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Fundamentals, Applications, and Perspectives of Solid-State Electrochemistry: A Synopsis

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Abstract

The opening chapter of this Handbook highlights the characteristic features of solid-state electrochemistry, including basic phenomena, measurement techniques, and key applications. Materials research strategies that are based on electrochemical insight and the potential of nanostructuring are detailed in particular. Fundamental relationships between the decisive thermodynamic and kinetic parameters governing electrochemical processes are also briefly discussed.

1.1
Introduction

Electrochemistry refers to the conversion of electrical (chemical) information and energy into chemical (electrical) information and energy, the interconnection being anchored in the central thermodynamic quantity, the electrochemical potential (of a species k) $\tilde{\mu}_k = \mu_k + z_k F \phi$ where μ is the chemical potential, $z_k F$ the molar charge, and ϕ the electrical potential.

Solid-state electrochemistry, as a subsection of electrochemistry, emphasizes phenomena in which the properties of solids play a dominant role. This includes phenomena involving ionically and/or electronically conducting phases (e.g., in potentiometric or conductometric chemical sensors). As far as classical electrochemical cells are concerned, one refers not only to all-solid-state cells with solid electrolytes (e.g., ceramic fuel cells), but also to cells with liquid electrolytes, such as modern Li-based batteries in which the storage within the solid electrode is crucial [1–3].

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1.2
Solid versus Liquid State

The key property of solids is their *rigidity*, which relies on the strong local bonds at a given temperature, and typically manifests itself in both long-range order and pronounced short-range order, the only exceptions being completely or partly amorphous materials, such as glasses or polymers. In many cases, no distinction can be made between intermolecular or intramolecular bonds, for example in NaCl or diamond crystals, which may even be termed three-dimensional (3-D) giant molecules. The strong bonds are typically associated with not only a great thermal stability but also a good mechanical stability in terms of shear resistance. The mechanical stability may not be pronounced in terms of fracture toughness; in fact, many crystals are brittle and can easily crack. Solids can often be used even at very high temperatures, they can be manufactured in highly reproducible fashion, and they may also be easily shaped and miniaturized.

In terms of ion conductivity, one huge advantage of solids is that of *transport selectivity*. The transference number of silver ions in α-AgI with its quasi-molten Ag^+ sublattice and its rigid I^- sublattice is unity [4] (see Chapter 7). This selectivity not only helps to avoid polarization effects, but is also of substantial advantage for chemical sensors. (Alternatively, such selectivity hampers the realization of supported electrolytes.) The greatest disadvantages of the strong bonds in this respect are the typically modest absolute values of the ionic conductivities. Exceptions here are superionic solids, such as the aforementioned α-AgI which has liquid-like silver ion conductivities. (The connection between bond-strength, thermal disorder and melting temperature was elucidated in Ref. [5]; see also Figure 1.1) [6]. To a substantial degree, this inherent problem makes solid-state electrochemistry a typical high-temperature science, with its specific advantages (fast reaction kinetics) and disadvantages (stability problems). A more modern strategy that allows solids to be electroactive even at room temperature – and which is outlined at the end of the chapter – is to improve overall transport in solids by down-sizing them. This emphasizes the significance of nanotechnology for solid-state electrochemistry (see also Chapter 4).

One major specificity of the ordered solid state is the appearance of quasi-free electronic conduction. Owing to the high number of overlapping orbitals, energy bands can form giving rise to excess electron conduction in the lowest not fully occupied band, and to hole conduction in the highest bond that is fully occupied at $T = 0$ K. (In reality, one finds the whole spectrum from delocalized motion to strongly localized polaron motion.) Hence, the "mixed conductor" is to the fore in solid-state electrochemistry from which – conceptually speaking – semiconductors and solid electrolytes emerge as limiting cases (see Chapter 3). There are various phenomena that are specific to mixed conductors, such as component permeation (transport of neutral component) or stoichiometry changes (storage of neutral component), which can be employed directly, in allowing for storage or separation, or indirectly by tuning transport properties.

