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Chemical resistance and chemical capacitance

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Abstract: The present contribution defines rigorously terms such as chemical resistance, chemical capacitance and exchange reactivity. Several examples of interest are presented whose treatments show the relevance of these parameters for chemistry, in particular for solid state chemistry.

Keywords: chemical capacitance; chemical kinetics; chemical resistance; interfaces; solid state.

Dedicated to: Professor Arndt Simon on the occasion of his 80th birthday.

1 Introduction

Chemical reactions are probably the most important processes of our world. They range from life-enabling biochemical reactions to solid state reactions providing functional materials [1]. They represent examples in which generalized fluxes (reaction rate, mass flux, electric current, heat flux, strain rate) are driven by forces (affinity, concentration gradient, voltage, temperature gradient, stress) [2]. In all these situations dissipation occurs which is due to the corresponding resistances but also pure storage, which is due to the corresponding capacitances. Close to equilibrium, fluxes and forces are proportional to each other and coupled via friction parameters (or their inverse quantities such as exchange rate, diffusion coefficient, electric or thermal conductivities, elasticity modulus). These friction parameters are proportional to resistances, a special role in this context being played by a chemical resistance. Far away from equilibrium one can define analogous differential parameters, but then it is usually more straightforward to apply master equations, which in the case of chemical reactions means applying chemical reaction kinetics [3, 4].

In the case of pure transport phenomena, storage effects occur only if flux divergences are involved (i.e. influx ≠ outflux). In chemical reactions, storage (i.e. local concentration variations) naturally occurs unless the product is quickly transported away. This coupling is directly referred to by the continuity equation (total storage = storage via flux divergence + storage via reaction rate). In the case of chemical reactions, it is straightforward to use master equations that include such effects implicitly. Close to equilibrium, storage effects can be, however, easily accounted for by introducing generalized capacities such as a chemical capacitance.

Using both chemical resistors and chemical capacitors allows for a very simple description of reaction networks, and by combining them with electric circuit elements, a simple description of solid state chemical processes or electrochemical processes is enabled in which transport plays a significant role. Let us first discuss these elements and then address a few selected problems that reveal the relevance for chemistry. More detailed but less intuitive treatments have been given in some of our earlier work (see e.g. [5]).

2 Exchange reactivity

The term "reactivity" is typically used in a rather undefined sense usually meaning the forward rate ($\vec{\mathcal{R}}$) of the fastest reaction that a substance can undergo. If the term is used to describe a specific, concentration-independent property, it is rather to be identified with the corresponding rate constant ($\vec{k}$).

A very clear definition can only be given close to equilibrium where forward and backward reactions are not very different, and it then refers to the exchange rate [3].

The simplest example considers $A \rightleftharpoons B$ with

$$\vec{\mathcal{R}} = \vec{k}[A], \quad \overleftarrow{\mathcal{R}} = \overleftarrow{k}[B], \quad \mathcal{R}^\circ = \sqrt{\widehat{[A]}\widehat{[B]}\vec{k}\overleftarrow{k}} \equiv \bar{c}\,\bar{k}. \tag{1}$$

The exchange rate, that can be identified with the exchange reactivity, is thus composed of the geometric mean of the involved equilibrium concentrations (equilibrium values are denoted by hat) and the geometric mean of the rate constants.

(For this first order reaction $\mathcal{R}^\circ$ can – owing to mass conservation – also be written as $\bar{k}\langle c\rangle$ where $\bar{k}$ is the arithmetic mean of the two rate constants and $\langle c\rangle$ the harmonic mean of the two equilibrium concentrations $\widehat{[A]}$ and $\widehat{[B]}$ [3]). The similarity to a conductivity $\sigma \propto u \cdot c$

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is obvious, where the mobility u corresponds to the rate constant of the hopping process and σ to its exchange rate. If the hopping process is viewed as a reaction with zero affinity (hop from one side to the next equivalent one), σ can indeed be shown to be the exchange rate of this process [3].

