

Short communication

# Size effects on mass transport and storage in lithium batteries

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## Abstract

The contribution deals with the significance of size effects for lithium-based batteries. The relevant size effects range from purely geometrical effects to effects in which the local thermodynamics is varied. In this context, several recent findings towards improved electrolytes and electrodes are discussed.

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**Keywords:** Electrochemistry; Transport; Storage; Size effects; Li-batteries

## 1. Introduction

Fig. 1 shows the three decisive mechanistic steps of a lithium battery. (For an overview see e.g. Refs. [1–3].) The first is the  $\text{Li}^+$  motion through the electrolyte. This transport step does not violate electroneutrality as there is a compensating electron flow through the outer wire. Transient phenomena in the electrolyte occur typically on the nanosecond scale and are dielectric in nature (electrostatic storage). Hence the transport in the electrolyte is essentially a steady-state process driven by gradients in the electrochemical potential of the ion ( $\tilde{\mu}$ ), the transport coefficient being the  $\text{Li}^+$  conductivity. At the electrolyte/electrode interface  $\text{Li}^+$  has to traverse the phase boundary with a driving force being the difference in  $\tilde{\mu}_{\text{Li}^+}$  on both sides; the related transport coefficient is determined by the exchange rate of that process (we refer to the proximity to equilibrium, otherwise electrochemical kinetics has to be employed). The respective storage process is characterized by the interfacial capacitance and typically occurs on the  $\mu\text{s}$  level. The proper time dependence comes into play when considering the storage of Li in the electrode for which a chemical diffusion of  $\text{Li}^+$  and  $\text{e}^-$  is necessary. The driving force is the gradient of the chemical potential of Li ( $(\partial/\partial x)\mu_{\text{Li}} = \partial/\partial x(\tilde{\mu}_{\text{Li}^+} + \tilde{\mu}_{\text{e}^-})$ ) and the transport coefficient the ambipolar conductivity  $\sigma^\delta = (\sigma_{\text{e}^-}^{-1} + \sigma_{\text{Li}^+}^{-1})^{-1}$  both influenced by  $\text{Li}^+$  as well as  $\text{e}^-$ . If the driving force is expressed in terms of Li concentration gradients ( $(\partial/\partial x)c_{\text{Li}}$ ), the transport coefficient becomes the chemical diffusion coefficient  $D^\delta$  that

contains, in addition to  $\sigma^\delta$ , the chemical capacitance  $C^\delta$  (i.e.  $\partial c_{\text{Li}}/\partial \mu_{\text{Li}}$ ). Even though the real picture can be much more involved (existence of phase boundaries, protection layers, etc.) these are the three major transport modes to be considered.

What is the significance of “going nano”? First, one can increase the fluxes by sheer geometrical effects (more precisely the geometrical part of the resistances is decreased). As  $\partial x$  appears in the denominator of the local flux expressions,  $j \propto L^{-1}$  if  $L$  is the sample thickness. As to the storage time ( $\tau_{\text{eq}}$ ),  $\tau_{\text{eq}}$  varies according to  $\propto L^2$  as  $\dot{c} \propto -(\partial/\partial x)j$ . Note that a reduction of  $L$  from 1 mm to 100 nm reduces, for a material with  $D^\delta = 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , the waiting time from 2 years to 1/2 s! Even though this is extremely important an effect (see also end of Section 3.2), in the following the more fundamental point of how transport coefficients depend on  $L$  will be to the fore. As transport coefficients depend on carrier concentrations and kinetic parameters (such as mobilities or rate constants) and as the latter ones are essentially determined by the structure, it is the defect concentration whose variation is of prime importance here (as we wish to consider the  $L$ -dependence of the invariant structure).

## 2. Size effects: nanoionics

In a series of papers such effects on transport and storage have been elucidated [4–8]; here only some major points will be summarized and directly applied to Li-based batteries.