Thermodynamically ionic carrier chemistry in normal (i.e., non-superionic) crystals is in fact similar to the electronic counterpart in semiconductors (the case of the superionic conductor may be compared rather with the metallic state; see

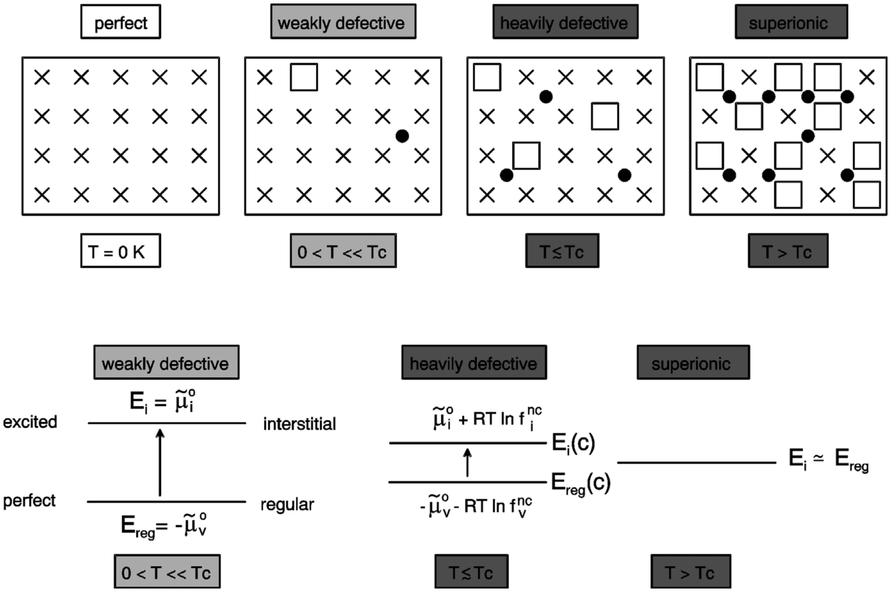

Figure 1.1 Depending on the bond strength, more or less point defects form on thermal excitation and will then alternatively interact and, owing to the formation avalanche, undergo sublattice melting or total melting [6]. The subscripts i and v refer to interstitial and vacancy defect; f denotes the activity coefficient owing to Coulomb interaction between these carriers. Reproduced with permission from Ref. [6]; © Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 1.1). Accordingly – and, again, similar to the situation in semiconductor physics – these normal ion conductors do not show exceedingly high conductivity values, but in turn offer the advantage of a pronounced variability. In analogy to excess and holes being electronic excitations of the ground state, typical ionic carriers such as interstitials and vacancies represent ionic excitations [7]. Thermal energy may excite ions out of regular sites into interstitial positions, either leaving vacancies or producing separated pairs of vacancies or interstitials. If this inherent dissociation is not perceptible, then dopants can be added, either substitutionally or additively. In the case of polymer electrolytes, both anions and cations can be dissolved simultaneously, the ground state then being the undissociated ion pair. There is a strong correspondence of charge carriers in solids to the aqueous state: there, the point defects are H_3O^+ or OH^-, corresponding to excess proton and proton vacancy, respectively. In fact, these centers belong to larger clusters of perturbed structures. Similarly, interstitials and vacancies are the centers of a perturbation zone of a much larger perimeter. The "energy levels" in Figures 1.1 and 1.2 [3] correspond to the electrochemical potentials minus a configurational contribution, in dilute cases they contain the local chemical ("standard") potential μ° and $z_kF\phi$ (i.e., $\tilde{\mu}^\circ$), whereas in non-dilute cases they also contain the non-configurational portion of the activity coefficient. Solid-state ionics allows one to treat each solid as a solvent and, by applying defect chemistry to tune its properties as aqueous ionics, this can be achieved successfully with liquid water.

