



A Physical Derivation of the Capacitive Brick Layer Model in Polycrystalline Ceramics from Fundamental Electrodynamic Equations

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The brick layer model in electrochemical impedance spectroscopy has been successfully used for decades to describe the behavior of polycrystalline materials. Equivalent circuits were created to obtain information about grain and grain boundary properties from electrochemical impedance spectroscopy measurements. Previous publications have expanded on initial interpretations and described grains and grain boundaries as plate capacitors filled with the grain and grain boundary material, respectively. However, this approach poses a number of significant issues, since key assumptions for the equivalent circuits do not match with the actual experimental situation of the material when exposed to an outer electric field, thus calling into question the entire approach for the interpretation.

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Manuscript submitted August 1, 2022; revised manuscript received September 23, 2022. Published October 12, 2022. *This work presents a physical derivation of the capacitive brick layer model exclusively based on fundamental equations of electrodynamics, and shows the real material-related reasons for the capacitors used in electrochemical impedance spectroscopy.*

Electrochemical impedance spectroscopy (EIS) is one of the main techniques used to analyze inorganic materials, especially polycrystalline samples, in order to distinguish, for example, grain and grain boundary properties. The brick layer model represents a simplified outline of the polycrystal that helps with the interpretation of results detected by EIS. The first approach for describing the experimental findings was introduced by Bauerle et al.¹ and an outline was described for *two* grains largely separated by *one* thin layer comprised of entirely different material and properties compared to the grains. An associated model was then derived for an equivalent electric circuit for the bulk and the interphase layer: The interlayer phase was assumed to be insulating, meaning that parts of the conductive grains separated by the interphase appeared to be like tiny plate capacitors. The key conclusion drawn was that such a geometry would deliver another equivalent circuit, and that the time constant of the equivalent circuit needed to be different from others in order to explain the EIS measurements. It is important to emphasize that only *one* additional capacitor resistor set is derived for a combination of good-conducting and insulating media within this interpretation. The brick layer model was subsequently developed in more detail by many other research groups e.g.,^{2–11} including polycrystals, where single-crystalline grains were separated by grain boundaries. For the latter case, this is a significant expansion of the model of Bauerle et al., since there are no longer any conductive grains with distinct regions with immediate contact and other regions where they are separated by insulating phases/voids. There are instead phases that continuously separate the grains and that are also conducting. In contrast to the initial model of Bauerle et al. with *one* additional capacitor resistor set, such a combination of two grains separated by a grain boundary was described by *two* additional capacitor resistor sets (as seen in Fig. 1). This accordingly leads to *two* semicircles in the Nyquist plot. The grains and grain boundaries may have “plate capacitors” directly associated with details of their microscopic properties: for example, the thickness of the uniform region is equal to the distance of the plates of the “plate capacitor” or the permittivity inside the “capacitors” is equal to the permittivity of the grains and grain boundaries, respectively. This is corroborated by the fact that the ratio of time constants roughly scales well with the ratio of the

widths of the grains and grain boundaries, respectively (here, “roughly” means that the individual ranges are given as several orders of magnitude in capacitance values¹⁰).

When taking a closer look at the actual microscopic situation in such a system, a number of questions can arise: Are there “capacitor plates” that can be charged (fast enough) despite all phases being somehow conductive? If yes, then the capacitors cannot be independent of each other (generally speaking the right plate of one capacitor is identical to the left plate of the next one). Why does the “outer capacitor” (i.e. the metal connect plates with the sample in between, where the current leads of the impedance spectrometer are connected) never appear experimentally in the case of blocking electrodes in the Nyquist plots of EIS measurements or in the equivalent circuit? It is a real capacitor with a capacitance in the range of 10% of the capacitance associated with the grain capacitance in EIS. The material in this real capacitor, when polarized, exhibits surface charges that have the *opposite* sign of charge of the outer capacitor, which means that it has the “wrong” sign of charge compared to a real capacitor in an electronic resistor capacitor resonator circuit. Since Coulomb forces are long range, virtually *all* available charges need to be considered in order to calculate the actual electric fields in the sample. And why can thousands of grains and grain boundaries be gathered so efficiently by just one capacitor instead of sophisticated networks of tiny capacitors?

