systems. In a preliminary note [5], the present authors showed that a combined analysis using both the complex impedance and the complex modulus formalisms had certain advantages over the earlier methods. This theme has been further developed in the present paper, and it is shown that modulus and impedance "spectroscopy" can be used to obtain a valuable insight into the heterogeneous electrical structure of solid electrolytes.

THEORY

Graphical displays of a.c. data

The a.c. response of an electrolyte or electrochemical cell can be expressed in any of four basic formalisms. These are most conveniently expressed as:

$$\text{the complex admittance, } Y^* = (R_p)^{-1} + j\omega C_p \quad (1)$$

$$\text{the complex impedance, } Z^* = (Y^*)^{-1} = R_s - j/\omega C_s \quad (2)$$

$$\text{the complex permittivity, } \epsilon^* = \epsilon' - j\epsilon'' \quad (3)$$

$$\text{the complex modulus, } M^* = (\epsilon^*)^{-1} = M' + jM'' \quad (4)$$

where the subscripts p and s refer to the equivalent parallel and series circuit components respectively. These functions separate into two groups representing essentially *parallel* and *series* formalisms. The two parallel or "admittance" functions are related.

$$Y^* = j\omega C_0 \epsilon^* \quad (5)$$

Similarly the series or "impedance" functions are related:

$$M^* = j\omega C_0 Z^* \quad (6)$$

where C_0 is the vacuum capacitance of the cell.

The quantities Y^* , Z^* and ϵ^* constitute standard textbook material, and have been in use for many years. Rather surprisingly, the fourth member of this tightly defined group, ϵ^{*-1} , was introduced into the literature only quite recently [6]. Macedo et al. [7-9] were the first to exploit the modulus and used it for analysing conductivity relaxations in glasses and in concentrated aqueous solutions. The extension of the modulus treatment to solid electrolytes [5] is crucial to the methods of analysis developed here.

Equivalent circuit simulations

The ideal solid electrolyte. In one theoretical treatment of polarisation in vitreous ionic conductors [8], conduction is visualised as a series process involving consecutive hops of an ion over potential energy barriers along the direction of the electric field. In the ideal case, where these energy barriers are assumed to be of equal height, the conductivity (σ) and the permittivity (ϵ') are independent of frequency [8]. Thus

$$\sigma = k/R_p \quad (7)$$

and

$$\epsilon' = C_p k/e_0 = C_p/C_0 \quad (8)$$

where k is the cell constant, and e_0 the permittivity of free space ($8.854 \times 10^{-14} \text{F cm}^{-1}$). It is convenient in the present context, to refer to such a material as an *ideal solid electrolyte*, defined as one whose properties are simulated by a single parallel RC element (Fig. 1). This circuit moreover is characterised by a single Maxwell time constant, τ_σ , given by

$$\tau_\sigma = R_p C_p \quad (9)$$

$$= e_0 \epsilon' / \sigma \quad (10)$$

Since this time constant represents the exponential decay of the electric field across the electrolyte caused by the conduction process, it is conveniently called the "conductivity relaxation time" [8].

The response of an ideal electrolyte has been simulated by setting $R_p = 10^6 \Omega$, $C_p = 10^{-12} \text{F}$ and $k = 1$ (Fig. 2). The graphs include complex plane diagrams (Y'' vs. Y' , etc.) and "spectroscopic displays" (Y'' , Z'' , etc. vs. $\log_{10} \omega$). The following points should be noted:

- (i) Graphs based on Y^* and ϵ^* are straight lines and indicate that σ and ϵ' are independent of frequency.
- (ii) The complex plane plots, Z'' vs. Z' and M'' vs. M' are semicircles.
- (iii) Plots of Z'' and M'' vs. $\log \omega$ appear as symmetric (Debye) peaks.
- (iv) The angular frequencies (ω) of the peak maxima and the centres of the

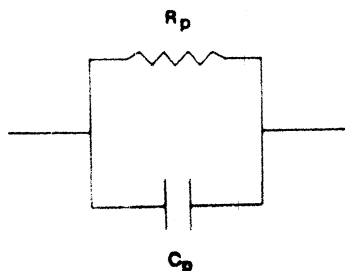


Fig. 1. The equivalent circuit of the "ideal solid electrolyte".

