Generalised equivalent circuits for mass and charge transport: chemical capacitance and its implications

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An exact equivalent circuit including terminal parts, which takes account of electrical and chemical control parameters in a unified way, is derived for a cell with a mixed conductor (or electrolyte) without internal sources or sinks. In one-dimensional problems electrochemical kinetics can be mapped by two-dimensional circuits exhibiting the spatial and the thermodynamic displacement as two independent coordinates. One main advantage of the exact circuits with respect to the underlying differential equations is the ability to simplify the description according to specific situations. As we show in several examples in the second part of the paper, it is straightforward to select the elements relevant for the particular experimental conditions and so to make appropriate approximations. This is most helpful for the description of electrochemical systems, such as fuel cells, membranes, pumps and batteries.

1 Introduction

In many electrochemical processes electrical driving forces cause chemical changes inside the sample and/or vice versa. Let us consider two examples from solid state electrochemistry: First, when a voltage is applied to a mixed conducting (i.e. electronically and ionically conducting) sample with electrodes which allow for only one of the two carrier species to be transferred across the contact (e.g. Ag$_2$S sandwiched between two Pt-electrodes$^1$ or a titanate ceramic capacitor under voltage stress at low temperatures,$^2$) stoichiometric gradients are built up internally. Second, a mixed conductor under a chemical gradient (e.g. SrTiO$_3$ separating two gas chambers with different oxygen partial pressures) gives rise to ambipolar fluxes inside. All these and related effects in the transient and in the steady state can be successfully treated by well-known transport equations combined with the continuity equations and Poisson’s equation at least as long as we restrict the conditions to proximity to equilibrium.

The sometimes complex situation becomes much more transparent when mapping the mathematical model by equivalent circuits obeying Kirchhoff’s laws. The application of such circuits is also extremely helpful in deriving relevant simplifications. In this paper we give a rigorous treatment of the sometimes complex situation becomes much more transparent when mapping the mathematical model by equivalent circuits obeying Kirchhoff’s laws. The application of such circuits is also extremely helpful in deriving relevant simplifications. In this paper we give a rigorous treatment of the

An example par excellence is diffusion. Respective capacitors in the transmission line describing diffusion are not related to the dielectric properties of the sample, but to the carrier density $c$. Their capacitance per unit length is given by $\frac{2\varepsilon^2c^2}{h^2} T$, where $T$ is the carrier’s charge number, $h$ the Boltzmann constant and $T$ the temperature. Further literature examples of non-electrostatic bulk elements are “redox” capacitors$^6$ or “electrochemical” capacitors$^7$ which characterise mixed conducting polymers. Referring to the interfacial process, “pseudo-capacitors”$^8,9$ mapping the adsorption of intermediates on electrode surfaces, are used. The capacitance of such adsorption capacitors is determined by $\frac{\partial\vartheta}{\partial\varphi}$, where $\vartheta$ stands for the fraction of the electrode surface covered by adsorbed intermediates and $\varphi$ denotes the electric potential at the electrode. Even an ordinary parallel metal-plate capacitor, if of mesoscopic size, cannot be described solely in terms of electrostatics.$^{10}$ The electric charge $Q$ stored in a mesoscopic capacitor is proportional to the difference in the electrochemical potentials of the electrons on both plates, $\Delta\varphi_{\text{elec}}$, rather than to $\Delta\varphi$ alone. Thus the respective capacitance is an electrochemical one: $e\frac{\partial\varphi}{\partial\varphi_{\text{elec}}}$ (where $e$ denotes the absolute value of the electronic charge).

Let us first consider purely non-electrostatic capacitors from a thermodynamic point of view. As pointed out by Pelton$^{11}$ a “chemical capacitance” $C_2$ of a thermodynamic system with regard to an exchangeable species $j$ can be defined, by analogy to heat capacity or compressibility, as the second derivative of the Gibbs energy $G$ with respect to the number of moles of that species $n_j$: $C_2 = \frac{\partial^2G}{\partial n_j^2} T$. Unlike the first derivative, $C_2$ is an extensive quantity thus being proportional to the thickness (volume) of the sample. An example of a system having high chemical capacitance is an aqueous solution of an acid–base pair which buffers pH with respect to additions of an acid. Another example is a solid state material the stoichiometry of which varies significantly upon small changes of the component partial pressure. In the field of solid state electrochemistry traditionally the inverse of $C_j$, known as the “thermodynamic factor”,$^{1,12}$ is used. Is the capacitance of “pseudo-”, “redox”, etc. capacitors always proportional to $e^2G/\partial n_j^2 T$? A question of equal importance is how to connect the circuit elements in an equivalent circuit. In order to take account of different carriers, spatial inhomogeneities, etc. the

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circuit elements are often constructed intuitively, e.g. on the basis of electrical impedance measurements as a function of frequency. The common problems of such constructions are well known: (i) the validity range of the circuit is difficult to estimate and (ii) the dependences of the circuit elements on the materials parameters (carrier mobilities, mass action constants, impurity concentrations, charge numbers, interfacial rate constants and cell dimensions) are often obscure. More precise construction relies on analytical25,26 or numerical27 solutions of the differential equations constituting a particular physical model. The circuit is still constructed intuitively, but the validity of the circuit and the meaning of the circuit elements are recast from the fitting of the circuit impedance to that predicted by the model.28

The next step is obviously the construction of the circuit directly from the physical model. Such “exact equivalent circuits” are a useful representation, mapping the underlying models. A very simple example is dielectric relaxation; the underlying model comprises Ohm’s law and Poisson’s equation and yields an equivalent circuit which combines the sample’s resistance and its electrostatic capacitance in parallel. In electrochemistry and semiconductor physics the situation is more complex and is usually described by drift-diffusion models. They consist of the Nernst–Planck–Poisson set of equations with Chang–Jaffe or Butler–Volmer boundary conditions.25–28 Using such a model, Sah13 derived exact equivalent circuits for the transport in semiconductors taking into account different generation–recombination mechanisms. Independently, in the field of liquid electrochemistry Barker14 found intuitively the exact equivalent circuit for a cell with a binary electrolyte and blocking electrodes. Later, Brumleve and Buck15 showed that Barker’s circuit is, close to equilibrium, isomorphic to the drift–diffusion model. It is interesting to note that in none of these studies (see also ref. 16 and 17) was the non-electrostatic capacitance identified as \( (\varepsilon^2 G/\eta n_F)^2 \) and hence given on a thermodynamic basis. In contrast, in the simplified equivalent circuit describing electrochemical polarisation of mixed conductors, the chemical capacitance (essentially the inverse of the thermodynamic factor) was used explicitly.18–21

Essentially, the treatments of the exact equivalent circuits discussed above can be viewed from the perspective of network thermodynamics. This theory2 provides the principles and tools for a graphical representation of time-dependent irreversible thermodynamic systems in general. Horno and co-workers23,24 applied the theory for the construction of equivalent circuits.

