



# Nano-Ionics: More Than Just a Fashionable Slogan

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**Abstract.** The paper considers and investigates the dependence of the ionic conductivity on the spacing of interfaces. Not only does a narrow spacing lead to an increased proportion of interfacial conductivity, it may also cause local size effects to occur. The present status as well as the perspective of this field are discussed and shown to justify the term “nano-ionics”.

**Keywords:** ion conductivity, transport, interfaces, nano-size

## 1. Introduction

Electronic properties of solids can be efficiently tuned by interfacial design as well as by varying the interfacial spacings. That is why nano-electronics became a well-established field of physics and materials science (see e. g. [1–6]). Of no minor importance for electroceramics are ionic properties, and the question is not only allowed but necessary to ask as to how important is a field that may be termed “nano-ionics” [7–12]. In order to answer this question we have to explore the behavior of ionic charge carriers at interfaces as well as the respective size effects. Note that in the nano-regime the interfacial spacing may be so narrow that we can no longer automatically assume semi-infinite boundary conditions.

The ionic charge carriers of electroceramics are the point defects, i.e., excess particles and vacant sites playing an analogous role as  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions do in aqueous solutions: they are the charge carriers that effectively transport the charge in a conduction experiment but they are also the acid/base active particles. In fact it can be shown that an acid-base concept can be constructed for ionic solids, that uses defect concentrations as a scale for acidity and basicity [13]. (The role of internal complex acids and bases, such as  $\text{CH}_3\text{COOH}$  or  $\text{NH}_3$  in water, is played by associates of impurities and the native point defect.) Surface point defects act as

acid-base active species concerning the reaction with the neighboring phase [14, 15]. Hence playing around with carrier concentrations is equivalent to tuning conductivities and reactivities. In addition the stoichiometry can be changed, and so then can storage properties.

In the following, results are presented demonstrating the relevance of the nano-regime for conductivity, reactivity and storage capacity.

## 2. Charge Carrier Distribution at Boundary Regions

### 2.1. Isolated Interfaces

As long as the free formation energy of point defects is sufficiently high and thus point defects are sufficiently dilute (this also poses constraints on temperature, doping content and component partial pressure) Boltzmann statistics can be applied. The (free) energy levels of ground state and excited state are then sufficiently distant. If there is a variability of the energy levels (e. g. density of states of electrons in solids, energy distribution of particles in space and/or time in the case of amorphous systems, liquids etc.) [16]), always a mean value can be extracted that defines the effective electrochemical standard potential, the distance of which to the generalized Fermi-level determines the defect concentrations (see Fig. 1(d)). If also Brouwer conditions (always valid if only two majority carriers have to

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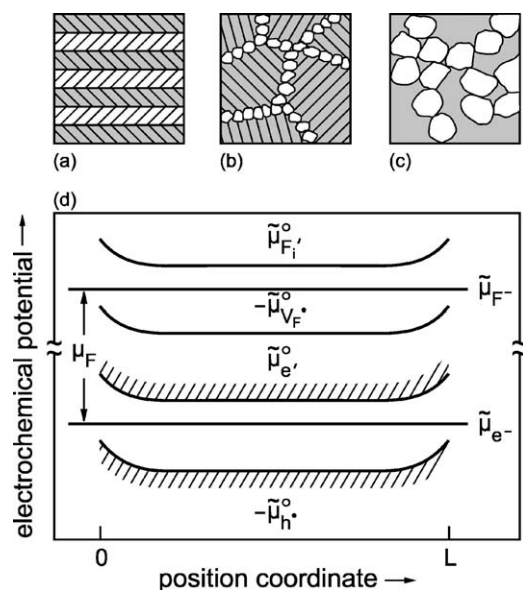


Fig. 1. Enhanced conductivities due to percolating conductive interfaces occur, e.g. in solid-solid dispersions (composite electrolytes (b)), heterolayer packages (a), or solid-liquid dispersions (“soggy sand” electrolytes (c)) (see Section 3). The bottom picture (d) illustrates the thermodynamic behavior of ions and electrons, their concentration (distance of  $\tilde{\mu}^o$ 's to  $\tilde{\mu}_{F^-}$  or  $\tilde{\mu}_{e^-}$ ) as well as their thermodynamic interrelation (distance between  $\tilde{\mu}_{F^-}$  and  $\tilde{\mu}_{e^-}$ ). The positions of the interfaces are designated as 0 and L.

be considered) are fulfilled, the bulk equilibrium concentrations follow a power law in the component partial pressure, the doping content and the mass action laws defining Arrhenius diagrams and Kröger-Vink diagrams [17].

