

Analysis of Immittance Spectra: Finding Unambiguous Electrical Equivalent Circuits to Represent the Underlying Physics

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An alternate approach of analyzing immittance spectra with electrical equivalent circuits, which not only eliminates circuit ambiguity but also directly extracts the system-specific parameters of the selected physical models, is proposed. To understand the underlying mechanisms, a fundamental electrical equivalent circuit, representing Maxwell's equations, is derived. Allowing nonlinear characteristics for the elements in the circuit results in a universal immittance that is neither limited to the fundamental frequency nor to linear response functions. Process-specific physical models with their intrinsic, potentially nonlinear, dependencies on external parameters are introduced as components of the circuit. This allows the extraction of the system-specific parameters of the models instead of single values for idealized components like resistors and capacitors. The resulting electrical equivalent circuits are unambiguous and can be fitted to measured immittance data for a whole set of varied external parameters instead of the frequency of the applied stimulus only. Furthermore, the different dependencies of the physical models on external parameters automatically weight the regions of their dominance. Exemplarily, for a well-known system, the impedance of a depletion layer in silicon is calculated by using models for the resistance and capacitance that are both dependent on the external parameters voltage and temperature. In addition to a detailed comparison with conventional electrical equivalent circuits, differences between the presented approach and analytical Poisson-Nernst-Planck models are discussed.

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I. INTRODUCTION

Immittance [1] spectroscopy is a well-established versatile method with a broad range of applications in very different fields. Besides its obvious application in (electrical) engineering, immittance spectroscopy is a very common method in the analysis of electrochemical systems, where it is better known as electrochemical impedance spectroscopy (EIS), and was used in this field of research starting from the end of the 19th century [4]. Examples of its applications in electrochemistry are the analysis of corrosion, observation of chemical reactions at the solid/liquid interface in general, and identification of processes in batteries [5]. The latter recently gained a lot of attention due to new requirements of batteries for electric vehicles [6], energy buffering for renewable energies [7], and the steady increase of the worldwide usage of mobile devices [8,9]. From the beginning, the investigation of biological samples has also been a common application of immittance spectroscopy (see Ref. [10], pp. 411–418). Measuring the impedance of human skin, for example, can be used to detect diabetes-related changes in the skin while being faster and less expensive than skin biopsies by microscopy [11]. Compared to competing measuring methods, immittance spectroscopy may often be a more cost-efficient and less time-consuming alternative.

These properties led to the use of impedance measurement in cardiac pacemakers [12]. Apart from that, immittance spectroscopy is an established method in material science [13] as well as geology [14].

In 1853, Helmholtz [15], utilizing Ohm's law and Kirchhoff's laws, formulated the principles of superposition of currents and voltages in spatially extended bodies and then, verbally, introduced the first electrical equivalent circuit (for details, see Ref. [16]). Among other things, he found that the distributed resistances can be lumped in "linear conductors" (lumped resistors). The description of linear systems by impedance dates back to the work of Heaviside, a telegrapher and nephew of Wheatstone [17], who coined the word *impedance* in 1886 (see Ref. [18], p. 64). Heaviside not only suggested the word impedance (derived from the verb "impede") but also generalized Ohm's law for ac signals and introduced the term "capacitance" as well as "inductance" [18].

A very common and comfortable method of interpreting immittance spectra is creating suitable electrical equivalent circuits (EECs) of idealized lumped components, especially resistors and capacitors (or, more generally, capacitive elements, like constant phase elements; see Sec. II F), and optimizing their values to resemble the measured immittance data as closely as possible [4].

Especially in *explanatory models* (see below), the arrangement of the idealized lumped components in an

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EEC is based on an idea of the underlying physics. Still, the use of idealized lumped elements only might entail certain drawbacks. EECs consisting solely of such components are well known to be ambiguous; i.e., different arrangements of components with the same number of capacitive elements and resistors can lead to the same immittance response over all frequencies [19,20]. Hence, although the arrangement of the idealized lumped components in the EEC might have been based on a certain idea of the underlying physics, it remains unclear whether the components really represent specific processes or parts in the investigated system. It is entirely possible that one idealized lumped component of the EEC is associated with multiple parts of the system. Hence, the selected network might not represent the underlying physics correctly [4], and this may, if it remains unrecognized, in the end, even lead to misinterpretations (see Ref. [10], p. 4). According to J. Macdonald, it is, however, possible to identify the most physically reasonable EEC by fitting the immittance data with a set of different plausible networks for a range of temperatures and/or potentials [20].

With respect to different types of models, this work uses the terminology of Grimnes and Martinsen (see Ref. [10], pp. 284–286). The terms *descriptive* and *explanatory* model in the context of electrical equivalent circuits for immittance data, their respective necessity in different situations, and the distinction between them are discussed in the mentioned source. As D. Macdonald notices, the step from a descriptive model (he calls this an “analog”) to an explanatory model (which he calls a “model”) is rarely done [4].

An existing approach of analyzing immittance spectra with the possibility to extract meaningful physical parameters for a broad variety of systems, which up to now was rarely used, is the analysis with models based on the Poisson-Nernst-Planck equations [21,22]. Using fundamental equations for current transport through mobile charge carriers, with opposite sign, varying concentrations, different mobilities, and specific valences in a potential landscape calculated by Poisson’s equation and certain boundary conditions, a broad variety of different systems can be modeled [23]. Such models could be used to describe spatially extended systems directly. For important situations usually observed in immittance spectra, analytic solutions of the Poisson-Nernst-Planck equations as lumped components exist [22–24]. The differences between process-independent Poisson-Nernst-Planck models and the suggested approach with process-specific physical models dependent on external parameters as well as a suggestion about how both approaches may be combined are discussed in Sec. III D.

In this work, an alternate approach of devising EECs for the analysis of immittance data is proposed. Derived from Maxwell’s equations, it is found that the fundamental EEC of a homogeneous, nonmagnetic material can be described by a parallel arrangement of the resistive and complex capacitive elements, hereafter called a generalized Voigt circuit element

[25]. Although the resulting arrangement of the components is already used in other works, it is not used exclusively; see Ref. [5], pp. 91–95, Fig. 2.2.3, and, most importantly, Fig. 2.2.4. Other arrangements are equally frequently found and, due to the ambiguity, not regarded as less reasonable, although the derivation from Maxwell’s equations renders many of the other used arrangements debatable.

Understanding the origin of the components of the generalized Voigt circuit element enables the direct introduction of process-specific physical models with their dependence on external and system-specific parameters. *External parameters* are those parameters the physical model is dependent on which can be externally controlled during the experiment, e.g., temperature, pressure, or bias voltage. Furthermore, the model can be dependent on *natural constants* and *system-specific parameters*; neither can be controlled. The latter may include material constants, volume fractions of inclusions, or energy barrier heights at interfaces. A well-known practical example, which is discussed in detail in Sec. II H, is the representation of the resistance and capacitance of a depletion layer in an EEC. The resistance is represented by a diode model, with the resistance dependent on the external parameters voltage and temperature as well as the system-specific parameters in place of a resistor with a single-valued resistance. When fitting the model against experimental data, instead of the single-valued resistance, nontabulated or unknown system-specific parameters of the diode model (e.g., the acceptor concentration) would be optimized by the fitting routine. The capacitive element of a depletion layer is represented by using the model for the voltage- and temperature-dependent depletion-layer capacitance from Ref. [26], p. 248.

The derivation of the universal immittance for a single, homogeneous piece of material and the corresponding representation as an EEC is shown in Sec. II. In Sec. II G, it is explained how the parts of systems with several pieces should be connected in an EEC and what approximations are useful as well as how to model multiple charge-transport and polarization processes in a single homogeneous part of the material.

To obtain reasonable values for the fit parameters and to evaluate if the correct physical processes are assumed, it is necessary to utilize the dependencies of the inserted models on their external parameters. In the example in Sec. II H, voltage and temperature dependence are used. To utilize the dependences of the depletion-layer model for fitting experimental data, the immittance is measured for a range of voltages and/or temperatures as suggested in Ref. [20]. The entire immittance data for all sets of parameters should be used as a whole (global optimization) to optimize the system-specific parameters of the used models that cannot be obtained from the literature. In separate plots of residuals of the immittances over frequency and each external parameter (in this example, one plot of residuals-frequency-bias voltage and one plot of residuals-frequency-temperature in the

investigated ranges), one can not only evaluate how well the EEC approximates the system for different regions but also identify missing components.

In contrast to first-order approximations like resistors and capacitors, process-specific models dependent on external parameters are inseparably linked to their corresponding underlying physical process. As a result, the dependence on certain different external conditions is restricted by the model. This restriction by an external-parameter dependence is the key to verifying whether the correct process is assumed: Since, usually, a mutually exclusive dependence on an external parameter can be found and used to distinguish between different models (examples of models are given in Table I). Additionally, due to their specific form, it is unlikely that a component based on process-specific models represents several parts of the system, which can, on the other hand, easily occur when using idealized lumped components. Furthermore, a plot of the residuals of a fit over the external parameters can be used to identify missing processes. As previously mentioned, instead of resistances and capacitances, the system-specific parameters of the models are fitted. These usually represent physical properties of the underlying system directly, e.g., carrier concentrations or energy levels of traps involved in the transport. Furthermore, since the dependence on external parameters is included in the model, there are significantly fewer fitted parameters for systems investigated for a set of different external parameters (compare the example in Fig. 5). Finally, the dependence on external parameters of the process-specific physical model weight the regions of importance of certain fit parameters, enabling global fitting and, consequently, resulting in better guesses for the parameters. On the other hand, to apply this approach it is necessary to measure immittance spectra at several different external conditions. While this approach has a lot of advantages for explanatory models, for descriptive models, where the quality of description might be most important, the approximation of the system is in this approach also limited by the quality of the utilized models to describe the real behavior of the corresponding process.

We believe that this extension to devise EECs will help immittance spectroscopists to extract more (and more precise) information about the system under investigation while, additionally, significantly reducing the risks for misinterpretations as compared to the usual procedure to create EECs consisting solely of idealized lumped components.

II. THEORY: DERIVATION OF A FUNDAMENTAL EEC FOR DIRECT EXTRACTION OF PARAMETERS OF THE UNDERLYING PHYSICAL PROCESSES

It is derived from Maxwell's equation of total current that a homogeneous, isotropic bulk of a nonferroelectric,

nonmagnetic ($\mu_r = 1$) material can be described by a generalized Voigt circuit element [capacitive element(s) in parallel to static resistor(s)]. Furthermore, sequential arrangement of multiple materials can be modeled by the serial combination of the corresponding generalized Voigt circuit elements.

In a first step, the possibility of a lossy polarization process is included by introducing a complex permittivity ϵ_r . In order to get from dimensionless quantities to an electrical equivalent circuit, geometry is, without loss of generality, added to the system. After the introduction of geometry, also for a material with susceptibility of unity, an alternating current leads to inductance, which has to be represented with an inductor in series with the circuit. Since inductance is usually of minor interest for immittance spectroscopy in science, it will be omitted in this derivation.

Charge-transport and polarization processes are usually dependent on external parameters. A resistance can, for example, be dependent on an applied magnetic field [27,28] or on pressure applied to the material [29]. Polarization processes can be dependent on external parameters as well, e.g., pressure [30]. A depletion-layer capacitance, for example, is strongly dependent on the externally applied electrical field [31]. Physical models may include the dependencies on certain external parameters. These dependencies can be used to distinguish between different processes and extract them as separate parameter-dependent resistors or capacitors. For that reason, these dependencies on external parameters are assumed throughout the derivation.