In this paper we consider the exact equivalent circuit in the light of solid state electrochemistry. We start with the derivation of the circuit from the drift–diffusion model. We introduce terminal parts, which take into account electrical and chemical driving forces. During the derivation several important questions which we mentioned in the Introduction will be addressed. In the second part the circuit is simplified and tailored for several cases of theoretical and practical interest. The lucidity of the circuit, when compared to underlying differential equations, makes this procedure very effective.

2 Transport equations

In the linear regime, which we refer to in this paper, the carrier fluxes are proportional to driving forces. The transport equations derived from irreversible thermodynamics impose no limitations on the carrier density,\(^\dagger\) \( c_j \) (\( j \) stands for the carrier type). The flux density, \( J_j \), is proportional to the gradient of the corresponding electrochemical potential, \( \mu_j = \mu_j + z_i e \phi \), \( \mu_j \) being the carrier’s chemical potential, \( z_i \) its charge number including sign, \( e \) the absolute value of electronic charge, and \( \phi \) the electric potential. If we neglect Onsager cross coefficients, the flux densities depend on the position, \( r = (x, y, z) \), and time, \( t \), as follows

\[
J_j(r, t) = -\frac{\sigma_j(r)}{(\varepsilon^2\rho_{\mu_j})} \nabla\mu_j(r, t). \tag{1}
\]

The conductivity \( \sigma_j \equiv z_i e c_j \mu_j \) is determined by the carrier mobility \( \mu_j \) and by the carrier density \( c_j \). At \( t = 0 \) the initial conditions of our experiments are established. In general, \( c_j(r, t = 0) \) and \( \sigma_j(c_j) \) may be position dependent, e.g. due to inhomogeneous doping (frozen-in profiles), or due to space charge regions adjacent to phase boundaries (e.g. p–n junctions). We assume further the absence of internal sources and sinks for carriers. Thus the continuity equation

\[
V \cdot J(r, t) = -\frac{\partial c_j(r, t)}{\partial t} \tag{2}
\]

is valid. If we neglect magnetic fields, the description is completed by Maxwell’s equation

\[
V \cdot D = e \sum_j z_j c_j(r, t). \tag{3}
\]

Considering a simple material (isotropic, non-ferroelectric) and long timescales, the dielectric displacement \( D \) depends on the electric potential \( \phi \) according to \( D_t(r, t) = \sigma(c_j) \varepsilon_j \varepsilon_r \phi / \varepsilon_0 \). The symbols \( \varepsilon \) and \( \varepsilon_0 \) denote the relative permittivity and the permittivity of free space, respectively.

The above formulation is not the most suitable for an equivalent circuit representation. For this we need relationships which relate fluxes and potentials, as does eqn. (1). The appropriate transformation of eqn. (3) is state of the art (see e.g. ref. 29): Taking into account the continuity equation for the charge density and the definition of the displacement current density, \( I_{\text{dis}} = \varepsilon_0 D_t / \varepsilon_r \), the flux–potential relationship reads \( J_{\text{dis}}(r, t) = \sigma(c_j) \varepsilon_j \varepsilon_r \phi / \varepsilon_0 \). The total current, \( I_{\text{dis}} + z_j I_j \), then has a vanishing divergence.

In order to recast eqn. (2) into a flux–potential relationship we write it as

\[
\frac{\partial \varepsilon_j}{\partial t} = \frac{\partial \varepsilon_j}{\partial \mu_j} \frac{\partial \mu_j}{\partial t}. \tag{4}
\]

Also here we neglect cross-coefficients, \( \varepsilon_j \delta_{ij} \delta_{\mu_k} \), and use the fact that the explicit \( t \)-dependence, \( \varepsilon_j / 2 \mu_j \), is zero. Although the substitution (4) seems trivial it has an enormous impact on the treatment and interpretation of mass and charge transport in terms of equivalent circuits. The reason is that the choice of the driving force defines the meaning of the circuit elements and their links. The derivative in eqn. (4) taken at constant \( t \) reflects the capability of the system to accept or release additional charge carriers of type \( j \) on a given variation of their chemical potential \( \mu_j \). Therefore it suggests the definition of chemical capacitance (defined per unit volume) allocated to the carrier \( j \) as

\[
\Psi_j = (\varepsilon_j)\left(\frac{\partial \mu_j}{\partial c_j}\right)^{-1}_{c_j=0}, \tag{5}
\]

which is in agreement with Pelton’s definition (see introduction) \( \Psi_j \propto (\varepsilon^2 G/\eta n_F)^{-1} \). We set \( t = 0 \) to emphasise that \( \Psi_j \) is a materials parameter, which is independent of the driving force in the linear regime. The thermodynamic stability theory31 demands that \( \Psi_j \) are all positive (more precisely, \( \Psi_{i,j} \) has to be positive definite) in order to ensure chemical

\(\dagger\) In the dilute limit, in which Boltzmann statistics applies, the flux equation derived from irreversible thermodynamics and the (linearised) Nernst–Planck–Poisson (drift–diffusion) equation are identical.

\(\dagger\) Many other substitutions are formally possible as well, see for example ref 24.
stability. Renormalising the chemical and electrostatic potentials according to \( \mu_T = (1/ez)\mu_T \) and \( \mu_T^* = \mu_T^* + \phi \), and replacing the flux densities \( J_i \) by the electric current densities \( I_j = \varepsilon_j e J_j \), we finally obtain

\[
I_j(r, t) = - \sigma_j(r)\nabla(\mu_T^* + \phi), \quad (6a)
\]

\[
I_{as}(r, t) = - \sigma_j(r) \frac{\partial \phi}{\partial t} \nabla \phi, \quad (6b)
\]

\[
\nabla \cdot I_j(r, t) = - \varepsilon_j(r) \frac{\partial \mu_T^*}{\partial t}. \quad (6c)
\]

We recognise that only in eqn. (6a) does the flux follow the time variations of the driving force without delay. In other words, both are “in phase”, which means that eqn. (6a) refers to an energy dissipative process. Eqn. (6a) defines a generalised “electrochemical” resistance via \( \tilde{\mu} \) as the generalised driving force: \( R_{\text{electrochem}} \propto \tilde{\mu}/I \) (see Fig. 1a). In contrast to eqn. (6a), the fluxes and driving forces in eqn. (6b) and (6c) are exactly “out of phase”, reflecting pure energy storage. At this point we see that only in the process of energy dissipation do the chemical and electrical potential appear symmetrically (eqn. (6a)), i.e. the dissipation of energy is independent of the partition of the total driving force in the chemical and electrical parts.