The major quantity in this context is the electrochemical potential of a charge carrier. In equilibrium it determines the carrier concentration and outside but close to equilibrium also the fluxes. It contains two classes of contributions: configurational

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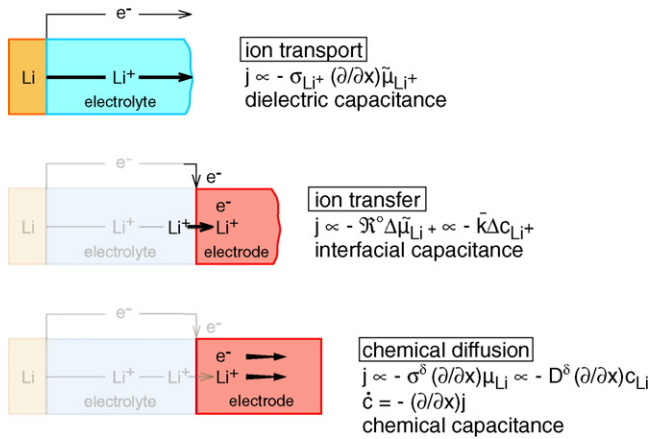


Fig. 1. Even in more complicated situations than the one shown, the decisive steps in Li-batteries are ion transport through the electrolyte, phase transfer to the electrode and chemical diffusion in there. The equations refer to small signal behavior. Size reduction acts on the transport coefficients as well as on the proportionality factors containing distances directly.

ones and local ones, the first being the result of the large number of statistical arrangement possibilities and of Boltzmann type in the ideal case (in non-ideal cases there are corrections such as the Fermi–Dirac correction once the number of sites (ions) or quantum states (electrons) is about to be exhausted). The local contributions play the role of “energy levels” in the generalized picture shown in Fig. 2 comprising a ground value ( $\mu^\circ$ : measuring the virtual free energy of forming an isolated defect without electrical influence), but also electrical potential terms and suitable corrections (such as interactions). Each of these terms has been shown to give rise to size effects.

Most important are effects due to electrical fields as a consequence of interfacial charging. Whenever an interface is introduced into a charge carrier containing bulk (such as a salt-containing solution or a solid with point defects) symmetry is

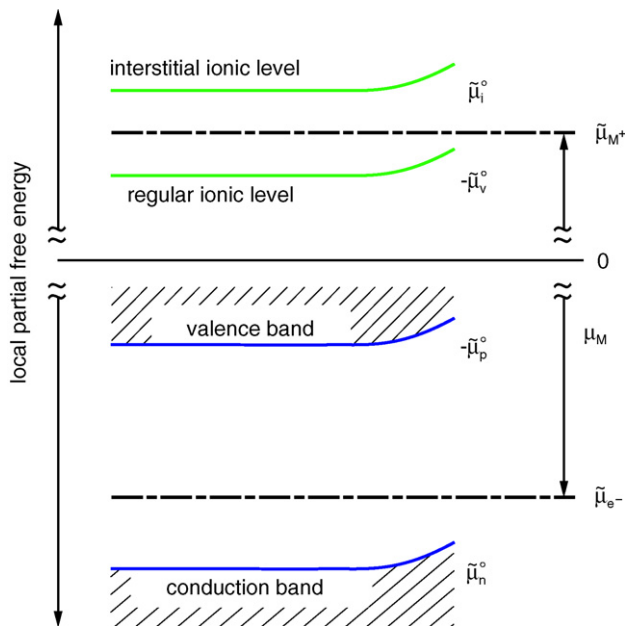


Fig. 2. Contact thermodynamics of a mixed conductor according to Refs. [9,10].