The aim of this work is to derive the capacitive brick layer model from fundamental equations for the description of electrical fields. The derivations show the opportunities and options for expanding the brick layer model as well as its prerequisites and limitations.

The following descriptions also contain a summary of very basic calculations of capacitors and a review of well-known characteristics. Nevertheless, they are important for assessing which properties of capacitors and materials and which assumptions are actually required.

Derivation of the Capacitance of a Capacitor Filled With Two Different Materials

It is clear that these two types of charge carriers are distinct in their electric properties, and it is therefore reasonable to describe them separately, such as in two “bands.”

We will now focus on the charge carriers that create polarization and do not move macroscopically, which means that this part of the sample can be regarded as insulating. An insulating material with

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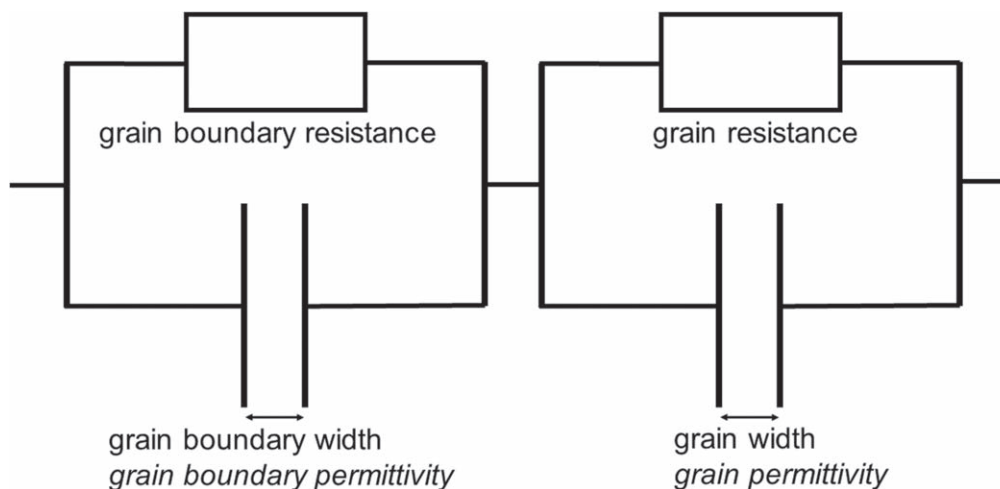


Figure 1. Typical equivalent circuit for the description of grains and grain boundaries in polycrystals analyzed by electrochemical impedance spectroscopy.

charges that can be slightly displaced by an electric field is referred to as *dielectric*.

The next paragraph is a short review of the derivation of the capacitances of capacitors, including certain materials with dielectric properties, taken from.^{12,13}

The first assumption is that the system acts in a linear manner (i.e. all equations including differential equations are linear), the electric field behaves like a vector, and the principle of linear superposition is given.

Here, we consider one plane of negligible thickness with an “infinite” planar extension that is positively and homogeneously charged with a certain areal charge density s , and no other charges are present anywhere. The term “infinite” here means that the extension may be large compared to other relevant length scales in the system. In anticipation of the future brick layer model, the constant charge density is one important aspect. The electric field vector of such a plane is perpendicular to the plane due to symmetry reasons. We then add a second plane that is parallel to the first one at a distance d and has the same areal charge density s but with the opposite sign of charge. The electric force is known to be long range, meaning that the calculation of the electric field at each position must take all charges into account. The resulting field is obtained by a linear superposition of the electric fields of the two planes: double electric field between the planes; no field outside of the planes. The electric field inside the plane can be calculated using the Maxwell equation $\text{div } \mathbf{E} = \rho/\epsilon_0$, where ρ denotes the charge density in a certain volume V , \mathbf{E} depicts the electric field vector resulting from all charges (including polarization charges) within such a volume V , and ϵ_0 represents the electric field constant. (All elements that exhibit vector-like transformation behavior are denoted in bold letters in this work.) By using the Gauss integral theorem $\oint_V \text{div } \mathbf{E} dV = \oint_S \mathbf{E} d\mathbf{A}$ for a given volume V and the entire surface S of this volume and by integrating the cuboid box-shaped integral volume depicted in Fig. 2, $E_0 = s/\epsilon_0$ is obtained for the field inside the planes.