The applied field (and, respectively, applied voltage) is the stimulus in most impedance experiments. Additionally, the deviation is not limited to linear systems. Therefore, to understand at which point nonlinear behavior plays a role, the applied field is explicitly given as a parameter. If not stated otherwise, any other dependency on external parameters is included in the parameter set $\mathcal{P}$; e.g., in the case of a diode, $\mathcal{P}$ would include the temperature.

Generally, a tilde above a function indicates that its time-domain representation is used; without a tilde, it is its frequency-domain representation. All external parameters, especially the applied field, can change over time and are, hence, explicitly time (respectively, frequency) dependent. To avoid unnecessarily long formulas, the explicit time (frequency) dependence of external parameters and the applied field is, if not stated otherwise, omitted.

A. Maxwell's total current density and the interpretation of its different terms

The total current density $\tilde{\mathbf{J}}(t, \tilde{\mathbf{E}}, \tilde{\mathcal{P}})$ through a nonferroelectric, nonmagnetic, isotropic material in the time domain can according to Maxwell be written as [32]

$$\tilde{\mathbf{J}}(t, \tilde{\mathbf{E}}, \tilde{\mathcal{P}}) = \tilde{\mathbf{J}}_{\text{free}}(\tilde{\mathbf{E}}, \tilde{\mathcal{P}}) + \frac{\partial \tilde{\mathbf{D}}(t, \tilde{\mathbf{E}}, \tilde{\mathcal{P}})}{\partial t}, \quad (1)$$

with current density $\tilde{\mathbf{J}}_{\text{free}}$ and electric displacement field $\tilde{\mathbf{D}}$ [33].

Following the interpretation of Jonscher (see Ref. [34], pp. 40–41), the two different contributions to the total current density in Eq. (1) are strictly separated in this work: While $\tilde{\mathbf{J}}_{\text{free}}$ is based only on the *dc conduction* mechanisms in the material, the derivative of the electric displacement field $\partial\tilde{\mathbf{D}}/(\partial t)$ exclusively includes *dielectric* processes, namely, the dielectric response of “free space” and the complex polarization in the material. The polarization is complex, because there is an unavoidable phase delay between the exciting signal and the polarization response of any material (see Sec. II C for details). This strict separation is not generally allowed. In Sec. III A, however, it is explained that this approximation is valid in the frequency ranges of *dielectric relaxation* (as defined in Ref. [34], p. 6) which is a superset of the frequencies used in immittance spectroscopy. The separation is necessary only since most conduction mechanisms that should later be introduced as parallel resistors (are developed to describe the static behavior of the material and) do not yet consider the effect that a stimulus varying with time (or frequency, respectively) has on their response. By using those conduction models, the mean free current over a full period of the stimulus is independent of the duration of the period. Any part of the derivation in this section remains valid if the conduction model includes a noninstantaneous response or gradient dependence to the variation of stimulus or other external parameters. Even when static conduction models are used, the variation of the external parameters with time still leads to an implicit time dependence of the free current $\tilde{\mathbf{J}}_{\text{free}}$. Their responses are, however, instantaneous and independent of the abruptness of the variation of the stimulus or any other external parameter with time. In contrast, the dielectric models consider the slope of the stimulus and include a delayed response.

Since for now only pure dc models are used to describe the free current $\tilde{\mathbf{J}}_{\text{free}}$, for the above-mentioned reasons, it is assumed purely real (no phase delay) and has no explicit time dependence.

The steady current density $\tilde{\mathbf{J}}_{\text{free}}$ arises from the continuous movement of charges across the dielectric material and does not change the “center of gravity” of the charge distribution in the material (see Ref. [34], p. 41). Although the index “free,” usually used in the literature, suggests otherwise, the charge carriers do not actually have to be free or even quasifree, like in a metal, where electrons propagate through delocalized states [35]. Dielectrics are insulators (see Ref. [34], p. 1) and their static charge transport is, as opposed to delocalized states in metals, usually conducted through (randomly arranged) localized states [36], by trapping and detrapping [37] or by ionic conduction, which can for the following arguments be treated equivalent to the conduction of charges through localized states [38]. Electrons in a disordered insulator [39], for example,

can percolate through defect-rich parts, i.e., hop from one localized defect to another, until they eventually migrate from one electrode to the other [40]. Disordered or not, in materials where current flow is the result of charge movement in localized states, the charge is bound to a specific defect between jumps and therefore not free [40]. Still, the resulting direct current density has to be ascribed to $\tilde{\mathbf{J}}_{\text{free}}$, since it is the only remaining term for a response caused by a time-independent stimulus.

B. dc processes

Generally, the static current in a material is not generated by a single but by multiple different transport processes. One might imagine the various parallel transport processes as a sum of the corresponding current densities or, in the picture of an EEC, as a parallel arrangement of resistors. Each resistor represents how many carriers in a time step would use the specific process of migration. If the separate dc transport processes in the investigated material are known, the corresponding models can directly be included as parallel, parameter-dependent resistors in the generalized Voigt circuit element. Otherwise, the sum of the unknown processes leads to a single parallel resistor which complicates the extraction of parameters, unless there is a single dominant process which might, hence, be identified.

Finally, static transport processes for the homogeneous piece of material are assumed to create the current density $\tilde{\mathbf{J}}_{\text{free}}(\tilde{\mathbf{E}}, \tilde{\mathcal{P}})$, which leads, as explained in detail later, to the parallel resistor(s) in the generalized Voigt circuit element [see parallel static resistors in Fig. 2(a)]. For sufficiently low frequencies, the impedance of any system is determined by the static transport processes only. Assuming a finite static conductivity for the system, a certain range of the low-frequency dielectric response is not measurable, since in the corresponding low-frequency range the static conductivity is the dominating part of the impedance (see Ref. [34], pp. 46–47).

C. Frequency-domain representation, complex permittivity, and dc conductivity

Since impedance spectra are usually analyzed in the frequency domain (see Ref. [5], p. 4), the work is continued in that domain. Because of the time derivative, the Fourier transform of the total current density in Eq. (1) is [41]

$$\mathbf{J}(\omega, \mathbf{E}, \mathcal{P}) = \mathbf{J}_{\text{free}}(\mathbf{E}, \mathcal{P}) + i\omega\mathbf{D}(\omega, \mathbf{E}, \mathcal{P}). \quad (2)$$

The dielectric displacement field $\mathbf{D}$ can be divided in the free space $\varepsilon_0\mathbf{E}$ and material component $\mathbf{P}$:

$$\mathbf{D}(\omega, \mathbf{E}, \mathcal{P}) = \varepsilon_0\mathbf{E} + \mathbf{P}(\omega, \mathbf{E}, \mathcal{P}). \quad (3)$$

The polarization $\mathbf{P}$ in a material is caused by (partial) alignment or induction of dipoles and can, using the susceptibility χ in the frequency domain, be written as

$$\mathbf{P}(\omega, \mathbf{E}, \mathcal{P}) = \varepsilon_0 \chi(\omega, \mathbf{E}, \mathcal{P}) \mathbf{E}. \quad (4)$$

As a result, in the time domain the polarization is the convolution of the electric field and the electrical susceptibility. As explained above, in the absence of alternatives, dc charge-transport models are used to calculate the current density $\mathbf{J}_{\text{free}}$ which do not consider the frequency dependence. The electrical susceptibility and all quantities derived from it (e.g., permittivity, polarization, and displacement field), on the other hand, take the frequency dependence into account. From Eqs. (3) and (4), it follows that

$$\mathbf{D}(\omega, \mathbf{E}, \mathcal{P}) = \varepsilon_0 [1 + \chi(\omega, \mathbf{E}, \mathcal{P})] \mathbf{E}.$$

Hence, one defines

$$\varepsilon_r(\omega, \mathbf{E}, \mathcal{P}) \equiv [1 + \chi(\omega, \mathbf{E}, \mathcal{P})].$$

As a result, $\mathbf{J}(\omega, \mathbf{E}, \mathcal{P})$ can be written as

$$\mathbf{J}(\omega, \mathbf{E}, \mathcal{P}) = \mathbf{J}_{\text{free}}(\mathbf{E}, \mathcal{P}) + i\omega[\varepsilon_0 \mathbf{E} + \mathbf{P}(\omega, \mathbf{E}, \mathcal{P})] \quad (5a)$$

$$= \mathbf{J}_{\text{free}}(\mathbf{E}, \mathcal{P}) + i\omega\varepsilon_0\varepsilon_r(\omega, \mathbf{E}, \mathcal{P})\mathbf{E}. \quad (5b)$$

Because of the fact that any dipole reaction is noninstantaneous [42], in general, $\mathbf{P}$ has an imaginary component, and χ as well as ε_r are consequently complex quantities, too [compare with Eq. (7)]. It can be seen that, in regions of low loss and frequency-independent relative permittivity ε_r , the amplitude of the current density linearly increases with frequency ω . This behavior results in a reactance that is inversely proportional to the frequency, while the resonances of the system [that are frequency regions where the relative permittivity is strongly dependent on frequency (see Ref. [34], p. 50)] are far off. Close to resonances in the polarization mechanism, the permittivity ε_r is strongly dependent on frequency (see Ref. [34], p. 50), resulting in a deviation from the reciprocal frequency dependence of the reactance.

As explained above, the dependence on external parameters, for example, applied field $\mathbf{E}$ and temperature T , is characteristic to the transport and the polarization process in the material. In the case of the static charge transport, the dependencies are included in the corresponding conductivity:

$$\mathbf{J}_{\text{free}}(\mathbf{E}, \mathcal{P}) = \sigma_{\text{stat}}(\mathbf{E}, \mathcal{P})\mathbf{E}(\omega). \quad (6)$$

As described in detail in Secs. II A and III A, an explicit time dependence (more precisely, a dependence on the gradient of the external parameters with time) of

conductivity σ arises outside of the frequency range of dielectric relaxation, which this work assumes.

Therefore, the use of models for *static conductivities*, denoted with σ_{stat} , is allowed. Furthermore, it should be noted that there is no explicit time dependence for the static conductivities and that σ_{stat} is purely real.

The derivation, however, remains valid for conductivities σ explicitly dependent on the slope of the applied field and, hence, current densities $\mathbf{J}_{\text{free}}$ dependent on the time derivative of the stimulus.

To stress the fact of the remaining implicit frequency dependence, the frequency dependence of the applied field is written explicitly in Eq. (6).

As explained below, there is no lossless polarization process. Hence, for any material (i.e., everything but vacuum), the permittivity $\varepsilon(\omega, \mathbf{E}, \mathcal{P})$ is a complex quantity (see Ref. [43], pp. 89–95). It can be written as

$$\begin{aligned} \varepsilon(\omega, \mathbf{E}, \mathcal{P}) &= \varepsilon_0 \varepsilon_r(\omega, \mathbf{E}, \mathcal{P}) \\ &= \varepsilon_0 \varepsilon'_r(\omega, \mathbf{E}, \mathcal{P}) - i\varepsilon_0 \varepsilon''_r(\omega, \mathbf{E}, \mathcal{P}) \\ &= \varepsilon'(\omega, \mathbf{E}, \mathcal{P}) - i\varepsilon''(\omega, \mathbf{E}, \mathcal{P}), \end{aligned} \quad (7)$$

where ε'_r is the real and ε''_r is the imaginary part of the relative permittivity (see Ref. [43], p. 94) [44].

If an external field is applied, the polarization response cannot be instantaneous [42], because a dipole has to be created or (at least partially) aligned to the external field. These processes require some time, which may for fast polarization processes be very, even negligibly, short but always different from zero. This time delay creates a nonzero phase shift of the polarization response. As a result, only a part, i.e., the real part, of the polarization is in phase with the applied field, and the remaining part in quadrature, the pure imaginary part. In summary, in any material the polarization has a time delay, and consequently there must be an imaginary part of the permittivity (describing the loss). Furthermore, it follows from the Kramers-Kronig relations (also valid for nonlinear materials; see Ref. [42]) that it is impossible to have a finite susceptibility in a loss-free or dispersion-free dielectric material (see Ref. [34], p. 49). In an experiment, however, the imaginary component of the relative permittivity might, far from resonances, be too small to be detectable within the given measurement accuracy.

