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Comparison and application of two methods for the least squares analysis of immittance data

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Two different, recent methods for complex nonlinear least squares fitting of the small-signal ac response of dielectric and partially conducting systems are described and compared. These methods, which are also appropriate for fitting mechanical relaxation, nuclear magnetic relaxation, and light-scattering complex data, simultaneously fit the real and imaginary parts of the data to an appropriate model. For small-range response data, the weighted, extended least squares, vector-minimization approach (Program LEVM) and the much more complicated unweighted matrix-determinant method are shown to yield indistinguishable results. For small-range data measured on a dielectric polymer, weighting is found to be unnecessary. Verification of some of the results is accomplished by Monte Carlo simulation. For large-range data sets, such as those usually arising from electrical response measurements on ionic or electronic conductors, data variances generally vary widely (high heteroscedasticity). Some kind of weighting is then essential in order to obtain low-bias fitting-model parameter estimates with small estimated standard deviations. This is demonstrated by fitting wide-range data for the admittance of hydrogen-doped lithium nitride over a wide frequency range. The results of fitting with the several different weighting schemes available as choices in the vector-minimization approach are compared and discussed. Such fitting was carried out using the general-purpose program LEVM, which runs rapidly on a PC/AT or equivalent machine. It is the only availabe complex nonlinear least squares fitting program which can use the data to produce least-squares estimates of the parameters of an error-variance (weighting) model as well as those of the fitting model. Thus, the data themselves can be used to determined the most appropriate weighting. An excellent fit of the Li_3N data was obtained, demonstrating that iterative reweighting, using variable weights proportional to the magnitude of the real and imaginary parts of the fitting-model function raised to a power near unity (a form of extended least squares), was the most appropriate way to treat the high heteroscedasticity of the data and to obtain minimum-bias, high-precision parameter estimates.

1. Introduction and background

The measurement and analysis of the small-signal ac frequency response of dielectric and partly conductive systems has come to be called impedance spectroscopy (IS) in recent times [1], although a more general designation is immittance spectroscopy. Here "immittance" represents any of the four levels important in IS: complex dielectric constant ($\kappa^* \equiv \kappa' - i\kappa''$) or complex capacitance level, admittance level ($Y \equiv Y' + iY''$), impedance level ($Z \equiv Z' + iZ''$), or complex modulus level ($M \equiv M' + iM''$), where $i \equiv (-1)^{0.5}$. The analysis of data at any of these levels is a crucial part of IS.

Since the work of Sheppard et al. [2,3] on dielectric response, the preferred method of analyzing IS data has been the use of complex nonlinear least squares fitting (CNLS). In such fitting, the entire immittance function (real and imaginary parts, or modulus and phase) is fitted to a model or equivalent circuit thought to represent the response. It has been found that CNLS fitting yields much more quantitative results than does graphical analysis and is more appropriate than fitting the real or imaginary parts of an immittance function separately to a response model. In CNLS fitting, one obtains a single set of parameter estimates based on all the data. In contrast, separate real and imaginary fitting yields two such sets of parameter estimates, each based on only part of the data. These results are often difficult to reconcile and are less precise than the CNLS ones [1].

Here, I first compare the results of using two quite different CNLS methods for the analysis of a typical set of narrow-range dielectric data [4,5], and I show what can also be learned with Monte Carlo (MC)

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simulation. Then, the simplest of the two CNLS methods is used to analyze conductive-system admittance data of extremely wide range, a common condition for such data, but one whose proper analysis requires special care because data variances are usually not constant and can vary greatly (termed a high heteroscedasticity situation by statisticians).

In CNLS fitting there are two dependent variables, both depending (wholly or in part) on the same set of model parameters. Although modulus and phase data may alternatively be used, here I consider only the Cartesian representation of complex variables, where the two dependent variables are the real and imaginary parts. Complex nonlinear least squares fitting was first applied in the dielectric area by Sheppard et al. [2]. Soon thereafter, a somewhat simpler approach, applicable for data at any immittance level, was presented by Macdonald and Garber [6]. This method was further described and developed by Macdonald et al. [7], Boukamp [8], Macdonald and Potter [9], and Macdonald [10,11]. Such work resulted in a very general CNLS program, LEVM, which is available in both source-code and executable form at nominal cost (no profit) from the author's department. This program was used to obtain most of the present results. It runs on a PC/AT machine, requires less than 400 KB of random access memory, and can fit typical IS data in a minute or less.

The current version of LEVM, V. 5.0, employs a method of solving the nonlinear least squares equations of the problem based on an approach called extended least squares (ELS) [12–15]. This approach will not be described in detail here since its description exists in the literature and is embodied in LEVM. ELS involves a form of iterative reweighting and was originally developed for fitting single-response (e.g., real) data. Except for its recent generalization and use in the IS area [11], it has been very little used, even for real data, because it cannot be implemented with most standard statistical packages [14]. Most real-data ELS fitting results, such as those of Beal and Sheiner [12], have only been obtained for data of limited range, and their particular ELS approach does not use geometrical averaging of weights, a vital element in LEVM and one which greatly improves iterative convergence during the fitting procedure for either real and complex data. In the present realization of the iterative ELS approach, the actual nonlinear least squares minimization procedure used at each iteration is based on a method of Moré [16].