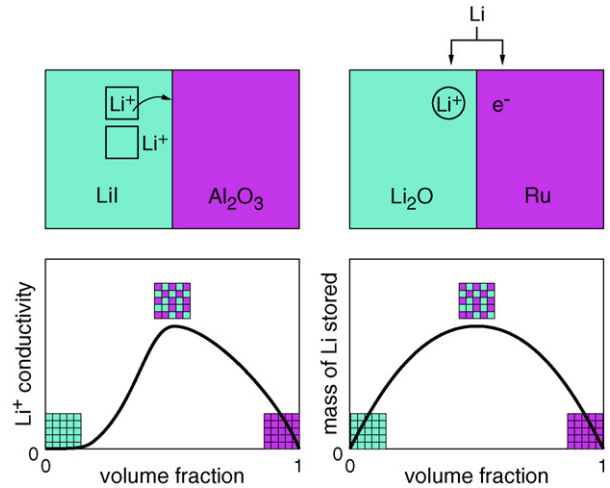


Fig. 3. Synergistic behavior of composites in terms of conductivity and storage. Conductivity and storage anomalies in two phase systems. The dissymmetry in the conductivity curve comes from percolation effects.

broken and the different affinity of the cation to get there compared to the anion matters. The charging can lead to extremely significant concentration variations. These are restricted to the immediate neighborhood of an interface (see level bendings in Fig. 2). In nano-sized systems, however, where the volume of the interfacial zones constitutes several tenths of the total volume, such effects can be tremendous. It has been shown that heterogeneities in solid state systems can turn insulators into conductors, electron conductors into ion conductors, interstitial type conductors into vacancy type conductors, etc. [10,8]. One example is the heterogeneous doping of halides (cf. Fig. 3), that can lead to 3 or 4 orders of magnitudes of conductivity enhancement if nanoporous alumina is employed as second phase [11–14]. Even mesoscopic phenomena can be realized in that the sample may become charged everywhere in the sample as the space charge zones overlap at extreme small spacing [15]. Examples are CaF<sub>2</sub>/BaF<sub>2</sub> heterostructures [16] or SrTiO<sub>3</sub> nanocrystalline ceramics [17]. In the former accumulation layers overlap, in the second depletion zones.

Also storage anomalies do occur. Let us consider a composite of two phases  $\alpha$  and  $\beta$ , whereby  $\alpha$  can store A<sup>+</sup> but not B<sup>-</sup>, while for  $\beta$  the opposite applies. Both phases then cannot store AB individually but the composite does [7,18,19]. (Fig. 3 gives an example for A<sup>+</sup> = Li<sup>+</sup>, B<sup>-</sup> = e<sup>-</sup>.)

Effects on the ground values of  $\mu$  (i.e. on  $\mu^\circ$ ) are [20,8] (i) size effects in which the perturbation zone around a defect or the electron cloud perceives confinement, (ii) elastic effects of longer range making  $\mu^\circ$  position dependent as well as (iii) curvature effects, (iv) effects of corners and edges or more generally effects for which the surface tension ( $\gamma$ ) becomes size dependent. Let us concentrate on the important curvature effects. If a solid is curved (inverse mean radius  $\equiv (r)^{-1} > 0$ ) as it is demanded for the equilibrium shape (Wulff shape) – the latter is characterized by a ratio  $\gamma_i/r_i$  that is constant with respect to the crystallographic plane  $i$  ( $\gamma_i/r_i = \langle \gamma \rangle / \langle r \rangle = \langle \gamma \rangle / \langle r \rangle$ ) – then the addition of a constituent does not just lead to an increase of the bulk but necessarily also of the surface. The extra impact on the chemical

potential is given by  $2(\gamma/r)v$  where  $v$  is the respective partial molar volume [21] and hence

$$\mu^\circ(r) = \mu^\circ(r = \infty) + 2(\gamma/r)v \quad (1)$$

The excess term can also be conceived as a result of increased internal pressure (note that  $\delta\mu/\delta p = v$ ). This increased internal pressure acts on the compound ( $\mu_{MX}^\circ$ ,  $v = V_{MX}$ ), the components (e.g.  $\mu_M^\circ$ ,  $v_M$ ), the ions as constituents (e.g.  $\mu_{M^+}^\circ$ ,  $v_{M^+}$ ) but also on the defects (e.g.  $\mu_V^\circ$ ,  $v_V$ ) [20]. Consequences of Eq. (1) are (i) decreased melting point of MX [22], (ii) increased partial pressures of M or X, (iii) partial charge transfer at interfaces of two differently curved materials (predicted in Ref. [20]), but also non-zero e.m.f. values in cells of the type

M (nano) | M<sup>+</sup>-conductor | M (micro) or MX (nano), . . .

| M<sup>+</sup>-conductor | MX (micro), . . .