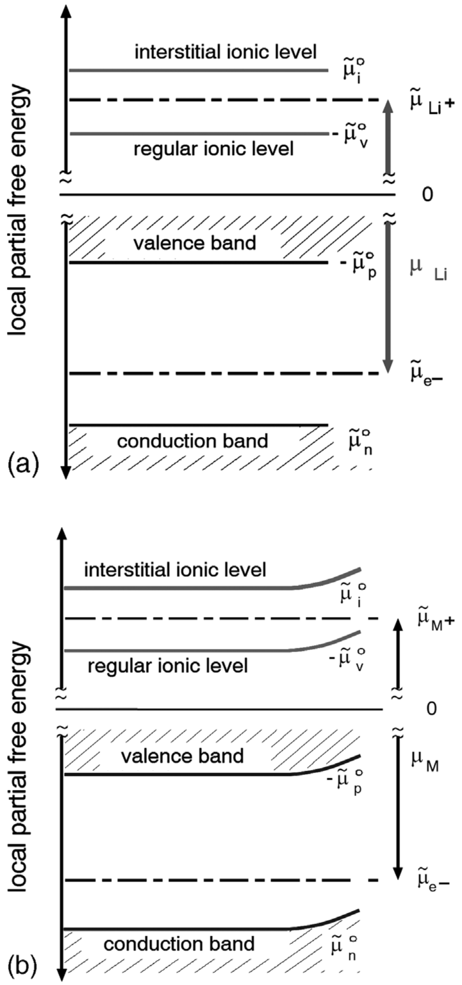

Figure 1.2 Representation of internal (Frenkel-) disorder in the (free) energy level diagram and its coupling with the fundamental electronic excitation in the bulk (a) and at boundaries (b) [3]. The illustrations correspond to particular cases when Li^+ (a) or generally monovalent M^+ cations (b) are excited in the lattice. ((a) Reproduced with permission from: J. Maier (2003) Defect chemistry and ion transport in nanostructured materials. Part II. Aspects of nano-ionics. *Solid State Ionics*, *157*, 327–334; © Elsevier Limited; (b) Reproduced with permission from Ref. [3]; © John Wiley & Sons, Limited.)

1.3
Thermodynamics and Kinetics of Charge Carriers

The statistics of the defects conceived as building elements (i.e., elements that can be added to the perfect structure to form the real structure) follow a Fermi–Dirac-type of statistics, whereas the statistics for the structure elements (i.e., elements that constitute the real structure) are of the Boltzmann type; hence, as a building element is a combination of two structure elements, consistency is preserved [8]. Figure 1.2a shows how ionic and electronic levels are connected through stoichiometry (μ of neutral component), and Figure 1.2b how they behave at a contact to a chemically compatible neighboring phase [3]. The utility of the energy level diagrams is particularly obvious at boundaries; for the description of bulk defect chemistry the usual approach of writing down explicitly defect chemical reactions that are dealt with by chemical thermodynamics is to be preferred on grounds of complexity. Note that at boundary zones the full account of Poisson's equation ($\rho = \Sigma_k z_k c_k = \nabla^2\phi/\varepsilon F$, where c is the molar concentration and ε the dielectric constant) must be made, while in the bulk it trivializes into the electroneutrality condition (charge density $= \rho = 0$).

In thermodynamic equilibrium, the equilibrium condition is $\nabla\tilde{\mu}_k = 0$ as regards the positional coordinate and $\Sigma_k \nu_{rk}\tilde{\mu}_k = 0$ (disappearance of the reaction sum of reaction r, where ν is the stoichiometric coefficient) as regards chemical displacement. Deviations lead to fluxes and generation/annihilation processes. Fluxes are – for not too-large driving forces – determined by the linear flux-driving force relationship $j_k \propto -\sigma_k\nabla\tilde{\mu}_k$. As a linear element of a Taylor expression, the partial conductivity σ_k refers to the equilibrium condition. Quite often, this equation is used even in cases where σ_k denotes a local non-equilibrium property, and this is allowed for local thermal equilibrium under small driving forces. At higher driving forces, however, higher orders in $\nabla\tilde{\mu}_k$ might be used or, preferably, the chemical kinetics approach via master equations might be applied [9]. In the latter case, local fields enter the rate coefficients and the driving force does not appear explicitly (only implicitly via concentrations and rate coefficients). We then obtain Butler–Volmer-type equations which can also be easily generalized for chemical reactions [10], viz.

$$j = \mathfrak{R}^\circ\left(g_1 \exp - \frac{\alpha\delta\Delta\varphi}{RT} + g_2 \exp - \frac{\beta\delta\Delta\varphi}{RT}\right) \tag{1.1}$$

where g_1 and g_2 refer to perturbations of the concentrations, $\mathfrak{R}^\circ$ is the exchange rate (the analogue to the conductivity for the reaction), and $\delta\Delta\varphi$ is the local drop of the applied bias. For the special case of transport, $g_1 = g_2 = 1$, $\alpha = \beta = 1/2$ and $\mathfrak{R}^\circ$ becomes the equilibrium conductivity.