It is straightforward to demonstrate (Appendix A) that close to equilibrium any chemical reaction ($\mathcal{A}$) reduces to a linear flux–driving force law

$$\mathcal{R} = \vec{\mathcal{R}} - \bar{\mathcal{R}} = \mathcal{R}^{\circ}(\mathcal{A}/RT), \tag{2}$$

where the affinity (negative reaction free enthalpy) plays the role of the driving force. Clearly the validity range of linearity is small in the case of chemical kinetics and very often exceeded.

3 Chemical resistance

A precise definition of the chemical resistance refers to eq. (2) and is possible via

$$R^{\delta} \equiv RT/\mathcal{R}^{\circ}. \tag{3}$$

(Do not confuse the different R's: resistance, gas constant, reaction rate).

In a sequence of reactions corresponding to a sum of R^{δ} values, it is the slowest step, i.e. the step with the largest R^{δ}, that determines the overall rate. In a parallel network (inverse R^{δ} values are summed) it is the fastest step (smallest R^{δ}) that determines the overall rate. In the steady state of such a reaction sequence all rates are equal. (The validity of Kirchhoff's laws follows directly from the isomorphicity of the flux-force relations). Then all the other steps with a higher exchange rate exhibit a rate that is much lower than their exchange rates. According to eq. (2), their affinities are virtually zero, meaning that all these steps are now in quasi-equilibrium ($\mathcal{A} \simeq 0$ i.e. $\vec{\mathcal{R}} \simeq \bar{\mathcal{R}}$) (see Fig. 1). The involved concentrations obey the specific (but not the global) mass action law but are time-dependent and different from true equilibrium concentrations.

A special role is met in the case of a diffusion controlled reaction [7], there $\mathcal{R}$ corresponds to a flux, $\mathcal{R}^{\circ}$ to an exchange flux and R^{δ} to an inverse conductance. In a typical chemical process, such as a diffusion controlled stoichiometry change, the overall rate is determined by electroneutrally coupled motion of two carriers. In the case of a diffusion-controlled simple redox reaction we refer to the coupled motion of ions and electrons (e.g. transport of Li^+ and e^- to change the lithium content, or counter transport of O^{2-} and $2e^-$ to change the oxygen content), yielding

$$R^{\delta} \propto \frac{\sigma_{\text{eon}} + \sigma_{\text{ion}}}{\sigma_{\text{eon}}\sigma_{\text{ion}}}. \tag{4}$$

Far from equilibrium the chemical resistance has to be defined differentially

$$R^{\delta}/RT = (d\mathcal{R}/d\mathcal{A})^{-1}. \tag{5}$$

A highly interesting case is met if an autocatalytic reaction is involved. Such reactions lead to growth, instabilities, oscillations, and structure formation. An autocatalytic reaction involves a negative chemical resistance. This is completely analogous to negative differential electric resistances that play a paramount role in electric nonlinearities and electronic structure formation in semi-conductors [8].

Let us consider the growth reaction

$$\mathrm{X} + \mathrm{F} \rightleftharpoons 2\mathrm{X} \tag{6}$$

where the X-population grows at the expense of the consumption of F ("food"). Here $\mathcal{R} = \vec{k}[\mathrm{X}][\mathrm{F}] - \bar{k}[\mathrm{X}]^2$ and $\mathcal{A} = RT\left(\ln K - \ln\frac{[\mathrm{X}]}{[\mathrm{F}]}\right)$ (cf. Appendix B for more details).

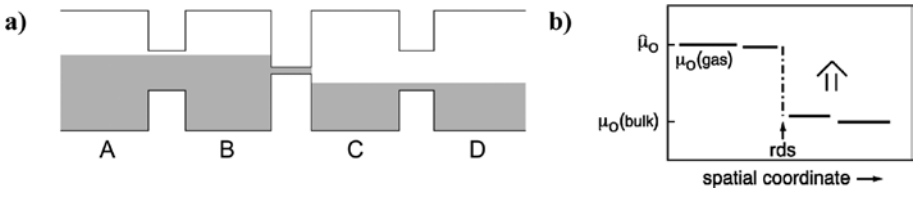

Fig. 1: (a) The rate determining step (rds: B ⇌ C) is the bottleneck, leading in the steady state to pre- and post-equilibria. These are quasi-equilibria as concentrations fulfil the respective mass action laws, but with time-dependent non-equilibrium concentrations. The water analogue shows then equal but time-variant water levels (for A ⇌ B and C ⇌ D). Reprinted from ref. [3]; (b) The oxygen chemical potential of an oxygen incorporation reaction into a solid whereby the surface step is the rate determining step. Reprinted from ref. [6] with permission from Elsevier.