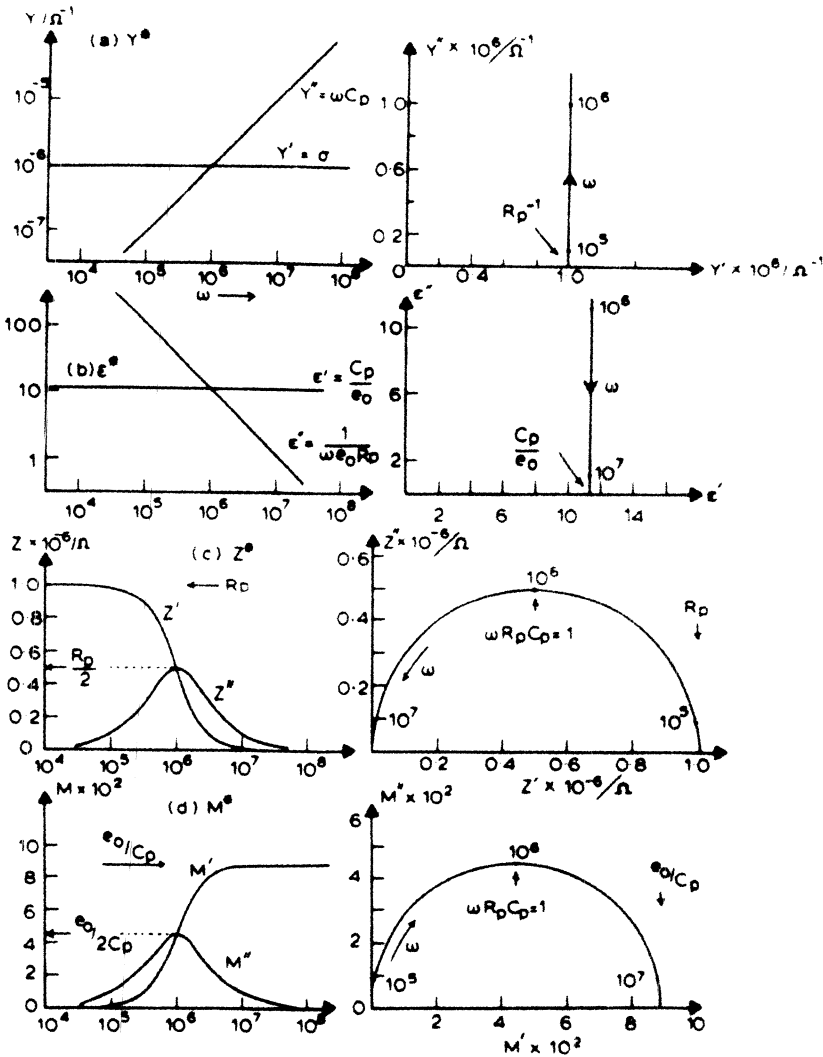


Fig. 2. Simulated "spectra" and complex plane diagrams for the ideal solid electrolyte, where $R_p = 10^8 \Omega$, $C_p = 10^{-12} \text{F}$, and the cell constant $k = 1$. (a) Y^* ; (b) ϵ^* ; (c) Z^* ; (d) M^* .

semicircles coincide, and are given by the reciprocal of the conductivity relaxation time, τ_σ :

$$\omega_{\max} = 2\pi f_{\max} = 1/\tau_\sigma = \sigma/e_0\epsilon' \quad (11)$$