As described in Ref. [11], such equations can be symmetrized for local thermal equilibrium to give, for example, for the transport case the relationship

$$j \propto -\sinh(\Delta\tilde{\mu}/2RT) \tag{1.2}$$

in the case of particle hopping (Δ refers to the variation over the elementary hopping distance). As the prefactor is now a generalized non-equilibrium conductivity, this is a useful local flux-driving force relation that does good service far from transport equilibrium [12]. A brief introduction into thermodynamics, together with several simple examples, can be found in Chapter 3.

A special problem consists of dealing with processes that do not lead to successful events, but rather to forward/backward hopping before the environment has acquired the opportunity to relax. Such phenomena give rise to frequency dependencies of the conductivity at very high frequencies, and form the transition to phonon dynamics [11].

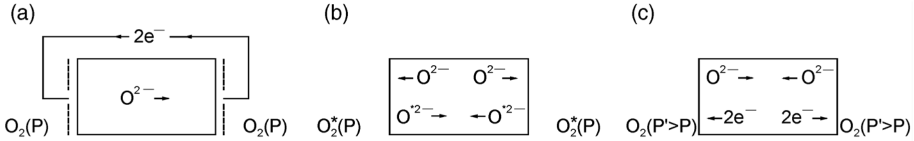

Figure 1.3 Three basic limiting experiments as discussed in the text. (a) Electrical; (b) Tracer; (c) Chemical [13]. The asterisk denotes an isotope. (Reproduced with permission from Ref. [13]; © Elsevier Limited.)

1.4
Usefulness of Electrochemical Cells

Figure 1.3 [13] shows the details of three key experiments in solid-state science representing limiting cases in practical experiments. The experiment shown in Figure 1.3c, refers to the pure chemical diffusion of an elemental compound such as oxygen in an oxide; this is a storage experiment for which a counter motion of ions and electrons is needed, as it changes the stoichiometry of the oxide (see Chapter 12). The experiment displayed in Figure 1.3b refers to a tracer exchange (Chapter 4); this requires the counter motion of two isotopes and not necessarily the explicit participation of electrons; the third experiment (Figure 1.3a) is the steady-state conductivity experiment in which the electrons are supplied by the outer circuit. These three processes can be connected with three diffusion coefficients (D^{δ}, D^{*}, D^{Q} for bulk transport) as far as the bulk is concerned. Accordingly, the three diffusion coefficients must be confronted with three relaxation rate constants (k^{δ}, k^{*}, k^{Q} for surface reaction), the relationships between which have been comprehensively discussed in Ref. [13].

Figure 1.4 [14] shows a typical battery cell in which conduction and storage occurs: conduction in the electrolyte, charge transfer through the boundary and storage in the electrodes. (The characteristic equations on the left-hand side refer to proximity to equilibrium.) Electrical and chemical resistors, electrostatic capacitors as well as chemical capacitors, are the basic ingredients of modeling electrochemical circuits even in complex cases. Owing to the normally huge value of the chemical capacitance, the time constant for the mass storage process dominates the overall process typically for Li-based batteries. Unlike the other processes addressed, this relaxation time depends sensitively on thickness (diffusion length), and can be efficiently varied by nanostructuring (see below).

As far as electrochemical cells relevant for applications or electrochemical measurements are concerned, we must distinguish between polarization cells, galvanic cells and open-circuit cells, depending on whether an outer current flows and, if so, in which direction this occurs. Table 1.1 provides examples of the purposes for which such cells may be used. In terms of application, we can distinguish between electrochemical sensors, electrochemical actors and galvanic elements such as batteries and fuel cells. These applications offer a major driving force for dealing with solid-state electrochemistry.