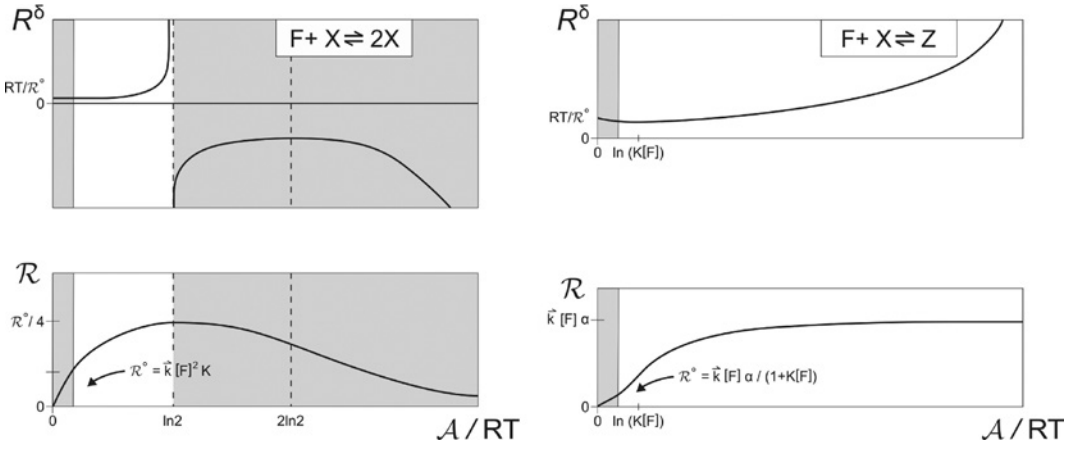

Fig. 2: Chemical resistances and reaction rates for two chemical reactions (left column: conversion reaction; right column: autocatalytic reaction), as discussed in the text. The shaded areas in the individual figures refer to the regimes of linearity (LHS) and positive feedback (RHS). (See Appendix B for technical details.)

In Fig. 2 the courses of the reaction rate and of the chemical resistance is shown for the autocatalytic reaction (6) and compared with the above considered conversion reaction ($X+F \rightleftharpoons Z$). Let us concentrate on the beginning of the reaction, here $\mathcal{R} \simeq \vec{\mathcal{R}} = \vec{k}[F][X] = \frac{d[X]}{dt}$. $\delta\mathcal{R}/\delta[X] > 0$, i.e. $\delta[X]^\bullet \delta[X] > 0$. This is the criterion of positive feedback [9, 10]. The same can be concluded from $\delta\mathcal{R} \cdot \delta\mathcal{A}$ which is also positive. It can be shown that this is equivalent to a positive variation of the entropy production, signifying the tendency of driving away from equilibria ([2], see also [3]). If the sign is opposite, the system moves toward equilibrium. The same is concluded from $\delta[X]^\bullet \delta[X] < 0$. Such an opposite sign develops when the back-reaction becomes significant.

Reference [5] gives a more detailed account and also shows why not only a chemical resistance but also a chemical capacitance is necessary for a network description of reactions. Table 1 refers to generalized currents driven by both electrical and chemical driving forces.

The electrical and chemical driving forces can be unified to gradients in the electrochemical potentials. Such a unification is generally not possible as far as dielectric and chemical capacitances are concerned, as here the mechanisms are different. As far as the dielectric effects are concerned (see Table 1), a displacement current (I_{dis}) is defined which is driven by the time derivative of the electric field. The missing equation is the mass conservation (continuity) equation that has to be written in terms of the chemical potential rather than concentration. This conversion from ∇c to $\nabla \mu^*$ then necessarily introduces a chemical capacitance.

Table 1: Flux-driving-force relations in electrochemical problems [5].