Both parts of the complex permittivity can, depending on the corresponding polarization process, have dependencies on various external parameters. They are obviously dependent on frequency, and their interdependence is described by the Kramers-Kronig relations [42]. Other dependencies vary with the polarization mechanism. For local dipoles caused by field-assisted hopping of carriers in an area of high defect concentration, for example, a dependence of temperature and electric field might be assumed (analog to the static transport in Ref. [37]).

Inserting both Eqs. (6) and (7) into Eq. (5b) yields

$$\mathbf{J}(\omega, \mathbf{E}, \mathcal{P}) = [\sigma_{\text{stat}}(\mathbf{E}, \mathcal{P}) + \omega \epsilon''(\omega, \mathbf{E}, \mathcal{P})] \mathbf{E} + i\omega \epsilon'(\omega, \mathbf{E}, \mathcal{P}) \mathbf{E}. \quad (8)$$

It can be seen that the imaginary part $\epsilon''(\omega, \mathbf{E}, \mathcal{P})$ belongs to the component of the current in phase with the driving field and therefore contributes to the power loss (see Ref. [34], p. 45). Thus, $\epsilon''(\omega, \mathbf{E}, \mathcal{P})/\epsilon_0 = \epsilon_r''(\omega, \mathbf{E}, \mathcal{P}) = \chi''(\omega, \mathbf{E}, \mathcal{P})$ is often referred to as the dielectric loss (see Ref. [34], p. 45). In contrast, the real part of the permittivity $\epsilon'(\omega, \mathbf{E}, \mathcal{P})$ is in quadrature with the driving field and, hence, in phase with the real part of the polarization and dielectric displacement field [compare Eq. (8) with Eqs. (2) and (5a)]. As a result, it does not contribute to the loss (see Ref. [34], p. 45).

D. Introducing geometry and universal immittance

Since the EECs consist of resistors and capacitors rather than conductivities and permittivities, spatial dimensions have to be introduced. For simplicity, but without loss of generality, the problem is described in a parallel plate geometry. More complex geometries will only lead to more complicated geometric factors. As explained above, an isotropic, homogeneous piece with conductivity $\sigma_{\text{stat}}(\mathbf{E}, \mathcal{P})$ and complex permittivity $\epsilon(\omega, \mathbf{E}, \mathcal{P})$ is assumed. Furthermore, all electric field lines are supposed to be parallel and the area of the conducting plates A large enough so that the field lines outside of the volume between the parallel plates can be neglected. Additionally, the distance between the plates d , which is gaplessly filled with the material, shall be sufficiently smaller than half of the wavelength of the applied signal. Consequently, the field becomes $E = V/d$ and the current density $J_{\text{tot}} = I_{\text{tot}}/A$, where V and I_{tot} are the externally applied voltage and current between the plates, respectively. As a result, Eq. (8) is multiplied by the area A and the field replaced by the applied voltage V [45]. Hence, the total current in the piece is

$$I(\omega, V, \mathcal{P}) = [\sigma_{\text{stat}}(V, \mathcal{P}) + \omega \epsilon''(\omega, V, \mathcal{P})] \frac{A}{d} V + i\omega \epsilon'(\omega, V, \mathcal{P}) \frac{A}{d} V. \quad (9)$$

It is now possible to identify the components of the fundamental EEC in Eq. (9) by partially expanding with the geometric factor A/d . The static conductivity multiplied with the geometric factor becomes $\sigma_{\text{stat}}(V, \mathcal{P})A/d \equiv R_{\text{stat}}^{-1}(V, \mathcal{P})$. For the term with the imaginary part of the permittivity, $\omega \epsilon''(\omega, V, \mathcal{P})A/d \equiv R_{\text{dyn}}^{-1}(\omega, V, \mathcal{P})$ is obtained [46]. And the last term is $i\omega \epsilon'(\omega, V, \mathcal{P})A/d \equiv i\omega C'(\omega, V, \mathcal{P})$. Equation (9) becomes

$$I(\omega, V, \mathcal{P}) = [R_{\text{stat}}^{-1}(V, \mathcal{P}) + R_{\text{dyn}}^{-1}(\omega, V, \mathcal{P})] V + i\omega C'(\omega, V, \mathcal{P}) V. \quad (10)$$

The quantity in brackets in Eq. (10) is almost the admittance, i.e., the reciprocal impedance $Z^{-1}(\omega, V, \mathcal{P})$. Almost, because impedance and admittance are defined only for linear systems. Nonlinear systems, like shown in Fig. 1, on the other hand, will, for a sinusoidal stimulus with a nonzero amplitude, generate harmonics [compare Fig. 1(b)] which cannot be represented by admittance or impedance. Depending on the curvature of the response

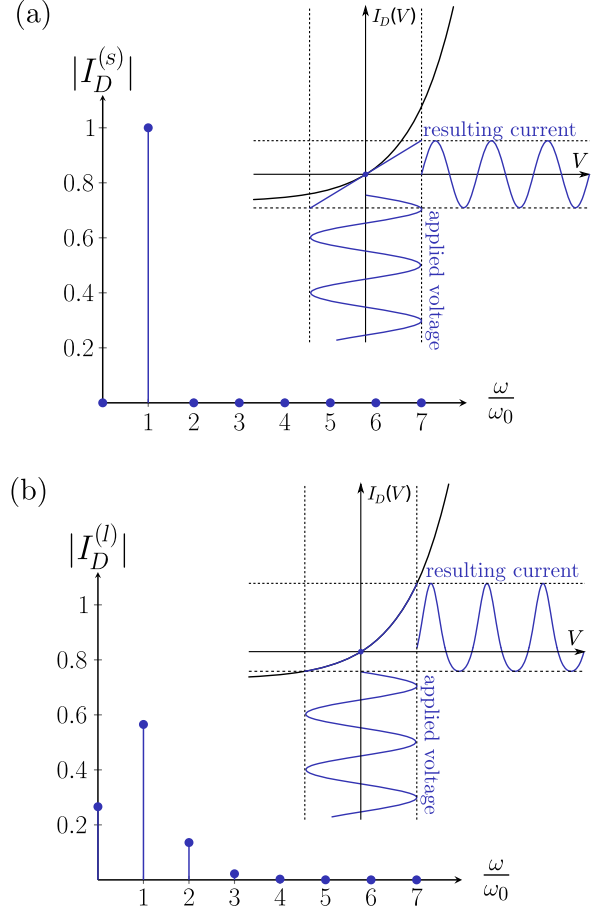


FIG. 1. The insets show the current-voltage curve of an ideal diode. In the inset in (a), the resulting current for a voltage signal oscillating around the bias voltage is calculated by using the small-signal approximation, that is, assuming the resistance at the bias voltage for all voltages of the signal as indicated by the tangent at the bias voltage. (a) shows the Fourier transform of the resulting current for the first six harmonics which due to the linear approximation consists only of the fundamental frequency of the applied voltage signal. In the inset in (b), on the other hand, the resulting current is calculated without the small-signal approximation, that means large-signal analysis. The applied voltage [identical to the applied voltage in (a)] leads to an oscillation on the current voltage curve instead of on the tangent in the operation point. As a result of the form of that curve, the resulting current is neither symmetric around zero current nor a pure sinusoidal. In (b), the Fourier transform of the resulting current is shown for the first six harmonics. The finite value at zero represents the mean value of the resulting current and the harmonics its asymmetric form.

of the nonlinear system and the signal amplitude, the small-signal approximation shown in Fig. 1(a) might not be a sufficiently accurate approximation. For an infinitesimally small amplitude, the large-signal response of the system and the small-signal response become identical. The derived general impedance can exactly describe the polyharmonic large-signal response of nonlinear systems. This new type of “admittance,” which is capable of describing any [47] response, may be designated universal admittance. Hence, the universal impedance of the system is

$$Z(\omega, V, \mathcal{P}) = \{R_{\text{stat}}^{-1}(V, \mathcal{P}) + R_{\text{dyn}}^{-1}(\omega, V, \mathcal{P}) + [iX'_C(\omega, V, \mathcal{P})]^{-1}\}^{-1}, \quad (11)$$

where a universal reactance is introduced as $X'_C = -(\omega C')^{-1}$.

The additional information of other harmonics in the response can be used to further confirm the choice of the selected models. This is especially important when characteristics of high-power devices, like rf amplifiers, are investigated [48]. Instead of using descriptive models, where additional circuit components are added to approximate a large-signal response [49], including process-dependent physical models as components in the EECs enables explanatory large-signal models based on the known nonlinear behavior of certain parts of the devices. The case of analyzing high-power devices has very specific requirements not present in most other areas of impedance spectroscopy. Hence, although the universal immittance seems promising for large-signal analysis, it is, in the focus of this work, only a by-product of the presented derivation. Its potential in that area will be investigated further elsewhere.

In many impedance spectroscopy experiments, the response to high amplitudes is of minor importance, and a selection of amplitudes below $k_B T$, at which a small-signal analysis is a good approximation (see Ref. [5], p. 6), is then a viable and less expensive alternative. Furthermore, in most cases, current frequency-domain measurement techniques give the “classical” immittance, that is, only the response with respect to the applied fundamental frequency, and amplitudes of the harmonics cannot be accessed. But, even in that latter case, the presented approach can help to identify a unique EEC where each component represents the underlying physics (see the example in Sec. II H). As previously mentioned, using an as-small-as-possible stimulating signal amplitude reduces the amount of power in the harmonics. Furthermore, if the harmonics are still not expected to be negligible, the classical immittance, measured in the linear measurement setup, can still be calculated from the universal immittance. In that way, the universal immittance is reduced to the corresponding fundamental frequency component and becomes comparable with the measured, classical immittance. In all cases, one may utilize the presented findings in the analysis: Process-specific physical models include a specific dependence on external parameters. If these are

included, instead of idealized lumped components, they force a certain form of dependence on the external parameters. Globally optimizing the unknown system-specific parameters of the models to immittance spectra measured for a set of external parameters (different conditions) then leads to better guesses for the fit parameters than subsequent analysis of fitted resistances and capacitances. The introduced restrictions validate whether correct models have been used. From residual plots, missing processes can be identified. Each process-specific model carries a physical concept and, hence, directly includes the underlying physics.

Since the differences are explained above and to make the remaining part of the manuscript easier to read, the (universal) response given in Eq. (11) is simply called the impedance.

E. Interpretation of the resulting impedance as EEC

The impedance given in Eq. (11) can be interpreted by a parallel arrangement of a resistor R_{stat} for the dc conduction mechanisms, another resistor R_{dyn} (frequency dependent and infinite at $\omega = 0$) for the dielectric loss, and finally a parallel (frequency-dependent) capacitor. The dependence of the dynamic components on the frequencies of the stimulus is described in the corresponding models [e.g., compare Eq. (12) or Eq. (14a)].

Other representations, e.g., a serial arrangement, of the dynamic components are possible. In any case, in the (equivalent) parallel circuit representation, the dynamic resistance R_{dyn} becomes infinite at $\omega = 0$. If, for example, the Debye model, where its serial representation allows easier extraction of parameters [50], is converted from its serial circuit representation into the equivalent parallel circuit representation, the resulting parallel dynamic resistor has infinite resistance at $\omega = 0$ as well. Also generally true is that the dynamic resistance $R_{\text{dyn}}(\omega, V, \mathcal{P})$ is always connected to the corresponding reactance $X'_C(\omega, V, \mathcal{P})$. The dynamic resistance is the loss of the respective polarization process and cannot be separated from its associated real part. It is consistent that the resistance in its parallel representation is infinite for zero frequency, since in the static case ($\omega \rightarrow 0$) dynamic resistors as well as capacitors have to vanish [see Eq. (2)].