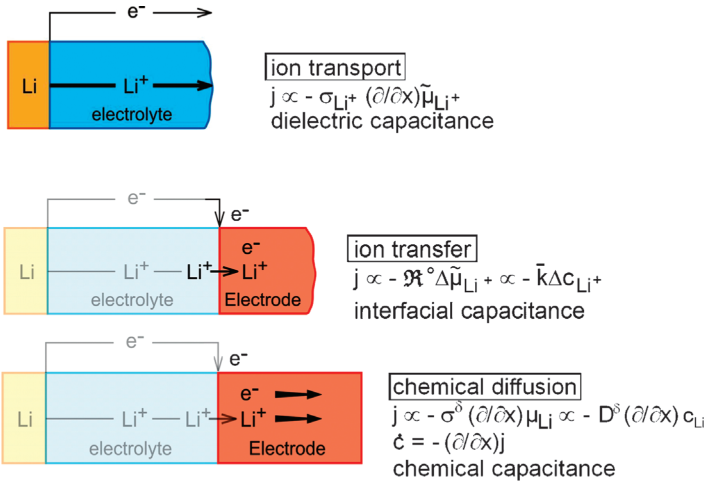

Figure 1.4 Resistive and capacitive processes in a Li-battery, and the targeted use of size dependence [14]. For simplicity, all relationships refer to proximity to equilibrium. Wherever the positional coordinate x appears, reduction of the transport path length is efficient. Moreover, the effective transport parameters can be sensitively varied by size effects, owing to local variations of defect chemistry. The superscript δ refers to the joint motion of Li^+ and e^-; D^{δ} is the chemical diffusion coefficient of Li, and σ^{δ} the ambipolar conductivity $(= \sigma_{e^-}\sigma_{Li^+}/(\sigma_{e^-} + \sigma_{Li^+}))$; $\bar{k}$ is the effective rate constant close to equilibrium. Reproduced with permission from Ref. [14]; © Elsevier Limited.

Figure 1.5 describes basic galvanic elements discriminated according to energy density (per mass) and temperature. All those galvanic cells that directly convert chemical into electrical energy, without thermal detours, are hence not bound by Carnot's efficiency, and offer high theoretical efficiencies. The application of solid

Table 1.1 An overview of electrochemical devices and measurement techniques based on various cell types [1].

Cell type	Measurement technique	Technological application
Polarization cell	Measurement of kinetic data by polarization	Electrochemical composition actors (electrolyzers, pumps, electrochromic windows), electrochemical composition sensors (amperometric, conductometric)
Current-generating cell	Measurement of kinetic data by depolarization	Electrochemical energy storage and conversion devices (batteries, fuel cells, supercapacitors)
Open-circuit cell	Measurement of thermodynamic formation data, transport number of electrons	Potentiometric composition sensors

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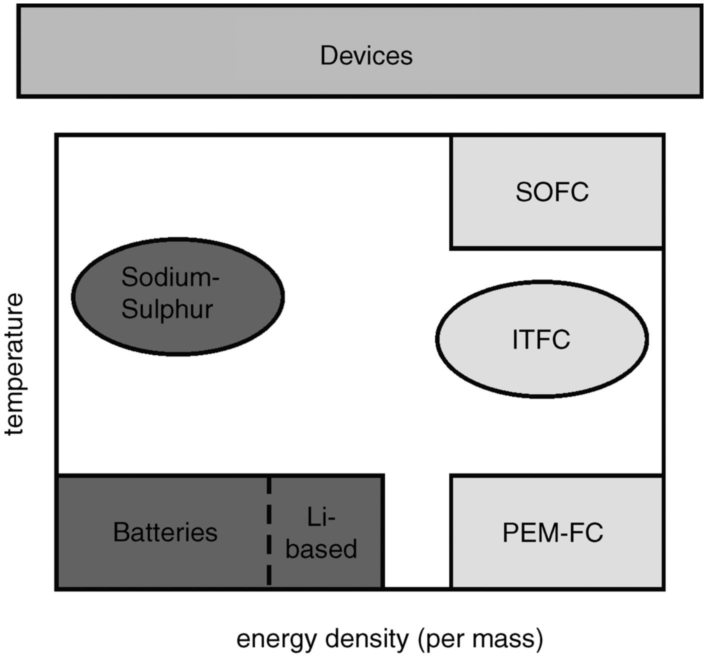