$I_j = -\sigma_j \nabla(\mu_j^* + \phi)$
$I_{dis} = -\varepsilon \frac{\partial}{\partial t} \nabla\phi$
$\nabla I_j = -\zeta \frac{\partial}{\partial t} \mu_j^*$

I_j, electric current density of carriers j; μ_j^*, normalized chemical potential, $\mu_j^* + \phi$ is the normalized electrochemical potential; ε, dielectric constant; ζ, normalized chemical capacitance.

4 Chemical capacitance

As chemical capacitance we define the increase of matter on varying the chemical potential. Note that in purely electrical processes the capacity is the increase of charge with increasing electrical potential.

As shown in a previous paper, generalized treatment of generalized capacitances is possible in an $\mu_1 n_2 TP$ ensemble [11]. In other words: We consider at given T, P a binary A_xB in which the A content is defined by the mole number of A (n_2), while the B content is determined via the chemical potential of B (i.e. μ_1), e.g. by establishing a partial pressure of B in the environment.

In the literature, this ensemble is referred to as an irrelevant one, the reason being that the intensive parameters are interrelated by an equation state. Yet this is only so if non-stoichiometries are neglected. In a material like PbO, to take an example, it is well possible to fix the particle number of Pb and then to independently fix the exact oxygen content by P_{O_2} corresponding to the

Table 2: Thermodynamics of a $\mu_1 n_2 TP$ ensemble.

$$\Gamma = U - TS + pV - \mu_1 n_1$$

$$d\Gamma = Vdp - SdT + \mu_2 dn_2 - n_1 d\mu_1$$
$$= Vdp - SdT - n_1 d\mu_1 \equiv \Sigma_i \ell_i d\lambda_i$$

As the generalized Gibbs-Duhem equation leads, for homogeneous systems, to $U = TS - pV + \mu_1 n_1 + \mu_2 n_2$, one finds $\Gamma = \mu_2 n_2$. For a one-component system, it results in $\Gamma = 0$, corresponding to the then irrelevant "intensive ensemble" referred to in Ref. [12].

homogeneity width ($PbO_{1+\delta}$). The ensemble is particularly applicable to multinaries such as perovskites ABO_3, where the ratio of A to B is often frozen while the oxygen content is still reversible. This ensemble is not only practically relevant, it moreover delivers, according to Table 2, the wanted capacitances as second derivatives of its characteristic thermodynamic function which we term Γ. (Note that Γ is at a minimum in an equilibrium for constant temperature, hydrostatic pressure and partial pressure of species 1.)

Considering Table 1, we can explicitly define generalized capacities via $\frac{\partial^2 \Gamma}{\partial \lambda_i^2}$ where λ is short for p, T or μ_1, namely the thermal capacitance $\left(\text{specific heat } C_p^T \equiv T\frac{\partial S}{\partial T} = -T\frac{\partial^2 \Gamma}{\partial T^2}\right)$, the mechanical capacitance $\left(\text{compressibility } \chi \equiv -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{V}\frac{\partial^2 \Gamma}{\partial P^2}\right)$ and our chemical capacitance, here for the component 1 $C_1^\delta \equiv \frac{\partial n_1}{\partial \mu_1} = -\frac{\partial^2 \Gamma}{\partial \mu_1^2}$. Interestingly a thermodynamic stability analysis [13] which relies on the second order variation of the respective thermodynamic potential function demonstrates that the specific heats, the compressibility but also a quantity such as C_1^δ must be positive. One realizes that the definition is also analogous to the electrical capacitance $C^q = \frac{\partial q}{\partial \phi}$ (q: charge, ϕ: electric potential) which can be introduced by generalizing the work term in the thermodynamic relations. As exemplified below, chemical capacitances play a prominent role in stoichiometric variations and more prominently in electrode storage. As used in Table 1, it connects concentration effects with the thermodynamic driving force

$$\text{div}\, I \propto \frac{\partial n}{\partial t} = \frac{\partial \mu}{\partial t}\frac{\partial n}{\partial \mu}. \tag{7}$$

Since in a battery $\partial \mu_{Li} = \partial V$ (V: electric voltage), there the chemical capacity translates into an electric effect as well. In usual battery language the storable mass Δn_{Li} is used as integral "capacity". This is sloppy but justified as then ΔV corresponds to the covered voltage window which stays invariant.

