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Analysis of dispersed frequency response for ionic glasses: influence of electrode and nearly constant loss effects

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Abstract

Analysis by D L Sidebottom of the dispersive frequency response of the real-part of the conductivity, $\sigma'(\omega)$, for many alkali phosphate and metaphosphate glasses, using a fitting model involving a ‘universal dynamic response’ power law with an exponent n and a constant-loss term, led to anomalous n behaviour that he explained as arising from variable constriction of the local cation conduction space. In order to obtain adequate fits, he eliminated from the data all low-frequency decreases of $\sigma'(\omega)$ below the dc plateau, ones actually associated with electrode effects. Such a cut-off does not, however, eliminate electrode effects possibly present in the high-frequency part of the data range. The results of the present detailed analysis and fitting of both synthetic data and several of his experimental data sets show unequivocally that his anomalous n behaviour arose from neglecting electrode effects. Their inclusion, with or without data cut-off in the fitting model, leads to the expected high-frequency slope value of $n = 2/3$ associated with bulk conduction, as required by recently published topological effective-dimension considerations for dielectric relaxation in conductive systems. Further, the effects of the inclusion in a full fitting model of series and possibly parallel complex constant-phase-element contributions, representing electrode and nearly constant loss effects, respectively, have been investigated in detail. Such composite models usually lead to best fitting of either the full or cut-off complex data when they include the semi-universal, topologically based K1 bulk model, one indirectly derived from the assumption of stretched-exponential temporal behaviour.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Appropriate analysis of dispersive frequency-response data is essential in establishing valid identifications and interpretation of the physical processes associated with such data. The use of physically inappropriate and improper data fitting models, even when they fit the data adequately, can thus yield misleading results. The present work identifies a problem with a widely used fitting model and shows how one type of response, constant loss, has been erroneously used to fit a response actually associated with electrode polarization effects.

Several years ago, Sidebottom considered power-law dispersion effects in the ac conductivity of ionic materials and invoked topological considerations to explain anomalous dependences of the power-law exponent, n , on metal type for a range of alkali-metal metaphosphate glasses, MPO_3 , and on doping level for superionic glasses formed by doping AgI into $AgPO_3$ [1, 2]. Values of the power-law exponent were estimated from wide-range frequency-response fitting of the real part of the conductivity data, $\sigma'(\omega)$.

He based his explanation of such anomalous behaviour on the expansion of phosphate chains comprising the glass network and proposed that the increase in n with expansion of the PO_3 network could best be understood in terms of the coordination of the local cation conduction space. He also proposed that when the phosphate chains are expanded enough relative to cation size that cation motion is unconstricted, one should expect to find estimates of n close to $2/3$, the value previously associated with three-dimensional motion, $d = 3$, but based on experimental rather than theoretical results [3]. On the other hand, when their motion is assumed to be constricted, he plausibly suggested that the effective dimensionality, d_e , should be less than 3, resulting in smaller n values [1–3].

Such dependence on d_e is related to recent, but quite different, topological considerations for field-forced response [4, 5 and references cited therein] that indicate, in agreement with a large amount of data fitting results on microscopically homogeneous glasses, single crystals, and polycrystalline materials, that, for materials involving a single type of charge carrier and allowing three-dimensional motion, d_e should equal 2. This value then leads directly to a power-law exponent and log–log slope of $n = d_e/d = 2/3$ at high frequencies. Hereafter for simplicity, the word ‘slope’ will be used in place of ‘log–log slope’.

The topological approach also leads, when only one-dimensional motion is allowed in a three dimensional material, to $d_e = 1$; so then one would expect $n = 1/3$. Further, these $1/3$ and $2/3$ slope values should be independent of temperature and mobile-ion concentrations when the latter are sufficiently larger than zero. For many materials, these expectations have been well verified over appreciable ranges of variation of such exogenous variables, in particular for situations leading to $n = 2/3$.

Here, it is demonstrated that estimates of n appreciably less than $2/3$ found by Sidebottom for his three-dimensional materials mentioned above arose from improper data analysis, and that adequate analyses indeed lead to values very close to $2/3$ in all cases considered, thus consistent with the field-forced topological predictions and rendering Sidebottom’s alternate explanations of such behaviour moot and unnecessary. Further, the important related question is examined of when to include a parallel nearly-constant-loss term in a composite frequency-response fitting model as well as a series term representing electrode effects.

2. Some alternate analysis models

The fitting model used by Sidebottom may be written as

$$\sigma'(\omega) = \sigma_0[1 + (\omega/\omega_0)^n] + A_0\omega^\alpha, \quad (1)$$

and was proposed earlier by Nowick and associates [6] with $\alpha = 1$, the value used by Sidebottom. Here σ_0 , the dc conductivity, and ω_0 are strongly thermally activated, while A_0 usually shows only weak temperature dependence, and $0 < \alpha \leq 2$, as demonstrated in [7]. The first term on the right has been termed universal dynamic response (UDR), but other models for ionic hopping have been shown to be superior to it [4, 5, 8].

The second term, with $\alpha = 1$, the value used by most earlier writers, leads to a frequency-independent constant loss (CL) contribution to the imaginary part of the complex dielectric constant, $\varepsilon(\omega) = \sigma(\omega)/(i\omega\varepsilon_V) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, where ε_V is the permittivity of vacuum. The more general form in equation (1) does not restrict the response to CL, and when $|1 - \alpha| \ll 1$ it can represent nearly constant loss (NCL).

As discussed elsewhere [7, 9–11], CL over a finite frequency range is physically impermissible and there is thus no Kronig–Kramers $\sigma''(\omega)$ pair corresponding to the $A_0\omega$ term. Therefore, equation (1) needs to be modified in order to be able to model fully complex data sets. Note, however, that in [3], whose table 1 lists a large number of materials with n values of 0.67 ± 0.05 , Sidebottom has stated that the $\sigma'(\omega)$ analyses leading to these estimates involved sufficiently high frequencies that the CL term of equation (1) could be neglected [1, 3].