The permittivity of a material is a result of all its electromagnetic resonances, which are well described by a quantum-mechanical treatment which, in general, leads to (compare Ref. [51], p. 19)

$$\varepsilon(\omega, \mathcal{P}_{\text{tot}}) = \varepsilon_0 + \frac{e^2}{m} \sum_{j>k} \frac{f_{jk}(\mathcal{P}_{\text{tot}})[N_k(\mathcal{P}_{\text{tot}}) - N_j(\mathcal{P}_{\text{tot}})]}{\omega_{jk}^2(\mathcal{P}_{\text{tot}}) - \omega^2 + i\omega\gamma_{jk}(\mathcal{P}_{\text{tot}})}, \quad (12)$$

where $\omega_{jk}(\mathcal{P}_{\text{tot}}) = \hbar^{-1}[E_j(\mathcal{P}_{\text{tot}}) - E_k(\mathcal{P}_{\text{tot}})]$ are transition frequencies, between lower energy levels E_k with

populations N_k and upper energy levels E_j with populations N_j , f_{jk} are the corresponding transition probabilities, γ_{jk} are the damping coefficients, m and e are the mass and charge of an electron, respectively, and $\mathcal{P}_{\text{tot}}$ indicates the dependence on all external parameters including the electrical field.

A single pair of dynamic resistor and frequency-dependent capacitor combining all transitions of Eq. (12) leads to unnecessarily complicated relations. This makes it difficult to introduce suited models. As described in Sec. IID, the complex permittivity can, by introducing dimensions, be interpreted as a complex capacitance (or pair of frequency-dependent capacitance and dynamic resistance). A sum of multiple complex permittivities, as in Eq. (12), therefore leads to a sum of the same number of complex capacitances and, as a result, a parallel arrangement of capacitors with a complex value. Each capacitor describes a specific polarization mechanism and may be separated into the corresponding in-phase (capacitance) and loss (dynamic resistance) components. Irrespective of whether parallel or serial arrangement of each component pair for the specific polarization process is chosen, all pairs are parallel to the dc resistance and, hence, to each other [see the dynamic resistor and capacitor pairs in Fig. 2(a), where parallel and serial representations are used].

Other simplifications are possible and are explained in the next section. This includes that, in regions of numerous adjacent resonant frequencies, e.g., caused by a defect band around the Fermi level, the corresponding large number of circuit elements may be combined in a single circuit element and that, for frequencies well above the highest frequency of the experiment, higher-frequency transitions may be combined in a high-frequency permittivity or high-frequency capacitor.

F. The constant phase element

For a large variety of even very different materials, the dynamic elements (dynamic resistance and frequency-dependent capacitance) obey a universal power law [52]. In those cases, the pair of dynamic elements is usually combined in a single circuit element: the constant phase element (CPE), which is also known as universal capacitance [denoted with “ K ” in Fig. 2(a)].

The constant phase behavior was first described by K. Cole [53], using a mathematical representation different from the one used today. In the same year Fricke, independently from K. Cole, proposed the CPE and used a mathematical formulation very close to the one used today [54]. The impedance of a CPE is given by a special relation between the frequency-dependent real and imaginary parts that ultimately leads to a more general complex capacitive element. Its reactance has a frequency dependence of ω^{-n} , with $0 \leq n \leq 1$, instead of allowing only the special case of an ideal, real-valued capacitor of ω^{-1} . Another, name-giving, consequence is

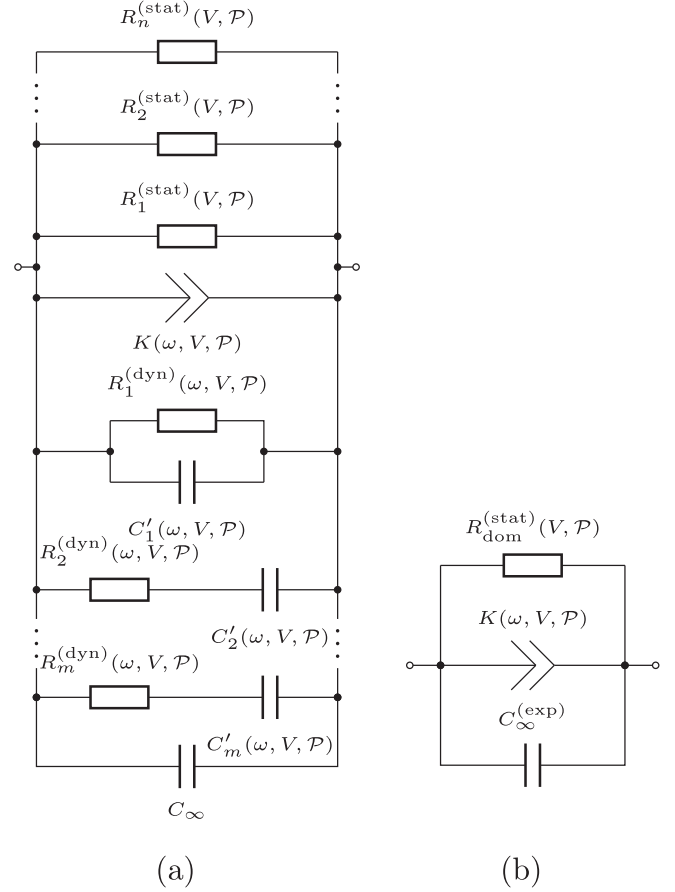


FIG. 2. (a) General EEC for a single homogeneous, nonmagnetic piece of material: n static current transport processes with their corresponding parameter dependence are each represented by parallel, parameter-dependent resistors $R_1^{(\text{stat})} \dots R_n^{(\text{stat})}$. The parameter-dependent total resistance at $\omega = 0$ is defined only by these resistors. Each of m separate polarization processes in the material is described by a pair of one dynamic resistor $R_1^{(\text{dyn})} \dots R_m^{(\text{dyn})}$ and one capacitor $C'_1 \dots C'_m$, both parameter-dependent and parallel to the static resistors. Either their parallel or equivalent serial representation can be used. In the parallel equivalent representation, the dynamic resistor has infinite resistance at $\omega = 0$. A broad distribution of adjacent resonances may be described by a constant phase element, denoted K , instead of many separate pairs of dynamic resistors and capacitors. The geometric capacitance which determines the highest resonance frequency in the system is represented by a frequency- and parameter-independent parallel capacitor C_∞ . (b) Experimentally relevant circuit (of the commonly investigated case) for one piece of material where the experimental conditions result in one dominating static transport process, represented by $R_{\text{dom}}^{(\text{stat})}(V, \mathcal{P})$, and the observed frequency range includes only the first dielectric resonance caused by a distribution of resonances represented by the constant phase element. The dielectric response of polarization processes with resonant frequencies well above the highest frequency in the experiment, including the free-space component, are included in the high-frequency capacitor $C_\infty^{(\text{exp})}$.

a constant phase $\theta = -n\pi/2$ instead of $\theta = -\pi/2$, which would be the phase of ideal, real-valued capacitors [54]. Written in the form of a complex capacitance, the relation between the real and imaginary parts is

$$C_n(\omega) = K(i\omega)^{n-1} \quad (13a)$$

$$= K \left[\sin\left(\frac{n\pi}{2}\right) - i \cos\left(\frac{n\pi}{2}\right) \right] \omega^{n-1} \quad (13b)$$

with the pseudocapacitance K , a constant that might depend on external parameters, and the phase $\theta = -n\pi/2$ [34,55]. Hence, the parameter n , which might generally be dependent on frequency and other external parameters (e.g., temperature as explained in Ref. [38]) as well, determines the constant phase and the power of the capacitive decay in the progression of absolute impedance with frequency. Having an approximately constant phase for a larger region of frequencies does mean that the ratio of the loss is approximately frequency independent in the corresponding region [56]. Regardless of which of many properties in the system actually shows a certain random distribution (see, for example, Refs. [56–59]), the deviation from an ideal capacitance is in the end explained by a distribution of resonance frequencies in the investigated frequency range [50]. Up to now, many different models have been proposed to explain the universal approximate power-law behavior of various different classes of materials [56–59]. Independent of the actual physical model, the result is always a distribution of time constants and, respectively, resonance frequencies. In summary, the CPE is observed in cases of broad ranges of adjacent resonance frequencies, whatever their cause might be. The distribution of resonance frequencies leads to a certain connection of the dielectric loss and real part of the permittivity which expresses itself in an approximate power-law dependence on frequency and a phase $\theta = -(n\pi/2)$, that is (compare Ref. [34]),

$$\varepsilon(\omega) = \frac{Kd}{A} (i\omega)^{n-1} \quad (14a)$$

$$= \frac{Kd}{A} \left[\sin\left(\frac{n\pi}{2}\right) - i \cos\left(\frac{n\pi}{2}\right) \right] \omega^{n-1}. \quad (14b)$$

Since the system is described as an EEC, the constant phase element is expressed as a reactance:

$$X_{\text{CPE}}(\omega) = -\frac{1}{\omega C(\omega)} \quad (15a)$$

$$= -\frac{1}{i^{n-1} \omega^n K} \quad (15b)$$

$$= -\frac{1}{\omega^n K [\sin(\frac{n\pi}{2}) - i \cos(\frac{n\pi}{2})]} \\ = -\frac{1}{\omega^n K} \left[\sin\left(\frac{n\pi}{2}\right) + i \cos\left(\frac{n\pi}{2}\right) \right], \quad (15c)$$

it follows that

$$Z_{\text{CPE}}(\omega) = iX_{\text{CPE}}(\omega) \quad (16a)$$

$$= \frac{1}{(i\omega)^n K} \quad (16b)$$

$$= \frac{1}{\omega^n K} \left[\cos\left(\frac{n\pi}{2}\right) - i \sin\left(\frac{n\pi}{2}\right) \right], \quad (16c)$$

with $0 \leq n \leq 1$. In many cases, n is around 0.8 [38]. In its formulation as the impedance, it can be seen that the absolute impedance decreases with a power of $-n$ with frequency and the phase is fixed at $\theta = -(n\pi/2)$.

While the parallel arrangement of the static resistor, dynamic resistor, and frequency-dependent capacitor can be used in a broad range of frequencies (especially as long as the inductance can be neglected), combining a dynamic resistor and a frequency-dependent capacitor into a single constant phase element is justified only for the frequency range of the corresponding distribution of resonance frequencies. All polarization processes with much higher frequency (e.g., phonon resonances in the infrared range) have either to be given explicitly, as further parallel pairs of components, or, which is sufficient for most impedance spectra, all higher-frequency processes can be included into a high-frequency capacitor for the specific experiment $C_{\infty}^{(\text{exp})}$ (which is in good approximation independent of frequency if other polarization processes are sufficiently far away from the highest frequency in the investigated range; compare Sec. II E). This simplified circuit is illustrated in Fig. 2(b). The geometric capacitance C_{∞} , shown in Fig. 2(a), will be introduced in Sec. II G.

Properties of the constant phase element

For a Voigt circuit element with an ideal capacitor, the cutoff frequency can be defined as either the frequency at which reactance and resistance both have the same absolute value, the frequency where the phase is $-\pi/4$, or the frequency where the power reduces to one-half. In the case of an ideal, parallel capacitor, all definitions lead to an identical frequency. When substituting the parallel ideal capacitor by a constant phase element, this ceases to be the case.

Since for a constant phase element the lowest phase is not $-\pi/2$, the phase of $-\pi/4$ loses its importance. In the ideal capacitor case, $-\pi/4$ is the limit between the system being resistive or capacitive. In the case of a constant phase element, this situation does not even have to exist.