2. Weighting schemes

Let y_i (with $i=1, 2, ..., N$) denote experimental data (usually complex) and define $F_{0i} \equiv F(x_i, \theta_0)$ and $F_i \equiv F(x_i, \theta)$ as the ith elements of the exact and actual fitting models, respectively. They may apply at any of the four IS levels. Here N is the number of data points; x_i is an independent variable value (angular frequency); θ_{0j} is the exact value of the jth parameter; and θ_j is an estimate of θ_{0j}. We use the same notation for estimates from a single fit and from MC simulations. The number of free fitting parameters is P. We thus assume that the form of the fitting model is appropriate for the data (negligible systematic errors) but that the θ_{0j}'s are unknown and are to be estimated by CNLS. For a single fit, the relative error of the jth parameter is $e_j \equiv (\theta_j/\theta_{0j}) - 1$. The relative bias is then the average of a large number of such e_j values obtained from fits of different data sets, each with different random errors but all drawn from the same error distribution. The bias, a measure of how accurate parameter estimates can be, on the average, thus must usually be estimated by MC simulation.

The proper choice of weighting is crucially important in allowing one to obtain a good CNLS fit of data of wide range and high heteroscedasticity. Such a fit should have minimum bias and small uncertainties of the parameter estimates obtained. Because IS fitting models are nearly always nonlinear in some of their parameters, there will always be some bias, but it can be minimized by using the most appropriate weighting, and the relative bias will often then be negligible [11]. In general, CNLS fitting requires both a fitting model and a weighting (variance) model [11,15]. The variance model is used to account as adequately as possible for the actual (unknown) random errors in the data and to reduce the effects of their heteroscedasticity if the variances of fitting residuals are not constant. In the IS area, data errors are often either approximately additive or are of approximately constant-percentage character, with proportionality constant σ_r. To account for more

general forms of random errors, let us assume that the individual data errors, $\epsilon_i \equiv \epsilon_i' + i\epsilon_i''$, are of the form

$$\epsilon_i' = \alpha_r P_1(0, I_i) + \sigma_r |F_{0i}'|^{\xi_0} P_2(0, I_i) , \quad (1)$$

and

$$\epsilon_i'' = \alpha_r P_3(0, I_i) + \sigma_r |F_{0i}''|^{\xi_0} P_4(0, I_i) , \quad (2)$$

where, for example, $\alpha_r P(0, I_i) \equiv P(0, \alpha_r^2 I_i)$ is a random sample from an independent, uncorrelated probability distribution of zero mean and standard deviation α_r. Although for actual data the ϵ_i's are all unknown, in MC simulations they can be constructed to be of exactly the above forms. By the choices of the four P's we can control the degree of correlation between the various components. Note that when $\sigma_r = 0$ the errors the additive, while if $\alpha_r = 0$ and $\xi_0 = 1$ they are of proportional form.

The general variance model used in LEVM, which involves the parameters ξ and U of table 1, can account for errors of the above character with both α_r and σ_r simultaneously non-zero [11]. Here, however, we shall need to deal only with those specific weighting choices (i.e., separate variance models) where either α_r or σ_r is zero. Weighting is just a transformation of both data and model values aimed at reducing the range of their difference after weighting (weighting residuals) and thus the heteroscedasticity of the problem. In the present work, I shall compare the effects of various weighting possibilities for both the small- and the large-range data sets mentioned above. Different weightings arise from different transformation choices. Define the ith transformed, or weighted, residual as

$$\begin{aligned} R_i &\equiv R_i' + iR_i'' \\ &\equiv [\{y_i' - F(x_i, \theta)'\}/T_i'] \\ &\quad + i[\{y_i'' - F(x_i, \theta)''\}/T_i''] . \end{aligned} \quad (3)$$

For simplicity, omit the real and imaginary designations and in the equations below take, for example, T_i as either T_i' or T_i'' as appropriate. The variance model is defined by the choice of the variances T_i^2 and the weights by $W_i \equiv 1/T_i^2$ [11,15]. Since it is important in ELS to use geometric averaging of weights, finally express T_i in terms of a quantity τ_i as

$$T_i = \tau_i / \prod_{i=1}^{N} \tau_i^{1/N} , \quad (4)$$

for specific choices of $\tau_i \neq 0$. We can now define the various weightings of interest by the choice of the τ_i's. When not shown separately, these choices will always be of the same form for the real and imaginary components.

The six weightings of present interest are determined for all i by the choices listed in table 1. CNLS fitting is simplest for unity weighting, UWT (equivalent to no weighting at all), data-proportional weighting, DPWT, and data-modulus weighting, DMWT because the T_i's are independent of parameter values for these choices. With such weighting, neither the geometric-mean normalization of eq. (4) nor ELS is needed, and these were the only weightings available for CNLS studies until the 1988 introduction of ELS in the LEVM program. But unity weighting is usually inappropriate for wide-range data, while data-proportional and data-modulus weighting lead to much greater parameter bias than does function-proportional weighting, FPWT, when proportional weighting is appropriate [11]. Since the last three weighting types listed in the table depend on the parameter values, which themselves vary during the least-squares iterations, they use ELS and eq. (4). By using function power-law weighting, FPLWT, where the ξ parameter of the weighting model is determined along with the fitting model parameters by

Table 1
Some weighting choices important in CNLS fitting of impedance spectroscopy data. (See eqs. (3) and (4).)