The development and stability of such e.m.f. values was investigated in more detail in Refs. [23–25]. In particular the accelerated growth in contact to the electrolyte was investigated.

Further size effects are caused by distribution anomalies and interaction phenomena. Please refer to Ref. [8] for more details.

### 3. Impact on Li-batteries

#### 3.1. Electrolyte

In the following let us directly address some consequences for Li-based batteries.

First of all let us ignore curvature effects ( $\delta(\gamma/r) = 0$ ) as well as structural variations within the material, except the necessary structural jump from the interfacial core to the bulk ( $\delta\mu^\circ(x) = 0$  except for  $x = s$ ). Then the major contact effects should stem from the charge carrier redistribution. As these effects are most important as far as conductivity aspects are concerned, they directly relate to the possibility of optimizing electrolytes.

Maekawa et al. [13] in a recent paper showed (following up early work by Liang [14]) that the conductivity of LiI can be driven towards remarkable conductivity values of almost  $10^{-3} \text{ S}^{-1} \text{ cm}^{-1}$  at room temperature by heterogeneously doping it with mesoporous  $\text{Al}_2\text{O}_3$  (see Fig. 4). According to our models of heterogeneous doping [10], the authors explained their effects by a vacancy generation as a consequence of  $\text{Li}^+$  adsorption. The enormous magnitude of the effect here simply stems from the huge interfacial area.

In recent years we have been successful in heterogeneously doping also liquid electrolytes [26]. Consider an organic solvent in which a lithium salt  $\text{Li}^+\text{X}^-$  has been dissolved (Figs. 5 and 6).

As typically the solvent’s dielectric constant is much smaller than that of water, much less ion pairs are dissociated into mobile free carriers. If now  $\text{SiO}_2$  is added (note that  $\text{SiO}_2$  unlike  $\text{Al}_2\text{O}_3$  preferentially adsorbs anions) anions are expected to be adsorbed setting free the  $\text{Li}^+$  counter ions. Indeed the conductivity versus  $\text{SiO}_2$  volume fraction curves show a percolation-peak type behavior.

We investigated the whole palette of parameters such as dependence on specific area, temperature, dielectric constant

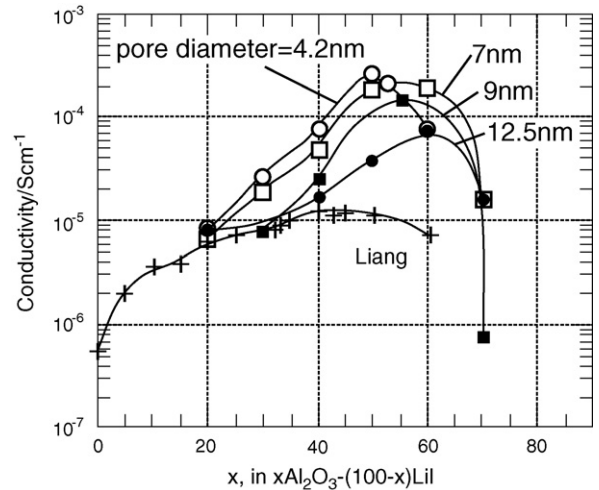


Fig. 4. Heterogeneous doping of LiI with alumina and mesoporous alumina according to Ref. [13].