On the other hand, the storage of energy does depend on this partition. In contrast to the previous case there are two fundamentally different proportionality constants characterising the storage: the electrical and chemical capacitance. Naively, by analogy to the “electrochemical” resistance, one might think that electrical and chemical capacitances could be also combined to form an “electrochemical” capacitor with the capacitance \( C_{\text{electrochem}} \propto (\tilde{\mu}/Q)^{-1} \), \( Q \) denoting the charge. Such an electrochemical capacitor as defined e.g. in ref. 10 can be conceived as a series combination of the electrical and chemical capacitances (Fig. 1b) as demonstrated by splitting \( \tilde{\mu}^* \) into its electrical and chemical part

\[
C_{\text{electrochem}} = \left( \frac{\tilde{\mu}^*}{Q} + \frac{\tilde{\mu}^*}{Q} \right)^{-1} \propto \left( \frac{1}{C_e} + \frac{1}{C_\text{chem}} \right)^{-1}. \quad (7)
\]

However, as will be explicitly shown later, the “charges” stored in electrical and chemical capacitors are not necessarily equal and therefore such a series representation only applies in a few cases and is generally not adequate; rather there may be additional branches connected to the node between both capacitors, as indicated in Fig. 1b. In steady state experiments (pure energy dissipation) the only relevant potential is \( \tilde{\mu} \) (splitting into electrical and chemical parts is meaningless).

This introductory discussion of circuit elements reveals already an important observation: apart from interfacial relaxations two different timescales may be associated with the transport processes: typically a short timescale involving electrical capacitances and a long timescale involving chemical capacitances.

3 Equivalent circuit

3.1 Bulk part

3.1.1 Constitutive relations of electrochemical resistance, electrical and chemical capacitances. Let us represent the set of equations (6) by an equivalent circuit. This is especially straightforward if the situation is quasi one-dimensional, i.e. we consider a laterally homogeneous sample of a cross-section area \( A \) extending along the \( x \)-coordinate from \( x = -L \) to \( x = L \) (see Fig. 2a). We divide the sample into \( n \) compartments of thickness \( s \), discretise the equations (6) and transform them from the time domain into the frequency domain (thus the time derivatives are replaced by \( j \omega \)). Although the potentials and currents now refer to complex-valued Fourier amplitudes we will keep the same symbols.\footnote{If the time domain variables are sinusoidal (usual case in impedance spectroscopy) amplitude and phase of the Fourier transforms reflect directly amplitude and phase of the sinusoidal time domain quantities.}

Note that the only approximation which we make here, is due to the discretisation. The transport eqn. (6) then read:

\[
I_{j,i}(\omega) = \frac{1}{R_{j,i}} \Delta_j \tilde{\mu}_j^i(\omega), \quad (8a)
\]

\[
I_{as}(\omega) = i\omega C_i^0 \Delta_j \phi(\omega), \quad (8b)
\]

\[
\Delta_j I_j(\omega) = -i\omega C_i^0 \delta \mu_j^i(\omega). \quad (8c)
\]

The subscript \( j \) denotes the type of the carrier and the subscript \( i \) the spatial location. If the sample is entirely homogeneous, \( i \) can be omitted. The operator \( \Delta \) calculates the difference between the centers of two compartments sandwiching the location \( i \), while the operator \( \delta \) calculates the deviation from the equilibrium \( (t = 0) \) values (Fig. 2c) within the compartments. The resistances \( R_{j,i} \), the electrostatic capacitances \( C^0 \) and the chemical capacitances \( C_i^{chem} \) are defined as

\[
R_{j,i} = \sigma_j \frac{S}{A}, \quad (9a)
\]

\[
C^0 \equiv \varepsilon_i \varepsilon_0 \frac{A}{\sigma}, \quad (9b)
\]

\[
C_{j,i}^{\text{chem}} = (e^2) \int \left( \frac{\tilde{\mu}_j^i}{k_B T} \right)^{-1} As. \quad (9c)
\]

While the chemical capacitances are assigned to the compartments (Fig. 2a), \( C^0 \) and \( R_{j,i} \) refer to the “transition” regions in between. The resistances \( R_{j,i} \) parametrise the carrier transfer and \( C^0 \) the electrostatic coupling between the compartments.

Whilst the electrostatic capacitances are inversely proportional to the compartment thickness, the chemical capacitances are directly proportional to it. In dilute situations Boltzmann statistics applies, thus \( \mu_j^i = \epsilon_j^i + k_B T \ln(c_j^i/N_j^i) \) (symbol \( \epsilon_j^i \) denotes the standard concentration independent term and \( N_j^i \) the density of available sites). Then the derivative in eqn. (9c) can be explicitly evaluated yielding

\[
C_{j,i}^{\text{chem}} = \frac{(e^2)^2}{k_B T} \frac{k_B T}{c_j^i / \text{As}.} \quad (10)
\]

Since \( C_{j,i}^{\text{chem}} \) is proportional to the volume, it can be very large compared to \( C^0 \). If the relative carrier density is 0.01%, the area 1 cm² and the thickness 1 mm, then the chemical capacitance at ambient temperature amounts to about 0.1 F. This is
10 orders of magnitude more than the sample’s electrostatic capacitance (if $\varepsilon = 10$).

Expression (10) has already been used in the context of equivalent circuits. In ref. 17 it is termed “Nernst–Planck capacitance”. Franceschetti$^{16}$ wrote two expressions for the “shunt” capacitance, as he called it: in the special case in which local electroneutrality applies, he used the shunt capacitance equals to ours (eqn. (10)), while in the case of the Nernst–Planck–Poisson model it surprisingly includes $\varepsilon$.

3.1.2 Construction of the circuit. After the three basic elements, electrochemical resistances, electrostatic and chemical capacitors have been defined, they just have to be connected such, that eqn. (8) are fulfilled. Since our system is relatively simple we do not necessarily need a bond-graph approach.$^{22}$ Nevertheless, different potentials ($\phi$, $\mu_j$) will appear in the circuit, thus the simple scheme displayed in Fig. 2b will be useful: the transport coordinate which is identical with the spatial coordinate $x$ describes the direction of transport: all the circuit elements, which are assigned to transport steps ($R_j$, $C^\phi$) have to appear aligned along the transport coordinate. The coordinate orthogonal to it is reserved for internal reactions. Since we assume local equilibrium we do not have to consider any reaction resistances, just chemical capacitors. A simple example of an internal reaction is the local dissolution of oxygen in an oxide or intercalation of lithium in graphite. The corresponding ions and electrons are stored in chemical capacitors.

Since we consider three transport mechanisms, we will have three rails aligned along the transport coordinate: the ionic, electronic and displacement rails (Fig. 2c). These three map eqn. (8a) and (8b). The coupling among the rails is described by eqn. (8c) (essentially part of Kirchoff’s law for the currents and flux-potential relation for chemical capacitors). The divergence of the carrier currents has to be balanced by storage of the carriers in chemical capacitors. Thus, $C^\phi$ will be attached to the nodes within the carrier rails (Fig. 2c) and aligned orthogonally (no electric potential drop is allowed across $C^\phi$). The remaining balance for the currents, $-\Delta I_1 - \Delta I_2 = \Delta I_{dis}$, will be obeyed if we connect the free terminals of $C^\phi$ to the nodes of the displacement rail. The circuit obtained is shown in Fig. 2d. Finally we verify Kirchoff’s law for the potentials. To do so, it is sufficient to restrict ourselves to the elementary loop indicated by the dashed line in Fig. 2e. Since the elementary loop refers to a single carrier we skip the subscript $j$. The potential drop along the loop equals \( \delta \mu^* + \Delta \mu^* - \delta \mu^*_{j+1} - \Delta \phi \). Taking into account that $\Delta \mu^* = \delta \mu^*_{j+1} - \delta \mu^*_{j} + \Delta \phi$, the sum obviously vanishes. Since any other loop can be composed of such elementary loops, Kirchoff’s law for the potentials (electrical, chemical and electrochemical) applies to any part of the circuit.