Unity weighting	UWT	$\tau_i = U = 1$
Data-proportional weighting	DPWT	$\tau_i = y_i$
Data-modulus weighting	DMWT	$\tau_i' = \tau_i'' = [(y_i')^2 + (y_i'')^2]^{0.5}$
Function-proportional weighting	FPWT	$\tau_i = \lvert F_i \rvert$
Fixed-function weighting	FFWT	$\tau_i = \lvert F_i \rvert^{\xi}$ (ξ fixed)
Function power-law weighting	FPLWT	$\tau_i = \lvert F_i \rvert^{\xi}$ (ξ free)

minimization of an objective function, one allows the data themselves to determine the character of the most appropriate weighting, a very valuable feature. For example, if the estimate of ξ is statistically indistinguishable from unity, it is very likely that one is dealing with a constant-percentage situation, while if the estimate is close to 0.5, the data involve Poisson statistics, such as one finds for radioactive decay measurements.

3. Comparison of methods: Objective functions

A principal difference between the multiresponse CNLS method of Bates and Watts [5], denoted BW, and the method described above and instantiated in LEVM is in the objective function employed: the function of the residuals which is minimized to obtain a least-squares solution. That used in LEVM and in all previous CNLS work except that of BW is

$$\boldsymbol{O}(\theta, U, \xi) \equiv \sum_{i=1}^{N} [(R_i')^2 + (R_i'')^2] . \tag{5}$$

As this expression shows, we minimize with respect to the parameters (both those of the fitting model and, when appropriate, those of the variance model, U and ξ), the sum of squares of the real weighted residuals and the imaginary weighted residuals with no cross-products. Thus, the squared-residual vector is of dimension $2N$. By contrast, BW [5] form a $N\times 2$ matrix of unweighted residuals, Z, whose left column involves real residuals and whose right column involves imaginary ones. They then minimize the 2×2 determinant $|Z^{\mathrm{T}}Z|$, where the T denotes the transpose.

Since both the above ELS vector method and the matrix approach yield maximum likelihood estimates, an important question in how large are the differences in the estimates? The matrix method leads to much added solution complexity, but it is different in that the objective function involves cross-product terms between real and imaginary residuals. Although no such terms occur in eq. (5), LEVM incorporates other ways of achieving coupling when needed. In favorable cases, the added BW terms probably speed convergence to an optimum solution, but there is also a problem not occuring in the LEVM vector approach, that of possible lack of positive-definite matrices in the BW analysis [5]. Another difference in the approaches is that D, the number of degrees of freedom, is $N-P$ for the BW matrix method and is $2N-P$ for the vector approach.

4. Fit quality measured and optimization

The variance of the fit, S_{F}^2, is calculated from the final converged value of $\boldsymbol{O}(\theta, U, \xi)$, $\boldsymbol{O}_{\mathrm{C}}$, in eq. (5). When convergence of the iterative least squares procedure is attained, $\boldsymbol{O}_{\mathrm{C}}$ is formed using the final values of the F_i's and T_i's, and S_{F}^2 is given by

$$S_{\mathrm{F}}^2 \equiv D^{-1} \Lambda \boldsymbol{O}_{\mathrm{C}} , \tag{6}$$

where

$$\Lambda \equiv \prod_{i=1}^{N} \tau_i^{-2/N} . \tag{7}$$

In addition, it is sometimes useful to calculate not only S_{F}, the standard deviation of the complex fit, but also the standard deviation associated with the real part of the data, S_{FR}, and that associated with fitting the imaginary part, S_{FI}. Comparison of the two values then yields a useful measure of how well the two separate parts fit the model. For good data with the proper fitting model and weighting, they should be essentially equal. The associated variances are defined as

$$S_{\mathrm{FR}}^2 \equiv (N-P)^{-1} \Lambda \sum_{i=1}^{N} [(R_i')^2]$$

and

$$S_{\mathrm{FI}}^2 \equiv (N-P)^{-1} \Lambda \sum_{i=1}^{N} [(R_i'')^2 .$$

For all weights involving the model function, F_i, S_{F} is an excellent estimate of σ_r, the standard deviation of the random error distribution, eqs. (1) and (2). Although LEVM allows one to obtain S_{FR} from a separate fit of the real part of the data and S_{FI} from a fit of the imaginary part, their comparison is most useful when they are obtained from a fit of the real and imaginary parts of the data together, the usual situation.

When S_{FR} and S_{FI} are unequal, we can invoke a simple iterative optimization procedure (denoted by

-O, as in UWT-O), which produces some coupling in the fit between the real and imaginary parts of the data and usually improves the solution. It consists of the following sequence: After convergence of the initial fit iteration, all the resulting real weights are multiplied by a single factor and all the imaginary ones by a related factor, both selected to bring S_{FR} and S_{FI} closer together. These modified weights are then used in a subsequent fit and the procedure iterated until near equality of S_{FR} and S_{FI} is obtained.