(variation of the solvent), surface acidity (variation of the second phase), concentration and nature of the salt. We measured zeta potential, viscosity as a function of shear rate and recently performed EX-AFS/XANES studies [28]. All the results are consistent with the proposed mechanism. Under the bottom line the final situation is similar to Nafion (where, however, anions are covalently bonded to the framework) [29] or particle hydrates (proton conductivity in the layer of surface water) [30]. For more details the reader is referred to the literature [26]. It may be specifically mentioned that we could also exclude possible introduction of  $\text{H}_2\text{O}$  as a reason for the conductivity enhancement.

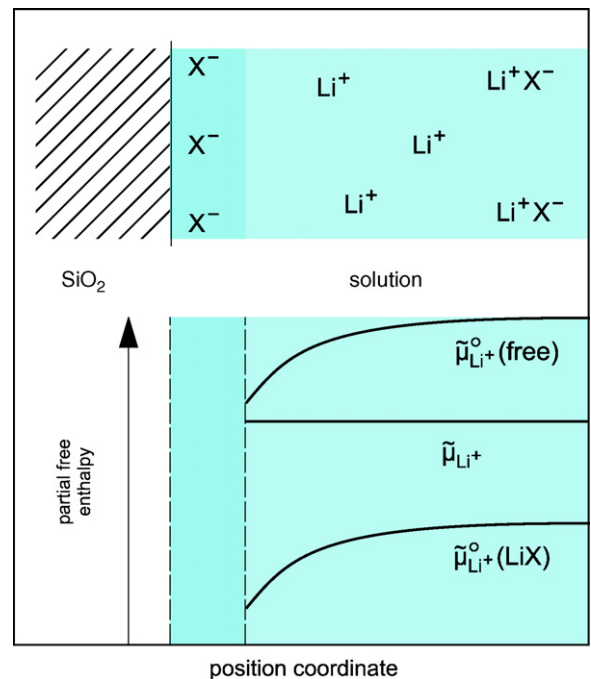


Fig. 5. Schematic representation of the influence of anion adsorption at the oxide surface on charge carrier concentration along with the energetics.  $\mu^\circ$ : standard electrochemical potential;  $\bar{\mu}$ : electrochemical potential.

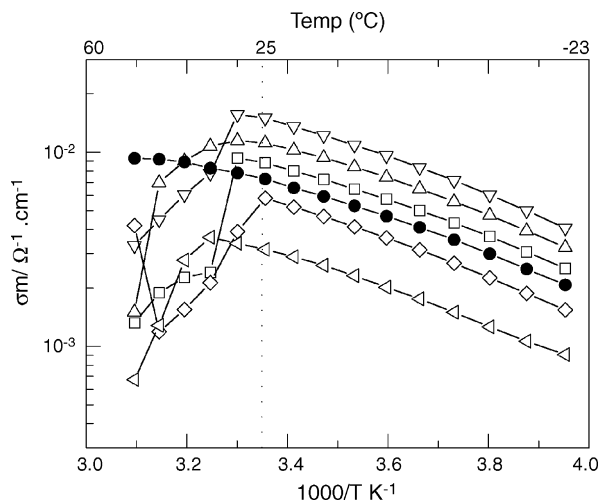


Fig. 6. Heterogeneous doping of battery electrolytes. Variation of  $\text{SiO}_2$  volume fraction ( $\phi$ ) in 1 M  $\text{LiPF}_6$  + EC/DMC (1:1 w/w) composite conductivity vs. temperature ( $-20$  to  $50$  °C):  $\phi = 0$  (●),  $\phi = 0.02$  (□),  $\phi = 0.03$  (△),  $\phi = 0.04$  (▽),  $\phi = 0.06$  (◇),  $\phi = 0.08$  (◁) (from Ref. [27]).

Not only is a conductivity increase achieved, also the mechanistic properties are distinctly better as the soft matter material is viscous and partially shapeable. First experiments showed that separators are dispensable if “soggy sand” is used and also safety is improved [27]. How far such effects are important for the kinetics at the contact solvent/oxide (e.g. solvent/electrode) is to be investigated in the future.

