Designing Solids

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Abstract: The rational design of an extended polymer or of a solid is an extremely difficult enterprise. Yet, only well-designed solids have a chance of constituting so-called intelligent materials – a necessary prerequisite for future technological materials. Three examples are given of how solids may be designed: a high energy battery material, tubular and fibrous nanoparticles, as well as semiconductor compounds.

Keywords: Building blocks · Design of solids · Li-ion battery · Manganese oxide · Nanofibers · Nanotubes · Zintl phases

Introduction

Ordering phenomena are the essence of our micro- and macroscopic world and in the latter mankind induces dramatic change, in many cases in a direct physical way in form of roads, houses, lakes, *etc.* Typically, in chemistry, the constituting particles of compounds and materials – atoms, ions, and molecules – cannot be handled directly. Consequently, chemistry has much to do with initiating self-organization of such particles by many different strategies. Although still far from perfect, design strategies of small molecules have been well developed in the last century to a relatively high level. In contrast to that, the design of collectives of particles, starting from the molecular scale to the so-called nano regime is still in its infancy. The availability of modern physical methods has pushed open doors for much more successful investigations on the design of nanoscopic entities than possible hitherto. These will be the clue to future materials research. A few examples may show how rational design can enter into solid state sciences.

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High Energy Battery

The presently best high energy battery – known as the Li-ion battery – delivers 120–130 mAh/g at about 4V. This is close to four times as much as can be achieved from the lead battery and not quite twice as much as from the nickel hydride battery. Another expression for this lithium accumulator is the rocking chair battery, the working principle of which is shown in Fig. 1. There are three main electroactive components: the positive electrode (Li graphite), the electrolyte, and the negative electrode (Li transition metal oxide). Dependent on the transition metal, the battery may exhibit an average potential of about 4V, which at the present stage is close to the stability limit of the available electrolytes. About 95% of the Li-ion batteries used worldwide utilize Li_xCoO_2 cathodes.

This material presents some shortcomings which one would like to overcome: 1. limited thermal safety; 2. high world market price of cobalt; 3. poisoning potential of cobalt; 4. much lower capacity than the presently available anodes; 5. independence from present patents.

In a common project with the Paul-Scherrer-Institute we are investigating alternative cathode materials which should preferably be based on manganese. However, many hitherto unsuccessful attempts have been undertaken to overcome the cycling instability of the thermodynamically stable spinel phase $Li_xMn_2O_4$ and to stabilize the metastable layered Li_xMnO_2. Even if one would be able to successfully cycle the spinel, its capacity is at least 10% lower than that of

the cobalt oxide. That is why we concentrated on the layered Li_xTO_2 type materials instead of spinels.

Considering HSAB theory and the knowledge from other stable Li_xTO_2 phases (T= transition metal) we attempted to stabilize a manganese-based compound of this type. The strategy was to introduce a more polarizing T cation as polarization favors the formation of layered materials. Consequently, we succeeded in synthesizing stable quaternary $Li_xMn_yNi_{1-y}O_2$ phases up to y = 0.5 which means up to 50% manganese content [1][2]. However, these phases exhibit fast decay during the electrochemical cycles which is generally traced back to Jahn-Teller distortions which breakup the TO_2 layers during the redox cycles.

To reduce the JT distortions, we investigated different small and polarizing but non-redox-active cations as a fifth component and found small amounts of aluminum to be a very useful dopant. The final chemically designed material is still a single phase compound reading $Li_xMn_{0.5}Ni_{0.4}Al_{0.1}O_2$. Despite focusing on this goal already quite early during the project it took several years to evaluate a synthesis route which allows the excellent properties of this new and environmentally friendly cathode material to be realized [3][4].

Further investigations revealed that there is not only an outstanding stability over many hundred redox cycles at room temperature but also at 55 °C where the already good capacity of 140 mAh/g increases to 160 mAh/g. This is an indication for an even larger potential electrochemical capacity of the material.