The frequency at which the phase becomes $-n\pi/4$ is the point where the sum of static resistance and dynamic resistance (representing the dielectric loss) becomes equal valued with the bypassing loss-free reactance. The frequency where the resistance and absolute reactance become equal valued is also not that special, since part of the absolute reactance partially belongs to the real part of the impedance.

The frequency where the power reduces to half, however, remains interesting for the manufacture of devices.

As a result, the definition where the cutoff frequency ω_{co} is defined as the frequency at which the absolute impedance has decreased from its static value $|Z(\omega \rightarrow 0|\mathcal{P})| = R_{stat}(\mathcal{P})$ to $|Z(\omega_{co}|\mathcal{P})| = [R_{stat}(\mathcal{P})/\sqrt{2}]$ is regarded in more detail. The above definition is valid only for linear, i.e., field-independent, systems [60]. For a Voigt circuit element with a constant phase element instead of a capacitor, this frequency deviates from the value of an ideal capacitor $\omega_{co}^{(ideal)} = (RC)^{-1}$. The cutoff frequency of a

constant phase element with pseudocapacitance $K(\mathcal{P})$ and $0 \leq n(\mathcal{P}) \leq 1$ is

$$\omega_{co}^{(CPE)}(\mathcal{P}) = \sqrt[n]{\frac{\sqrt{\cos^2[\frac{\pi}{2}n(\mathcal{P})] + 1} - \cos[\frac{\pi}{2}n(\mathcal{P})]}{K(\mathcal{P})R_{stat}(\mathcal{P})}}. \quad (17)$$

If the capacitor is replaced by a constant phase element, the phase at the cutoff frequency $\omega_{co}^{(CPE)}$ is

$$\theta_{co}^{(CPE)}(\mathcal{P}) = \arctan \left(\frac{-\sin[\frac{\pi}{2}n(\mathcal{P})]}{\left\{ \sqrt{\cos^2[\frac{\pi}{2}n(\mathcal{P})] + 1} - \cos[\frac{\pi}{2}n(\mathcal{P})] \right\}^{-1} + \cos[\frac{\pi}{2}n(\mathcal{P})]} \right). \quad (18)$$

G. Modeling a heterogeneous specimen

Above, it is derived directly from Maxwell's equations that a piece of nonmagnetic material can, in a frequency range around one polarization mechanism, without loss of generality be described by a parallel arrangement of one resistor for dc current transport R_{stat} , one dynamic resistor R_{dyn} , linked with the corresponding (real-valued) frequency-dependent capacitor C' , and a (real-valued) parallel capacitor $C_{\infty}^{(exp)}$, for all resonances with frequencies much higher than the highest investigated frequency $\omega_{max}^{(exp)}$.

Except for the case of broadband dielectric spectroscopy, where several resonances are observed and have to be individually described by further pairs of parallel dynamic components, this is the appropriate circuit for describing a single material in an immittance spectrum.

Impedance spectroscopy is commonly used to observe the region around an isolated first dielectric loss peak, usually broadened by a distribution of resonances which can be described by a CPE. This specific region may be described by the circuit shown in Fig. 2(b) with the following three parallel components: First is the resistor $R_{stat}(V, \mathcal{P})$ representing the dc transport in the material. This resistor shows a stronger temperature dependence than the dynamic components [38]. It is generally beneficial to find its correct dc model, because it helps to understand the underlying physics and forces a unique arrangement of circuit elements. Furthermore, it can be used to identify which circuit element represents which part of the system. In general, all known dependencies on the external parameters of every element are useful to identify the corresponding component correctly. Second is the parallel constant phase element which describes the dielectric loss peak in the observed frequency range. Third is the parallel constant capacitor $C_{\infty}^{(exp)}$ which includes the responses of all high-frequency polarization processes.

A sequential arrangement of different homogeneous pieces (e.g., different materials) leads, therefore, to a serial

connection of the corresponding generalized Voigt circuit elements. A piece does not necessarily mean a whole layer of a certain material; e.g., in a system with stacked layers of two different materials (A and B), there are often three pieces: material A, material B, and the interface of both materials. For example, the formation of barriers due to different electrochemical properties and a high number of interface states is quite common (e.g., Ref. [61]) and often leads to very different electric as well as dielectric properties of the interface. This volume has, of course, to be represented by a separate generalized Voigt circuit element with the corresponding models for dc and ac conductivity.

Sometimes other arrangements of circuit components than a serialization of the derived generalized Voigt circuit elements are used to fit the corresponding measured impedance spectra. If parameter-dependent models are introduced in the circuit elements, the fit either does not resemble the measured data at all or leads to unrealistic values for the fitted system-specific parameters. Using only resistors and capacitors, their fitted values might not look suspicious. In that case, however, each element would possibly represent multiple parts of the system. As a result, the other arrangements of elements should be used only if either finding a descriptive EEC purely mimicking the response, without any physical meaning of the values of its components, is sufficient or the geometry is not a serial arrangement of pieces. A serial arrangement of static and dynamic components for a single part of the system (homogeneous piece) is not recommended, as well: Any capacitive element in series leads to an infinite resistance for zero frequency, but the dc mechanism has to be the remaining resistance. Furthermore, the variation of the dielectric displacement field leads to an additional current through that material. It contains the free-space component of the volume between the electrodes and the additional current because of the polarizability of the material. Both are currents capacitively bypassing the dc resistor; i.e., they are zero for frequency $\omega \rightarrow 0$ and increase with frequency. In the same way the different dc transport processes are complementary, hence, parallel paths through

the same volume of material, the different polarization processes are parallel processes with their corresponding current contribution.

If one polarization process with a broad distribution of resonance frequencies is extracted into the CPE, all other polarization processes with higher frequency remain in the high-frequency capacitor. All polarization processes can be written as a sum of the corresponding parts of the permittivity [see Eq. (12)], which leads to a parallel arrangement of each dynamic pair representing a single polarization process (see Sec. II E). Hence, a parallel arrangement of the static resistor, CPE (or other pairs of separate capacitive elements which could themselves also be serially arranged), and high-frequency capacitor is preferable. Furthermore, there should not be any capacitive element in series to the dc resistance of a piece.

In a real experiment, only a finite range of frequencies can be observed. As a consequence, two deviations from the generalized Voigt circuit element can be useful.

If the highest frequency investigated is in a region which is still dominated by the distribution of resonances (that is, the CPE), it might be preferable to omit the high-frequency capacitor, since its information in the data points is limited and consequently leads to a high uncertainty for the fitted capacitance.

Parts of the investigated system may have cutoff frequencies far higher than the highest frequency $\omega_{\max}^{(\text{exp})}$ in the experiment and have only low, Ohmic resistances, e.g., leads, the metal contacts themselves, substrates. Hence, their capacitive bypasses cannot be observed, and there is no possibility to distinguish between the different contributing elements. As a result, all these parasitic resistances can be combined in a single resistor $R_{\infty}^{(\text{parasitic})}$ without capacitive bypass in series to all generalized Voigt circuit elements. The missing bypasses are, however, even beneficial if the investigation of these components is not of interest. Hence, the experiment should be designed to minimize those parasitic resistances and, respectively, increase their cutoff frequency far enough to be sufficiently higher than $\omega_{\max}^{(\text{exp})}$.

In some experimental setups, especially in electrochemical impedance spectroscopy, the system under examination is geometrically complicated and stretched out. In such cases as well as when the frequencies are sufficiently high, the introduction of a geometric capacitor $C_{\infty}^{(\text{geo})}$ spanning all parts of the system might be useful (see Ref. [5], p. 99). The smallest time constant in the EEC is then given by $\tau_{\min} = R_{\infty}^{(\text{parasitic})} C_{\infty}^{(\text{geo})}$ (see Ref. [5], p. 15). As long as $\omega_{\max} \tau_{\min} \ll 1$, the geometric capacitor might be omitted. However, the geometrical capacitance is still useful, since it can be used to normalize different geometries and it is the only purely real capacitance. This capacitance is not parameter dependent, except implicitly, e.g., if the dimensions of the system are changed through the variation of other parameters.

H. Example: Impedance of a depletion layer

In this section, the application of the proposed models on a well-known, well-understood example is presented. The characteristics of a depletion layer in silicon fulfill these criteria and are, furthermore, interdisciplinary familiar.

Both static conductivity and capacitive physical models dependent on external parameters are available for the description of a depletion layer (compare Fig. 3). In this

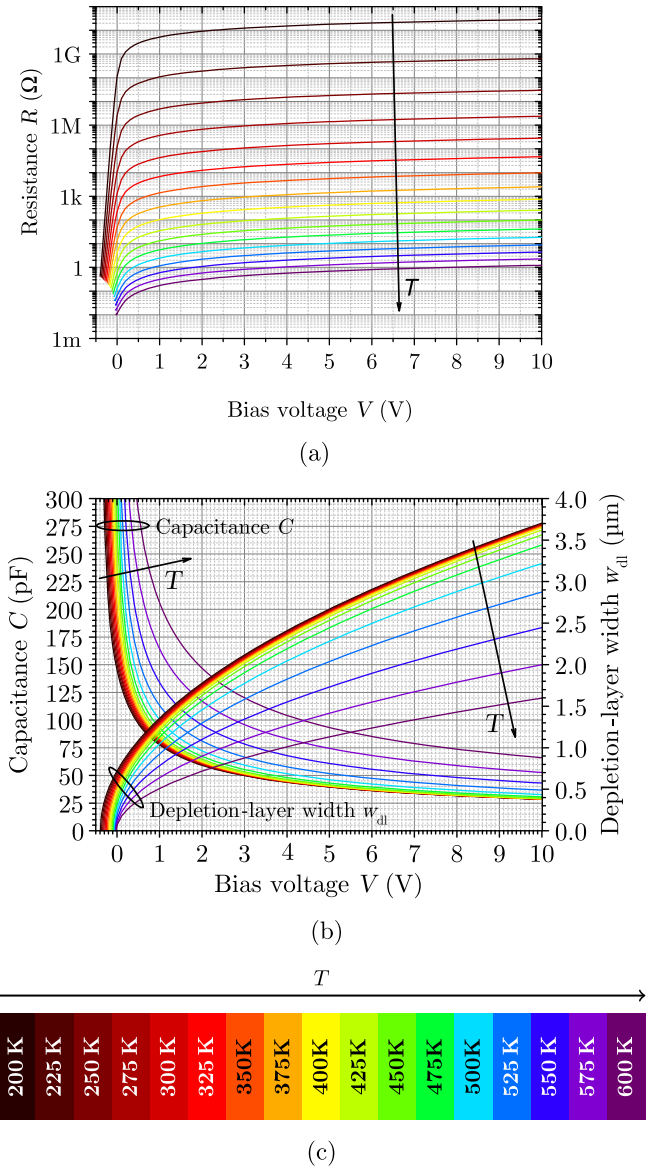


FIG. 3. (a) Resistance-voltage curve of the depletion layer described in Sec. II H for the temperatures shown in (c). (b) Capacitance-voltage curve and depletion-layer width versus voltage curve for the same depletion layer at identical temperatures. As described in Sec. II H, only the depletion layer is modeled; i.e., remaining silicon bulk is not included. The calculated resistance and capacitance are used to calculate the corresponding impedance for the depletion layer shown in Fig. 4.

example, the dependence on temperature as well as applied voltage is utilized. However, it is important to notice that it is not necessary to vary several external parameters, e.g., temperature and voltage. Depending on the sensitivity of the different components in the system on the corresponding parameters, one varied external parameter might be enough to find the one unambiguous circuit representing the underlying physics.

As explained in Sec. II G, the resistance and capacitance of the depletion layer are arranged in parallel.