### 3.2. Electrode

As far as the electrode is concerned, effects on  $\phi$  (interfacial storage), on  $\gamma/r$  (e.m.f., storage contact, ripening) as well as reduction of the relative diffusion length are to the fore [7]. Let us start with the capillary effects.

If we can assume equilibrium within the particles, the chemical thermodynamics is straightforward. While for large particles the equilibrium condition (arc denotes equilibrium values) for a chemical reaction (between reaction partners  $j$  with the stoichiometric coefficients  $\nu_j$ ),  $\sum \nu_j \mu_j = 0$  leads to electrochemical mass action laws  $\prod_j \hat{c}_j^{\nu_j} = K \bar{\alpha}$ , where  $K$  is the conventional mass action law and  $\bar{\alpha}$  refers to the electric potential effects. Taking account of curvature effects of the reaction partner  $j$  with stoichiometric coefficient  $\nu_j$ , the mass action law is to be modified according to

$$\prod_j \hat{c}_j^{\nu_j} = K' \bar{\alpha} \quad (2)$$

where

$$K' = K \times \exp - \frac{\sum_j \nu_j (2\gamma_j/r_j) \nu_j}{RT} \quad (3)$$

Let us consider the simple case of a local reaction ( $\bar{\alpha} = 0$ ) in which only one nano-sized phase is to be considered, e.g.



Then the varied e.m.f. compared with having M (macro) on both sides is given by  $(2\gamma/r)V_M$ . By considering typical values for  $\gamma$ ,

$r$ ,  $V_M$  we expect variation of the order of 100 mV or less in the cell voltage. (Please note that in many cases additional contributions come into play if the nano-material is amorphous [31].) A more detailed analysis showed that in a simple cell such as M (nano) |  $\text{M}^+$  (electrolyte) | M (nano) it is the tension of the M-particles at the electrolyte contact, that is decisive [23–25].

The sluggish  $\text{M}^+$  transport within the metal particles or from particle to particle is the reason for the (kinetic) stability of a nanocrystalline arrangement of M-particles the grains of which are in contact.

Once such an arrangement is brought in contact with the  $\text{M}^+$  electrolyte, a peculiar situation arises. Now the  $\text{M}^+$  ions can take the path through the electrolyte and the M-particles rapidly grow [32,25], even if they are not in direct contact as long as they are electrochemically connected as it is the rule for a good electrode. Particles of an alloy or compound MX could still behave metastably if X is immobile; in spite of the rapid equilibrium of the Li content. If, however, the alloy partner (or anion) is also exchangeable over the interfaces and the ions mobile in the electrolyte, grains grow.

It also follows from Eq. (1) that grains of different curvatures (i.e. different grain sizes) or different surface free energies have different Li content if they are in equilibrium (as regards  $\mu_{\text{Li}}$ ), i.e. a size distribution demands a variation in the Li content [7].

Another consequence of Eq. (1) [7] affects the slope of the discharge curve: a variation in  $\gamma$  or  $r$  during charging or discharging demands a variation of  $\mu_{\text{Li}}$  and hence a variation of the cell voltage even if the situation would be non-variant in the macroscopic case. In such a case a regime expected to be flat would be sloped. But note that typically polarization effects are expected to dominate realistic discharge–charge curves.

The pioneering paper by Poizot et al. [33,34] on conversion reactions in Li-based batteries revealed the enormous difference in transport behavior between micro- and nanoscale phases on the nano-scale in Li-batteries. It refers to the fact that the capacity of electrode materials can be largely extended beyond the homogeneity range of a solid accessible via easily reversible intercalation by making use of the full reduction to the metal (or even to the alloy). Observing the tiny diffusion lengths the nanocomposite behaves quasi-fluid as to the possibility of at least partly reversing the reaction, i.e. to extract lithium out of the  $\text{Li}_2\text{O}$ /metal composite to form the initial oxide again. Also fluorides, nitrides and sulfides can behave analogously [35,36]. We could show that  $\text{RuO}_2$  [37] shows almost 100% extractability. We attribute this to the necessity of electron conduction,  $\text{Li}^+$ -conduction,  $\text{O}^{2-}$  and/or metal ion conduction, all of them being established in  $\text{RuO}_2$ . In  $\text{IrO}_2$ , e.g., which does not exhibit a similarly good  $\text{Li}^+$ -conductivity only 2/3 of the Li can be extracted in the first cycle [38].