Since the chemical capacitors once built into the circuit are treated as the electrical ones we use the same symbol (Fig. 2). In contrast to $R$ and $C^\phi$, the two terminals of the chemical capacitor refer to the same locus yet to different potentials (states): one terminal is held at zero potential (i.e. at equilibrium potential) and the other at variable potential $\delta \mu^*_{j+1}$. In contrast to an electrostatic capacitor there is no separation of electric charge in a chemical capacitor. While in an electrostatic capacitor the Gibbs energy $\Delta G = \frac{1}{2}C^\phi \Delta \phi^2$ is stored electrostatically, in a chemical capacitor Gibbs energy $\Delta G = \frac{1}{2}C^\phi \delta \mu^* e^2$ is stored as entropy changes (in non-dilute cases energy changes also). In general the ionic and electronic capacitors connected to the particular node in the displacement rail are not charged equally (with the negative sign). Referring to the circuit, the currents flowing through them are not equal. This difference is compensated by the current in the displacement rail in the middle. In this way the electrical cur-

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**Fig. 2** (a) Discretisation of the sample, (b) coordinate system used in construction of the circuits, (c) basic circuit branches: carriers and displacement rails (d) final equivalent circuit and (e) Kirchoff’s voltage law for the loop indicated in the circuit.
rents due to the carrier flow (the top and the bottom rail) can switch over to the displacement rail. Such a switching, which is always accompanied by a local electrical charging, necessarily occurs e.g. at interfaces which do not allow for the transfer of ions and/or electrons (e.g. Pt/AgCl or SiO\textsubscript{2}/Si).

On the other hand, in homogeneous regions the subscript \(i\) can be dropped in \(R_i, C_i, C_{i}'\) far away from interfaces, local electroneutrality usually holds. Then the chemical capacitors are charged and discharged evenly and no current redistribution takes place in the nodes of the displacement rails (Fig. 2b). In such cases ionic and electronic chemical capacitors behave as truly connected in series. Thus it is advantageous to define a component chemical capacitance,

\[
\frac{1}{C^e} = \frac{1}{j} \sum_i \frac{1}{C_i'}.
\]

the reciprocal of which is well-known in solid state electrochemistry under the term “thermodynamic factor”\textsuperscript{11,12} (e.g. in an oxide, \(\propto \delta \mu_O / \partial c_O\), where the subscript O denotes the component, oxygen in our case). The component chemical capacitor with the capacitance given by eqn. (11) has been proven to be a useful element in approximate equivalent circuits of mixed conductors.\textsuperscript{18–21}

The “charge” stored according to the constitutive relation \(\delta Q = C^e \delta \mu_{\text{comp}}^e\) (the normalised component chemical potential is defined as \(\delta \mu_{\text{comp}}^e = \delta \mu_{\text{ion}}^e - \delta \mu_{\text{ion}}^d\)) refers in this case to the amount of neutral species stored: \(\delta Q = e z_0 \, V \, \delta \mu_{\text{comp}}^e, V\) being the volume. The “charging” of \(C^e\) means changing the chemical composition rather than changing the electric charge density. The most familiar examples of this kind of “charge” storage are batteries.\textsuperscript{9}

3.2 Terminal parts

The terminal parts of the circuit are defined by the boundary conditions. Since at phase boundaries many different experimental situations are encountered the set of possible boundary conditions is large. Though being a non-trivial part of the overall problem, little attention has been devoted to this topic so far.\textsuperscript{11–13} For the following discussion it is worthwhile to treat cases with and without electrodes separately.

3.2.1 Electrode boundary conditions. A situation very often encountered in the solid state refers to electrochemical reactions in which the reaction product and/or educt is in the gas phase. The morphological changes at such interfaces can, at least to a first approximation, be neglected. On the other hand, the geometry of the reaction sites may be quite complex and, on the microscopic level, far from being planar (purely electronically conducting electrodes are usually porous). We consider here, as an example, a mixed conducting oxide in contact with very thin electrodes which serve as current collectors and are basically permeable for oxygen (Fig. 3a, top). The sample must first be equilibrated in an atmosphere with the same oxygen partial pressure at both sides (\(x = L\) and \(x = -L\)). This procedure defines the initial situation. Besides the difference of electron electrochemical potential, \(\Delta \phi_{\text{eon}}\), applied we also allow for external chemical driving forces, i.e. for deviations of the oxygen chemical potential from the initial values, \(\delta \mu_{\text{gas}}^d\) and \(\delta \mu_{\text{gas}}^g\), referring to the left- and right-hand side of the sample, respectively. Note that \(\delta \mu_{\text{gas}}^d = \frac{1}{2} \delta \mu_{\text{gas}}^g\). All three independent driving forces, \(\Delta \phi, \delta \mu_{\text{gas}}^d, \delta \mu_{\text{gas}}^g\), are control parameters and may be time (frequency) dependent. Next, we have to clarify the discretisation of the terminal parts. As already mentioned the sample is divided into compartments of thickness \(s\). To both sides we add an additional compartment which stands for the electrodes (Fig. 3a). The adjacent compartment refers to the core of the interfaces, i.e. in our case to a transition region of varied structure between the metal and mixed conductor. The chemistry of the electrode compartments is often highly complicated: the electrodes may be porous, there may be adsorbed oxygen, reactions may be complex, etc. In this paper we consider them on a ‘‘black box’’ level which does not require any particular mechanistic model, but assumes a quasi-steady state approximation (see remarks at the end of this section and also ref. 30). Under these conditions the construction of the terminal part of the circuit is as follows: transition of electrons between the metal and core compartment is characterised by the “electrochemical” resistance \(R_{\text{eon}}^L\) (see Fig. 3a). The displacement rail is connected to the electrode via the electrostatic capacitance, \(C_{\text{ion}}^L\). Since, in the metal compartment, the density of electrons is very high, \(\delta \mu_{\text{ion}}^e\) is vanishing there. Consequently the terminals of the displacement and electronic rails have to be at the same potential, which is satisfied by short-circuiting the two terminals as shown in Fig. 3a, bottom. Finally we are left with connecting the ionic rail to the electrode. The overall reaction relevant to this reads

\[
\frac{1}{2} O_2(gas) \rightleftharpoons O_{2e}^- - 2e_{\text{electrode}}^-.
\]