In this paper we will use the following functional to describe the local electrochemical potential of a defect [18, 19]:

$$\tilde{\mu}_j = [\mu_j^* + \mu_j^{\text{int}} + zF\phi + \mu^r] + RT \ln c_j + \mu^{\text{ex},c}. \quad (1)$$

The first term ( $\mu_j^*$ ) refers to the purely chemical partial free formation energy of an isolated defect and also includes locally changed bond lengths and bond strengths owing to elastic effects. The second non-configurational term ( $\mu_j^{\text{int}}$ ) takes account of interactions (typically being proportional to  $\sqrt{c}$  or  $\sqrt[3]{c}$ ,  $c$  = concentration [20, 21]), in the case of inhomogeneities as it is the case with interfaces it will also

contain gradient effects and hence a term which is proportional to  $\nabla^2 c$  [22]. The third term takes account of the charge and the influence of the electrical potential  $\phi$ . Term number 4 ( $\mu^r$ ) is due to curvature effects and in the simplest case proportional to surface tension ( $\gamma$ ), inverse curvature ( $r$  = radius) and partial molar volume of the defect [23]. These terms constitute what may be called “energy levels” (but of course also including local partial molar entropies), while the following terms stem from statistics of the defect distribution over these levels. For dilute, randomly distributed defects, the Boltzmann-term is the relevant one; the correction term  $\mu^{\text{ex},c}$  takes account of multiplicities, site exhaustibilities (FermiDirac correlation) or corrections due to non-random distributions.

The simplest case is an interaction-free, random system with a stress-free abrupt junction; then simply

$$\tilde{\mu}_j = \mu_j^* + RT \ln c_j + zF\phi \quad (2)$$

Combination of the equilibrium condition ( $\nabla \tilde{\mu}_j = 0$ ) with Poisson's equation leads to the Poisson-Boltzmann equation, which has to be solved in order to obtain the equilibrium concentration profile. The resulting charge carrier profile leads to space charge accumulation and/or depletion effects on the electrical conductance which can be very strong and very dependent on whether the charge carrier moves along or across the interface (Fig. 2(a)). In addition to these space charge zones, the core of the interface may also provide marked conductance/resistance effects. In Ref. [24] such phenomena are studied in detail in particular with respect to ion transport.

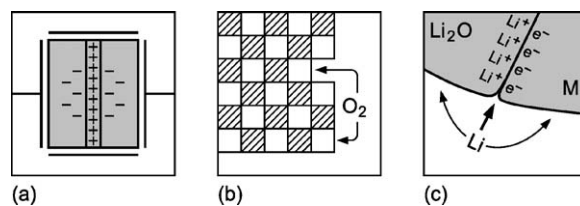


Fig. 2. The (anisotropic) effect of a charged boundary on the conductance (cf. Section 3) (a), the different reactivities of surface ions, ions at edges/corners and defects within the surface ( $\text{O}_2$  reacts preferentially with metal corner atoms and oxygen vacancies) (cf. Sections 3, 4.1, 4.3) (b), the excess storage of Li at the  $\text{Li}_2\text{O}$ /metal interface (cf. Section 4.2) (c) (see text).

## 2.2. Nano-Crystalline or Nano-Composite Samples

Referring to systems that contain many interfaces, not only the nature, form and chemistry of the individual interfaces are important but also their relative orientations and spacings (see Fig. 2(a)). In the simplest case of non-interacting interfaces and as long as the anisotropy of the interfacial tension as well as edge and corner effects can be neglected, the bricklayer model may be used to study the superposition of  $\bar{\sigma}_L^\perp$ ,  $\bar{\sigma}_L^\parallel$  and  $\sigma_\infty$  to the overall measured conductivity

$$\sigma_m = f(\bar{\sigma}_L^\perp, \bar{\sigma}_L^\parallel, \sigma_\infty; \varphi); \quad (3)$$

$\sigma_\infty$  denotes the bulk conductivity, while  $\bar{\sigma}_L^\perp$ ,  $\bar{\sigma}_L^\parallel$  designate the mean boundary conductivities across and along the boundary. The bar indicates that these quantities are averaged over core and space charge zone. The volume fraction of the layer ( $\varphi_L$ ) determines the impact of  $\bar{\sigma}_L^\perp$ ,  $\bar{\sigma}_L^\parallel$  on the overall property leading to interfacially controlled materials for sufficiently high  $\varphi_L$ -values. As long as these transport parameters do not change with  $\varphi_L$  we may speak of trivial size effects. This also includes the possibility of structural effects on  $\mu^*$  (graded junction, elastic effects of long range etc.) as long as they decay to the bulk values between the boundaries.

More sophisticated effects [12] appear if the boundaries perceive each other (true size effects). Such phenomena refer to the  $zF\phi$ -term (space charge overlap) but also—if the interfacial spacing is of the order of the effective size of the defect (defect including structurally perturbed neighborhood)—to  $\mu^*$ . This is particularly relevant in the case of elastic effects of long range or for wide band semiconductors in which the electrons are effectively very extended. Apart from this, the distance of interfaces may also be not large enough for defect pairs (excitons, Frenkel pairs etc.) to be separated.