A plate capacitor is defined by a set of two parallel thin planes with lateral dimensions that are large compared to their distance d . In the future, for EIS, fast charging and discharging of the capacitor planes by AC voltage will be required. However, there has so far been no need for any real metal plates or similar to have a capacitor. There are no “shielding” effects of a metal, no electrical grounding, or any other voltage/current sources connected. The area of one plate is A and the charge accumulated on one plate is Q_0 . The areal charge density s is then $s = Q_0/A$. This is now the model of the “outer” capacitor which was briefly outlined in the introduction. In an EIS

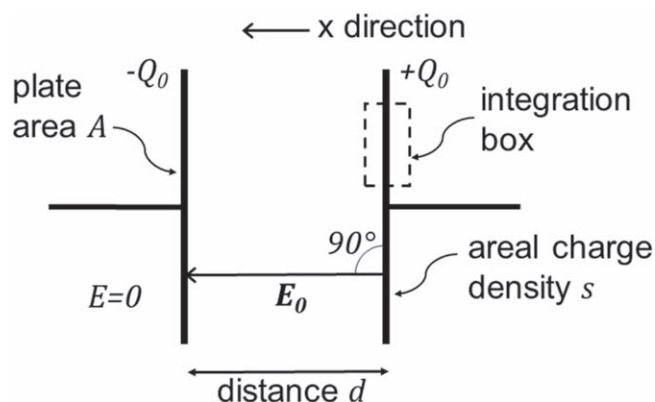


Figure 2. Diagram of a cross section of a plate capacitor. (The requirement of large (“infinite”) capacitor plates compared to distance d is not depicted in the diagram for the purpose of clarity).

experiment, the casing with metal plates, which connect the polycrystalline sample to the current leads, acts as the outer capacitor.

Here, we consider the work W of a (virtual) test charge q going from one plate to the other (the electric force $\mathbf{F} = q\mathbf{E}$ is used here):

$$W = \int_0^d \mathbf{F} ds = \int_0^d qE_0 dx = qE_0 \int_0^d dx = q \frac{Q_0}{\epsilon_0 A} d \quad [1]$$

The potential U is defined by $U = W/q$. Potential differences define the voltage (specifically the voltage in absence of chemical potentials in order to accept that voltages in general are differences in the electrochemical potential).

The capacitance C is defined by the charge Q that an object can accumulate when a voltage U is applied

$$C = Q/U \quad [2]$$

The definition does not depend on any particular geometries, designs, or technical construction peculiarities of the capacitor. All objects that can accumulate charge by applying a voltage, regardless of their construction, are capacitors. Since the analysis here is restricted to linear systems, a linearity of Q and U is also presumed in the following. This proportionality is necessary for deriving the semicircles in the Nyquist plot for an electrical network set of a resistor and a capacitor connected in parallel, which is used in EIS, for example.

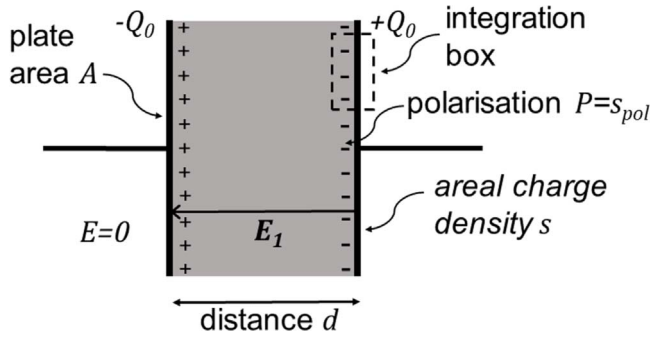


Figure 3. Diagram of a cross section of a plate capacitor completely filled with a material that is polarized by the electric field of the outer capacitor.