The concept of chemical capacitance proved to be very helpful in the case of stoichiometric variation as here C^δ can be given explicitly. If the non-stoichiometry is established by neutral defects such as in alloys ($CuZn_{1+\delta}$) or in ionic crystals at low T (where ionic and electronic defects are strongly correlated, e.g. $YBa_2Cu_3O_{6+\delta}$), it simply holds that

$$C^\delta \propto \delta. \tag{8}$$

In ionic crystals where point defects are rather dissociated

$$C^\delta \propto \left(\frac{\chi_{ion}}{c_{ion}} + \frac{\chi_{eon}}{c_{eon}}\right)^{-1}. \tag{9}$$

The χ-factors are unity if trapping effects are not important, and c_{ion}, c_{eon} are sums of point defect concentrations [14].

In dilute systems ionic and electronic defects (j) follow characteristic power laws (power N) [15]

$$\frac{\partial \ln c_j}{\partial \ln a} = N_j = \frac{\partial \ln c_j}{\partial \mu} = \frac{\partial c_j}{c}\frac{1}{\partial \mu}. \tag{10}$$

In such cases, it follows

$$C_j^\delta = N_j \cdot c_j \tag{11}$$

showing that C_j^δ is only significant if both N_j and c_j are large. If the storage is due to a redox process (e.g. oxygen incorporation in an oxide), this is realized in regimes where ionic defects are compensated by electronic defects.

5 The use of chemical resistance and chemical capacitance for solid state processes

In the solid state, diffusion processes are usually important and coupled to interfacial reactions. Some selected examples given now will shed light on the use of the above introduced parameters.

5.1 Protection layers

Here we consider layers of reaction products that slow down or inhibit further reactions [3, 7].

Let us consider Al as an example. In spite of the huge affinity to form Al_2O_3 under air, Al can be safely used as

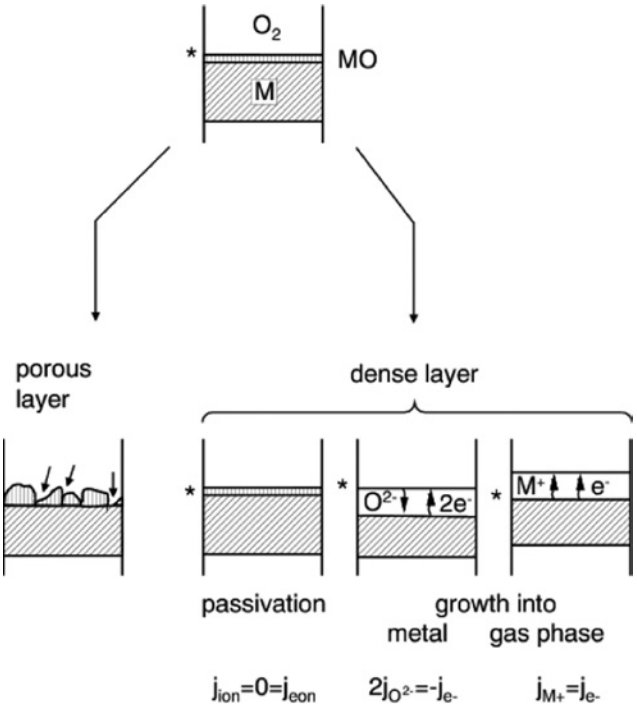

Fig. 3: Transport controlled growth of a passivation layer on top of a metal M exposed to oxygen. Reprinted from [16] with permission from Wiley & Sons.

construction metal. This is due to the very low transport rates which limit the oxide layer thickness to very small values and prevents – even for such small thicknesses – oxygen from reaching Al and Al from reaching the oxygen side. The low conductivities correspond to a high chemical resistance [cf. eq. (4)]. In other cases the oxide layer grows either towards the gas phase or into the metal depending on whether metal ions or oxygen ions are more mobile in the layer (Fig. 3).

A similar situation is met in Li batteries [17] where the electrolyte is almost exclusively unstable with respect to the positive and/or the negative electrodes (e.g. Li). Here the formed protection layers named SEI (solid electrolyte interphase) are a prerequisite for battery stability. The difference to the Al_2O_3 example is that the ionic conductivity is (desirably) not small (and required), but the very low electronic conductivity suffices to depress R^δ [cf. eq. (4)].