The above distinction becomes less clear if we have to consider anisotropies, curvatures or edges and corners. In the case of curvature effects the above effective transport parameters may change with  $\varphi_L$  even though the interfaces are non-interacting. In the simplest case this can be attributed to changed concentrations of edges and corners, and then, to a certain extent, the distinction between non-trivial and trivial size effects can be continued on a higher level by taking account of well-isolated or interacting edges/corners [25].

Similarly, boundary phase transformations may occur isolated at interfaces or strongly affected by neigh-

boring interfaces in confined systems. Amongst other complications and sophistications owing to the small number of constituents, the discreteness of charge distribution or geometrical complexity, only one more point may be addressed here: While the concentration fluctuations from grain to grain may not so much affect thermodynamic statements about mean defect concentrations, resulting inhomogeneities and differences from grain to grain may lead to severe complications with regard to percolation and overall transport property.

Eventually, at extremely tiny sizes one leaves the range of validity of such top-down approaches and one enters the regime of cluster chemistry that is better tackled by bottom-up considerations (e. g. ab initio calculations).

In the following selected examples, experiments and perspectives of nano-ionics are discussed with regard to electrical conductivity (Fig. 2(a)), reactivity (Fig. 2(b)) and storage (Fig. 2(c)) effects also in the view of possible applications.

## 3. Materials Examples

An important starting point for exploring solid state ionics is the impact of interfacial engineering on transport properties. Distinguishing between core and space charge effects (the latter are expected to be particularly pronounced in materials with low disorder and high mobilities), it has been shown [26] that it is not only possible to increase or decrease ionic conductivities by designing homo- or heterojunctions; it is also possible, e. g., to turn ionic into electronic conductors and vice versa, to turn anion conductors into cation conductors or changing the transport mechanism from interstitial to vacancy type. Useful strategies for directing the effect are chemical modification of boundaries by acid/bases molecules, insertion of second phases (Fig. 1(b)) with appropriate surface properties or generation of junctions of two ionically conductive particles (Fig. 1(a)). One example for which for a limited time a practical application as heart pacemaker solid electrolyte was envisaged, has been LiI:Al<sub>2</sub>O<sub>3</sub> composites [27]. Admixing Al<sub>2</sub>O<sub>3</sub> to LiI leads to an increased vacancy conductivity which cannot be achieved by homogeneous doping owing to low solubilities. Oxide admixtures to Li<sup>+</sup>-conducting polymer electrolytes have led to relevant candidates for high power Li batteries with exible electrolytes [28, 29]. The mechanism may be more

complicated than in the case of inorganic materials but recent results indicate that an analogous mechanism may be operative, adsorption of one charge carrier and setting free the counter ion (in the inorganic crystals, e. g. adsorption of  $\text{Li}^+$  and setting free mobile vacancies; in the case of polymer electrolytes: breaking up ion pairs) and setting free the non-adsorbed ion sort.

The recently proposed “soggy sand electrolytes” [30, 24] consist of oxides wetted by Li-salt containing liquid non-aqueous electrolytes and rely completely on this effect (Fig. 1(c)). The related conductivity effects are remarkable, indeed [30]. Similarly as in Nafion the solid/liquid network provides internal space charge proton conductivity. By combining high conductivity, stability and mechanical properties of soft matter they are of significant potential for battery application.

Conductivity effects can be significantly increased by going to the nano-regime as been evidenced by the investigation of nanocrystalline  $\text{CaF}_2$  or nano-sized ionic  $\text{CaF}_2/\text{BaF}_2$  heterostructures (Fig. 1(a)) [31]. The individual spacing of the latter can be made much smaller than the Debye length, i. e. transferred to a regime in which electrostatic size effects become important. Similar heterolayer effects seem to occur in stacking faults at  $\beta$ -AgI interfaces which lead to very high ion conductivities [32].

In oxides such as  $\text{SrTiO}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$  mostly positive space charge potentials have been observed leading to depletion effects. Fe-doped  $\text{SrTiO}_3$  is definitely the best investigated material in this respect (see e. g. [24]): high angle and low angle boundaries show positive potentials. In the case of high angle boundaries the effect roughly increases with the structural perturbation introduced by the boundary while in the case of low angle grain boundaries the effect increases with decreasing spacing of the boundary dislocations (i. e. increasing with misfit angle). The positive potential leads to severe depression of the  $p$ -type conductivity and even stronger effects on the vacancy conductivity (in agreement with the double charge of oxygen vacancies). The depletion of both  $\text{h}^+$  and  $\text{V}_\text{O}^\bullet$  has been shown to lead to severe effects on the chemical diffusivity of oxygen [33, 34]. Simultaneously an increase of the electron concentration is expected. While there are only some indications for this in acceptor-doped  $\text{SrTiO}_3$ , the effect has been clearly investigated for  $\text{CeO}_2$  which exhibits a higher electron concentration in the bulk. A positive space charge potential of  $\sim 0.3$  V, which was also inferred from measurements of macro-crystalline  $\text{CeO}_2$  [35], explains all the features