Close to equilibrium the rate of reaction (12) will be proportional to the difference of the (electro-) chemical potentials referring to the left- and right-hand side of the equation. Thus, the oxygen flux density \(J_O\), reads

\[
J_O = A_O (\mu_{\text{gas}}^\text{gas} - (\mu_{O_2} - 2\mu_{e})).
\]
The proportionality constant, $A_O$, is, in our approximation, a frequency-independent materials parameter referred to equilibrium. Eqn. (13) is actually the boundary condition we had been looking for, however, it is much easier to visualise it graphically, by introducing normalised quantities: We replace $J_{ion}$ by the equivalent electrical current density $I_{ion} = -2e\delta\phi$, define resistance of reaction (12) $1/R_{ion} = 4eA_O$ and normalise the chemical potential of $O_{2(gas)}$ according to

$$\delta\mu_{O_{2(gas)}} \equiv \frac{1}{2e} \delta\mu_{O_{2(gas)}}.$$ 

Then eqn. (13) may be rewritten

$$I_{ion} = \delta\mu_{O_{2(gas)}} - \delta\mu^*_0 - \Delta\phi.$$  

(14)

The electric potential difference, $\Delta\phi = \phi_{core} - \phi_{electrode}$, appears, since the ions and electrons in reaction (12) refer to different loci. The boundary condition (14) is implemented into the circuit as shown in Fig. 3a. The chemical potential of $O_{2(gas)}$, which corresponds to one of the externally applied driving forces, is implemented as an ideal voltage source (its potential is independent of the current). The source is displayed in Fig. 3a as an ellipse with two terminals. One can easily verify the terminal part of the circuit by applying eqn. (14) as Kirchhoff’s voltage law to the loop indicated in Fig. 3a by a dashed line. Please note, that according to our rules, the electrical potential changes only from one carrier compartment to the other (along the $x$-coordinate), while along branches in $y$-direction (reaction coordinate) it remains invariant.

The circuit elements, $R_i^+$ and $C_i^+$, which appear as a consequence of the boundary conditions, deserve some comments. The oxygen exchange reaction (12) is a multi-step process, thus $R_{ion}^+$ stands for the sum of resistances of all the individual steps. If just one step is rate determining, then $R_{ion}^+$ can be interpreted as the inverse of the exchange current density in the Butler–Volmer formalism or as the inverse of the corresponding rate constant in the Chang-Jaffe description (see ref. 30). The description of the overall reaction rate with a resistance only assumes that the output flux instantaneously follows the time-dependent driving forces—a quasi-steady-state approximation. Under general conditions, a transfer function offers a proper description. The frequency dependence stems from the inclusion of energy storage mechanisms, e.g. oxygen adsorption, surface diffusion, etc. As in the bulk, these storage processes can easily be taken into account by chemical capacitances. A detailed treatment in this respect which highlights the power of the proposed tool for handling electrode kinetics will be given elsewhere.

As far as $C_i^+$ is concerned, we should stress that the relative permittivity of the corresponding transition-compartment located between electrode and core certainly differs from the bulk values (see in-depth studies concerning liquid electrochemistry). In terms of liquid electrochemistry the interfacial core refers to the inner Helmholtz plane (IHP), thus $C_i^+$ to the capacitance of the region between the electrode and the IHP. The capacitance due to the diffuse (Gouy–Chapmann) layer is already included in the “bulk part” of the transmission line (see Section 4.1, also ref. 13 and 15); thus, there is no need to include it explicitly in the terminal part, as has been done in the literature.17

3.2.2 Free surface boundary conditions. In the field of solid state electrochemistry, samples are not necessarily electrically contacted. An important example is a mixed conducting membrane separating two chambers with different component partial pressures. Here different charge carriers move in an ambipolar and effectively electroneutrality fashion. If the mobilities of the carriers, e.g. $O^{2-}$ and $e^-$ in the case of oxygen permeation, differ, the membrane surface will become charged albeit not contacted externally (see for example ref. 31).

In the simplest case the sample ends with the surface core (no electrode compartments) (see Fig. 3b) and the only driving forces are $\delta\mu_{O_{2(gas)}}$ and $\delta\mu_{core}$, the overall reaction between the gas phase and the carriers in the surface core, which occurs in several steps, can be written as

$$\frac{1}{2}O_2(gas) \rightleftharpoons O_{2(core)}^2 - 2e_{core}^-, \quad (15)$$

which is quite similar to reaction (12). The only difference is that here the electrons refer to the core, not to the electrode. Using almost the same procedure as in the previous section (we denote the surface reaction resistance by $R_s$) we derive

$$\pm I_{ion} R_s = \delta\mu_{O_{2(gas)}} - \delta\mu_{core}^* - \delta\mu_{core}^* - \Delta\phi \quad \text{at } x = \pm L. \quad (16)$$

The source of oxygen chemical potential, $\delta\mu_{O_{2(gas)}}$, is connected to the terminals $T_1$ and $T_2$ (see Fig. 3b) through $R_s$, which, on the level of the equivalent circuit, describes the internal resistance of the source. The division of the external driving force $\delta\mu_{O_{2(gas)}}$ into $\delta\mu_{core}^*$ and $\delta\mu_{core}^*$ is determined by the structure of the circuit. Please note that the core chemical capacitors for ions and electrons are in general not filled evenly, thus storing an excess surface charge, which was mentioned above. This charge is needed in order to enable the existence of the drag electric field within the sample, which is characteristic for ambipolar diffusion. In the literature dealing with chemical diffusion the surface reaction is usually characterized by a phenomenological rate constant $k_s$. It is straightforward to show that $k_s$ is related to $R_s^{-1}$ through the component chemical capacitance of the whole sample, viz.: 

$$k_s = \frac{L}{R_s C_s^+}. \quad (17)$$

From eqn. (17) we see immediately, that $k_s/L$ plays the role of a time constant which characterises the transient behaviour of the surface controlled diffusion.

4 Applications of the equivalent circuit

4.1 A single carrier conductor polarised with blocking electrodes

One of the simplest situations, which is met in solid state electrochemistry, is a single carrier system contacted by electrodes which do not allow for any carrier transfer across the interface (completely blocking electrodes). Such a cell is approximately realised by PtAgCl/Pt or C/β-alumina/C (as long as we do not consider the low frequency part of the impedance spectra near the dc conditions). Another single carrier system with blocking electrodes is the MOS (metal-oxide-semiconductor) structure M/SiO$_2$/Si/SiO$_2$/M. Here, the material under focus is Si doped such that only electrons or holes are of importance. If we neglect ions in SiO$_2$, the SiO$_2$/Si contacts perfectly block the carriers in Si. The impedance of these systems has been treated in detail on the continuum level as well as on the level of intuitive and exact equivalent circuits. Our aim here is to derive from the equivalent circuit some interesting properties of the electrode capacitance (Is it electrostatic and/or chemical by nature?) and of Maxwell–Wagner relaxation. Before doing so, let us reproduce the well-known impedance relations.