(v) The peak heights of Z'' vs. $\log \omega$ and M'' vs. $\log \omega$ are proportional to R_p and $1/C_p$, respectively, as shown by the equations:

$$Z'' = R_p \omega \tau_\sigma / [1 + (\omega \tau_\sigma)^2] \quad (12)$$

$$M'' = (e_0/C_p) \omega \tau_\sigma / [1 + (\omega \tau_\sigma)^2] \quad (13)$$

All the diagrams given in Fig. 2 are valid ways of presenting data but it can be seen that different plots highlight different features. In particular, the modulus and impedance spectra (M'' vs. $\log \omega$ and Z'' vs. $\log \omega$, respectively) highlight the time constant (conductivity relaxation time) of the ideal electrolyte. Equation (11) shows that the frequencies of both peak maxima are determined by the ratio σ/ϵ' , and since the permittivity of ionic conductors varies little from one material to another, the position of the peaks in the impedance and modulus spectra is very largely determined by the electrolyte conductivity. In essence, this is the basis of the proposed method for characterising real (heterogeneous) solid electrolytes by using impedance and modulus spectroscopy to obtain the *distribution of conductivities* in the sample.

Practical solid electrolytes. In favourable circumstances, ionic solids can be obtained conveniently as single crystals and may approximate in their properties to the "ideal solid electrolyte" described above. This can be exemplified by the work of Haven and others [10,11] on dielectric loss in doped alkali halide crystals, where it is found that (discounting a small Debye-Falkenhagen effect) the conductivity of the electrolyte remains constant up to frequencies which lie well above those at which the maxima in the impedance and modulus spectra would occur.

However, most "practical" solid electrolytes cannot be represented by the simple equivalent circuit shown in Fig. 1. Thus, polycrystalline materials will generally show intergranular or grain boundary impedances which may differ in R and/or C from the individual crystals. In the absence of surface conduction, polycrystalline solid electrolytes can be represented by a series array of parallel RC elements, as shown by Armstrong et al. [3]. Such an equivalent circuit, with additional series capacitance to represent blocking electrodes, is given in Fig. 3. To get a physical picture of this distribution of RC elements, consider the highly *schematic* diagram of the solid electrolyte given in Fig. 4. Different physical features in the electrolyte are represented by layers of varying thickness, as in Maxwell's model of the layered dielectric [12]. To a first approximation, the permittivity of the material is assumed to be uniform throughout, so that only fluctuations in resistivity occur [13]. On this assumption, *low* capacitances (ca. 10^{-12} F) can be assigned to the thick layers (representing the crystal grains or "bulk" material), and rather higher capacitances (ca. 10^{-11} – 10^{-6} F) to the thin layers representing grain boundaries, electrode double layers, etc. However, depending on their resistivity, grain boundary resistances may be negligible or may be large in comparison with the resistances of the crystal grains.

In terms of the above discussion, a simple circuit which could be used to simulate the properties of a real (nonideal) electrolyte would contain a pure capacitance to represent blocking electrodes, and two elements, R_1C_1 and R_2C_2 each representing different parts of the electrolyte. Using this type of circuit it is possible to compare the effects of making R_1 different from R_2 and C_1 different from C_2 .

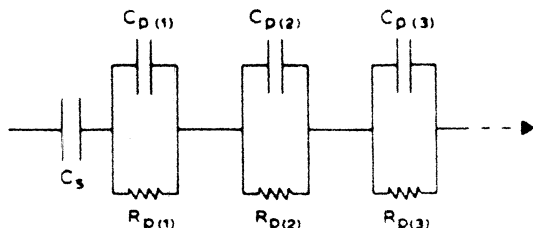


Fig. 3. The series equivalent circuit for a polycrystalline solid electrolyte (appropriate only when surface conductivity is negligible).

Modulus and impedance spectra for two such equivalent circuits are shown in Figs. 5 and 6. In Fig. 5, the capacitances are equal but the resistances differ by two orders of magnitude. This circuit simulates the behaviour of an electrolyte containing a mixture of two crystalline phases of different conductivity. It can be seen that the modulus spectrum separates into two peaks corresponding to the two RC elements — equal in height since the capacitances are equal (eqn. 13), whereas the impedance spectrum is dominated by the RC element with the larger resistance.