An expression that can represent complex data and provide results comparable to those from the equation (1) model for $\sigma'(\omega)$, except when γ_{PC} is exactly zero, is

$$\sigma(\omega) = \sigma_0[1 + (i\omega\tau_o)^n] + \varepsilon_V A_{PC}(i\omega)^{1-\gamma_{PC}}, \quad (2)$$

where $-1 < \gamma_{PC} \leq 1$. The first term on the right has been designated the ZC (or ZARC) fitting model because it is a form of the venerable Cole–Cole response when written at the complex resistivity or impedance level [8, 12]. The second power-law expression is denoted by PCPE or P, and represents a parallel complex phase element. The quantity A_{PC} reduces to a pure dielectric constant when $\gamma_{PC} = 0$, but the PCPE can also model NCL when $0 < |\gamma_{PC}| \ll 1$ and then A_{PC} still approximates a pure dielectric constant.

When the data lead to estimates of n and $1 - \gamma_{PC}$ that are appreciably different, all the free fitting parameters in equation (2) can usually be adequately estimated with weighted least squares fitting. Nevertheless, the ZC model, while more general than the UDR one of equation (1), is inferior to the Kohlrausch KWW1 frequency-response model, now designated as the K1 [4, 5, 7–11], a response model that is indirectly derived from the K0 model, one that involves stretched-exponential response in the temporal domain with an exponent of β_1 . This quantity is also the frequency-response shape parameter of the K1, a unique model that has been derived from both macroscopic and microscopic theoretical analyses [5].

Further, the K1 is one of the very few models whose shape parameter value has been theoretically established [4, 5], rather than just determined by experimental fitting. When β_1 is fixed at $1/3$, the resulting model, involving only the two free parameters, σ_0 and its characteristic relaxation time, τ_o , leads to the high-frequency power-law slope of $1 - \beta_1 = 2/3$, the topological value discussed in section 1. This specific K1 model is a universal one when the conditions listed above for the applicability of the field-forced topological result of $2/3$ are satisfied. It will then be designated by the letters UN. Although the K1-model temporal and frequency response must be calculated numerically for arbitrary values of β_1 , methods allowing it to very accurately calculated for both data fitting and simulation are included in the LEVM complex nonlinear least squares (CNLS) fitting and inversion program [13].

For satisfactory data fitting, one must usually employ a composite fitting model, such as those of equations (1) and (2), in order to adequately model the data. A scheme for designating such composite models needs to identify those parts of the total response that are in parallel with the bulk mobile-ion part and those that are in series with the rest of the model; see, for

example, table 1 in [11]. A useful expression for representing series electrode effects is the SCPE, also denoted by S, expressed at the conductivity level as $\sigma_{SC} \equiv \varepsilon_V A_{SC} (i\omega)^{\gamma_{SC}}$, with $0 \leq \gamma_{SC} \leq 2$ [7, 10].

In the present model nomenclature scheme, letters representing parallel elements appear to the left of those for the bulk model, and letters identifying series elements appear to its right. Thus, the equation (2) model is designated as PZC, and the replacement of the ZC model by the UN one and the addition of a series model as well would lead to PUNS. For real-part conductivity data fitting when the second term on the right of equation (1) is used in place of the P response on the right of equation (2), the resulting composite model is named the NCLUN one, or the CLUN when $\alpha = 1$. Finally, fully complex experimental data always involve responses associated with the presence of bulk dielectric effects, usually well approximated by a dielectric quantity $\varepsilon_{D\infty}$ that is frequency independent in the frequency range used for investigating the conductive-system response. Its presence in a composite model is represented by the letter C, as in the CUNS model.

There is a little-recognized complication in fitting $\sigma'(\nu)$ data with a model including a series electrode-effects part, a complication that is not present for such fitting that instead involves a parallel part such as the PCPE, NCL, and CL ones defined and discussed above. Although for models such as the CUN or CK1, a free fitting parameter ε_x , always included in the fit, represents $\varepsilon_{D\infty}$ and plays a role only in the $\sigma''(\nu)$ part of the data and none in the $\sigma'(\nu)$ part, this state of affairs no longer applies for such models such as the CUNS, CK1S, and CZCS. For them the presence of a serial part of the full model couples together, to a considerable degree, the real and imaginary responses of these models. Therefore, for such $\sigma'(\nu)$ fits, ε_x should be either fixed at the value obtained from a full complex fit or it should be taken free to vary when it can be adequately estimated.

UN and K1 models contribute an effective dielectric constant term, $\varepsilon_{C1\infty}$, that is entirely associated with mobile charge, to the full high-frequency-limiting dielectric constant ε_∞ , so that it is given by $\varepsilon_\infty = \varepsilon_{C1\infty} + \varepsilon_{D\infty}$ [5, 14]. For the ZC and other conductive-system dispersion models, however, no non-zero $\varepsilon_{C1\infty}$ term is present and ε_x is then an estimate of ε_∞ . If the actual data are well represented by a UN or K1 model, the usual case, then the ε_∞ value estimated from ZC fitting is not just that of $\varepsilon_{D\infty}$ but implicitly includes $\varepsilon_{C1\infty}$, as above. The conventional $\Delta\varepsilon$ quantity may be expressed as $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty = \varepsilon_{C10} - \varepsilon_{C1\infty}$, and, like $\varepsilon_{C1\infty}$, it is entirely associated with mobile charge effects. Here ε_{C10} is the low-frequency limiting value of the real part of the effective dielectric constant associated with the K1 model. For the UN model, it turns out that $\Delta\varepsilon = 9\varepsilon_{C1\infty}$ [5].

3. Fitting results and model comparisons

In this section, several data sets kindly provided by Professor Sidebottom are analysed by various models using the LEVM program with CNLS and NLS fitting involving proportional weighting. The equation (1) fitting model with $\alpha = 1$ that he used to estimate values of n includes no account of electrode effects, effects that can be important at both low and at high relative frequencies [7, 9], as discussed below. It is demonstrated here that this omission can indeed lead to n values less than $2/3$, and, concomitantly, to the misidentification of part of the experimental response as being of CL character rather than being associated with electrode effects. When available, it is always appropriate to fit full complex data sets rather than just their real or imaginary parts. Here, however, complex $\sigma(\nu)$ data sets will be fitted as well as just their $\sigma'(\nu)$ parts (often misleadingly written as $\sigma(\nu)$ rather than $\sigma'(\nu)$), as in the work of Sidebottom and many others.