Figure 1.5 Selected galvanic cells (for details, see the text). SOFC = (high-temperature) solid oxide fuel cells; ITFC = intermediate-temperature fuel cells; PEM-FC = polymer electrolyte membrane fuel cells.

oxide fuel cells is driven by the fast electrode kinetics at high temperatures that enables the easy consumption of fuels such as hydrocarbons. The main advantage of near-room temperature fuel cells are the ease of performance and the lack of severe thermal stability problems. Here, however, the catalytic activity of the electrodes is much more demanding. Relevant batteries use solid storage materials, and are particularly relevant if Li is the element to be stored, owing to its extremely high reduction energy per mass.

Electrochemical cells can also be used for the precise determination of kinetic and thermodynamic parameters. Such cells can be classified according to the combination of reversible and blocking electrodes. Cell types and parameters to be determined are compiled in Table 1.2 [15–17]. The determination of kinetic parameters makes use of the condition that, in an experiment with a mixed conductor, the flux densities are composed of a drift and a stoichiometric term:

$$j_{\{\}} = -\frac{\sigma_{\{\}}}{\sigma}\frac{i}{z_{\{\}}F} - D^{\delta}_{\{\}}\nabla c_{\{\}}. \tag{1.3}$$

In Equation (1.3) only the total current i and the total conductivity σ carry no indices, the other quantities do ($\{\}$). If associates do not play an important role, the indices simply refer respectively to ions or electrons or to the respective component

Table 1.2 Combination of reversible ((O^{2-}, e^-|, typically porous Pt) and blocking electrodes ((e^-|, i.e., only reversible for e^-, a typical example being graphite; or (O^{2-}|, i.e., only reversible for O^{2-}, a typical example being a Pt-contacted zirconia electrolyte) leads to a variety of measurement techniques applied to the oxide MO.

Cell	Quantities to be determined
$(O^{2-}, e^- \vert MO \vert e^-, O^{2-})$	Resistances and capacitances
$(O^{2-}, e^- \vert MO \vert e^-, O^{2-})'^{a}$	Transport numbers, chemical diffusion coefficients
$(O^{2-}, e^- \vert MO \vert e^-)$	Electronic conductivities as a function of activity, chemical diffusion coefficients
$(e^- \vert MO \vert e^-)$	Electronic conductivities, chemical diffusion coefficients
$(O^{2-}, e^- \vert MO \vert O^{2-})$	Ionic conductivities as a function of activity, chemical diffusion coefficients
$(O^{2-} \vert MO \vert O^{2-})$	Ionic conductivities, chemical diffusion coefficients
$(O^{2-} \vert MO \vert e^-)$	Stoichiometry, thermodynamic factor, chemical diffusion coefficients

[a] A different oxygen partial pressure was used on the right-hand side.

(in j, D^δ, c) [18]. If associates, however, play a substantial role, the respective "conservative ensemble" must be considered [19].

If, for example, oxygen vacancies ($V_O^{\cdot\cdot}$, denoting a missing O^{2-}) and electrons are present and then also associates such as $V_O^{\cdot}$ (one electron trapped by an oxygen vacancy) and $V_O^{\times}$ (two electrons trapped by an oxygen vacancy), the flux and conductivities in Equation (1.3) address the total oxygen ensemble, $\sigma_{\{O\}} \equiv \sigma_{V_O^{\cdot\cdot}} + 2\sigma_{V_O^{\cdot}}$ ($V_O^{\times}$ does not contribute being effectively neutral). The ensemble diffusion coefficient $D^\delta_{\{O\}}$ is essentially composed of $\sigma_{e'} - \sigma_{V_O^{\cdot}}$ and $\sigma_{V_O^{\cdot\cdot}} + 2\sigma_{V_O^{\cdot}}$, as well as of respective differential trapping factors [19]. (Of course, interaction can also formally be put into Onsager's cross-coefficient, but this does not provide any mechanistic insight [20].)