An important prerequisite for all these cases is the formation of dense layers. Otherwise fast parallel transport takes over (see Fig. 2).

5.2 Intercalation batteries

In a battery electronic current (from the outer circuit) and ionic current (from the electrolyte) meet at a chemical capacitor (electrode) (cf. Fig. 4). It implies that a steady-state current is only achievable by internal short-circuits, e.g. if the electrolyte exhibits electronic conductivity. To be precise, the two species meet at the electrode boundary wherefrom the component (e.g. Li) diffuses into the material by a chemical diffusion. The chemical diffusion coefficient is composed of an internal chemical resistance R^δ and a differential chemical capacitance composed of electronic and ionic point defect concentrations in the electrode. Interestingly, the storage time τ^δ is given by $R^\delta \cdot C^\delta$ exactly as the dielectric relaxation time is given by the product of an electrical resistance and a dielectric capacitor. Note that in batteries C^δ determines the energy density and τ^δ the power density (if transport is rate-determining).

5.3 Transport kinetics if the surface reaction is sluggish

Figure 5 shows the equivalent circuit for an impedance measurement of a high-temperature fuel cell cathode whereby the rate of the oxygen reduction reaction is important, i.e. influences the current to be extracted. As a consequence the corresponding reaction resistance matters and can be detected by the electric measurement. Storage only occurs in the electrode, but not in the electrolyte whose chemical capacitance is hence neglected. For details see [19].

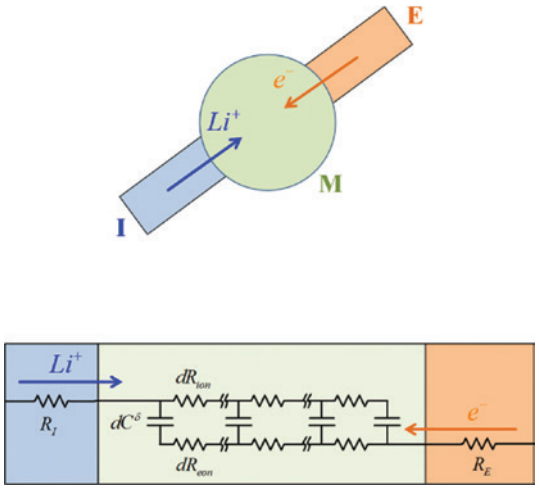

Fig. 4: Equivalent circuit for a battery exhibiting electric and chemical circuit elements. The upper figure displays the electrode (M) with its electronic and ionic contacts. Reprinted from [18] with permission from The American Association for the Advancement of Science.

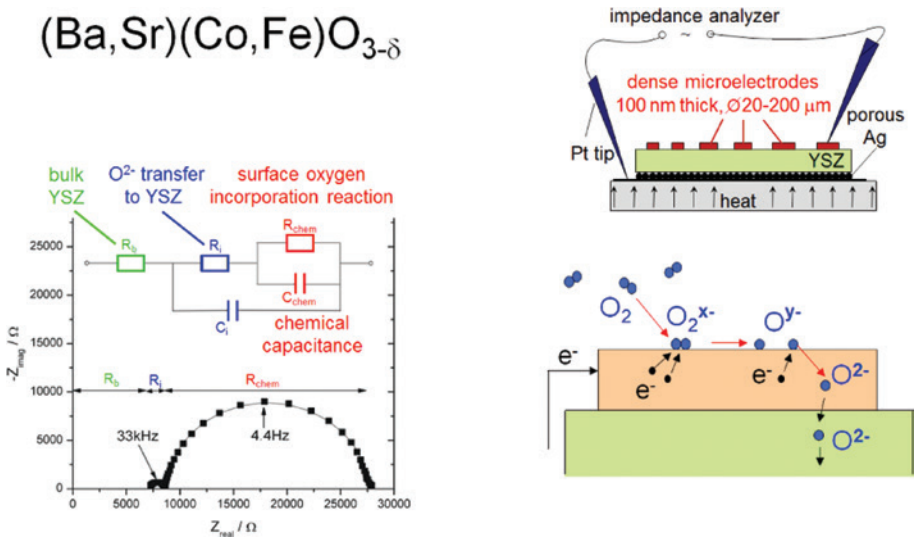

Fig. 5: Surface reaction dominated impedance of a high-temperature fuel cell cathode. Adapted from ref. [19].