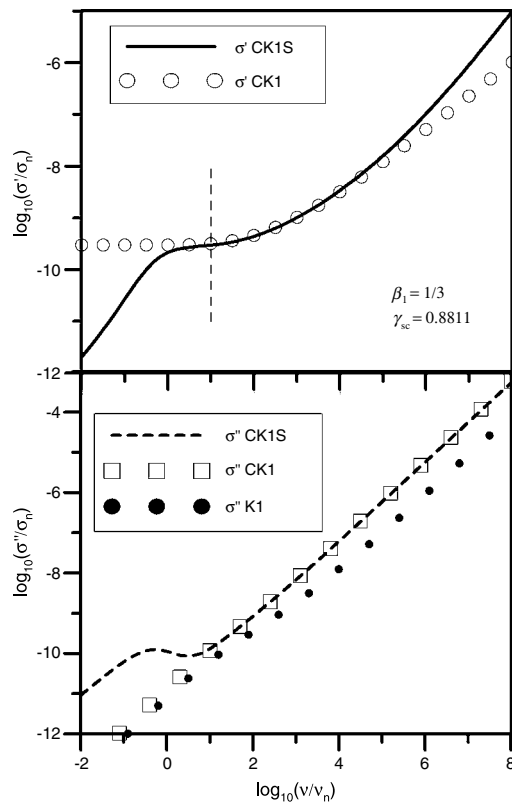


Figure 1. Log–log plots of exact $\sigma'(\nu)$ and $\sigma''(\nu)$ frequency responses for the CK1S composite response model with its β_1 shape parameter fixed at $1/3$. The $\varepsilon_{D\infty}$ part of the model is denoted by 'C'. The composite model is then named the CUNS one. Also shown are the separate responses of the CK1 and K1 parts of the model. Here and elsewhere the normalization quantity ν_n is 1 Hz and σ_n is 1 S cm^{-1} .

3.1. Behaviour and ZC-model fitting of wide-range $\sigma(\nu)$ synthetic data

Unfortunately, it has not been well known what part partially blocking electrode effects play in the overall immittance frequency response since they are rarely included in $\sigma'(\nu)$ data fits. It is therefore useful to identify their influences for the typical example presented in figure 1; two other figures are included in [7] that additionally demonstrate low- and high-temperature instances of such effects. For the composite CK1S model used to generate the synthetic data of figure 1, there are six parameters, and the values used for the four of them not listed in the figure itself were $\varepsilon_{D\infty} \approx 9.24$, $\rho_o \approx 3.32 \times 10^9 \text{ } \Omega \text{ cm}$, $\tau_o \approx 7.11 \times 10^{-5} \text{ s}$, and $A_{SC} \approx 1235$. The source of these values is discussed in section 3.3.

Typical low-frequency characteristics of non-negligible electrode polarization are the decrease in the $\sigma'(\nu)$ response below the dc limiting value, σ_0 , associated with bulk hopping response, and the peak and subsequent decrease in the σ'' response. The low-frequency-limiting slopes of both are just γ_{SC} , here about 0.88, but are not physically plausible in that limit [9, 11], although these decreases are often apparent over appreciable frequency ranges in some experimental data sets [15, 16]. Because of the common perception that electrode effects are only relevant in the low-frequency part of an experimental data range, they have been frequently unmentioned and omitted from published and fitted data, and only data such as

those for frequencies above the dashed vertical line in figure 1 are then fitted (e.g., [1, 2]). This is, however, somewhat inconsistent when such effects are nevertheless identified as present in the low-frequency part of the same cut-off data when transformed to $\varepsilon'(\nu)$ form [1, 17].

Comparison between the behaviours of the $\sigma'(\nu)$ responses of figure 1 for the full CK1S model and the CK1 part of it show that for the present situation there is a large and growing difference in the responses at the high-frequency end of the range. In fact, the limiting slope of the K1 model is just $(1 - \beta_1) = 2/3$ here, and for the present CK1S model the slope is about 1.06 at $\nu = 10^8$ Hz, reaches a maximum of about 1.08 near 10^{10} Hz and then very slowly decreases. Earlier work [7, 9] has shown that for composite models this slope can potentially reach a value near $(2 - \gamma_{SC})$ and then decrease toward γ_{SC} . It is noteworthy that Le Stanguennec and Elliot [18] some time ago used equation (1) for fitting and found a superlinear high-frequency exponent of $\alpha = 1.2$ for the same metaphosphate glass material investigated by Sidebottom [1] and considered herein.

The approximate frequency at which the two high-frequency $\sigma'(\nu)$ responses shown in figure 1 begin to diverge increases by a factor of 10 or more as the value of the electrode-effects parameter, A_{SC} , is increased by a factor of 10. Such an increase also causes the low-frequency point of divergence to move to lower frequencies as well, leading to a wider plateau at $\sigma'(\nu) \cong \sigma_0$. In practice, however, the behaviour of these transition points depends on the values of all the composite model parameters, with σ_0 and τ_o usually showing appreciable thermally activated response and A_{SC} only increasing slowly as the temperature is increased [7].

It is of interest to see how well a model involving ZC bulk response can fit the synthetic data shown in figure 1. Separate fitting of the full $\sigma(\nu)$ and $\sigma'(\nu)$ data sets with the CZCS model rather than the exact CUNS one led to the following results for S_F and n : 0.0190, 0.617, and 0.0140, 0.604, respectively, with γ_{SC} estimates both very close to the original value of 0.8811. Here S_F is the relative standard deviation of the fit residuals. Clearly, although the ZC model leads to good fits of the data, because of the presence of electrode effects it does not yield estimates of n very close to the actual high-frequency limiting slope of $2/3$ of the original UN response model. No adequate fits of the present data were found to be possible using the PZC, NCLZC, or CLZC models.