Another important feature of a high energy battery is the safety aspect. One of the main threats is the spontaneous reaction of the cathode with the electrolyte under evolution of CO_2 at higher temperatures which leads to an explosion of the battery. With the novel quinternary Mn-based material this reaction does not start before 270 °C, which is about 50 °C higher that for Li_xCoO_2 and Li_xNiO_2 [5][6] (Fig. 2).

Inorganic Nanotubes and Nanowires

Nanotubes and nanorods or fibers are anisotropic nanoparticles which have, as a result of their morphology, many interesting basic properties. This makes them an ideal part of a nano toolbox – an important prerequisite for future nanotechnology. However designing nanoparticles is somewhat beyond a circus director trying to tame all his animals at one time in one ring. Let's just assume simple sodium chloride: a crystal with a radius of 0.5 nm contains 27 atoms – like a medium-sized molecule; at 1 nm radius we find 203 atoms, at 2 nm 1647, and at 10 nm – still a small nanoparticle – 205876 atoms in the particle. Now, if one wishes these many atoms to behave in a certain way, *i.e.* build just a very specific anisotropic structure out of many possible arrangements, one has to find out specific synthesis routes during which morphology can be designed. This means not all of the particles should behave in the same way because that would mean the formation of a simple small crystal.

Nanotubes are becoming an increasingly fascinating research field because they seem to be quite outstanding nanoparticles that leave many possibilities open for modification, functionalization, exchange/topochemistry, and alignment into larger ordered arrays. We believe we have established a quite general way to generate nanotubes or nano scrolls from layered materials. The precursor has to be an, in principle, arbitrary layered compound. So the first step is formation of the layered compound; then the inter layer interactions have to be weakened, either by chemical or by physical means, and finally – after having lost the contact to neighboring layers – the separated layers scroll up to get at least into their own contact. This procedure has been proven to work for a number of oxides and layered salts [7]. However, it should be noted that the layered precursor compound need not be identical to the final nanotube, but may just be an intermediate
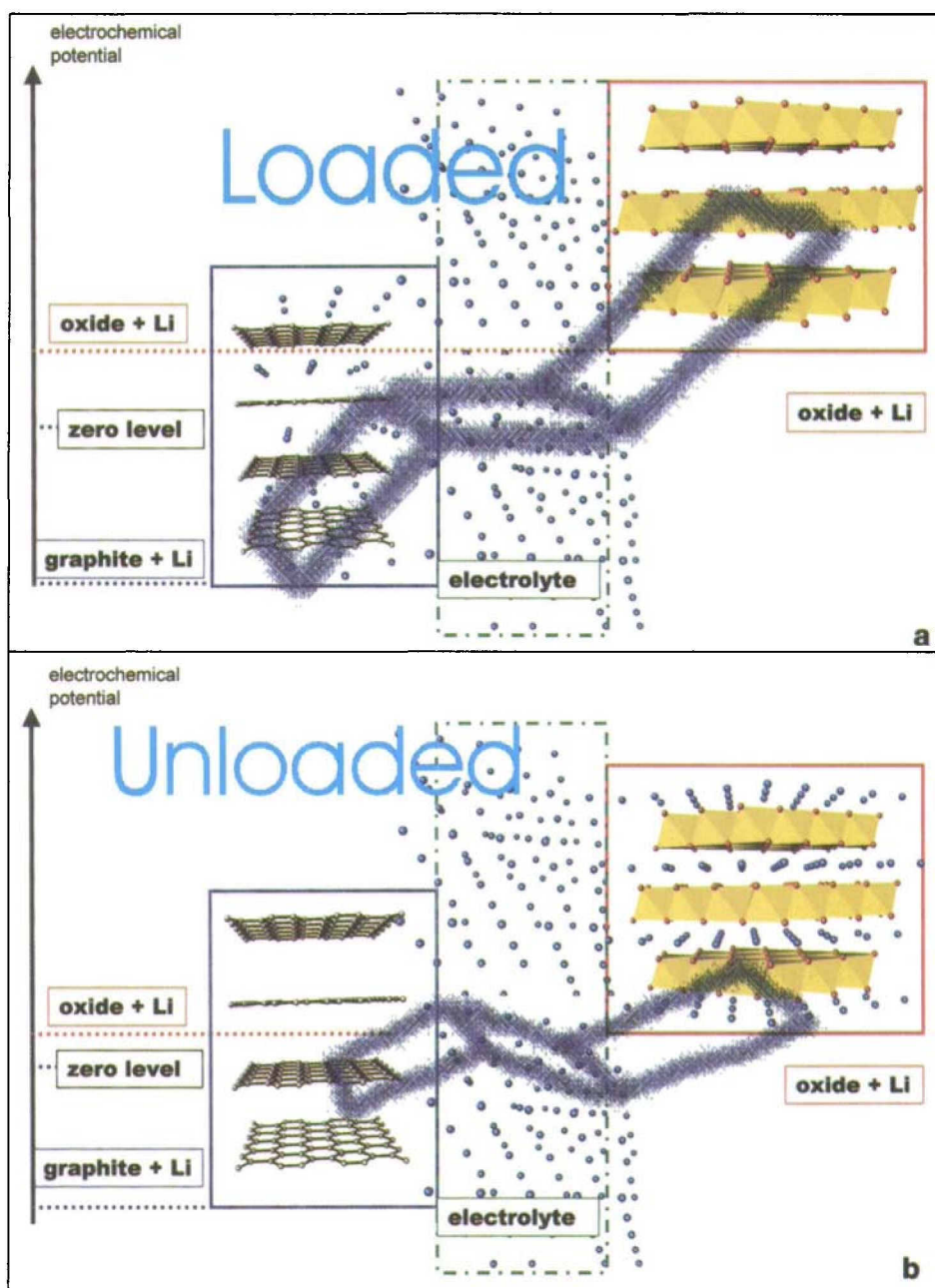