4.1.1 Impedance. Since we have just one charge carrier to consider, the general circuit simplifies (here we take for example the ions as charge carriers, but the circuit would have the same topology also for electrons): The electronic rail as well as the chemical capacitors due to electrons can be omitted (see Fig. 4a). In the case of blocking electrodes the interfacial resistance is infinitely large, thus the ionic rail is simply disconnected from the electrodes. First we assume arti-
4.1.2 Diffuse layer capacitance. As derived previously by Sah and Brumleve and Buck, the second term refers to the diffuse layer capacitance, $C_{\text{diff}}$. Interestingly, $C_{\text{diff}} \equiv \sqrt{C^0 C^\text{dl}}$ is the geometric mean of the sample’s dielectric and chemical capacitances. Further evaluation of the geometric mean according to eqn. (9b) and (9c), yields the more familiar expression of the “flat band” diffuse layer capacitance

$$\sqrt{C^0 C^\text{dl}} = \frac{\kappa_0 A}{\sqrt{\varepsilon_0 kT}} \frac{A}{L_D} = A$$

The Debye length, $L_D$, i.e. the screening length, reveals a further interesting meaning. The chemical capacitance of the whole sample increases with the sample’s thickness, while its electrostatic capacitance decreases. Therefore, there must be a critical thickness at which $C^\text{dl} = C^0$. In single carrier systems this thickness is exactly the Debye length: if the sample is thinner than $L_D$, its electrostatic capacitance will be larger, if the sample is thicker the chemical capacitance will predominate.

As we noted, $C_{\text{dl}}$ is a “mixture” of an electrostatic and a chemical capacitance (Fig. 4b). Since the capacitors are arranged in a transmission line, the term “diffuse layer capacitance” is very meaningful. A straightforward calculation shows that one half of the free energy in such transmission line is stored electrostatically, and the other half chemically (configurational entropy term). Although $C_{\text{dl}}$ can thus be considered as an element in which the energy is stored “electrochemically” it is not an electrochemical capacitor in the sense of its definition (see Fig. 1b). The chemical and electrostatic capacitors are connected in a transmission line rather than in series. Already this shows that the concept of an electrochemical capacitance is not general.

4.1.3 Interfacial capacitance including core effects. The diffuse layer capacitance of cells with solid ionic conductors has never been clearly measured. The values found were almost always much higher (orders of magnitude) than expected from $L_D$. Although different interpretations have been given in the literature, we propose an explanation which follows directly from the circuit. In the treatment above we assumed that the sample is completely homogeneous. In reality, the carrier density in the interfacial core will be different from the bulk since there the underlying structure differs from the regular structure in the bulk. Thus the core chemical capacitance should be distinguished from the chemical capacitances of the subsequent compartments. The equivalent circuit for the interfacial capacitance, $C$, is then composed of $C^\text{dl}$ and $C_{\text{core}}$, as shown in Fig. 4c and derived earlier from the steady state considerations. If the core carrier density is very high, then $C_{\text{core}} > C_{\text{dl}}$ and $C$ will appear as a series combination of the electrostatic $C^\text{dl}$ and chemical $C_{\text{core}}$. Thus an interpretation of $C$ as an electrochemical capacitance is indeed possible in this case (see also Fig. 1b). If a partial charge transfer between the metal and core takes place, $C^\text{dl}$ will effectively be very large and $C \approx C_{\text{core}}$. Such a situation is met in supercapacitors, in the case of underpotential deposition or the electrosorption process of $e.g.$ Pb on Au (see e.g. ref. 9). Our core defects in these cases refer to the electrosorbed species comprising a part of the monolayer on the top of the electrode. To make this point clear let us calculate the core capacitance explicitly. According to eqn. (9c) the capacitance is defined as $\kappa e_{\text{core}} / c_{\text{max}}$. Using the surface coverage, $\theta \equiv c_{\text{core}} / c_{\text{max}}$, rather than the concentration, and taking into account that the density of core defects is limited by $c_{\text{max}}$, their chemical potential reads $\mu_{\text{core}} = \mu_{\text{core}} + k_B T \ln \theta/(1 - \theta)$.
The capacitance obtained \( C = (e\varepsilon_0) / K_0 \cdot T \cdot V(1 - \theta) \) is identical to the pseudo-capacitance derived from the electrochemical Langmuir isotherm.

### 4.1.4 Maxwell–Wagner relaxation

There is another point worth mentioning in a single carrier system. Let us consider a material which exhibits a Schottky contact with the metal. Then the equilibrium carrier density in the space charge layer will be significantly depleted and the \( C \) referring to the compartments within the space charge layer will be much smaller than in the bulk. To a first approximation, \( C \) can be omitted, and the equivalent circuit of the space charge layer will consist of the layer’s resistance in parallel with the layer’s electrostatic capacitance. If, on the other hand, the carrier density changes significantly only on a scale large compared to \( L_0 \), then the opposite limit is realised: the discretisation can be coarser (\( s > L_0 \)), and the \( C \) will be relatively large (when compared to \( C \)). Thus, the \( C \) can, to a first approximation, be short-circuited, resulting in a series of \( RC \) terms. This description, which is known in the literature under the term Maxwell–Wagner relaxation, does not assume local electroneutrality but rather neglects the relative changes of carrier density. As we have shown, the Maxwell–Wagner approximation is very good for single carrier systems on a scale much larger than \( L_0 \). Therefore, only the opposite limit is realizable.

### 4.2 Quantum-confined capacitor

So far we have neglected the changes in electron densities in metal electrodes upon applied potential difference. Since the number of electrons in metal electrodes is very high when compared to the number of carriers in an ionic conductor, the relative changes in the metal are indeed negligible. The situation is different, however, if the size of the electrodes becomes very small (Fig. 5a). Let us briefly consider such a mesoscopic parallel plate capacitor using our equivalent circuit. If we neglect, for simplicity, the spatial variations within the plates, the equivalent circuit shown in Fig. 5b results. Since the chemical and electrostatic capacitors, unlike in the case considered in Section 4.1, appear in series then the system capacitance in this case is a proper electrochemical one, as derived earlier. At \( T = 0 \), and to a good approximation also at finite temperatures, the chemical capacitance of electrons \( C_{\text{con}}^a = (e^2 / k_0 T) V(\mu_{\text{con}} / \varepsilon_{\text{con}}) \) is proportional to the density of states at Fermi energy multiplied by the electrode volume. As we already mentioned, due to the high number of states, \( C \) is usually much greater than \( C \) and thus negligible in the overall expression. Interesting effects appear at mesoscopic sizes. If the width and thickness of the electrodes are of the order of a few nm, the electrodes behave as quantum wires (Fig. 5a). Then the chemical capacitance is not proportional to the volume but to the length, \( L \), of the wires, \( C = L / (h_{\text{eff}}) \), \( h \) being the Planck constant. Assuming \( L = 1 \mu m \) and the velocity of electrons at the Fermi energy \( v_F \) to be \( 10^6 \text{ cm s}^{-1} \), then the chemical capacitance \( C \) is approximately \( 0.05 \text{ fF} \), becomes comparable to \( C \).