3.2. Fitting of $\sigma(\nu)$ synthetic data with low-frequency cut-off

When the low-frequency decrease in $\sigma'(\nu)$ shown in the figure for $\nu < 1$ Hz is cut off and eliminated, it has been shown that a composite fitting model including either serial SCPE electrode-effect response or parallel PCPE NCL can well represent the remaining data [7, 10, 15]. Even the CL term of equation (1), as used by Sidebottom, can often adequately approximate high-frequency data that actually involve electrode effects. Unfortunately, the recognition that such effects could be important at high frequencies [7] appeared later than the work of Sidebottom in 2000 [1], but still early enough to be of relevance to his similar 2003 work [2] had he referred to the earlier work.

Since most prior analyses by others eliminate the low-frequency series electrode effect contributions, in order to obtain results comparable to those of Sidebottom [1] new fits were carried out of the present synthetic data set with a minimum frequency of 10 Hz, as indicated by the vertical line in the top part of figure 1. A PK1 fit of the resulting $\sigma(\nu)$ data led to S_F , β_1 , and $(1 - \gamma_{PC})$ estimates of about 0.0371, 0.552, and 0.975, respectively. For the $\sigma'(\nu)$ part of the data, the PK1 model seemed to converge toward a value of γ_{PC} of zero, so the CLK1 model was used and yielded estimates of 0.0277 and 0.541 ± 0.007 , with α fixed at unity. For these parallel composite models it is clear that the K1-model β_1 estimate is far from the value of $1/3$ of the original UN one, even though the fits here are again quite good. Thus, the parallel P

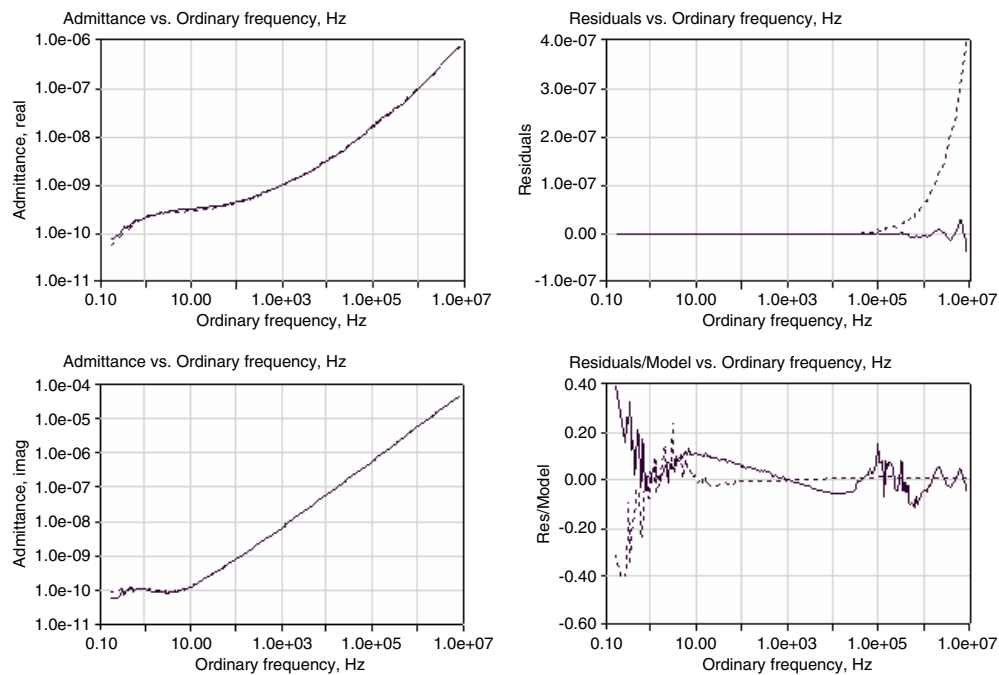


Figure 2. Direct graphical output obtained from LEVMW CNLS fitting of $\text{CsPO}_3 \sigma(\omega)$ data at 298.15 K using the CUNS composite model with proportional weighting. The left two plots show the data as solid lines and the fit results as dashed lines. The two right plots show real-part residuals and relative residuals by solid lines and imaginary-part ones by dashed lines.

and CL parts of the composite fitting model are evidently far less appropriate for the K1 than is the proper series-effects addition.

Fitting of the $\sigma(\nu)$ cut-off data with the PZC model led to S_F , n , and $(1 - \gamma_{PC})$ estimates of 0.0273, 0.490, and 0.990, while CLZC fitting of its $\sigma'(\nu)$ real part yielded the estimates 0.0325 and 0.491 ± 0.007 . Again it is clear that the ZC model with parallel power-law additions yields inadequate estimates of the actual slope of the main bulk ionic-motion part of the total response and better, but still unsatisfactory estimates when a series electrode-effects power law is included.

3.3. Fitting of $\text{CsPO}_3 \sigma(\nu)$ and $\sigma'(\nu)$ experimental data

3.3.1. Fitting of full experimental data with models that include electrode effects. Figure 2 shows CNLS fitting results for CsPO_3 data at 298.15 K [1]. It is especially useful when log-log plots involve data that vary over wide ranges to show the associated residuals as well. Here, although very little difference is evident between the data and the fit results in the left-hand parts of figure 2, the fit, with $S_F \approx 0.085$, was actually far from excellent, as shown by the lower right-hand-side plots of relative residuals. Particularly evident are large low-frequency relative residuals and ones that suggest that the measuring apparatus was changed for $\nu \geq 10^5$ Hz. The parameter estimates obtained from this fitting, listed in section 3.1, were used to generate the synthetic data shown in figure 1, thereby eliminating random errors and allowing easy extension of the frequency range by a decade at both its low- and high-frequency ends.

Fitting of the $\sigma'(\nu)$ part of the data with the CUNS and CK1S models led to nearly identical parameter values since the CK1S estimate of β_1 was about 0.334 with a S_F value of 0.044. In

contrast, CZCS fitting of the $\sigma(\nu)$ and $\sigma'(\nu)$ data led to S_F and n estimates of 0.075 and 0.572, and 0.047 and 0.551, respectively.