Another relevant feature of these nanocomposites is the pseudo-capacitive behavior at low potentials which we attribute to the interstitial storage effects addressed above [7,18]. While both  $\text{Li}_2\text{O}$  and Ru are not expected to dissolve Li perceptibly, the composite can as  $\text{Li}_2\text{O}$  can dissolve  $\text{Li}^+$  and Ru the electron [37]. We have experimental support for this by NMR [39] and could also exclude formation of SEI or storage in the SEI to be

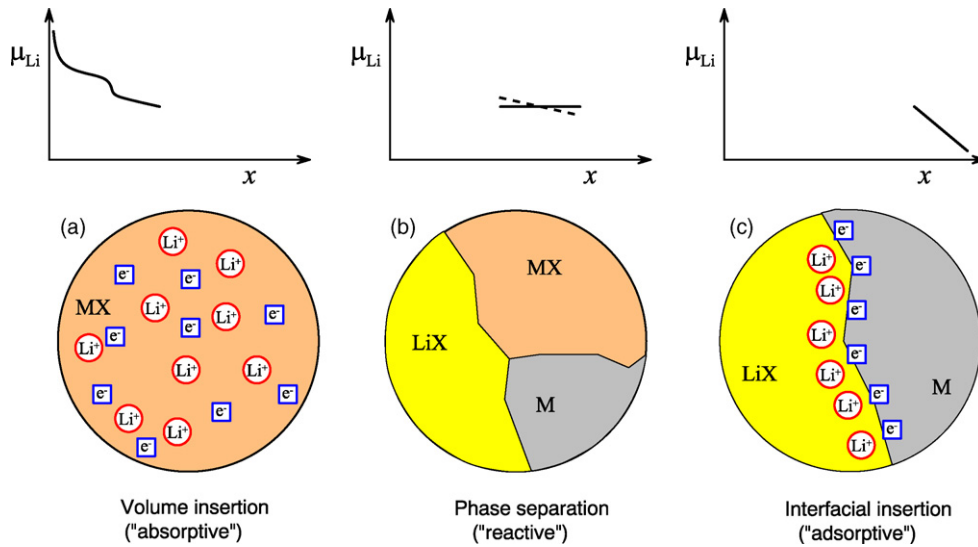


Fig. 7. Different stages of Li storage in MX. Bulk insertion (a). Conversion reaction (b). For simplicity Li dislocation in LiX and M is ignored. Interfacial charging as novel mechanism (c) [7].

responsible (note that significant Li storage in SEI would make it mixed conducting and de-passivate it); moreover, detailed DFT calculations showed the relevance of the effect [19]: lithium can – in a thermodynamically favorable way – indeed be brought to the interface or close to the interface while becoming ionized and the electrons being transferred to the metal. Surprisingly also Li storage at free interfaces is found to be possible with the electrons transferred to the oxide conduction band. This sheds light on the significance of modified stoichiometries of small particles or nanocomposites (see also [40,41]). A detailed treatment of this is given recently [18].

Calculating the specific capacitance for such a storage, it is no surprise in the retrospect that by these interfacial mechanisms values can be achieved that approach the homogeneous limit if the space charge layers overlap. In such a mesoscopic situation this mechanism forms the bridge between an electrostatic capacitor and a battery electrode.

Fig. 7 shows the basic storage mechanisms in Li batteries: homogeneous introduction (intercalation/insertion), formation of new phases, and interfacial storage (heterogeneous storage) [7].