5. Analysis of Havriliak–Bates–Watts complex dielectric constant data

A CNLS analysis of data on the complex dielectric constant, κ, for the polymer *s*-PMMA has appeared recently in the statistical literature [4,5]. The unity-weighting analysis used the BW multiresponse approach discussed in section 3, a method developed entirely independently of earlier CNLS work. The fitting model employed was the five-parameter empirical Havriliak–Negami (1967) function expressed by BW in the form

$$\kappa_i = \kappa_i' - i\kappa_i'' = \kappa_\infty + (\kappa_0 - \kappa_\infty)/[1 + (i\omega_i e^{-\theta_T})^\alpha]^\beta, \qquad (8)$$

where ω_i is an angular frequency, and the possible ranges of α and β are $0 \leqslant \alpha \leqslant 1$ and $0 \leqslant \beta \leqslant 1$. The expression $e^{-\theta_T}$ may be identified with a relaxation time, τ, but should, for dimensional consistency, be written as $\tau_0 e^{-\theta_T}$, where τ_0 is held fixed at unit value but must have dimensions of time.

The data analyzed by Havriliak and Watts [4] and by BW [5] were originally obtained by Havriliak and Negami [17] and were corrected, in the later work, to remove systematic errors. These data involve 21 points and cover the small ranges of 1.5 for the real part and 2.3 for the imaginary part. Since the range is so small, there should be little difference between unity-weighting and function-proportional-weighting fit results. Nevertheless, it will be instructive to compare them. In table 2, line 1 summarizes the fit results obtained by BW using their multiresponse method. For quantities of the form $\theta \pm (\mathrm{SD})_\theta$ in the table, θ, is a parameter value estimate and $(\mathrm{SD})_\theta$ is its approximate (linearized) standard deviation es-

Table 2
Analysis of Bates–Watts complex dielectric constant data. Lines 1–7: individual CNLS fit results. Lines 8 and 9: MC results for line-1 parameter choices; line 8: S_{JC} estimates for $\rho_{RI} = 0$; line 9: S_{JC} estimates for $\rho_{RI} = 1$. In lines 8 and 9 the simulation used normal errors. In the weight column -O indicates that an optimization procedure (section 4) was used. The symbol @ indicates that the result was not available.

Line	Weight	S_{FR}	S_{FI}	S_F	S_{NE}	κ_0	κ_∞	θ_T	α	β
1	UWT-BW	0.003	0.0024	@	@	4.398 ± 0.006	2.451 ± 0.010	8.245 ± 0.074	0.487 ± 0.007	0.571 ± 0.021
2	UWT	0.00414	0.00242	0.00315	0.1483	4.394 ± 0.0072	2.447 ± 0.0129	8.218 ± 0.0867	0.490 ± 0.0084	0.561 ± 0.0253
3	UWT-O	0.00337	0.00337	0.00313	0.1311	4.398 ± 0.0055	2.451 ± 0.0098	8.240 ± 0.0701	0.487 ± 0.0064	0.570 ± 0.0200
4	FPWT	0.00127	0.01013	0.00672	0.3039	4.397 ± 0.0058	2.445 ± 0.0076	8.187 ± 0.0520	0.491 ± 0.0045	0.557 ± 0.0134
5	FPWT-O	0.00719	0.00719	0.00668	0.1214	4.397 ± 0.0041	2.446 ± 0.0076	8.204 ± 0.0620	0.490 ± 0.0056	0.561 ± 0.0165
6	FFWT	0.00309	0.00337	0.00301	0.1301	4.398 ± 0.0049	2.449 ± 0.0088	8.231 ± 0.0655	0.488 ± 0.0059	0.568 ± 0.0183
7	FFWT-O	0.00323	0.00323	0.00301	0.1266	4.398 ± 0.0051	2.449 ± 0.0091	8.231 ± 0.0672	0.488 ± 0.0061	0.568 ± 0.0188
8	UWT-O/MC			0.00314	S_{JC}:	0.0072	0.0127	0.0882	0.0083	0.0260
9	UWT-O/MC			0.00314	S_{JC}:	0.0054	0.0146	0.0923	0.0081	0.0268

timate. Finally, because S_F values obtained with unity weighting and with function weighting are not directly comparable, we have included in the table the values of S_{NE}, a negative entropy (logarithmic) measure of fit that can be so compared [9,18]. Its range is 0 to 1, and it approaches zero as all the squared (weighted or unweighted) residuals, R_i^2, approach equality. Thus, a minimum value of S_{NE} is usually desirable, but we do not minimize it directly here.