3.3.2. Fitting of cut-off experimental data with models that include electrode effects. The results discussed in this section should be compared to those in section 3.2. The following fitting results illustrate the effect of the coupling between real and imaginary parts of the data when an SCPE is a part of the composite fitting model, as discussed in section 2. For simplicity, let 'F' indicate a fixed parameter value and 'X' denote 'C' complex fits, 'R' real-part fits, or 'I' imaginary part fits. The results are presented here in the format: X, S_F , $\varepsilon_{D\infty}$, ε_∞ , $\Delta\varepsilon$, and β_1 . No γ_{SC} estimates are shown here since they were all of the order of 0.88.

For the CUN model, results are: C, 0.027, 9.60 ± 0.04 , 10.82, 11.05, and 1/3F; R, 0.038, 9.43 ± 1.91 , 10.62, 10.72, and 1/3F; and I, 0.004, 9.59 ± 0.03 , 10.84, 11.22, and 1/3F. When $\varepsilon_{D\infty}$ is fixed at 9.43, the other R-fit results are the same as shown above. But when it is fixed at zero, one obtains R, 0.053, 0.0F, 1.34, 12.04, and 1/3F, yielding an appreciably poorer fit and an entirely inadequate estimate of ε_∞ . Clearly, when a composite model includes a series term and well represents the data, a value of $\varepsilon_{D\infty}$ obtained from a C or I fit should be held fixed in an R fit.

A complex CK1S fit of the present cut-off data yields C, 0.027, 9.80 ± 0.04 , 10.76, 12.07, and 0.309 ± 0.001 . When $\varepsilon_{D\infty}$ is fixed at the above CUN value of 9.595, the resulting β_1 estimate is 0.331 ± 0.001 , closer to 1/3, as might be expected. For this same fixed value one obtains from an R fit a β_1 estimate of 0.316 ± 0.031 . All these CK1S results indicate that, in view of the errors in the data, the CUN model is the most appropriate one.

Fitting with the CZCS model does not yield an estimate of $\varepsilon_{D\infty}$ and there are no $\Delta\varepsilon$ and ε_{C10} limits associated with the ZC part of the model. Therefore, the appropriate fit-results notation is X, S_F , ε_∞ , and n , and fittings with this model led to C, 0.028, 10.763 ± 0.033 , and 0.607 ± 0.003 . Fitting with ε_∞ fixed at this value yielded R, 0.038, 10.763F, and 0.595 ± 0.005 , and no significant estimate of ε_∞ was possible for R fits.

3.3.3. Fitting of cut-off experimental data with models that include parallel effects but no series effects. Here fitting results will be shown in the form X, S_F , n or β_1 , and $(1 - \gamma_{PC})$ or α . For the CUN model S_F was about 0.18, an unsatisfactory fit particularly in the high-frequency region. For the PUN model the results were C, 0.0450, 1/3F, and 0.9924, while the NCLUN model led to R, 0.0384, 1/3F, and 1.097. For the CLUN model, the results were R, 0.0484, 1/3F, and 1.0F, the worst of these three fits.

For the PK1 one finds C, 0.0303, 0.172, and 0.9926. Here the value of β_1 is far from the proper value of 1/3, and since the high-frequency slope associated with the K1 model is $(1 - \beta_1) \approx 0.83$, the K1 and PCPE responses are together leading to a high-frequency slope near 0.88, that which is associated with electrode effects. For the NCLK1, the results are R, 0.0382, 0.273, and 1.097. In contrast, the CLK1 fit yielded R, 0.0418, 0.179, and 1.0F. Here, the NCLK1 fit was worse than that of the PK1 one, but it led to an estimate of β_1 closer to the expected value.

For the CZC model, the fit results were C, 0.0975, and 0.758. Although the fit was quite poor, the n estimate is an approximation to the electrode-effect slope. Matters are better for the PZC where one finds C, 0.0286, 0.519, and 0.9912. The NCLZC fit led to R, 0.0384, 0.574, and 1.067, while the CLZC one yielded R, 0.0397, 0.527 ± 0.007 , and 1.0F. It is noteworthy that Sidebottom's CL result from fitting with the present equation (1) led to an estimate of n of 0.530 ± 0.005 [1], very close to the present result for this situation, suggesting that his results for the present material also involved a temperature of 298 K and that his low-frequency data cut-off was similar to that used here.

All of the section 3.3 results for fitting the Sidebottom CsPO₃ data, as well as the section 3.1 and 3.2 results for the synthetic data based on this experimental data set, show that such full data should be fitted by a composite model that includes series electrode effects. Even for data from which measured low-frequency electrode effects have been eliminated or are initially absent, present results indicate that although it is then often possible to fit such data adequately with only a parallel added response term, such as the PCPE, the NCL, or CL one, the resulting estimates of the bulk-model parameters β_1 or n are inadequate when electrode effects are present in the high-frequency region of the data.

3.4. Fitting of other $\sigma(\nu)$ and $\sigma'(\nu)$ experimental data sets

Section 3.3 dealt with data whose analysis using the CL version of equation (1) led to the smallest n estimate, 0.53, found by Sidebottom in [1]. This value deviated the most from his 'low-constriction' expected value of $2/3$. In table 1 he includes n estimates of 0.67 ± 0.005 , however, for several other materials [1]. It is therefore important to consider what conditions may lead to such results. Therefore we shall consider data sets for LiPO₃ at 295.0 K and those for AgI_{0.4}(AgPO₃)_{0.6} at 151.8 K and at several other temperatures.

3.4.1. Fitting of LiPO₃ $\sigma(\nu)$ and $\sigma'(\nu)$ experimental data. Here we use the notation: X, S_F , n or β_1 , and γ_{SC} or α . For CUNS fitting the results were C, 0.0518, $1/3F$, and 0.383. From this γ_{SC} value one would expect a maximum slope of the $\sigma'(\nu)$ data of about 1.62. In fact, the actual slope at the highest frequency is close to this value. CNLS fitting with the CK1S model yielded results very close to those for the CUNS, with an estimate of β_1 of about 0.326 ± 0.003 . For real-part fitting, the K1S model led to $\beta_1 \cong 0.324 \pm 0.004$.