1.5
Materials Research Strategies: Bulk Defect Chemistry

Ultimately, we should be concerned with the strategies to optimize electrochemical parameters by materials research. The most momentous strategy is to seek new phases (new structures and compounds) and, indeed, many simple phases have already been explored. Yet, examining any higher compositional complexity increases the possibility that the new phases are chemically unstable when in contact with neighboring phases, and that is why the modification of given phases is of key significance.

One very decisive way to optimize a given phase (Figure 1.6) is the targeted variation of defect chemistry. The property window that can be addressed by defect chemical variation is often greater than the alteration of the mean property when going from one phase to the next. The key parameters are component activity (partial

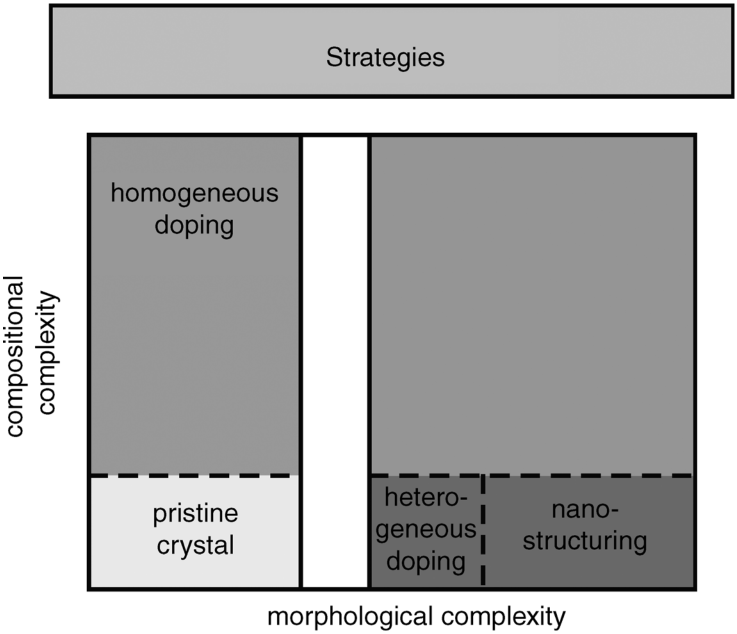

Figure 1.6 Strategies to optimize given phases.

pressures), the temperature, and the doping content. In reality, not all sublattices are in equilibrium with the neighboring phase, and these frozen concentrations then enter as the doping content C rather than being controlled by additional partial pressures ("component activities"). In the case of simple defect chemistry [21], which is characterized by the fact that all defects are randomly distributed (interactions can be taken into account by assuming randomly distributed associates), defect concentrations are typically given by

$$c_k(T, P, C) \propto P^{N_k} C^{M_k} \Pi_r K_r(T)^{\gamma_{rk}}. \tag{1.4}$$

where P is the component partial pressure and K_r the mass action constant of defect reaction r.

The exponents (N, M, γ) qualitatively follow simple rules and represent simple rational numbers [1, 3, 21]. Let us concentrate on the influence of the doping content a little more in detail, as it is – as far as application is concerned – the real relevant optimization parameter. The consequence of introducing a given dopant with known effective charge on any charge carrier k is simple; it is described by the "rule of homogeneous doping" [1, 3]

$$\frac{z_k \delta c_k}{z \delta C} < 0 \quad (\text{for any } k) \tag{1.5}$$

with z being the charge number. This means that an effectively positive (negative) dopant k increases the concentration of all negatively (positively) charged defects c_k, and decreases the concentration of all positively (negatively) charged ones individually.

If the power law of Equation 1.4 is valid, this can be rewritten as:

$$\frac{z_k}{z} M_k < 0 \quad (\text{for any } k). \tag{1.6}$$

Deviations from random distribution greatly modify and complicate the picture. Debye–Hückel corrections [9] do usually not lead very far; corrections by cube root terms do better service in many respects, but lose validity in heavily doped systems [5].