Now let us assume that the BW results of table 2, line 1, are good parameter estimates. How well do our results compare? Our unity-weight results of line 2 are generally close to those of BW but show slightly larger uncertainties. But our optimized unity weighting results, UWT-O, are exceedingly close to the BW ones and have slightly smaller uncertainty estimates. Thus, our simpler, quicker fit is quite satisfactory here. Line 4, for function-proportional weighting, shows a large difference between S_{FR} and S_{FI}, a difference reflected in the large value of S_{NE}. But optimization, line 5, leads to considerable improvement and to smaller estimated SDs than in the BW analysis.

A fit with optimized function power-law weighting (FPLWT-O) led to a ξ estimate of 0.2545|0.49, thus poorly defined. In this notation, 0.2545 is the parameter estimate and 0.49 is its relative standard deviation, $(SD_\xi)/\xi$. If, in spite of the poor definition of ξ, we take it fixed at the above value in a run with fixed-function weighting, FFWT, line 5 in table 1, we obtain the results shown in line 6 of table 2, results which indicate that taking ξ fixed at its predicted value makes the S_{FR} and S_{FI} values approach each other closely. The parameter estimates are now appreciably nearer to the BW ones. The finally fitting run, line 7, also with $\xi=0.2545$, shows that optimization has little further effect since the S_{FR} and S_{FI} values are already close without it. In addition, the approximate parameter correlation matrix presented by BW and that found in the line-7 run are very nearly identical.

When different ways of fitting a single data set are compared, one can always ask the question: How typical are the results? Perhaps with a different set of data taken on the same material under conditions as similar as possible, comparison might lead to different conclusions. When many such sets are unavailable, the usual case, uncertainty of this type can generally be resolved by means of a Monte Carlo simulation study. Thus, I carried out such a study here using optimized unity weighting. The BW parameter values of line 1 were first used to generate error-free data from the model; these values were then employed as the basis of the MC study. For each MC replication, independent errors of the form of eqs. (1) and (2) were then added to the error-free values. Although all these errors were drawn from normal error distributions, it was found, as expected, that using uniform error distributions led to little difference in the parameter estimates [15]. Sufficient MC replications were used to ensure that the last figure in each quoted result was significant.

In order to obtain a MC S_F value close to that of line 3, I used in eqs. (1) and (2) $\sigma_r=0$ and an α_r choice of 0.00322, which led to $S_F=0.00314$, as shown in table 2, lines 8 and 9. Further, MC results were obtained for two choices of the P_1 and P_3 error distributions (and their individual elements): (a) P_1 and P_3 entirely independent, and (b) $P_1=P_3$. Thus the correlation between real and imaginary errors, ρ_{RI}, was statistically zero for choice (a) and unity for (b). Relative bias values depended only slightly on these choices and were all of negligible magnitude: less than 10^{-4} in magnitude for the first two parameters, less than 3×10^{-4} for the second two, and about $+1.6\times10^{-3}$ for the parameter β.

Lines 8 and 9 in table 2 list results for the estimated standard deviations of the parameter distributions, S_{jC} (termed $(SD)_\theta$ above for a single fit), with each value based on averaging 2×10^5 individual fit results. Again, we see very little dependence on the correlation between real and imaginary errors. Further, comparison of the S_{jC} values in line 8 with the corresponding SD values of line 2 shows remarkable agreement, while comparison of such quantities in lines 9 and 3 indicates somewhat less agreement. The correlation coefficients between the real and imaginary unweighted residuals for the lines 2 and 3 fits were about -0.21 and -0.22, respectively. When one takes into account that all the imaginary data values are negative, the signs of these values should be changed for comparison with error correlations. All these results suggest that the correlated Havriliak–Negami data set is indeed representative of the actual experimental situation (e.g., it contains errors whose distribution is well approx-

imated by a normal distribution) and that one can have confidence in the results of the present comparison of fitting methods.

An examination of the estimated SD's of all the parameter estimates of table 2 suggests that there is no particular basis to prefer one of the line-3, line-6, or line-7 solutions to the others. Although fixed or variable weighting is clearly unnecessary for these small-range data, it is essential for IS data with large ranges. Thus, generalization of the BW procedure to include various weighting schemes such as those used here, or generalization of the present approach based on weighted residuals with a residual matrix rather than a residual vector, might be helpful to ensure convergence from poorer parameter starting estimates than possible in the present procedure. It is not clear, however, that, given convergence to a least-squares condition, such a generalized procedure will lead in a practical sense to any better parameter estimates. Nevertheless, I hope to investigate this matter further in future.

6. Analysis of large-range admittance data

Electrochemical IS data are usually experimentally determined as either impedances or as admittances (impedance level or admittance level). Given data at one of these levels, they can be directly inverted to yield results corresponding to the other level. In order to avoid bias introduced by inversion, however, CNLS fitting should preferably be carried out at the measurement level.

Since it is worthwhile to compare both small-range and large-range CNLS data fitting using the present methods, the 45°C admittance data for a hydrogen-doped lithium nitride (Li_3N) single crystal with evaporated gold electrodes [19] were analyzed. For future reference and for use with other fitting methods which may be developed in the future, the Li_3N data are listed in table 3 and involve 49 logarithmically distributed frequencies extending from 1 Hz to 277 300 Hz.