The diode resistance is calculated with the thermionic emission theory assuming an aluminum/*p*-type silicon Schottky contact (see Ref. [26], pp. 255–258) with an area of 1 mm². The model is extended to allow for Schottky-barrier lowering (see Ref. [26], pp. 281–282). Furthermore, instead of assuming that all acceptors are ionized, the concentration of ionized acceptors is calculated and also concentration of intrinsic charge carriers considered using the Misiakos and Tsamakis empiric formula [62]. The effect of spin orientation and the number of hole bands is taken into account for the calculation of carrier concentrations using Fermi-Dirac statistics. All calculations for carrier concentration, Fermi level, etc., are also used for the calculation of the capacitance in the system. Since *p*-type silicon is assumed, the diode is reversely biased for positive bias voltages.

For the purpose of this example, the impedance is modeled for the depletion layer only, which means that the depth of the simulated region, the depletion-layer width, is limitlessly varying with temperature and voltage and, furthermore, that neither the leads nor the bulk silicon are simulated. As a result, the depletion-layer width converges against zero at a certain bias value which leads to a diverging capacitance. In addition, only bias voltages where a depletion layer exists are calculated, although the resistance model is valid for forward bias voltages as well. Furthermore, the selected model, the thermionic emission theory, is not suited to describe very low or very high temperatures, since other effects, e.g., tunneling through the barrier or a high-current limiting process, become important in those regions and are not included in the model.

The capacitance of the system is modeled assuming a spatially homogeneous carrier concentration in the depletion region which ends abruptly after the depletion-layer width. The same properties, e.g., carrier concentrations, Fermi level, etc., as used for the resistance of the depletion layer are used for the capacitance. Since the capacitance does implicitly include the geometric capacitance, the simulated circuit to calculate the impedance of the depletion layer looks like the circuit shown in Fig. 2(b). In a real depletion layer at a metal-semiconductor interface, there is likely to be some random element (e.g., random fluctuations of the doping concentration, interface roughness, etc.) which might lead to a constant phase element

with a slope of the capacitive decay very close to unity rather than an ideal capacitor. As there is no theoretical prediction for that value and its temperature dependence in this specific case, unity is chosen for the simulation.

The resulting resistance and capacitance for the depletion layer of the system can be seen in Figs. 3(a) and 3(b), respectively.

Assuming impedance, the spectra of a depletion layer in silicon with the above properties are measured for different voltages and temperatures.

The *classical analysis*, which is often omitted [4], is to fit the resistance and capacitance of the ideal, lumped resistor and capacitor in the Voigt circuit for different external conditions. Subsequently, the system-specific parameters (e.g., the Schottky barrier height) of the resistance model would then be optimized to fit the experimentally found resistance of the different conditions. Then, the same would be done with the capacitance [63].

In the *presented approach*, the models are combined to calculate the impedance of the system for different conditions (see Fig. 4). Subsequently, the whole data are fitted with the combined impedance model in a global fit. It might seem unnecessarily complicated for this very simple example, since only one separate part of a system is analyzed, which could never be separately measured like this. Real systems, on the other hand, consist not only of a single part but various parts and parallel transport processes per part, etc., which make ascribing different processes separately to the corresponding idealized lumped components almost impossible. The differences and advantages of this approach for this example are now discussed in detail. A general comparison of this approach with analysis using conventional EECs consisting solely of idealized lumped components can be found in Sec. III C.

Figure 4 shows the impedance of the depletion layer in a parameter-dependent Bode plot. For low temperatures, the impedance is capacitive. At 100 K, the phase is -90° and the absolute impedance has a slope of -1 in the direction of increasing frequency for almost all parameter values. Mainly due to the high static resistance, the cutoff frequency is even smaller than 10 Hz. For gradually increasing temperatures, the absolute impedance is decreasing, while the phase is increasing for each parameter point. The absolute impedance surfaces do not cross each other; the phase surfaces merge at -90° and 0° . Since the capacitance of the depletion layer is less strongly varying with temperature than the resistance (compare Fig. 3), it seems as if all absolute impedance values cling almost to the same layer of capacitive bypass. In other words, with higher temperatures the cutoff frequencies are increasing in frequency mainly due to changes in the resistance. For high temperatures the resistance is so low that the cutoff frequencies are higher than 1 GHz. For low bias voltages, the resistance is rapidly decreasing. In this region the resistance is so low that it is resistive for all temperatures up to the highest plotted frequency.

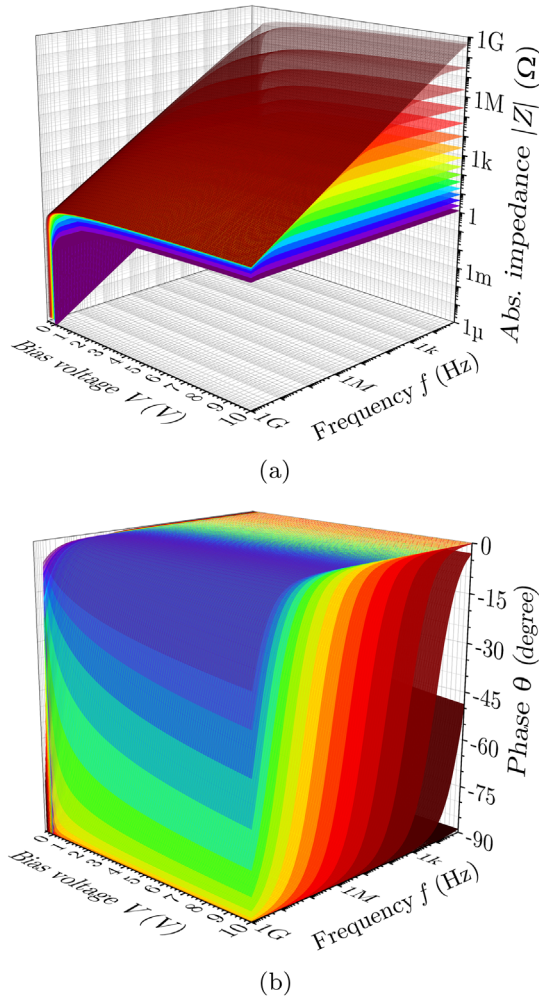


FIG. 4. (a) Absolute impedance of the depletion layer described in Sec. II H versus frequency and bias voltage for the temperatures listed in Fig. 3(c). (b) The corresponding phase versus the same parameters for identical temperatures. The parallel pair of resistance and capacitance shown in Fig. 3 are assumed. The capacitance does implicitly include the geometric capacitance. As a result, the simulated circuit looks like the one shown in Fig. 2(b).

The parameter-dependent model for the static resistance of the depletion layer and its capacitance is dependent on various different parameters which we can divide into four different groups: *natural constants*, *system-specific parameters*, *external parameters*, and *fit parameters* (a subset of the system-specific parameters). Natural constants are of course fixed and tabulated. System-specific “constants” are the temperature-dependent band gap of silicon $E_g(T)$ (its equation is given in Ref. [26], p. 15), the temperature-dependent intrinsic carrier density $n_i(T)$ given in Ref. [62], the effective masses of silicon for holes $m_h^{(\text{eff})}$ and electrons $m_e^{(\text{eff})}$, respectively, given in Ref. [64], the permittivity of silicon, given, e.g., in Ref. [26], p. 849, the acceptor concentration N_A usually specified by the wafer supplier (here an acceptor concentration of 10^{15} cm^{-3} is assumed), and its energetic distance to the valence band E_A , usually tabulated as well

(here Ref. [65], p. 416, is used). With the exception of the acceptor concentration N_A , all these values come from literature sources and should not be used as fit parameters.

The external parameters are in the simulated case here the temperature T and the applied bias voltage V . These parameters are set by the conditions of the experiment. The temperature can usually be set explicitly but the applied bias usually only indirectly, since in an experiment other components might be in series.

There is only one fit parameter for both the static resistance of the depletion layer and its capacitance, the Schottky barrier height Φ_{SK} . It depends not only on the involved materials at the interface but is also known to be dependent, e.g., on the deposition method. In a conventional EEC, the static conductivity is modeled by a resistor and a parallel capacitor (and the geometric capacitance). The corresponding resistance and capacitance are fitted. These values can describe the depletion layer correctly only at one point of the parameter set $\mathcal{P}_0 \in \mathbb{P}$; here $\mathcal{P}_0 = (V_0, T_0) \in \mathbb{V} \times \mathbb{T}$. For each other point in parameter space, two additional fit parameters are necessary (compare Fig. 5 and Sec. III C), and due to circuit ambiguity they might even not be only for one part of the system but for a number of different parts. With the parameter-dependent model, only one fit parameter describes the full parameter space. Furthermore, this parameter is neither a resistance nor a capacitance, potentially representing a combination of different parts, but a physically meaningful parameter like the Schottky barrier height. Since the models are fitted against the measured data, the physical constant is, in the margin of the accuracy of the fit and if the global minimum of residuals is found, the statistically best guess for the assumed models.

Since the model for the capacitance uses (a subset of) the same parameters as the static resistance and represents the same physical phenomenon as the resistance, both models cannot accidentally include other parts of the system. Hence, the resulting circuit is not only *unambiguous* but is also forced to represent the *underlying physical processes* correctly.

Another example: Assuming the acceptor concentration is unknown, it is a fit parameter as well. Fitting experimental impedance data for a range of different bias voltages and/or temperatures gives directly the best guess for the acceptor concentration for the used model. Since this parameter is present in the capacitance as well as in the resistance, it shows how well the model is suited for the experimental situation.

As already mentioned before, it is important to notice that it is not necessary to vary several external parameters, e.g., temperature and voltage. Depending on the sensitivity of the different components in the system on the varied parameter, one varied external parameter might be enough to find the one unambiguous circuit representing the underlying physics.

III. DISCUSSION AND OUTLOOK

D. Macdonald reminds us that the ultimate goal of electrochemical impedance spectroscopy is to find the underlying mechanisms [4]. Furthermore, the mere creation of an analogue, that is, without further analysis any EEC reproducing the measured impedance spectra, would represent an incomplete analysis of the data [4]. It is the opinion of the authors that these points of criticism should not be limited to the analysis of electrochemical impedance spectra but extend to other scientific branches of impedance spectroscopy as well.

Of course, immittance spectroscopy is applied not only in science and research. For some applications in engineering, for example, the device under test might only be a small part of a larger system and understanding of the processes involved in that part is not of interest. Instead, the goal is to know as precisely as possible how this part reacts under certain operation conditions. In that case, a descriptive model (D. Macdonald calls this an analog; see Ref. [4]) is sufficient, and the primary criterion is a good approximation of the impedance response. It should, however, be noted that the extraction of statements over underlying processes from a descriptive model involves certain risks and should be avoided.

The goal in science is usually to understand the underlying mechanisms which lead to the specific immittance of the system under investigation [4]. Therefore, an explanatory model has to be found. This work proposes an approach to finding explanatory models.

Taking up the differentiated discussion from Grimnes and Martinsen (see Ref. [10], pp. 284–286) over different approaches to devise models, the suggested model is similar to what they call “model 2,” which is a special case of “model 1.” Different from their suggestion of representing only the largest contributions, the proposed model replaces, if possible, the parts of the EEC with the largest contributions by physical models including their dependence on external parameters. However, other parts are not omitted but simply still represented by idealized lumped components. If the significance of the latter is of minor importance, this usually also means that they do not have a pronounced part in the immittance spectra. A typical reason for that is, for example, that the cutoff frequency is far from the boundaries of the measurement range. In such a case, all parts of minor interest which have much higher cutoff frequencies than the maximal frequency in the experiment can be lumped in a serial resistor, since they are all resistive in the measured frequency range and with respect to frequency indistinguishable. In contrast, all parts not of interest which have much lower cutoff frequencies than the minimal frequency in the experiment can be lumped in a capacitor, since they are all capacitively bypassed. Naturally, the measured frequency range should include all cutoff frequencies of parts of the system which are of interest.