For the CZCS model, the fit led to C, 0.0408, 0.669 ± 0.007 , and -0.152 , implying a maximum slope of about 2.15. The two SCPE parameters were, however, not very well estimated for either this fit or for the above CUNS complex fit. On the other hand, the n estimate is here very close to $2/3$, in agreement with the $(1 - \beta_1)$ results for the CUNS and CK1S fits. A CZC complex-data fit yielded S_F and n estimates of 0.115 and 0.762, respectively, a poor fit. Further, a CLZC $\sigma'(\nu)$ fit produced R, 0.103, 0.398 ± 0.063 , $1F$, as well as an n estimate of about 0.55 when the highest frequency decade of the data was eliminated. Both n estimates are far from Sidebottom's n estimate of 0.670, possibly because his published value involved data at a different temperature than the present 295 K. Finally, an NCLZC fit gave R, 0.0501, 0.692 ± 0.011 , and 2.27 ± 0.14 . Figure 3 shows results for this fit. For the present LiPO₃ data set, either series or parallel terms in a composite fitting model yield comparable fits, and the data do not extend to sufficiently low frequencies to allow an unambiguous choice between them. Clearly, however, fitting with the CL version of equation (1), as in the work of Sidebottom, is unsatisfactory.

3.4.2. Fitting of AgI_{0.4}(AgPO₃)_{0.6} $\sigma(\nu)$ and $\sigma'(\nu)$ experimental data at $T = 151.8$ K. We start with analysis of the 151.8 K data since Sidebottom shows $\sigma'(\nu)$ -fit results for this temperature in his figure 2 [1], involving low-frequency cut-off at about 2 Hz, and he lists the estimate $n = 0.678$ in this figure and 0.670 ± 0.005 in his table 1. CNLS fit results for this situation are shown in figure 4. It is clear that, without cut-off, electrode effects are evident, at least at the lower frequencies. Their influence is shown in a different way in figure 5, one that emphasizes the low-frequency response and makes the irregularities in the low-frequency data particularly evident. Present fit results will be summarized in the form X, S_F , n or $(1 - \beta_1)$, $1 - \gamma_{PC}$ or α , and γ_{SC} . For the PUNS composite model fit, estimates were C, 0.0404, $2/3F$, 0.9839 ± 0.0003 , and 0.898 ± 0.005 . Fitting with the PK1S model led to very similar results with $\beta_1 \approx 1/3$, but

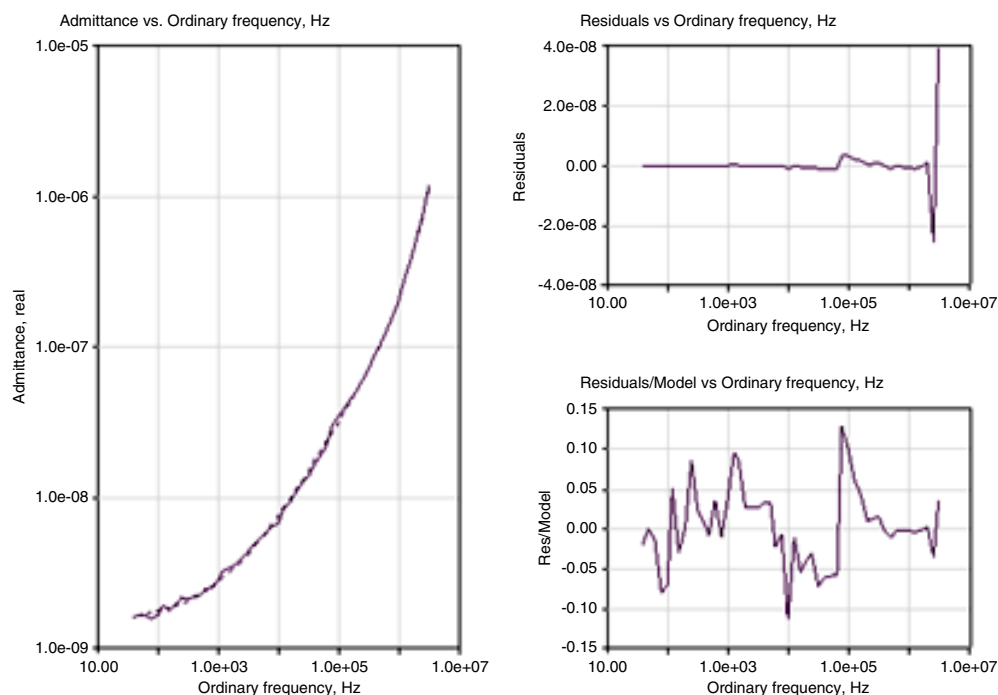


Figure 3. Direct graphical output obtained from LEVMW NLS fitting of LiPO_3 $\sigma'(\omega)$ data at 295.0 K using the NLCZC composite model with proportional weighting. The left plot shows the data as a solid line and the fit result as a dashed line. The two right plots show real-part residuals and relative residuals by solid lines.

its estimated value was somewhat dependent on the accuracy selected for the K1 fitting model, probably arising from the appreciable errors present in the data. As usual, the UN model is found to be the most appropriate choice.

It is noteworthy that, as shown in figure 4, there is a plateau in the $\sigma'(v)$ data extending for nearly three decades before the low-frequency series electrode-effect decline begins, appreciably different from the results presented in figure 1. It is therefore not surprising that a plot of the present fit results with those associated with the SCPE part of the model removed eliminates the low-frequency electrode responses but makes no difference in the high-frequency $\sigma'(v)$ response. The actual slopes of this part of the model predictions (which average out data irregularities) are about 0.75 at 10^6 Hz and 0.80 at 5×10^6 Hz. Since these are larger than $2/3$, it is clear that a parallel part, such as the PCPE, is needed in the full composite model. That estimated from the PUNS fitting clearly involves NCL behaviour. The data range would have to extend to considerably higher frequencies for the SCPE part to begin playing a significant role in the high-frequency $\sigma'(v)$ response. For completeness, the PZCS fit results are C, 0.0446, 0.715 ± 0.005 , 1.038 ± 0.001 , and 0.940 ± 0.006 .