### 4.3 Warburg diffusion and stoichiometry polarisation: General

In general, in solid materials ionic and electronic charge carriers are mobile. Here we discuss such a mixed conductor with one ionic and one electronic charge carrier sandwiched between electrodes which are nearly reversible for electrons and nearly blocking for ions. We use the word “nearly” since we discuss a realistic cell. Such cells are often used in solid state electrochemistry in order to investigate separately the ionic and the electronic conductivity and to measure the component diffusion coefficient. The electrochemical cells mentioned in the previous section but now observed over the entire frequency range are appropriate examples. Others are \( \text{C}/\text{PbO}/\text{C} \), and also cells in which the electronic carriers are blocked. For this purpose pure ionic conductors are used as electrode phases, e.g. Pt, \( \text{O}_2/\text{yttria-stabilised-zirconia (YSZ)} \), contacted to \( \text{PbO} \), or BaTiO\(_3\), or \( \text{Yb}_2\text{Cu}_3\text{O}_{x+y} \). We further assume, just for simplicity, that the mixed conductor is a single crystal and that the component partial pressures at both sides of the sample are kept equal and constant. At high frequencies of the applied voltage the electrode influence is negligible; the dielectric relaxation in the bulk yields a semi-circle in the complex plane described by the “non-blocked bulk resistance” \( R_{\text{con}}(R_{\text{ion}} + R_{\text{con}}) \) and the dielectric capacitance of the sample. In this regime both carriers contribute fully to the bulk conductivity. At lower frequencies, however, the selectively blocking electrodes prevent ions from crossing the interfaces: ions periodically accumulate at one side of the sample while becoming depleted at the other. Of course, this accumulation and depletion over larger distances is only possible if the density electron changes accordingly, such that the sample remains locally electroneutral. In this frequency range chemical diffusion (45° Warburg diffusion turning over into a semicircle) takes place: in an oxide, the “oxygenu” effectively swings between both halves of the sample, and thus the composition changes as well. In ref. 20 and 21 we introduced intuitively an approximate equivalent circuit for such a cell and showed that it applies in a very broad materials parameter window. However, we could not derive it directly from the basic equations. Here we show how this is possible (we will use an exact equivalent circuit rather than differential equations as the starting point).

The exact equivalent circuit of a mixed conductor is shown in Fig. 3a (we omit outer chemical driving forces here). On the basis of the previous single carrier study the following simplifications of the circuit can be made: (i) the bulk of the sample is electrically homogeneous which suggests that local electroneutrality will be a good approximation there. Thus \( C_{\text{con}} \) and \( C_{\text{ion}} \) will be charged evenly, and there will be no current leakage into the displacement rail; Consequently the bulk \( C \) behaves as truly connected in series. We replace the \( C \)s from the bulk part of the displacement rail by a single geometrical capacitance of the sample connected externally (see Fig. 6a). This is an approximation since the interfacial \( C \)s are now counted twice, but as long as \( L \gg L_0 \), the approximation is good. Now the bulk ionic and electronic chemical capacitors allocated to the same compartments also appear to be connected in series—thus they can be replaced by the chemical capacitance of the component, \( C \), as derived previously. This first simplification step yields the circuit shown in Fig. 6a.

In the interfacial regions local electroneutrality is clearly violated. In this region we neglect, besides \( R_{\text{ion}} \), all other resistances.
3.2 Local current and charge carriers: Concentration and current distribution

The capacitive network that remains (Fig. 6b) is a three-terminal element which can in general be described by three impedances (see for example ref. 43) and taken into account explicitly in the evaluation of the overall impedance. This description is, however, beyond the scope of this paper, and we rather make further approximations as shown in Fig. 6c. We replace the capacitive network by two capacitors with well defined values obtained as follows: First we neglect electronic carriers (the bottom part of the network). The remaining two-terminal transmission line (see Fig. 4b) exactly reflects the diffuse layer capacitance due to ions, $C_{dl}^{ion}$. Second, we neglect ions and substitute the bottom part of the network by $C_{dl}^{ion}$. Of course such a substitution of the three-terminal network by that composed of $C_{dl}^{ion}$ and $C_{dl}^{ion}$ (Fig. 6b) is an approximation, yet, as the detailed analysis shows, the error is less than 50%. This is still acceptable, especially in view of the fact that the impedance of the resulting circuit (Fig. 6c) can be obtained in a closed form and applies for a very broad materials parameter window. The obtained closed form impedance explains, for example, a long lasting “paradox” in the field of impedance spectroscopy, referring to the transition of 45° Warburg impedance to 90° rise which we expect if we start with a mixed conductor and then neglect one of the charge carriers. For details see ref. 20 and 21.

It is interesting to note that the interfacial capacitance (the three terminal capacitive network) in general does not refer to charge carriers. For details see ref. 20 and 21.

4.4 Warburg diffusion and stoichiometry polarisation: SOFC kinetics

In this section we apply the circuit just derived above to the interesting example of the electrode kinetics of solid oxide fuel cells. To be specific, we consider the impedance of the cell (see Fig. 7a) $O_{2(gas)}/(La, Sr)CoO_3-(YSZ/Pt, O_{2(gas)})$. From the point of view of the SOFC cathode this is the set-up of a Wagner–Hebb polarisation cell in which the electronic conductivity is blocked by YSZ electrolyte. Since (La, Sr)CoO$_3$-s (LSC) is a mixed conductor with relatively high electronic conductivity the circuit shown in Fig. 6c can be further simplified by short-circuiting the electronic resistors and by connecting the external lead to LSC directly ($R_{ion}$ is not necessary). We use highly permeable LSC instead of the manganate since we can then consider quasi-one-dimensional transport. The oxygen exchange reaction is taken into account by the resistance $R_s$ in parallel with the interfacial capacitor $C_{dl}^{ion}$, as derived previously (see Fig. 6c). The right-hand side terminal part of the circuit refers to the interface between the mixed and ionic conductor. Here the electrons are blocked, thus only $C_{dl}^{ion}$ remains in the electronic rail. The ionic transfer is characterised by $R_{ion}$. Let us assume that a reference electrode is used, connected to YSZ close to the interface, such that further transport steps are not of importance. The resulting circuit is shown in Fig. 7b.