observed with respect to the electronic ( $e'$ ) and ionic ( $\text{V}_\text{O}^\bullet$ ) conductivity of nanocrystalline  $\text{CeO}_2$  [36]. The electronic conductivity is increased, the ionic one decreased. Reports on excess conductivities in nanocrystalline  $\text{ZrO}_2$  are contradictory [37]. Enhanced conductivities could not be explained by the space charge effects observed in macro-crystalline  $\text{ZrO}_2$ . Its positive space charge [38] potential rather leads to depletion effects and an inverse sign would hardly cause substantial conductivity effects in such a highly disordered oxide.

A beneficial reduction of overall size is often helpful without invoking trivial or non-trivial size effects in the conductivity. In these cases one just uses the improved cell geometry which gives rise to a higher conductance. Such effects are one driving force to use thin film electrolytes or generally reduced transport length.

## 4. Applications

### 4.1. Fuel Cells

As already mentioned nano-sized effects are involved in the transport in ion exchange membranes commonly used in low temperature fuel cells: In Nafion the channel width is so small that there should be deviation from charge neutrality everywhere [39]. The protons dissociated away from the fixed counter ions bound to the polymer backbone are highly mobile within the tiny water-containing channels. Meanwhile a lot of activities exist which try to replace water by other donor-acceptor molecules (organic heterocycles) to even integrate these into the side chains of the network [40]. A variety of materials have been proposed to bridge the gap between low and high temperature application [41]. These intermediate fuel cells are still to be optimized to a degree that makes them worthwhile for applications.

The highly doped solid oxide electrolytes used in high temperature fuel cells can hardly be improved by making them nanocrystalline unless there will be severe interfacial effects on the oxygen ion mobility. Thin film electrolytes may improve the performance owing to a decreased conductance as a consequence of a reduction of the transport path; similarly the size reduction of electrode particles may facilitate the kinetics by increase of the interfacial area and of the number of edges, corners etc., as well as of the length of the three-phase boundaries [42, 43].

Problems of the stability of the nano-structure may be overcome by using nano-composites. The significance of size effects (e. g. interfacial reactivity) with respect to the specific reactivity parameters may, as a rule, be expected to be less pronounced at higher temperatures.

#### 4.2. Li-Batteries

Similarly, the use of greatly diminished transport lengths leads to an increased performance in Li-batteries. So, reactive storage of Li accompanied by the formation of new phases can be reversible in the nano-sized or even amorphous state [44–47]. In addition, greatly modified local transport parameters may be expected at low operation temperatures.

The interface can also be the source/sink of an enhanced nonstoichiometry [26, 48–52]) leading to an excess storage capacity in nanocrystalline systems. As regards the above mentioned reactive Li-storage by reducing a metal oxide to  $\text{Li}_2\text{O}$  and metal, a detailed mechanism has been proposed that consists in incorporating additional  $\text{Li}^+$  at  $\text{Li}_2\text{O}$  side of the interface while electrons are incorporated at the metal side (Fig. 2(c)) [52].

#### 4.3. Sensors and Catalysts

Amongst many other beneficial applications of nano-sized materials, essentially those which make use of the enhanced surface reactivities of surface defects are worth being mentioned. Such effects may explain enhanced sensor sensitivities of small  $\text{SnO}_2$  crystallites [53] or the modified catalytic activity in reaction engineering ( $\text{AgCl}$  [14, 15],  $\text{CeO}_2$  [54],  $\text{TiO}_2$  [7]).

A systematic presentation of this field is beyond the scope of this paper. Nevertheless, it may be generally stated that the surface point defects are excitations within the higher-dimensional defect “surface”, are present due to configurational entropies, non-equilibrium effects or mass constraints and possess a higher local energy and hence reactivity.

### 5. Conclusions

The significance of nano-ionics has been discussed and corroborated by a variety of experimental examples. It relies on the following points:

- (1) Interfacial effects on ionic charge carrier concentrations (and mobilities) can be very pronounced. Reduction of the spacing of interfaces leads to interfacially controlled overall properties (size effects on overall conductivity).
- (2) Size effects on the local conductivities occur if interfaces interfere.
- (3) Nano-sized systems can be sufficiently durable during operation at not too high temperatures, particularly if composites are used. Owing to the mobility of one ion sort this point is more delicate than for nano-electronics.
- (4) Beneficial effects of the nano-regime for electrochemical applications or for catalysis are demonstrated.

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