Define the ith admittance data value as $y_i \equiv y_i' +$

Table 3
Real and imaginary admittance components (Siemens) versus frequency, f, in Hz for a lithium nitride single crystal at 45°C [19].

f	y'	y''	f	y'	y''
1.000	0.615300E-05	0.209760E-04	598.5	0.882210E-03	0.600950E-03
1.287	0.775400E-05	0.260300E-04	773.2	0.954670E-03	0.663240E-03
1.663	0.987500E-05	0.323110E-04	999	0.103412E-02	0.742810E-03
2.148	0.127330E-04	0.398800E-04	1287	0.112074E-02	0.834489E-03
2.775	0.164690E-04	0.491020E-04	1663	0.122121E-02	0.955872E-03
3.586	0.213750E-04	0.601400E-04	2148	0.133692E-02	0.109845E-02
4.633	0.278870E-04	0.730640E-04	2775	0.147638E-02	0.126872E-02
5.985	0.363170E-04	0.883530E-04	3586	0.164006E-02	0.146794E-02
7.732	0.472720E-04	0.106032E-03	4633	0.184047E-02	0.169870E-02
9.99	0.612220E-04	0.126425E-03	5985	0.208200E-02	0.196115E-02
12.87	0.787520E-04	0.149059E-03	7732	0.239430E-02	0.224461E-02
16.63	0.100867E-03	0.174399E-03	9990	0.273670E-02	0.258351E-02
21.48	0.128417E-03	0.202238E-03	12870	0.318163E-02	0.292923E-02
27.75	0.161130E-03	0.231336E-03	16610	0.368816E-02	0.326404E-02
35.86	0.199751E-03	0.261772E-03	21460	0.428890E-02	0.364087E-02
46.33	0.243680E-03	0.293630E-03	27730	0.499211E-02	0.396094E-02
59.85	0.297240E-03	0.321590E-03	25820	0.581406E-02	0.421096E-02
77.32	0.352510E-03	0.350160E-03	59789.9	0.763076E-02	0.443093E-02
99.9	0.413470E-03	0.376600E-03	77240	0.856872E-02	0.435872E-02
128.7	0.475800E-03	0.404370E-03	99800.1	0.945813E-02	0.415920E-02
166.3	0.542110E-03	0.431270E-03	128600	0.102969E-01	0.384986E-02
214.8	0.610120E-03	0.454380E-03	166100	0.109867E-01	0.353381E-02
277.5	0.677130E-03	0.482420E-03	214600	0.115701E-01	0.306196E-02
358.6	0.744560E-03	0.514960E-03	277300	0.120370E-01	0.264509E-02
463.3	0.813960E-03	0.551330E-03			

iy_i'' and the corresponding impedance value as $y_i^{-1} \equiv z_i \equiv z_i' + iz_i''$. The ratios of maximum to minimum values of z', $|z''|$, y', and y'' are, respectively, 1956, 211, 164, and 3290. Since the data have already been analyzed by Macdonald et al. [19] using CNLS with data-proportional weighting and the results interpreted in terms of the various conduction processes present, I restrict attention here to the results of new more appropriate fits of the data.

For complex dielectric data, one usually deals with a single physical process (represented, for example, by the Havriliak–Negami function of eq. (8)), which allows a single, relatively simple, fitting function to be employed. For partially conducting materials, however, four or more separate processes may be present, making the determination of the most appropriate fitting model much more difficult. In the earlier work on the present Li_3N data, the fitting model was an equivalent circuit with seven free parameters, and it led to $S_F \simeq 0.07$. Using the more appropriate circuit of fig. 1, which involves eight free parameters, the best fit (see below) led to a S_F more than 25 times smaller. In this circuit $- \gg -$ designates the constant phase element (CPE), a response function whose admittance may be written as $A(i\omega)^n$, where A and n are free parameters and $0 \leqslant n \leqslant 1$.

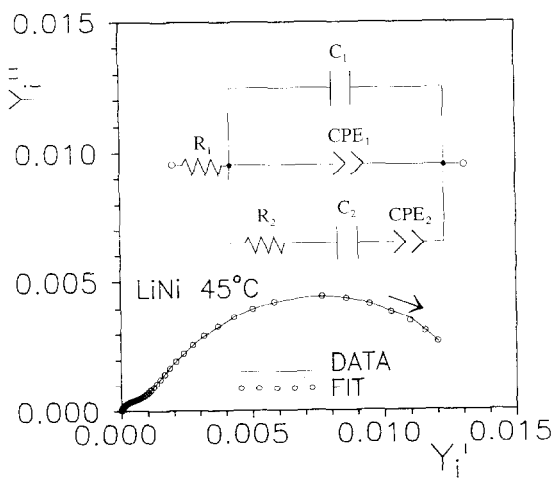

Fig. 1. Top: circuit used for fitting Li_3N admittance data and their inverses. The symbol $- \gg -$ designates a constant phase element (CPE). Bottom: complex-plane admittance plots of the Li_3N data and of its optimized fixed-function weighting (FFWT-O) CNLS fit of line 6, table 4. The arrow indicates the direction of increasing frequency.