Fig. 1. Schematic display of the functional parts of the rocking chair lithium ion battery: (a) loaded state with most of the lithium ions intercalated into the graphite; (b) unloaded state with most of the lithium ions in-between the transition oxide layers.
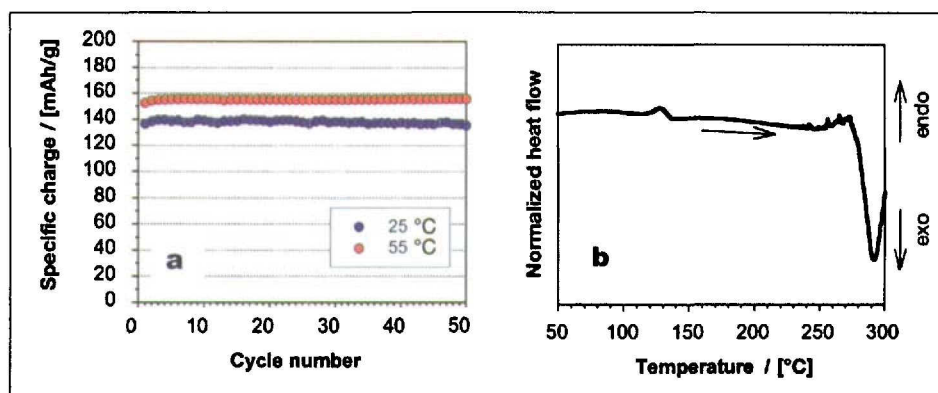

Fig. 2. Electrochemical performance of $Li_xMn_yNi_{1-y-0.1}Al_{0.1}O_2$: (a) cycling stability at room temperature and at 55 °C showing no loss of capacity; (b) temperature stability in contact with a typical electrolyte solution. Decomposition starts at about 270 °C which is about 50 °C higher that for Li_xCoO_2.

which can react under scrolling to a final composition and structure which may be no longer layered [8]. The scrolled nature of VO_x [8–17] and TiO_2 [18] nanotubes is beautifully displayed in Figs. 3b and 3f. It has also been shown that in some cases layered nanotubes undergo topochemical reactions, *i.e.* they can exchange molecules and ions and at the same time readjust their morphology thanks to their scrolled nature [16]. In cross-sectional TEM images (Fig. 3c) with elemental mapping the distribution of vanadium (Fig. 3d, light areas) and of carbon-containing template molecules (Fig. 3e, light areas) can clearly be discriminated.