Rather than cut off the data to eliminate the responses below about 2 Hz, as Sidebottom did for his fitting of $\sigma'(v)$ for the present material [1], it is likely to be more appropriate to fit such real-part data with a composite model including the SCPE part. Then one finds for the NCLUNS model: R, 0.0341, $2/3F$, 0.804 ± 0.014 , and 0.898 ± 0.013 , and for the CLUNS one: R, 0.0435, $2/3F$, $1F$, and 0.924 ± 0.017 . The NCLZCS fit yields R, 0.0350, 0.668 ± 0.039 , 0.912 ± 0.371 , and 0.946 ± 0.015 , and the CLZCS one leads to R, 0.0350,

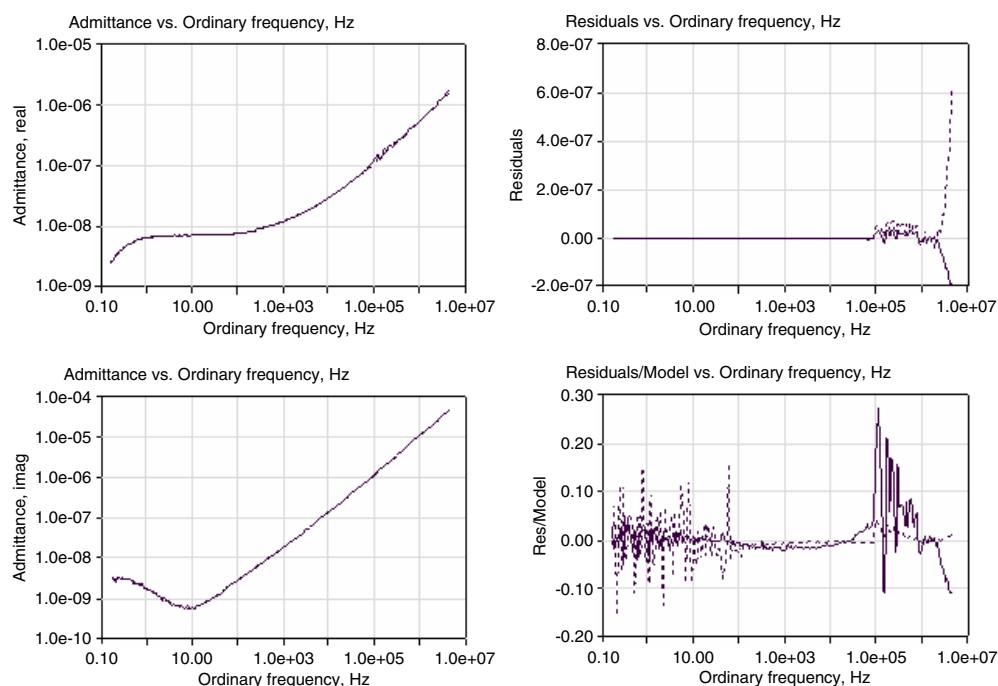


Figure 4. Direct graphical output obtained from LEVMW CNLS fitting of $\text{AgI}_{0.4}(\text{AgPO}_3)_{0.6} \sigma(\omega)$ data at 151.8 K using the PUNS composite model with proportional weighting. Identification of lines is the same as in the caption of figure 2.

0.674 ± 0.006 , 1F , and 0.945 ± 0.014 . The n estimate of 0.674 here is very close to the 0.678 one of Sidebottom [1], and it is also consistent with the PUNS-model fixed value of $2/3$.

3.4.3. Fitting of $\text{AgI}_{0.4}(\text{AgPO}_3)_{0.6} \sigma(\nu)$ and $\sigma'(\nu)$ data at other temperatures. In sections 3.3 and 3.4 above, we identified and analysed data situations for different materials where composite models required an SCPE part, SCPE and PCPE parts, or, with low-frequency cut-off, sometimes only a PCPE, NCL, or CL additional part. What is the situation, however, for a single material at various temperatures? To investigate and describe such behaviour, consider the results obtained from fitting the present material at temperatures of 183.8, 151.8 K (see above), 138.6, and 84.5 K. The last value is the lowest temperature for which Sidebottom provided data for this material. The actual $\sigma'(\nu)$ data points and curves for these four temperatures are presented in figure 6. New fit results will be only briefly summarized here.

The figure shows that electrode response dominates the low-frequency $\sigma'(\nu)$ behaviour of the 183.8 K data set. Further, its high-frequency effects turn out to fall well beyond the highest measured frequency, and the entire $\sigma'(\nu)$ data curve is well fitted by the CUNS model with $\gamma_{\text{SC}} \approx 0.8$. It turns out that good fitting of both the 151.8 and 138.6 K data sets requires the inclusion of a PCPE term in the composite model, so the PUNS one is used for both, although for the 138.6 K data the PCPE parameters are better determined than are the SCPE ones because of the large noise present in the low-frequency region.

For the present material, Sidebottom [1] quoted a σ_0 activation energy of 0.341 eV. It follows that for the 84.5 K data, σ_0 will be less than $10^{-17} \text{ S cm}^{-1}$, far below the low-frequency resolution limit of the measurements, as shown by the scattered solid points for $\nu < 10^3$ Hz.

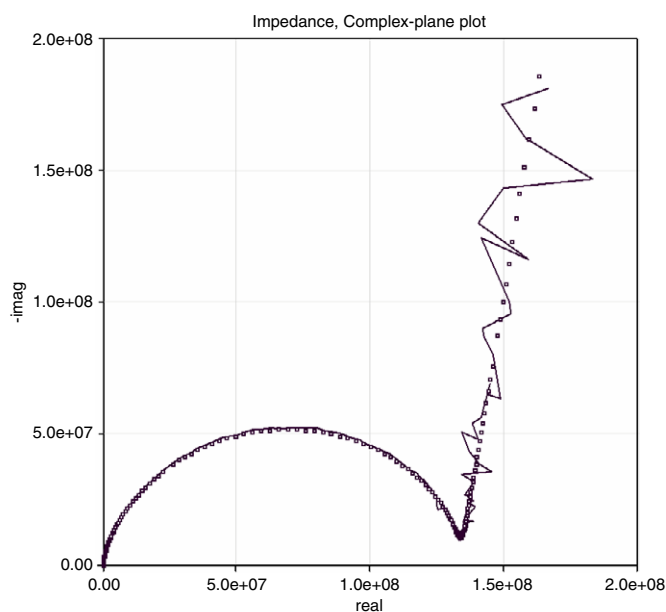


Figure 5. Complex-resistivity-plane plot of output obtained from LEVMW CNLS fitting of $\text{AgI}_{0.4}(\text{AgPO}_3)_{0.6} \sigma(\omega)$ data at 151.8 K using the PUNS composite model with proportional weighting. Data: solid lines; fit: solid circles.