A. Validity of describing J_{free} with the corresponding dc current model

Beginning in Sec. II A, the two terms on the right-hand side of Eq. (1) are identified as exclusively representing dc and ac properties of the material. This interpretation is continuously used in all following equations up to the final general EEC for a piece of nonmagnetic material. Although this separation is used by Jonscher (see Ref. [34], pp. 40–41) (and J_{free} had even been already linked with Ohm’s law by Maxwell in 1865 [32]), it can be only an approximation. Maxwell explicitly ascribes the polarization to the dielectric displacement [32]. However, he only mentions the proportionality of the free current and applied field (“electromotive force”) with the proportionality constant of “specific resistance” ρ , that is, using the syntax in this manuscript, for a homogeneous, isotropic material [32]

$$\mathbf{J}_{\text{free}} = \rho^{-1} \mathbf{E}. \quad (19)$$

In Maxwell’s publication [32], there is no restriction that the specific resistance might not be dependent on the frequencies of the stimulating signal and that it has to be identical to the dc value. In this paragraph, it is shown that the interpretation of Jonscher as the dc value ($\mathbf{J}_{\text{free}} = \sigma_{\text{dc}} \mathbf{E}$) is in the frequency range of dielectric relaxation, which is the only frequency regime considered in his book, a valid assumption.

Inserting the dc conductivity means assuming that the dc current transport mechanism, independently of the frequencies of the applied signal, creates a current completely *in phase* with the driving field. Furthermore, at any given point in time, the current corresponds to the dc value for the currently applied field.

Two classes of materials are considered. For systems where conduction is through delocalized states, i.e., metals, the dc conductivity can be applied up to frequencies that are sufficiently smaller than the inverse of the damping constant (which is in the terahertz range) (see Ref. [51], p. 21). In a system with conduction through localized states, this separation is valid as long as the inverse of the frequency of the stimulus is large compared to the frequency for which the absorption or emission of modulation quanta (see below) is possible. The validity of the separation in a material that is dominated by hopping or detrapping of localized charges is now considered in more detail. An important time constant in such a system is the *lifetime* of an occupied trap, that is, the time in a trap before the charge performs the jump to the next trap or the corresponding conductive band. From the lifetime of the charge in the trap (and the corresponding trap density, occupation, attempt to jump frequency, energy differences, different final states, etc.), one can calculate a jump rate r_i for charges in traps. Generally, the jump rate $r_i(\tilde{\mathbf{E}}(t), \tilde{\mathcal{P}}(t))$ might depend on external parameters, e.g., the applied field and temperature.

The total number of successful jumps in a time interval (t_1, t_2) can be calculated by integration:

$$n_i = \int_{t_1}^{t_2} r_i \left(\tilde{\mathbf{E}}(t), \tilde{\mathcal{P}}(t) \right) dt, \quad (20)$$

even for frequencies higher than the jump rate. These higher frequencies just lead to a reduced total number of successful jumps. Each possible conducting path in the material has a rate of charges it can conduct in a time interval, i.e., a contribution to the total current density, based on all individual jump rates. Analogue to the above explanation for a single trap, this does not invalidate the assumption of $\mathbf{J}_{\text{free}}$ being calculable by dc conduction models. For even higher frequencies, there are two mechanisms that could invalidate the separation.

According to Büttiker and Landauer, a *traversal time* is needed for the trapped charge to actually traverse the barrier [66]. As long as the frequency of the applied field is much lower than the inverse of the traversal time and below frequencies to emit or absorb modulation quanta, the total number of successful jumps in a time interval can still be calculated by Eq. (20), and the charge in the trap sees an effectively static barrier [66]. When the inverse of the frequency of the applied signal is in the same magnitude or even higher than the traversal time, a charge in a trap continues to see effectively the same barrier [66]. However, it can absorb or emit modulation quanta which changes the probabilities of jumps and, hence, also the jump rate [66]. Not because of reaching field periods in the order of the traversal time [67], but because of reaching the frequency range where the emission and absorption of modulation quanta is possible (the corresponding time constant does not necessarily have to be in the range of the traversal time), the dc current models in the material can in the latter frequency range not be used to calculate $\mathbf{J}_{\text{free}}$. According to the definition in Ref. [34], p. 6, the dielectric relaxation is the “‘low-frequency’ subquantum” limit and therefore ends for frequencies below the above-described interaction with modulation quanta. For frequencies around or larger than this modulation quantum regime, the conductivity $\sigma_{\text{stat}}(\mathbf{E}, \mathcal{P})$ in Eq. (6) has to be replaced by a dynamic conductivity $\sigma_{\text{dyn}}(\omega, \mathbf{E}, \mathcal{P})$ which depends on the frequencies of the stimulating signal but should still describe only the conduction processes contributing to the free current. As a result, the assumed separation of the dynamic part exclusively in $\partial \tilde{\mathbf{D}}/(\partial t)$ and the static part in $\tilde{\mathbf{J}}_{\text{free}}$ breaks.

Assuming dissipative tunneling introduces a friction coefficient γ and might lead to longer traversal times and decreased transmission rates [66]. It does, however, not change the frequency limit as described above. Dissipative tunneling is highly probable in any real material, since energies or (directions of) momenta of the final and initial states are likely not identical. In such a case, the hopping process must, independently of the

frequency range, be assisted by phonons, etc., to ensure conservation of momentum and energy. With this in view, the definition of Jonscher (see Ref. [34], p. 6) for the dielectric relaxation to be in the “subquantum limit” might be misleading.

B. Underlying mechanisms for polarization and static charge transport

Interestingly, the same jumps that lead, over a longer path of (spatially or energetically) randomly arranged states, to a direct current can also contribute to the polarization. For higher frequencies, jumps over undesirable barriers (high or wide) are too slow, so that the carriers preferably oscillate only in regions of easy jumps [68] or even perform jumps only between pairs [69]. This results in the formation of dipoles (induced polarization) in these regions of easy jumps. The sum of these microscopic dipoles leads to a macroscopic polarization (see Ref. [51], p. 16). A previous example illustrates that the static current at low frequencies and the polarization at higher frequencies can be, and often is, due to the same mechanism (see the Barton-Nakajima-Namikawa relation in Ref. [70]). Since these jumps are phonon assisted [38] as well as noninstantaneous, they result in the dissipation of energy into heat in the static as well as in the dynamic case. As explained, this forces the electric displacement field, or, more precisely, the polarization, to be a complex quantity.

C. Comparison with conventional EECs

Conventional EECs use solely idealized lumped components, like ideal resistors, ideal capacitors, or constant phase elements. A resistance is a first-order approximation of a current transport process and, hence, a physical model, though not one dependent on external parameters. Thus, conventional EECs can also be, and often are, explanatory models.

If the system is studied at different conditions (sets of external parameters), the resistance changes according to the parameter dependence of the underlying process (compare with the examples in Table I). For each different condition, the value of each component, e.g., the resistors, is determined by refitting the same arrangement of components to the experimental data acquired under the corresponding condition, resulting in a potentially large number of fitted parameters equal to the number of values of components in the circuit times the amount of different conditions (see Fig. 5). It is well known that circuits consisting only of idealized lumped components are ambiguous [20]. Since another arrangement of the same components can lead to an equally good agreement, one cannot be sure whether in the selected arrangement the resistance really is the first-order approximation of a charge current process. Although J. Macdonald suggests to vary the bias voltage and/or temperature to identify the correct arrangement of components, in many experiments the

Example: Fitting the impedance of a depletion layer at 10 temperatures and 50 bias voltages

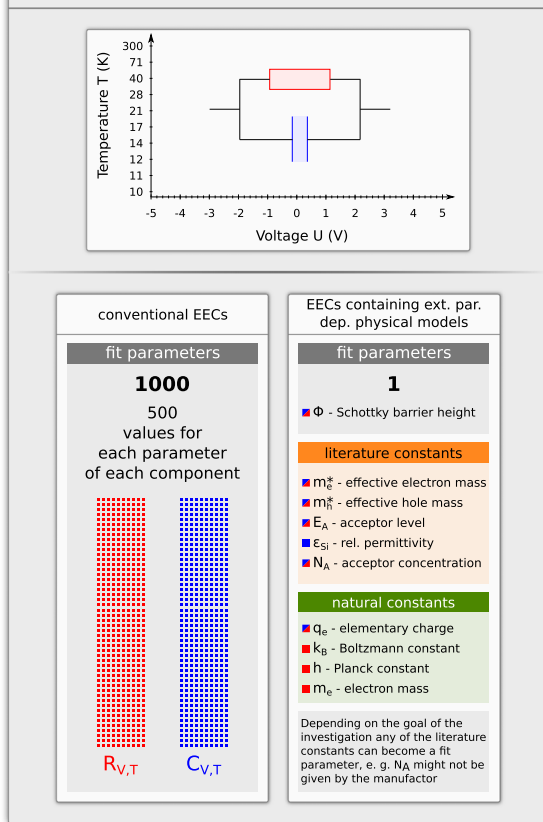


FIG. 5. Typical practical example: Fitting a depletion layer using the shown circuit for ten different temperatures and 50 different bias voltages (see the axes representing the parameter space, temperatures equidistant in the reciprocal temperature scale). A small square corresponds to a fitted parameter value. On the left side, the system is described by using a conventional EEC containing only idealized lumped components. The values for the resistive (red) and capacitive (blue) components are independent of each other. On the right side, the models dependent on external parameters are used for resistive and capacitive elements. The *one* remaining fit parameter characterizes resistive and capacitive properties simultaneously (half red and half blue squares), resulting in a consistency check of whether the correct processes are assumed.

frequency of the signal is still the only varied parameter. If other dependencies are used, there are still challenges: Often, there are multiple different transport processes, even in a single homogeneous part of a system, and the resulting parallel resistors are impossible to separate in a model consisting only of idealized lumped components. As a result, the obtained resistance is a combination of several first-order approximations of charge-transport processes and the single contributions cannot be extracted. Aside from multiple processes in one homogeneous part, it can also not be ruled out that several processes forming different parts of the sample are simultaneously described by one component.

Although there are certain challenges using conventional EECs, it has been and still is a major pillar for the analysis of experimental immittance data. The process of finding the right arrangement of idealized lumped components and the subsequent look at the resulting resistances and capacitances (and their change with alteration of certain external parameters) are usually the most enlightening phases during the analysis of immittance spectra. The presented approach should rather be seen as a valuable supplement, that eliminates certain risks, than as a replacement of the analysis with EECs consisting solely of idealized lumped components.