5.4 Kinetics of stoichiometric changes in a polycrystalline ceramic

The precise evaluation of such examples in composites can be very complex even in simple brick-layer morphologies (see Fig. 6).

Let us recall that in a single crystal the time constant for stoichiometric changes τ^δ is given by $R^\delta C^\delta \propto \frac{L^2}{D^\delta}$.

Let us first consider the situation that the grain boundary transport is very fast (Fig. 5 LHS). Then the relaxation time is determined by the diffusion in a single grain (size d) as the transport to all individual grains is fast. If the effective diffusion coefficient D^δ_{eff} is defined by $\tau^\delta \propto \frac{L^2}{D_{\text{eff}}}$ (as it were for a homogeneous situation) then obviously

$$D^\delta_{\text{eff}} = D^\delta \frac{L^2}{d^2} \tag{12}$$

where L is the total size. As the overall chemical capacitance is not varied by the grain boundary (as long as the storage in the boundaries is negligible) and the chemical resistance is very much reduced, the effective diffusion coefficient is strongly increased if $d \ll L$.

If on the other hand the grain boundaries are hardly permeable, the ambipolar conductivity $\sigma^\delta \equiv \left(\frac{\sigma_{\text{eon}}\sigma_{\text{ion}}}{\sigma_{\text{eon}}+\sigma_{\text{ion}}}\right)$ is determined by the grain boundaries, while C^δ is still determined by the bulk (i.e. by c^δ). The simple result is

$$D^\delta_{\text{eff}} \propto \frac{d}{d_{\text{gb}}}\frac{\sigma^\delta_{\text{gb}}}{c^\delta} \propto D^\delta \frac{d}{d_{\text{gb}}}\frac{\sigma^\delta_{\text{gb}}}{\sigma^\delta}. \tag{13}$$

Unless the grain boundary thickness d_{gb} is very small, D^δ_{eff} is largely diminished as $\sigma^\delta_{\text{gb}} \ll \sigma^\delta_{\text{b}}$. Should the bulk be absolutely impermeable unlike the boundaries, the storage time is determined by the product of the R^δ_{gb} values and the now very small values of C^δ_{gb}. This little storage was neglected in eq. (11). (Ref. [20] gives technologically relevant examples of Li storage, and thus of a high chemical capacitance, at heterointerfaces).

The reader may imagine that the same formalism can be used to describe much more complicated reactions or reaction-diffusion networks without or with electric contributions [5].

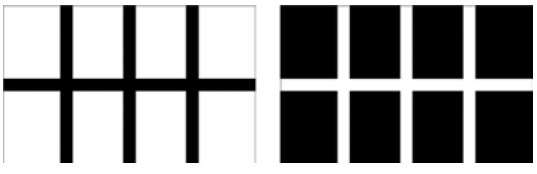

Fig. 6: Simple model of a polycrystalline oxide in which oxygen is dissolved: LHS: Grain boundaries quickly transport the oxygen to the grains. RHS: Grain-boundary transport is sluggish, but oxygen is finally dissolved in the grains [11].

6 Summary

Precise definitions of chemical resistance and chemical capacitance are given. The terms are shown to be useful in particular in complex systems. Differentially defined

they do also great service far from equilibrium. Used as elements of electrochemical circuits, simplifications are easily possible and intuitive even for conditions where the analytical treatment is intricate or impossible.

Appendix

A Rate and affinity in chemical kinetics

The rate is given by

$$\begin{aligned}\mathcal{R} &= \vec{k}\Pi_{\text{educt}} - \overleftarrow{k}\Pi_{\text{product}} \\ &= \vec{k}\Pi_{\text{educt}}\left(1-\frac{Q}{K}\right)\end{aligned}$$

and the affinity (negative reaction free enthalpy) by

$$\mathcal{A} = RT\ln\frac{K}{Q}$$

where the reaction product $Q = \Pi_{\text{product}}/\Pi_{\text{educt}}$; $K \equiv Q(\mathcal{A}=0) \equiv$ mass action constant; Π denotes the product of the concentrations to the powers given by the stoichiometric coefficients for educts or products.