1.6
Materials Research Strategy: Boundary Defect Chemistry

So far, one important characteristic of solids that relies on the low mobility of at least one structure element, has not been addressed, namely the (meta)stability of higher-dimensional defects, and in particular of interfaces (see Figure 1.6). Although grain boundaries are often detrimental, there are cases in which they may be even deliberately generated with the purpose of improving transport properties. This includes the use of fine-grained ceramics, composites or heterolayers. Even in cases in which the interfaces do not give rise to significantly different mobilities, the conductivity effect at interfaces can be enormous. This is due to the greatly varied defect chemistry in boundary zones. Here, a similar rule – the rule of heterogeneous doping [1, 3] – is valid; that is:

$$\frac{z_k \delta c_k}{\delta \Sigma} < 0 \quad (\text{for any } k) \tag{1.7}$$

in which the charge of the dopant in Equation 1.5 is replaced by the surface Σ charge of the interface. By heterogeneous doping, the ion conductivities can be enormously modified, poor conductors may be changed into good conductors, and even the type of conduction mechanism can be changed, for example from vacancy to interstitial, from anion to cation conductivity, or from ionic to electronic [22].

1.7
Nanoionics

Even more intriguing are changes in which the local properties are varied throughout the sample; this is, for example, possible by curvature (capillary pressure), by the overlap of elastic effects or by space charge overlap [23]. In this way, not only synergistic transport phenomena but also synergistic storage phenomena can be verified, providing a bridge between multiphase systems to new artificial, “almost homogeneous”, systems. Figure 1.7 [23] provides an overview of effects that can be dealt with in the context of what we refer to as “nanoionics”. Most striking are the qualitatively novel conductors or storage materials which are arrived at in the limit of space charge overlap in two-phase systems. A systematic exploration of size effects in

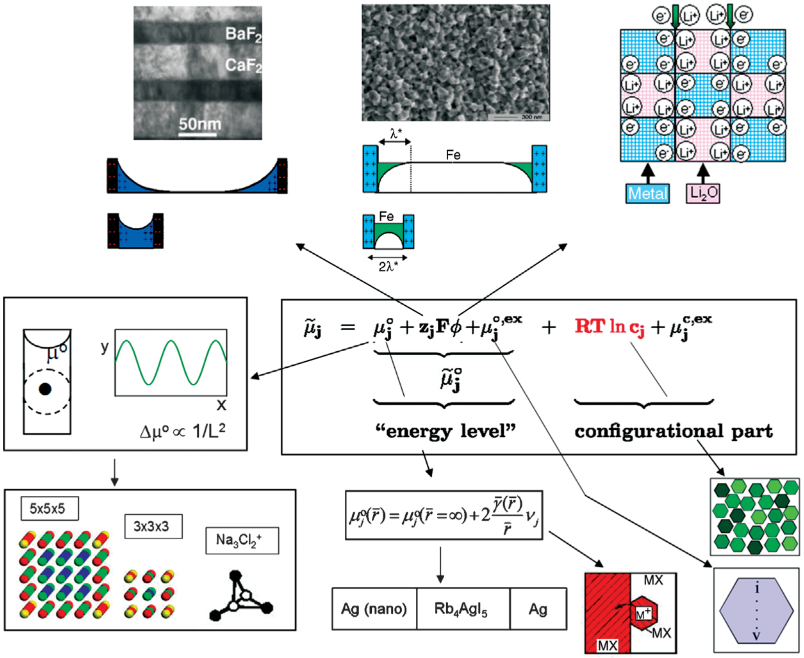

Figure 1.7 Typical true size effects (i.e., local property depends on size) on the ionic charge carrier j [23]. ($\bar{\gamma}$ = mean surface tension; $\bar{r}$ = mean radius of the particle with the composition M^+X^-.)

terms of Li-based batteries has recently been provided [14]; additional information can be found in Chapter 4 of this Handbook.

From a more conceptual point of view, it is the introduction of higher-dimensional defects that allows the transition to a "soft materials science", characterized by an enhanced information content even in systems in which the atomic bonds are not covalent. The future will be witness to increased research and applications in the field of metastable materials characterized by increased local complexity, with the possibility of further systematic collaboration with semiconductor physics and biology.

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