Table 4
Individual CNLS fit results for Li_3N admittance data. Lines 1–6: fits at the admittance level. Lines 7–12: fits at the impedance level. A quantity written as A|B represents a parameter estimate and its estimated relative standard deviation (RSD).

Line	Weight	S_{FR}	S_{FI}	S_F	$S_{N\cdot E}$	R_1	$10^8 C_1$	$10^6 A_1$	n_1	R_2	$10^6 C_2$	$10^5 A_2$	n_2
1	UWT	7.1×10^{-6}	9.7×10^{-6}	8.1×10^{-6}	0.366	74.4|0.0010	1.90|0.021	3.65|0.061	0.613|0.009	1426|0.036	3.12|0.21	1.13|0.35	0.665|0.065
2	UWT-O	8.4×10^{-6}	8.4×10^{-6}	8.0×10^{-6}	0.321	74.4|0.0011	1.92|0.020	3.75|0.058	0.611|0.009	1443|0.034	3.00|0.18	1.15|0.33	0.665|0.061
3	FPWT	4.5×10^{-3}	5.8×10^{-3}	4.96×10^{-3}	0.170	73.9|0.0014	1.47|0.024	2.11|0.017	0.666|0.003	1119|0.006	2.98|0.013	2.41|0.028	0.555|0.008
4	FPWT-O	5.2×10^{-3}	5.2×10^{-3}	4.95×10^{-3}	0.157	73.9|0.0015	1.47|0.024	2.11|0.016	0.666|0.003	1122|0.006	2.97|0.012	2.41|0.026	0.555|0.008
5	FPLWT-O	4.0×10^{-3}	4.0×10^{-3}	3.82×10^{-3}	0.157	73.8|0.0015	1.46|0.025	2.10|0.018	0.667|0.003	1123|0.006	2.99|0.014	2.39|0.028	0.557|0.008
6	FFWT-O	2.8×10^{-3}	2.8×10^{-3}	2.71×10^{-3}	0.163	73.8|0.0014	1.45|0.024	2.09|0.019	0.667|0.003	1124|0.006	3.00|0.014	2.37|0.028	0.558|0.008
7	UWT	19.8	22.9	20.5	0.100	108|0.051	7.89|0.035	1.80|0.015	0.262|0.121	573|0.032	3.85|0.023	3.21|0.042	0.515|0.016
8	UWT-O	21.3	21.4	20.4	0.115	106|0.046	7.64|0.035	1.84|0.017	0.314|0.098	559|0.031	3.71|0.024	3.42|0.041	0.502|0.017
9	FPWT	6.9×10^{-3}	5.8×10^{-3}	6.05×10^{-3}	0.168	74.1|0.0027	1.57|0.022	2.23|0.016	0.659|0.003	1119|0.008	2.84|0.013	2.64|0.032	0.542|0.010
10	FPWT-O	6.3×10^{-3}	6.3×10^{-3}	6.04×10^{-3}	0.165	74.1|0.0029	1.56|0.021	2.21|0.017	0.660|0.003	1122|0.008	2.87|0.014	2.59|0.032	0.545|0.010
11	FPLWT-O	3.2×10^{-3}	3.2×10^{-3}	3.01×10^{-3}	0.150	74.1|0.0021	1.56|0.019	2.21|0.018	0.660|0.003	1122|0.008	2.87|0.014	2.58|0.033	0.545|0.010
12	FFWT-O	3.3×10^{-3}	3.3×10^{-3}	3.17×10^{-3}	0.151	74.1|0.0022	1.56|0.019	2.21|0.018	0.660|0.003	1122|0.008	2.87|0.014	2.58|0.032	0.545|0.010

Although the primary fitting here will be carried out at the measured admittance level, it is of interest to examine how much results are changed by the inversion from the admittance level to the impedance level. Thus, table 4 contains results for various individual fits of the Li_3N data: those at the admittance level in lines 1–6 and those for the impedance level in lines 7–12. As usual, resistances are in Ohms, capacitances are in Farads, and the CPE A values have units of Siemens x Hz^n. If one takes the line-6 results as the best, then all others may be compared to them. First, it is clear that all the unity-weighting fits are poor, that optimization does not improve them, and that the admittance-level fits with unity weighting are much better than the impedance-level ones. The better results obtained with function-proportional weighting and with function power-law weighting strongly suggest that these weightings far better match the actual errors in the data. The S_{NE} values of lines 7 and 8 indicate that this measure can be misleading, especially for very poor fits. Although fits cannot be improved for these data by setting both the U and ξ parameters simultaneously free in a variance model, such improvement has been observed for other IS data [11].

Comparison of the results of lines 3 and 4 with those in lines 9 and 10 indicates that, with function-proportional weighting, Y-level fitting is not significantly better here than Z-level and, because the S_{FR} and S_{FI} values are already close for such weighting of these data, optimization is not much needed. The line-5 and line-11 fits with optimized function power-law weighting are slightly better than the optimized function-proportional weighting ones and led to $\xi_Y \simeq 0.9193|0.049$ and $\xi_Z \simeq 1.0919|0.047$, respectively. These values were taken fixed for the line-6 and line-12 fits. Here we see that the ξ estimates are quite well determined, unlike those for the low-range data of section 5. Their sum is 2.011|0.048, quite close to 2, the expected value for real data with small errors [15].