It follows that

$$\mathcal{R} = \vec{\mathcal{R}}\left(1-\exp-\frac{\mathcal{A}}{RT}\right)$$

For vanishing affinity the forward reaction rate approaches the exchange rate and a linear flux-driving force relation (eq. 2) results.

B Rate and resistance for two examples

B1 Simple first order kinetics

$$\mathrm{X} + \mathrm{F} \rightleftharpoons \mathrm{Z}$$

X at the expense of an infinitely available food (F) reversibly transforms to Z. The standard kinetic approach leads to

$$\mathcal{R} = \vec{k}[\mathrm{F}]\alpha\frac{\exp(\mathcal{A}/RT)-1}{K[\mathrm{F}]+\exp(\mathcal{A}/RT)}$$

with the abbreviations $\vec{k}$ for forward reaction constant, $K \equiv \vec{k}/\overleftarrow{k}$ for the mass action constant with $\vec{k}$ referring to the back reaction. $\mathcal{A}$ (negative reaction free enthalpy) is the affinity and given by

$$\mathcal{A} = RT\ln\frac{K}{Q}$$

whereby $Q \equiv [\mathrm{Z}]/[\mathrm{F}][\mathrm{X}]$. α denotes the invariant sum of [X] and [Z]. (If starting e.g. with no Z, then $\alpha = [\mathrm{X}](t=0)$.) The exchange rate is

$$\mathcal{R}^\circ = \frac{\vec{k}[\mathrm{F}]\alpha}{K[\mathrm{F}]+1}$$

The differential chemical resistance $R^\delta \equiv \mathrm{d}\mathcal{A}/\mathrm{d}\mathcal{R}$ follows as

$$R^\delta = \frac{(K[\mathrm{F}]+\exp(\mathcal{A}/RT))^2}{\vec{k}[\mathrm{F}]\alpha\exp(\mathcal{A}/RT)(K[\mathrm{F}]+1)}$$

For zero $\mathcal{A}$ the constant chemical resistance is

$$R^\delta(\mathcal{A}=0) = \frac{RT}{\vec{k}[\mathrm{F}]\alpha}(K[\mathrm{F}]+1)$$

The graphs of $\mathcal{R}$ and R^δ vs. $\mathcal{A}$ are sketched in Fig. 2.

B2 Simple autocatalytic growth/decay reaction

$$\mathrm{F} + \mathrm{X} \rightleftharpoons 2\mathrm{X}$$

with constant food supply.

Simple kinetics lead to

$$\mathcal{R} = \vec{k}[\mathrm{F}]^2 K\exp(-\mathcal{A}/RT)(1-\exp(-\mathcal{A}/RT))$$

with the exchange rate

$$\mathcal{R}^\circ = \vec{k}[\mathrm{F}]^2 K$$

and to the differential resistance

$$R^\delta = \frac{RT}{\vec{k}[\mathrm{F}]^2 K}\,\frac{\exp(2\mathcal{A}/RT)}{2-\exp(\mathcal{A}/RT)}.$$

which for zero $\mathcal{A}$ reduces to $RT/(\vec{k}[\mathrm{F}]^2 K)$

The graphs of $\mathcal{R}$ and R^δ vs. $\mathcal{A}$ are sketched in Fig. 2.

C The (partially) intensive ensemble

An ensemble in which temperature, pressure and mole numbers for certain components but partial pressures for others are fixed, is – even though exotic from a theoretical

point of view –rather the usual case in experiments of multinary systems. In $SrTiO_3$, e.g. the exact oxygen content (stoichiometry) is established by preparing the oxide under given oxygen potential pressure while the Sr/Ti content is frozen. The variation of the Sr/Ti ratio requires much higher temperatures. The relation between frozen and non-frozen structure elements is treated in J. Maier, *Phys. Chem. Chem. Phys.* **2003**, *5*, 2164–2173. In this context, the author wants to acknowledge Dmitry Tsvetkov for drawing his attention to related work in the geochemical literature (P. Holba, *Czech. J. Phys.* **1992**, *42*, 549–575).

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