Let us return to mass transport. Fig. 8 shows four modes for Li transport in a predominantly Li<sup>+</sup> conducting material: (i) Li<sup>+</sup>

in the electrolyte accompanied by e<sup>-</sup> flowing in the outer circuit, (ii) Li<sup>+</sup> flux accompanied by e<sup>-</sup> flux in the crystal and (iii) Li<sup>+</sup> flux accompanied by e<sup>-</sup> flux along a second phase or (iv) along the grain boundaries. Only the last three are relevant for mass storage within the material shown.

In the case of a predominantly electronically conducting material analogous mechanisms have to be considered. If the material shows both a poor Li<sup>+</sup> conductivity as well as poor e<sup>-</sup> conductivity, another approach is advisable, namely introducing mixed conducting networks.

In this context our recent work on anatase might be mentioned [42]. First mesopores are introduced in TiO<sub>2</sub> which can take up electrolyte. As we metalized them internally by RuO<sub>2</sub>, the channels provide electronic conduction, too, and hence represent mixed conducting wires. The situation is schematically shown in Fig. 8. As the spacing between the channels is of a few nm only, the equilibrium time for Li storage in TiO<sub>2</sub> is negligible in spite of the low diffusion coefficients. As such a monolith is hardly preparable and would be, in addition, hardly infiltrable, a clever design uses a similar superstructure on a microstructure and hence a functionally self-similar network. The performance of such electrodes is excellent even at extreme rates as high as 30 °C (still 90 mAh g<sup>-1</sup>).

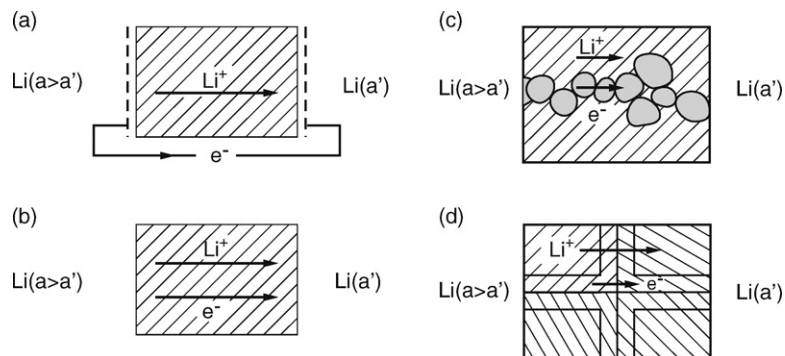


Fig. 8. Various modes of Li transport in solids.

### Materials Research of Li-based Batteries

- Nano-Networks: Decreasing overall resistances and waiting times
- New Materials: New properties
- Given Materials: Homogeneous and heterogeneous modification of materials parameters

Fig. 9. See text.

### 4. Strategies for materials research

Fig. 9 refers to the materials strategies for achieving better performance of electrochemical devices. One is the just described possibility of playing around with geometric parameters. Even if these do not affect the local transport parameters, the overall effect may be drastic. The very opposite is to prepare new compounds and structures generating changed mobilities ( $u$ ) and carrier concentrations ( $c$ ). In addition, there is the possibility to vary the transport parameters of given compounds and structures. In the bulk this is possible with the help of the adjusting screws, temperature ( $T$ ), (pressure), component partial pressures ( $P$ ) as well as freezing parameters since usually not all the components achieve thermodynamic equilibrium. Homogeneous doping (doping content  $C$ ) is known to be very efficient by introducing impurities irreversibly. As extensively shown, the (irreversible) introduction of higher dimensional defects (in particular interfaces) is an extremely efficient means (heterogeneous doping), too. It unfolds its whole strength if the interfacial density is so large that the materials are completely interfacially dominated or even show mesoscopic properties.

Not only the nature but also the spacing of interfaces is important and can lead to non-trivial effects. As the improvements caused by interfacial effects are most pronounced at not too high temperatures, the field of nanoionics has great potential to bring about a strong impetus to the field of Li-based batteries.

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