Since both ξ estimates are quite close to unity here, it might be reasonable to assume that the errors in the data are, indeed, of proportional form ($\xi = 1$) and to use the Y-level optimized function-proportional weighting solution, even though it does not fit the data quite as well as the corresponding optimized fixed-function weighting one. Because the present data lead to ξ values very close to unity, there is relatively little difference in the results for function-proportional weighting fits and function power-law weighting fits here. But in many situations, the most appropriate ξ will not be near unity; then the unquestioned use of the traditional weightings of lines 1 through three of table 1, or even of function-proportional weighting, will lead to poor fitting-model parameter estimates; and it will then be essential to use function power-law weighting in order to determine the weighting parameter value most appropriate to the data and so to optimize the parameter estimates of the fitting model.

The Y-level data and the line-6 fit results are plotted together in the admittance plane in fig. 1. (Y-level data values, y_i, are in unit of Siemens.) Although the fit appears excellent and the estimated SD's of the parameter estimates are all small, the fig. 2 plot of the real and imaginary weighted residuals against the logarithm of frequency (actually normalized dimensionless frequency) shows some small remaining problems. In spite of the great ranges of the original data, these results show little heteroscedasticity. It is clear that although the real and imaginary residuals are not entirely independent, it turn out that their cross correlation is a negligible −0.14. The figure suggests, however, that appreciable autocorrelation

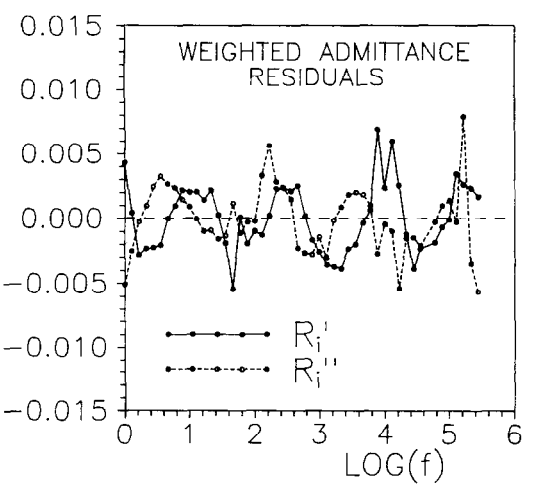

Fig. 2. Dependence of the real and imaginary weighted residuals on log(f) for the optimized fixed-function weighting (FFWT-O) fit of fig. 1 (line 6, table 4). Lines have been drawn between discrete values to guide the eye and to help distinguish between the two residual components.

is present. Calculation of the lag-1 autocorrelation before and after differencing yields 0.61 and −0.12, respectively, for the real components, and 0.39 and −0.26, respectively, for the imaginary ones. Thus, differencing removes much of the large lag-1 autocorrelation. But its presence, even when the weighted residuals are as small as they are here, indicates that some systematic error remains. Although most of it could probably be eliminated by adding one or more further parameters to the fitting model, the present fit is sufficiently good for all practical purposes and well illustrates the application of the present methods to highly heteroscedastic complex data. For such data, one should compare optimized unity weighting (UWT-O) fits with function power-law weighting ones (FPLWT-O), choose the better of the two, which will nearly always be the optimized function power-law weighting one, and use the ξ estimate obtained in a final optimized fixed-function weighting (FFWT-O) fit.

7. Summary

Two quite different approaches to the CNLS fitting of small-signal immittance data have been compared and shown to yield indistinguishable results for small-range dielectric response data fitted without weighting. By contrast, fitting of wide-range admittance response data for single-crystal Li_3N with a variety of weighting schemes showed that strong weighting is required to transform the data to a desirable equal-variance (homoscedastic) condition. Such variable weighting, which can be automatically determined during the fitting itself, is often found to be of proportional or near proportional character for wide-range data and ensures low-bias parameter estimates with small estimated uncertainties.

The multiresponse, matrix-determinant CNLS fitting method of Bates and Watts does not incorporate weighting possibilities and is not available as a computer program for general use. The LEVM CNLS program is readily available as a complete program and provides a choice of many different weighting schemes. In particular, it has the important practical advantage of being the only CNLS program which allows variable weighting, where the data itself is used to determine the most appropriate weighting to yield minimum bias and high-precision parameter estimates. Since LEVM and the more complicated matrix-determinant method evidently lead to the same estimates in unweighted situations where they can be compared, one can have confidence in the LEVM estimates.

For the analysis of IS data, where weighting is nearly always necessary and appropriate, all other currently available CNLS programs, such as that of Boukamp [8], yield appreciably more biased parameter estimates than does LEVM [11]. It follows that for any wide-range experimental data (e.g., dielectric, conductive, mechanical relaxation, nuclear magnetic relaxation, light scattering, etc.) which can be expressed in terms of two related dependent parts (e.g., real and imaginary or modulus and phase), simultaneous fitting of the entire data set to a model should be carried out with LEVM, or its equivalent, in preference to other programs with less general weighting.

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