Alternatively to the first-order approximation of a current process by a resistance, one might use process-specific physical models dependent on external parameters. In that case, the values of the components, e.g., resistances, are not fitted separately for each condition, since the progression of values with the variation of an external parameter is prescribed by the model. Instead, the measured data for all conditions are globally fitted to extract the parameters of the underlying physical model which are system specific and cannot be found in the literature. In the case of the impedance of a depletion layer (see Fig. 5), only the Schottky barrier height has to be fitted. If the part of the system really is a depletion layer, then with only one fit parameter the resistive as well as the capacitive contributions to the impedance are described correctly within the possibilities of the model. The fact that both resistive and capacitive components are fitted by the same parameters also verifies consistency, ensures that only one specific part of the system is modeled by the components, and makes sure that the right processes are assumed. In comparison, the modeling with idealized lumped components can reach a better resemblance, since there are no restrictions imposed by the model or arrangement of components, and parameters are optimized for each condition separately. If the researcher is not interested in how the part of the system works but just wants to model the response, a conventional EEC with separate fits for every condition might be superior due to a better approximation of the measured results. On the other hand, a larger set of conditions leads to a very high number of fitting parameters. In order to identify the transport process, some authors analyze the progression of the value of certain fitted components in the conventional EEC, e.g., by fitting a resistance over temperature. Correlating the progression of the value of a component with physical models *after* fitting the parameters of the EEC then gives the parameters of the underlying model. This intermediate step through local fits leads to either the same parameter or, more likely, a less accurate one, due to information loss in the intermediate fits, e.g., by partially wrongly assigned contributions to different components. In comparison, in a global fit with the parameter-dependent physical model, wrongly assigned contributions are not as likely since the model is more

restrictive. Furthermore, all data points are used directly to extract the relevant parameters. The problem of separating parallel processes is also resolved, since different transport processes have different dependencies on external parameters. One only has to find the relevant external parameters to vary. It is also not necessary to know every transport process in the system. Only relevant models, or even one relevant model, dependent on external parameters have to be included. A subsequent look at the residuals can then help to identify the missing processes, and they can then be added accordingly. A requirement for the presented approach is that it becomes obligatory to analyze the system under different conditions that have to lead to distinguishably different behavior of the corresponding processes. Furthermore, the possibly involved processes must be known.

D. Comparison with Poisson-Nernst-Planck models

Poisson-Nernst-Planck (PNP) models are a group of process-independent models that can be used to analyze immittance data and extract relevant physicochemical parameters from any material exhibiting one dominating transport process for each of the up to two charge carriers with opposing signs.

The development of these models started in the 1930s [21,72]. The first version by Jaffé [21,72] is not intended to

be used with electrolytes. Hence, discharges of the charge species at the surfaces are prohibited. A first step to make the theory applicable to electrolytic solutions was done in 1952 by the same author together with Chang [73] by including discharging at the surfaces. In 1953, J. Macdonald extended the model of Chang and Jaffé to describe the situations of electrolytes more realistically [24]. Different mobilities for the charge carriers (since they can be arbitrary, one species might be immobile), incomplete dissolution of a neutral species into charge carriers of opposing sign, and generation and recombination of the charge carriers are included. The next milestone in the development of PNP models to describe immittance data was done in 1978 [23]. The charge carriers of arbitrary valence can be generated from and recombined into neutral centers, as well as immobile charged donor or acceptor centers. Although PNP models for analyzing immittance data have incrementally been refined to account for more and more details, like anomalous diffusion processes, they have not yet found widespread application in the analysis of experimental data [22].

PNP models are based on a fundamental microscopic interpretation of a system and can, as a result, be used to interpret a wide range of matter, including semiconductors, electrolytes, or ionic conductors. For given boundary conditions and surrounding effective medium (continuous,

TABLE I. To clarify what is meant by process-specific physical models dependent on external parameters, a few examples of such models for current transport processes in solids and their interfaces, which are commonly found in dielectric films in CMOS technology, are given [71]. All these models have a nonlinear dependence on the applied field and, hence, show the importance for allowing nonlinear field dependence in the derivation. Symbols: μ , electron drift mobility; N_C , density of states in the conduction band; $e\Phi_T$, trap energy level; $\epsilon_r^{(d)}$, dynamic relative permittivity (at frequencies of visible light); a , mean hopping distance; n , electron concentration in the conduction band; ν , frequency of thermal vibration of electrons at trap sites; d , thickness of the dielectric thin film; A^* , effective Richardson constant; $e\Phi_B$, Schottky barrier height; h , Planck constant; and m_T^* , tunneling effective mass in the dielectric.

Bulk-limited conduction processes
Frenkel-Poole conduction:
$J_{FP}(E, T) = e\mu(E, T)N_C E \exp\left\{(-e/k_B T)\left[\Phi_T - \sqrt{eE/\pi\epsilon_r^{(d)}\epsilon_0}\right]\right\}$
Hopping conduction:
$J_H(E, T) = ean(T)\nu(T) \exp\{(-e/k_B T)[\Phi_T - aE]\}$
Trap-filled limited/space-charge limited conduction:
$J_{TFL/SPL}(E, T) \propto \mu(E, T)(E^2/d^5)$
Electrode-limited conduction processes
Schottky emission:
$J_{SE}(E, T) = A^*T^2 \exp\left\{(-e/k_B T)\left[\Phi_B - \sqrt{eE/4\pi\epsilon_r^{(d)}\epsilon_0}\right]\right\}$
Fowler-Nordheim tunneling:
$J_{FN}(E) = (e^2 E^2 / 8\pi h \Phi_B) \exp\left[-\left(8\pi\sqrt{2em_T^*}/3hE\right)\Phi_B^{3/2}\right]$
Thermionic-field emission tunneling:
$J_{TE}(E, T) = \left(e^2\sqrt{mk_B T}E/2h^2\sqrt{\pi}\right) \exp\{(-e/k_B T)[\Phi_B - (e\hbar^2 E^2/24m(k_B T)^2)]\}$

mean-field), the equations for the point-charge distribution, and the resulting movement of the point charges by drift or diffusion, are directly solved. Charges can be mobile or immobile, and recombination and generation into or from charged or neutral centers can be included in addition to reactions at and interaction with the surfaces. Instead of resistances and capacitances, fitting with PNP models gives physical constants like the reaction rates and density of charge carriers as well as their mobilities and valences and the density underlying neutral undissolved species.

In general, PNP models are extremely versatile and limited only by the effective medium approach and the disregard of the spatial extent of the species. Any processes that can be described in an effective medium theory should be possible to include. By utilizing finite element methods, also inhomogeneous systems can be modeled with PNP equations. In principle, nonlinear models, like Frenkel-Poole conduction or Schottky emission, could be included by introducing carrier generation dependent on the local field in the bulk or at boundaries. They then profit from the application of the specific local fields.

It is the scope of this work to find unambiguous EECs. Hence, theories should take the form of lumped components, as some solutions of PNP equations for specific problems do [23]. In the remaining part of this section, only those PNP models are discussed. Furthermore, the applicability of PNP models using point charges in situations like electrochemical double layers is not evaluated.

To gain useful values for the mentioned parameters of the PNP model, several requirements have to be fulfilled. The boundary conditions must apply. The material should have only one dominating process of transport for each of the mobile charges. There should be only the species present that are included in the model.

Assume a material where several processes lead to the migration of mobile negative charges, e.g., electrons hopping through localized energy levels (variable range hopping [74]) and electrons that are thermally and field-assisted excited into the conduction band or over the mobility edge (Frenkel-Poole conduction [37]). Using the usual PNP model still gives a value for the mobility and a concentration of charge carriers, but they are only effective values [75]. Parallel arrangement of PNP models, on the other hand, leads to coupling between the parameters.

There are two solutions to get the different transport processes decoupled. The first one is directly the one suggested in this work, instead of PNP models. Include the corresponding parameter-dependent transport processes as parallel parameter-dependent resistances in the part of the equivalent circuit that should describe the material [76]. Subsequently, fit the parameters of the model that cannot be taken from the literature or those that shall be determined anyway. In the above example, the density of defects that participate in the variable range hopping and the concentration of defects from which electrons are thermally

excited can both be decoupled and, therefore, extracted separately. Furthermore, the energetic distance to the mobility edge of the defects that are involved in the Frenkel-Poole conduction process are obtained. At least a hint to the decision about whether the same traps participate in both processes or that different traps are involved in the processes is then given by the determined energetic distances to the conduction band or mobility edge, respectively.

In addition to the use of the pure concept presented in this work, a combination of that concept with PNP models is possible and presented in the following paragraphs.

Sometimes, specific physical processes that define the internal properties, like the number of carriers, are known. The Frenkel-Poole process increases the number of electrons in the conduction band dependent on the applied field and temperature [37]. Also, the rate of electrons injected into the material from the electrodes can depend on the applied field and temperature (see Ref. [26], pp. 250–254).

The central idea of this work, i.e., including process-specific physical models dependent on external parameters, can be applied to PNP models as well. In semiconductors, the mobility and number of mobile charge carriers is dependent on the temperature and the total donor concentration. Utilizing the main concept of this work, instead of fitting mobilities directly (where, e.g., a set ten of different temperatures would result in ten different fitted mobilities), insert the physical model for the mobility in the PNP model. As a result, the general dependence of the mobility and number of carriers on temperature is given by the underlying physical model. Furthermore, the donor concentration is a parameter in the mobility and quasifree electron concentration as well. The donor concentration is, hence, correlated with two distinct properties in the system and forces self-consistency. Similarly as for the mentioned, well-known example of mobilities and charge carrier concentrations in semiconductors, many restrictions through dependencies on external parameters can be found for various materials and processes.

Instead of fitting parameters ignoring the external dependencies and interpreting them afterwards, it is suggested to include the physics as early as possible to include self-consistency, understand the underlying physical processes, and fit globally, resulting in better estimates for the physically relevant parameters. If the model does not fit, either the model cannot be applied to the system and extracted parameters would not have the expected interpretation anyway, or the system consists of more parts or has more processes than expected. The former suggests using different models; the latter forces one to reevaluate the expected structure or processes. In either case, more information is gained, since the PNP fit would just map anything on the available fit parameters. In short, process-specific models impose more restrictions which, as a result, make it easier to validate if the model can be applied. The

price is the requirement to measure at a sufficient number of different external conditions.

Whether the presented approach is used directly or in combination with lumped PNP models, the dependence on external parameters can decouple parallel processes, allows global fitting of all data at once, and automatically weights the importance of the specific parameters in certain regions which in the end leads to better guesses for the important physical parameters.

In contrast to the usual lumped PNP models, the advantages are global fits with automatic weighting, understanding the underlying physics by being process specific, easier validation of whether the model is applicable, and, dependent on the process, further information is gained, e.g., the involved energetic levels for charge carrier generation.

E. Summary and conclusion

In this work, a method of devising EECs is introduced, where the underlying physics is directly attached to its components. It is known that analyzing more external parameters than solely the frequency eliminates circuit ambiguity [20], and at least the additional bias voltage dependence used also in the example of this work could easily be included in most of the existing experimental setups. The introduction of process-specific physical models themselves as components of the EEC guarantees that the underlying physics is recognized. Furthermore, it allows one to extract the relevant physical constants directly. That is, instead of using information of certain regions, all data points are used, resulting in a statistically better guess of the optimized parameters. The analysis of EECs with idealized lumped components can, however, create lower sums of squared residua and respectively better approximations. In applications where a good approximation is more desirable than the understanding of the system, the approach with those components can be superior. The close resemblance of such calculated data with measured data is, however, deceptive, since a better approximation does not necessarily mean a better understanding of the system. On the contrary, when using parameter-dependent models, the deviations from the measured values can be used to identify missing processes.

The presented idea is not only beneficial for EECs but can also be applied to PNP models. In that case, external-parameter-dependent physical models, e.g., for the mobility of a conducting species, can be included in the PNP model. In the end, the resulting PNP can be globally fitted to the immittance spectra for various conditions.

The introduction of voltage-dependent models in the EEC does even open new possibilities. As the variation of an element with voltage is known, large-signal analysis respecting the underlying physics lies within one's reach. Since the applied signal is time dependent, the voltage currently applied at each component varies, and the response of the component to it is included in the model.

The logical next step is to exploit this new possibility. Combining time-domain simulations (especially including the progress of the states of charge of the capacitors with time) with the proposed layout of EECs containing models for fitting the impedance is believed to have great potential.

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- [1] Immittance is a coinage by Bode that should generalize the equivalent representations of *impedance* and *admittance* [2]. Later, it was generalized further as a designation for any equivalent representation of the impedance, most importantly, admittance, (complex) permittivity, (complex) conductivity, and modulus [3]. Since this work focuses on electrical immittance spectroscopy, the prefix “electrical” will be omitted for any type of immittance.
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