An interesting situation occurs, if the transport in LSC is surface controlled, then the ionic resistance of the mixed conductor vanishes and the chemical capacitors, which are now all in parallel, can be replaced by a single $C^o$ which refers to the whole sample. The resulting circuit (Fig. 7c) becomes even more transparent when presented in a nested form (Fig. 7d): it yields two impedance semicircles in the complex plane, the high frequency one referring to the interface LSC/YSZ while the low frequency one is composed of the surface exchange resistance $R_s$ and the chemical capacitance of LSC. Since $C^o$...
is, unlike \( R_1^2 \), proportional to the thickness, we expect the relaxation time to scale linearly with the thickness of LSC. This was indeed observed and also properly explained.\(^{44} \) This example is interesting, since \( C^e \) appears as a part of an \( RC \) term just like the electrostatic capacitances which we are used to. In general the chemical storage of energy always occurs locally and is therefore necessarily combined with the transport steps which supply the carriers; thus the storage and dissipation of energy is inherently distributed in space with the consequence of dispersive impedance spectra (transmission lines). If, however, the transport steps are relatively fast, as in the case here, the chemical storage is reflected in its pure form, \textit{i.e.} as a perfect capacitor without any frequency dispersion.

### 4.5 Intercalation battery

In this section we discuss two ionically and electronically reversible electrodes separated by an ionic conductor, \textit{e.g.} \( \text{Pt}/\text{Li}_x\text{Mn}_{2}O_4/\text{Li}^-\text{-electrolyte}/\text{Li}_xC \) which is the set-up of a modern rocking chair battery in which Li swings forth and back from one intercalation electrode to the other. From the point of view of the intercalation electrode (\textit{e.g.} \( \text{Li}_x\text{Mn}_{2}O_4 \)) this is a set-up of a coulometric titration cell, in which \( \text{Li}_x\text{Mn}_{2}O_4 \) as the mixed conductor is sandwiched between a metal electrode (blocking for ions) and an ionically reversible electrode (\( \text{Li}^-\text{-electrolyte}/\text{Li}_xC \)) being blocking for electrons. A detailed description of the electrochemical impedance of such cells is possible but requires numerical simulations.\(^{46} \) Nevertheless, several basic features can also be derived from our equivalent circuit.

The cell is depicted schematically in Fig. 8a. In reality, the intercalation electrodes are often porous, we assume here for simplicity that the conductivity within the pores is very high and consider only a single “grain” of the intercalation electrode. The electrolyte, which is \textit{e.g.} a lithium ion conductor, is contacted with an intercalation electrode material (\( \text{Li}_x\text{Mn}_{2}O_4 \)) being capable of accepting or releasing lithium in the form of ions and electrons: ionic transfer takes place at the electrode/electrolyte interface and electronic transfer at the current-collector/electrode interface. For this situation the circuit shown in Fig. 7b is sufficiently general. Disconnecting the ionic rail from the current collector and neglecting the electronic resistances within the electrode the circuit reduces as shown in Fig. 8b. It is obvious that at low frequencies the circuit describing a battery is blocking; the imaginary part of the impedance will be determined by \( C^e \); the charge is swinging between the two chemical capacitors (two electrodes). The chemical capacitance \( C^e \) is a differential quantity by definition. Thus, the overall charge stored in a battery is obtained by integration:

\[
Q = \mu_1 \int_{\mu_2}^{\mu_1} C(\mu)d\mu,
\]

which is just the average chemical capacity of the electrodes. In other words \( \bar{C} \) is the integral chemical capacitance, just by analogy to the integral electrostatic capacitance.

### 4.6 Pure chemical diffusion

As the final example we discuss the appropriateness of the derived circuit for mass transport with vanishing net current flow. This type of transport refers to chemical diffusion of a component, \textit{e.g.} oxygen, in the form of oxygen ions and electrons, through an oxide. Owing to its selectivity with respect to the species transferred, the process can be used for gas separation \textit{e.g.} to filter out oxygen from air by simply applying a pressure difference across an oxide membrane.

A properly terminated general circuit for this situation was developed in Section 3.2.2 and is shown in Fig. 3b. On a timescale large compared to the dielectric relaxation time and with a spatial resolution well above the Debye length we may assume electroneutrality which simplifies the circuit substantially (see Fig. 9a). Transmission lines of this form are a well-known description of diffusion transport in general.\(^{5} \)

\begin{align*}
\text{(9) the more familiar form} \\
D^f = \frac{L^2}{(R_{\text{ion}} + R_{\text{eon}})C^e},
\end{align*}

Substituting \( R \) and \( C^e \) in eqn. (22) by their defining equations (9) the more familiar form \( D^f = t_{\text{eon}}D_{\text{ion}} + t_{\text{ion}}D_{\text{eon}} \) is readily reproduced (note that internal trapping reactions\(^{47} \) are neglected here).

\textbf{Fig. 9} (a) Approximate equivalent circuit for chemical diffusion in a polycrystal with blocking grain boundaries. (b) Further reduction of the circuit for situations in which the grain boundary chemical resistance prevails over the bulk one.

The circuit becomes a useful tool if the sample is not homogeneous. Let us consider a polycrystal in which grain boundaries are “blocking” for chemical diffusion (e.g. Fe-doped SrTiO₃ ceramics). We assume a brick layer model for the polycrystal, such that a quasi-one-dimensional approximation is reasonable. The resistances and chemical capacitances which refer to the grain boundary regions will differ from the elements within the grains. The complexity of this circuit in general requires a numerical approach. However, a simple analytical solution can be given, if the resistances in the grain boundary regions are high when compared to the resistances of the grains, \( R_{\text{grain}} \) may be neglected, and if in addition the grain size, \( L_{\text{grain}} \), is large compared to \( L_0 \), the boundary volume and thus the boundary chemical capacitance is negligible. The correspondingly tailored circuit (Fig. 9b) is then just a superstructure of a transmission line for a single crystal: the transport on a scale larger than the grain size appears as diffusion in a homogeneous material but characterised with resistances \( R_{\text{gb}} \) and capacitances \( C_{\text{grain}} \). The corresponding diffusion coefficient reads:

\[
D_{\text{gb}} = \frac{L_{\text{gb}}^2}{R_{\text{gb}} + R_{\text{grain}} C_{\text{grain}}}.
\]  

(23)

Please note that in eqn. (23) the resistances and the capacitances refer to different loci (boundaries and grains, respectively).

5 Conclusions

An equivalent circuit, which exactly maps the drift-diffusion model of an effectively one dimensional mixed conductor contacted with two electrodes, has been derived. Under conditions of time-invariance and linear response the circuit consists of only three basic elements: (i) “electrochemical” resistance, (ii) electrostatic capacitance and (iii) chemical capacitance, which are defined in terms of the chemical and electrical properties of the cell. The connection of the elements has to satisfy the fact that the spatial and thermodynamic displacement occur along two “orthogonal” coordinates. As we showed in several examples in the second part of the paper, it is very easy to identify in the exact circuit the elements relevant for the particular experimental conditions and to neglect the unimportant ones. This is most relevant for solid state electrochemistry, since it allows for the description of different experimental set-ups as well as of a variety of devices, e.g. fuel cells, oxygen membranes and pumps, batteries. As simple as the tailored circuit finally is, it has two advantages when compared to empirically constructed circuits: (i) the validity range of the circuit is well defined and (ii) the circuit elements are clearly related to basic materials parameters.

References

34. K. W. Wagner, Arch. Elektrotech., 1914, 2, 371.