The capacitance of a plate capacitor is $C_{\text{plate capacitor}} = \varepsilon_0 A/d$ (see Eq. 1), with a proportionality of Q and U , and thus a constant capacitance (i.e. independent of Q and U) is given.

In this paragraph, the case of a capacitor filled with one *homogeneous* material is discussed. As previously highlighted, the effects of part of the material being polarized are described by charge carriers that cannot leave their local environment by applying a voltage. This means that the system can be described as a dielectric that has a polarization P (Fig. 3). P has a fundamental connection to the superficial charge density s_{pol} of the sample: $s_{\text{pol}} = P$.¹³

Considering the additional charges originating from the polarization P of a material inside a charged capacitor, the Maxwell equation comprising all charges is as follows:

$$E = \frac{s}{\varepsilon_0} - \frac{P}{\varepsilon_0} \quad [3]$$

For subsequent EIS, it is essential that there is a linearity between E and P , otherwise overtone-like modulations and more deviations would appear.¹⁴ Therefore, the derivation would not be valid for ferroelectric materials, for instance. The proportionality of P and E is typically written as $P = \chi \varepsilon_0 E$, and the constant χ defined in this way is referred to as the electric susceptibility. For subsequent EIS, it is further assumed that the electric susceptibility does not depend on the frequencies used in EIS, and also does not have imaginary parts.

Putting $P = \chi \varepsilon_0 E$ into Eq. 3 leads to:

$$E = \frac{s}{\varepsilon_0} \frac{1}{1 + \chi} \quad [4]$$

This shows a reduced effective electric field inside a capacitor filled with a dielectric compared to a capacitor with a vacuum between the capacitor plates, since the polarization charges of the material have the opposite sign compared to the charge of the capacitor plates.

The capacitance of the capacitor with material can be calculated analogously to Eq. 1 as

$$C = (1 + \chi) \frac{\varepsilon_0 A}{d} = \frac{\varepsilon_0 A}{d} + \chi \frac{\varepsilon_0 A}{d} \quad [5]$$

The factor ε_r which is determined by $\varepsilon_r = 1 + \chi$, the ratio of the capacitance of a plate capacitor filled with material to the capacitance of an empty capacitor is the definition of the dielectric constant or permittivity of the material.

The second part of Eq. 5 states that the material along with the locally mobile charge carriers that create a polarization can be described in the same way as a capacitor (provided the polarization is proportional to the electric field). Since a capacitor is only defined by Eq. 2, $C = Q/U$, the material itself is a capacitor, regardless of its specific construction.

Only the charge Q is relevant, not the type of charge carrier. It could be any cation or anion in a crystal, and, with respect to EIS, it

is not necessary that these charge carriers are the same as the type of charge carriers that are responsible for a macroscopic charge flow (a current).

Here, a sample comprising two different materials in a capacitor is analyzed. Figure 4 shows a capacitor filled with a material 1 with a thickness of x , followed by a different material 2 with a thickness of l , which is again followed by a material 1 with a thickness of $d-x-l$. Both materials are assumed to be homogeneous, including a homogeneous polarization. With the same approach as for one homogeneous material in a capacitor (integration of Maxwell law in the region of the plates, integration boxes 1 and 2), the electric field E_1 in material 1 is $E_1 = \frac{E_0}{\varepsilon_{r,1}}$, where $E_0 = s/\varepsilon_0$.