In Fig. 6, the resistances are equal and it is the capacitances which differ by two orders of magnitude. This circuit simulates the properties of an electrolyte containing about 1% of intergranular material with resistivity about 100 times larger than that of the crystal grains. In this case, the impedance spectrum contains two peaks — equal in height since the resistances are equal (eqn. 12) — whereas the modulus spectrum suppresses the low-frequency peak, which corresponds to the high-capacitance intergranular material.

It is clear from Figs. 5 and 6 that impedance and modulus spectra display complementary information. In both cases, the resulting spectrum is the summation of two Debye peaks, one for each RC element. However, differences occur because the two methods apply different weighting schemes to the ex-

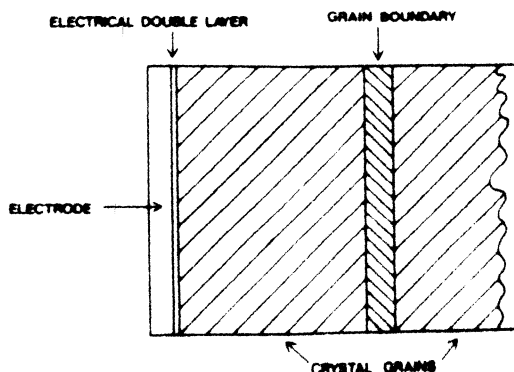


Fig. 4. A physical representation of the equivalent circuit shown in Fig. 3 in terms of Maxwell's layered-dielectric model.

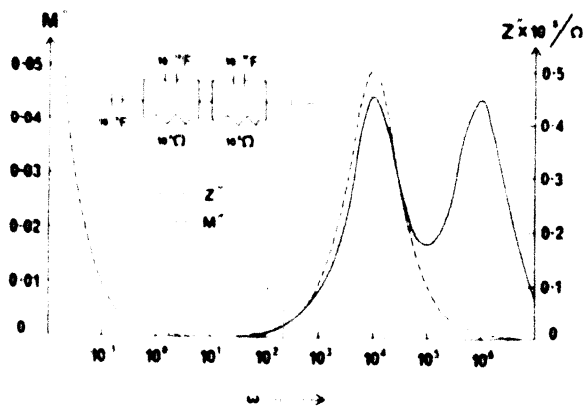


Fig. 5. Simulated impedance and modulus spectra for a "real" electrolyte containing two different crystalline phases.

perimental data. In the modulus the height of each peak is proportional to $1/C$ for that RC element, eqn. (13), and so information about thin layers, such as the electrode/electrolyte double layer and intergranular effects, will tend to be suppressed. On the other hand, the peak heights in the impedance spectrum are simply proportional to R of each RC element, eqn. (12), and so the most resistive element will dominate the spectrum. For solid electrolytes in general (even though the simple equivalent circuits shown in Figs. 5 and 6 are unlikely to give an adequate description) the two types of spectrum will always place a different emphasis on bulk and interfacial effects.

Electrode effects show up this difference most clearly. Thus, blocking electrodes are completely "invisible" in the modulus spectrum, but show up as a low frequency spike or "cutoff" in the impedance spectrum. Whichever formalism is used, there are clear advantages to be gained from the use of good blocking electrodes in studies of polycrystalline electrolytes (where ideally

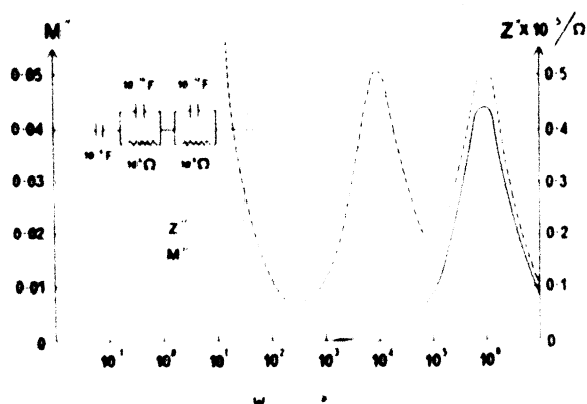


Fig. 6. Simulated impedance and modulus spectra for a "real" electrolyte exhibiting a grain boundary effect.