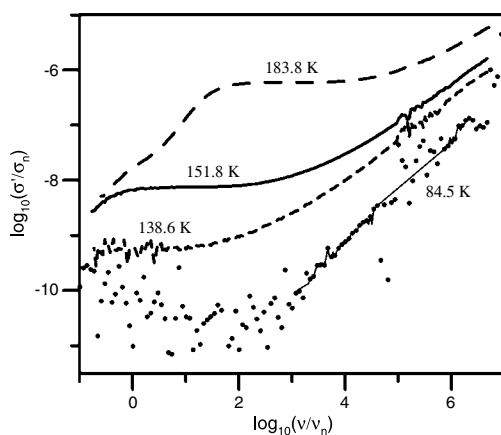


Figure 6. Log-log plots of $\text{AgI}_{0.4}(\text{AgPO}_3)_{0.6} \sigma'(\omega)$ data for four temperatures. For the 84.5 K data, every other measured value is shown by a dot. Fitting of this data set involved only the approximately straight-line part, obtained by docking the data at both ends and by eliminating the large outlier points, particularly those in the neighbourhood of 10^5 Hz.

Thus, no bulk K1-model fitting was possible, and fitting involved only the data between 10^3 and 2.5×10^6 Hz. The PS, P, and S models were used for fitting here. The latter two are equivalent, and PS-model fitting led to no significant improvement in fit over that obtained with either separately, ones that led to an estimated slope of 0.94. In addition, the PS-model SCPE parameter estimates were far more uncertain than the PCPE ones for this composite-model fit. It therefore seems most physically reasonable to pick the PCPE rather than the SCPE

model as being most appropriate for this data set. Then it may be interpreted as exhibiting NCL behaviour.

One finds for the three highest temperatures that γ_{SC} increases monotonically as the temperature decreases, reaching a value of about 1.5 for 138.6 K. On the other hand, the quantity $(1 - \gamma_{PC})$ varies from about 0.98 at 151.8 K, to about 0.87 at 138.6 K, and reaches 0.94 at 84.5 K, all NCL behaviour. Both A_{SC} and A_{PC} estimates decreased superlinearly and monotonically with decreasing temperature, and although the dependence of A_{SC} was noisy and not closely of Arrhenius form, its estimated activation energy was 0.15 ± 0.05 eV. That of A_{PC} was better determined and, for the three lowest temperatures, was 0.029 ± 0.004 eV. It is noteworthy that an A_{PC} activation energy value of 0.06 eV was found to be appropriate for the crystalline fast ionic conductor $\text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3$ [10].

In 1999 Hsieh and Jain [19] concluded that NCL observed for high-temperature, high-frequency conditions and that observed at low-temperature, low frequency ones is the same phenomenon. Recently, molecular dynamics simulations [20, 21], including ion–ion Coulomb interactions, have suggested that NCL involves the coupled motion of caged ions and the smaller correlated motion of the caging atoms, that the simulation results are relevant to experiment over a wide frequency range, and that they are more appropriate than are single-particle percolation response models. The present bulk UN model involves a continuous-time random-walk percolation model [22, 23], however, and fits the data for many different glasses excellently. The independence of its β_1 value of ionic concentration and temperature [4, 5, 14] does not necessarily imply the absence of ion–ion correlations but just shows that β_1 is not an appropriate measure of such interactions.

The present results clearly show that observed high-frequency slopes of $\sigma'(\omega)$ of the order of unity are not associated with a bulk hopping process and model but arise from either series electrode effects represented by the SCPE, or parallel PCPE NCL effects, or both. The molecular dynamics simulations of [20] and [21] apply only to the parallel PCPE contribution to the total response. Further, it is evident that when electrode effects are significant they may totally dominate any NCL processes present, as in the 183.8 K data and fit, so that no NCL parameter estimates may be extracted from such a fit. As the temperature is decreased, SCPE contributions to the response eventually decrease sufficiently that they become of less importance than do PCPE ones, with only the latter NCL contribution remaining at even lower temperatures.

4. Conclusions

The present results suggest that when there is a flat σ_0 low-frequency plateau several decades wide apparent in the $\sigma'(\nu)$ data, it is possible that the high-frequency limit of the data may not extend high enough that the data in this region are affected by electrode effects. If a low-frequency decrease is present below the plateau, however, the data should certainly always be fitted with a composite model that includes the SCPE, or another electrode-effects part, to take proper account of this behaviour. But even when no such decrease is present, or when the data have been cut off at low frequencies to eliminate it, the SCPE should still be included initially in a composite fitting model to account for possible high-frequency electrode effects.

Much published $\sigma'(\nu)$ data do indeed show only a wide plateau, and, for such data, equation (1) with $\alpha = 1$ should be satisfactory, if and only if fitting leads to a well-determined n value close to $2/3$, explaining the many n estimates in the literature that use such a CL equation and approximate this value. It will generally be more appropriate, however, to fit with α free to vary, leading to NCL results with $|1 - \alpha| \approx 0$, but not exactly equal to 0, more physically plausible than pure CL response.

Finally, it is always better to fit full complex data rather than its real or imaginary part. Initial fits should be made using the CUNS and PUNS models to establish the presence and importance of electrode and NCL contributions to the data. Such fits, which involve $\beta_1 = 1/3$, are not only supported by topological considerations, but generally lead to better fits and to better parameter estimates than do CZCS or PZCS models. Should this not be the case and/or if CK1S and PK1S fits lead to appreciably better fits than those with β_1 fixed at $1/3$, it is likely that the material investigated is not microscopically homogenous and/or involves more than a single type of charge carrier.

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The newest WINDOWS version, LEVMW, of the comprehensive LEVM fitting and inversion program may be downloaded at no cost from <http://www.physics.unc.edu/~macd/>. It includes an extensive manual and executable and full source code. More information about LEVM is provided at this www address.
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