Using the larger integration volume (box 3) in Fig. 3, the electric field E_2 in material 2 can be calculated as:

$$\begin{aligned} E_2 A &= \oint_S \mathbf{E} d\mathbf{A} = \oint_V \mathbf{div} \mathbf{E} dV = \oint_V \frac{\rho}{\varepsilon_0} dV \\ &= \frac{Q_{\text{in box}}}{\varepsilon_0} = \frac{s - s_{\text{pol}2}}{\varepsilon_0} \end{aligned}$$

The overall charge (i.e. surface charge) contributions of material 1 level out, as the polarized material as a whole remains electrically neutral. It follows with $s_{\text{pol}2} = P_2 = \chi_2 \varepsilon_0 E_2$ and $\varepsilon_{r,2} = 1 + \chi_2$ that $E_2 = \frac{E_0}{\varepsilon_{r,2}}$.

The capacitance of such a capacitor is derived in the same way as for the empty capacitor, using Eqs. 1 and 2:

$$\begin{aligned} U &= \int_0^d \mathbf{E} ds = \int_0^d E dx = \int_0^x E dx + \int_x^{x+l} E dx + \int_{x+l}^d E dx \\ &= \int_0^x E_1 dx + \int_x^{x+l} E_2 dx + \int_{x+l}^d E_1 dx \\ &= E_1 \int_0^x dx + E_2 \int_x^{x+l} dx + E_1 \int_{x+l}^d dx \\ &= E_1 x + E_2 l + E_1 (d - (x + l)) \end{aligned}$$

Using the equations $C = Q/U$, $E_1 = \frac{E_0}{\varepsilon_{r,1}}$, $E_2 = \frac{E_0}{\varepsilon_{r,2}}$ and $E_0 = Q/\varepsilon_0 A$, it follows that:

$$C = \frac{A \varepsilon_0}{\frac{x}{\varepsilon_{r,1}} + \frac{l}{\varepsilon_{r,2}} + \frac{d-x-l}{\varepsilon_{r,1}}} \quad [6]$$

Here, the inverse value of C in Eq. 6 is analyzed:

$$\begin{aligned} \frac{1}{C} &= \frac{\frac{x}{\varepsilon_{r,1}} + \frac{l}{\varepsilon_{r,2}} + \frac{d-x-l}{\varepsilon_{r,1}}}{A \varepsilon_0} = \frac{x}{A \varepsilon_0 \varepsilon_{r,1}} + \frac{l}{A \varepsilon_0 \varepsilon_{r,2}} + \frac{d-x-l}{A \varepsilon_0 \varepsilon_{r,1}} \\ &= \frac{1}{\frac{A \varepsilon_0 \varepsilon_{r,1}}{x}} + \frac{1}{\frac{A \varepsilon_0 \varepsilon_{r,2}}{l}} + \frac{1}{\frac{A \varepsilon_0 \varepsilon_{r,1}}{d-x-l}} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} \end{aligned}$$

These formulae are such that the overall capacitance of the entire set of the outer capacitor and two different materials with individual polarizations within the capacitor plates can be described by a serial connection of *three* distinct capacitors, C_1 , C_2 and C_3 , with the following capacitances:

$$C_1 = \frac{A \varepsilon_0 \varepsilon_{r,1}}{x}, \quad C_2 = \frac{A \varepsilon_0 \varepsilon_{r,2}}{l} \quad \text{and} \quad C_3 = \frac{A \varepsilon_0 \varepsilon_{r,1}}{d-x-l}$$

They look like capacitors that exactly match the properties and dimensions of individual parts of the sample with materials 1 and 2 between the outer capacitor plates: for example, the distance of the “plates” is equal to the thickness of the individual homogeneous regions, and they have the correct single $\varepsilon_{r,i}$ values. For the purpose

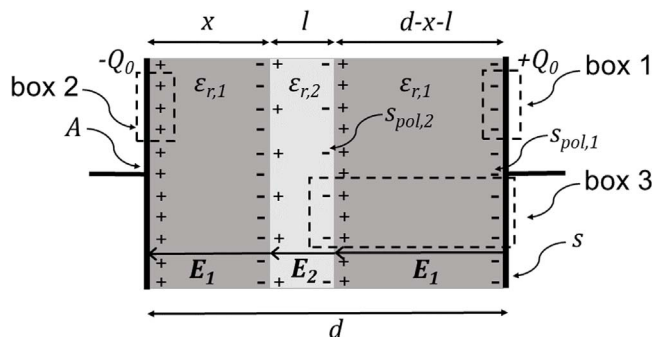


Figure 4. Diagram of a cross section of a plate capacitor filled with two distinct materials with permittivity values $\epsilon_{r,i}$, which are polarized by the effective electric fields within the capacitor plates.

of clarity, there are no real capacitors consisting of “capacitor plates” or similar, but the outer capacitor has been “absorbed” to this new equivalent circuit. It is also important to stress that the capacitors of the constructed capacitance equivalent circuit are not independent of each other, but are linked by the parameter l .

The term x in the formulae can be completely disregarded—it was purposefully not deleted in order to illustrate the shape of the equivalent circuit with the three capacitors. In other words, the position of the region of material 2 can be arbitrarily shifted between the outer capacitor plates. This provides a degree of freedom in the construction of the brick layer model.

Another important aspect for the capacitances is the expansion to even more complex series. The result would be exactly the same if there were two separated areas with $\epsilon_{r,2}$, each with a thickness of $l/2$, and three surrounding regions with $\epsilon_{r,1}$ filling the rest of the capacitor, or a sample with a thickness of $d \approx 1$ cm, with 10,000 grains with an individual length of $d_{\text{grain}} = 1 \mu\text{m}$, and 9,999 grain boundaries each with a thickness of $l_{\text{gb}} = 10$ nm between them ($l \approx 1 \mu\text{m}$ in this example).

The ratio of grain capacitance to grain boundary capacitance is given by:

$$\begin{aligned} \frac{C_{\text{grain}}}{C_{\text{gb}}} &= \frac{\epsilon_{r,\text{grain}} \epsilon_0 A / (d - l)}{\epsilon_{r,\text{gb}} \epsilon_0 A / l} = \frac{\epsilon_{r,\text{grain}}}{\epsilon_{r,\text{gb}}} \frac{l}{d - l} \\ &= \frac{\epsilon_{r,\text{grain}}}{\epsilon_{r,\text{gb}}} \frac{l_{\text{gb}}}{d_{\text{grain}} - l_{\text{gb}}} \end{aligned}$$

This is an extension of the corresponding formula 4 in.¹⁰

In summary, even the situation with many grains and grain boundaries is described by only *one* capacitor for *all* the grains, and *one* for *all* the grain boundaries. This is the reason why the simple equivalent circuit, as shown in Fig. 1, works so well for the description of a large number of grains and grain boundaries rather than using a huge network of capacitors for the description of EIS data.

$\epsilon_{r,1} \neq \epsilon_{r,2}$ is a prerequisite for having more than one effective capacitor in the equivalent circuit (the length l cannot be determined if $\epsilon_{r,1} = \epsilon_{r,2}$). If $\epsilon_{r,1} = \epsilon_{r,2}$, Eq. 6 would only describe a capacitor filled with one homogeneous material, meaning that only one semicircle would appear in the Nyquist plot.

The derivation can be expanded in the same way to more layers with different permittivities at any position within the outer capacitor, provided that all layers are plane-parallel, as outlined in Fig. 4. Each additional layer with a different permittivity adds one more capacitor with a capacitance of $C_i = \frac{\epsilon_0 \epsilon_{r,i}}{x_i}$ to the equivalent circuit, with x_i denoting the (overall) thickness of the layer and $\epsilon_{r,i}$ depicting the permittivity.

As previously mentioned, the thicknesses of the material layers in Fig. 4 do not necessarily need to be identical (e.g. $1 \mu\text{m}$). It is

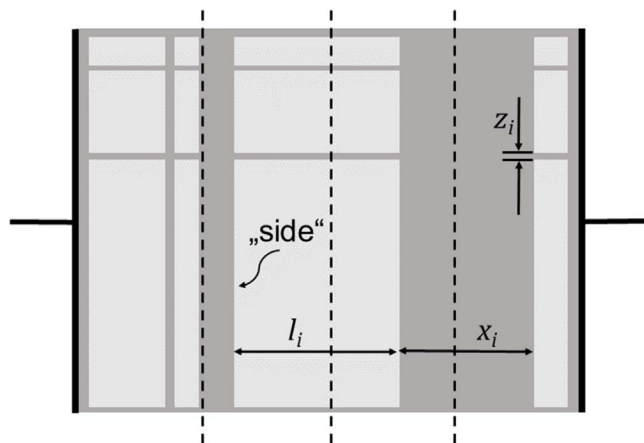


Figure 5. Diagram of a cross section of a plate capacitor filled with two distinct materials in a more complex manner as an expansion of the brick layer model (see e.g. Fig. 2 in¹⁰). The dashed lines illustrate the approximated equipotential lines. The values of x_i and l_i may be arbitrary, as long as the “sides” of the grains are parallel to the equipotential lines of the electric field. The values z_i may be small to mimic the situation shown in Fig. 4.

therefore tempting to fragment real grains with an irregular shape into tiny bricks (e.g. crystal unit cells in a cubic system) and to apply the calculations of the previous sections accordingly. However, this is not a valid approach, since the dimensions of the capacitor plates need to be large compared to the other relevant dimensions in order to obtain the homogeneous electric field oriented perpendicular to the capacitor plates. For other geometries, corrections of local fields (i.e. local currents in EIS) need to be taken into account, for example depolarization factors.⁷ For this reason, the model can only be applied in a brick layer model where bricks may have varying thickness in the x direction (as defined in Fig. 2) but always with common grain boundary layers in between them (Fig. 5).

In a real crystal, phases with different conductivities may appear, meaning that the current flow may be locally irregular. As the electric field is always perpendicular to the local current flow, the geometry of the effective capacitances and resistances becomes even more complex. A more detailed description requires more complex resistor capacitor networks (see e.g.¹⁵).

At first glance, Figs. 2 to 5 might exclusively provide a description of an electrostatic problem and its solution. However, the fundamental equation for electrostatic problems, $\text{rot } \mathbf{E} = 0$, was not required at any stage. Therefore, the figures can also be interpreted as flashlight images of an electrodynamic system.

Conclusions

The description of the electrochemical impedance spectroscopy of polycrystals using a capacitive brick layer model was reviewed. In addition, the description of grains and grain boundaries by capacitors was strictly derived from fundamental equations for the electric fields in matter, and previous equations for its description were expanded. The current collector/casing as an outer capacitor in conjunction with the polarization charges of the materials within this capacitor accurately create all capacitances observed experimentally in EIS as well as in the equivalent circuits. Thus, no other mechanisms are required to build up more capacitors. In particular, the charge carriers in the “conduction band” (i.e. those that can leave their local environment) only contribute to pure charge transport through elements that are associated with electrical transport in resistors. There is, of course, the exception of blocking electrodes, where the mobile charge carriers move inside the sample more or less freely in the electric field of the outer capacitor and accumulate at the charge carrier blocking interface, thus creating another capacitor with a higher capacitance value than, for example, bulk or grain boundary polarization.¹⁰

It was highlighted that differences in the permittivity values for grains and grain boundaries are required for the description with two distinct capacitors in the typical equivalent circuits. Not all single grains or grain boundaries of a polycrystal need to be described by separate capacitors, but they can be integrated in one capacitor for each permittivity value.

The results also inform about two aspects of the experimental set-up for EIS. Firstly, the dimensions of the outer capacitor plates may be large compared to their distance. Secondly, the sample should be cylindrical in shape, and the top cylinder surfaces should exactly match the shape of the outer capacitor plates: it was essential for the derivation that the outer capacitor and the sample both have an identical area A . For larger samples, the stray fields of the outer capacitor may impact the actual capacitance. If the plate capacitor has a larger plate area than the sample, there will be an additional effective capacitor parallel to the capacitor-sample set-up, which needs to be taken into consideration in the equivalent circuit.

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