As already mentioned, besides changes of the tube radius, severe changes of chemical bonding in the tube walls may also occur under ion exchange. We have encountered that ion exchange for the small protons leads in many cases to a compacting of the structures during which intermediate nanotubes are transformed into nanorods or nanofibers. The latter may also be called nanowires. In extreme cases, these wires may have diameters of just 50nm but lengths of several centimeters. This is an extraordinary case of anisotropy or aspect ratio ($\sim 10^6$).

Due to their extreme morphology, numerous applications are envisaged for nanotubes and nanofibers, which are presently more a focus in physics than in chemistry. However already now, it seems quite probable that the chemical reactivity of such materials is different from conventional powders. This will have an impact on many different fields of chemistry, for example on heterogeneous catalysis. Just to mention one example: we synthesized a novel kind of fibrous MoO_3 (Fig. 3g), which exhibits an excellent activity in the methanol oxidation process, becoming active about 100 °C lower than conventional MoO_3 materials and showing at the same time a high thermal stability.

The generation of a toolbox set of nanoparticles is only the beginning of making available nanoparticles with designed functionalities. For this goal, selective surface coating reactions are being explored to generate multishell particles, to allow for a tuning of surface potentials and selectively dock particles at designated sites. One quite obvious example of a secondary nanoparticle would be a tube-in-tube case (Fig. 3i).

Semiconductor Cluster Compounds

Silicon is still the fundamental electronic material of the last and the present century. Although metal silicon contacts are quite frequent junctions in electronic devices, metal silicon compounds – so-called Zintl phases – are still a vast, widely unexplored field. As just recently shown by IBM, specific silicide compounds may have a pivotal influence on the performance of strongly miniaturized wire connections (carrier velocity of copper silicides). We have been exploring Zintl phases of group 13 and 14 of the periodic table for more than two decades and found in this steadily growing family interesting hierarchical building features. There are frequently occurring building blocks which allow a variety of complex solid structures to be composed from simpler blocks [19][20]. Out of a number of different topological building-block families, only one is mentioned here: the ternary dumb-bell compound $BaMg_2Si_2$ is the aristotype (hierarchical root) of a number of observed and hypothetical phases in which the ratio of large cation/small cation(s) = 1:2 is selectively changed [21]. Instead of forming completely new structural variants, these phases use the basic building principle of the aristotype and insert variational blocks to match their stoichiometry. The composition $BaMg_2Si_2$ contains all the necessary essentials to coordinate an Si–Si bond and highly charged terminal Si^{3-} (naked silyl) groups (Fig. 4a). In the ternary Si_6 chain compound $Ba_2Mg_3Si_4$ a lack of small cations occurs which favors an increase of Si–Si bonds. As a consequence this phase may be understood as consisting of the silyl group coordinating block $[BaMg_2Si_2]$ and an $[BaMg_1Si_2]$ chain-linking block which is deficient of small cations (1 stands for a missing Mg atom; *cf.* Fig. 4a).

In the same way the quaternary six-chain compound $Ba_6Mg_{5.3}Li_{2.7}Si_{12}$ and the quaternary infinite chain compound $Ba_2M_2Si_4$ (M = Mg, Li) can be formulated as $[BaMg_2Si_2]$ $[BaMg_{0.3}Li_{0.7}1Si_2]_4$ $[BaMg_2Si_2]$ or $[BaMg_2Si_2]$ $[BaM1Si_2]_4$ $[BaMg_2Si_2]$, and $[BaMg_1Si_2]$ $[BaMg_1Si_2]$, respectively (Fig. 4b and c). Tuning this building principle allows us to design different silicon chain lengths in the solid. On varying the mutual block locations, predictions for developing different chain conformations can be made. This is shown in Fig. 4d by comparing the quaternary infinite chain compound $Ba_2M_2Si_4$ (M = Mg, Li) and the hypothetical infinite chain compound $M'_2M_2Si_4$
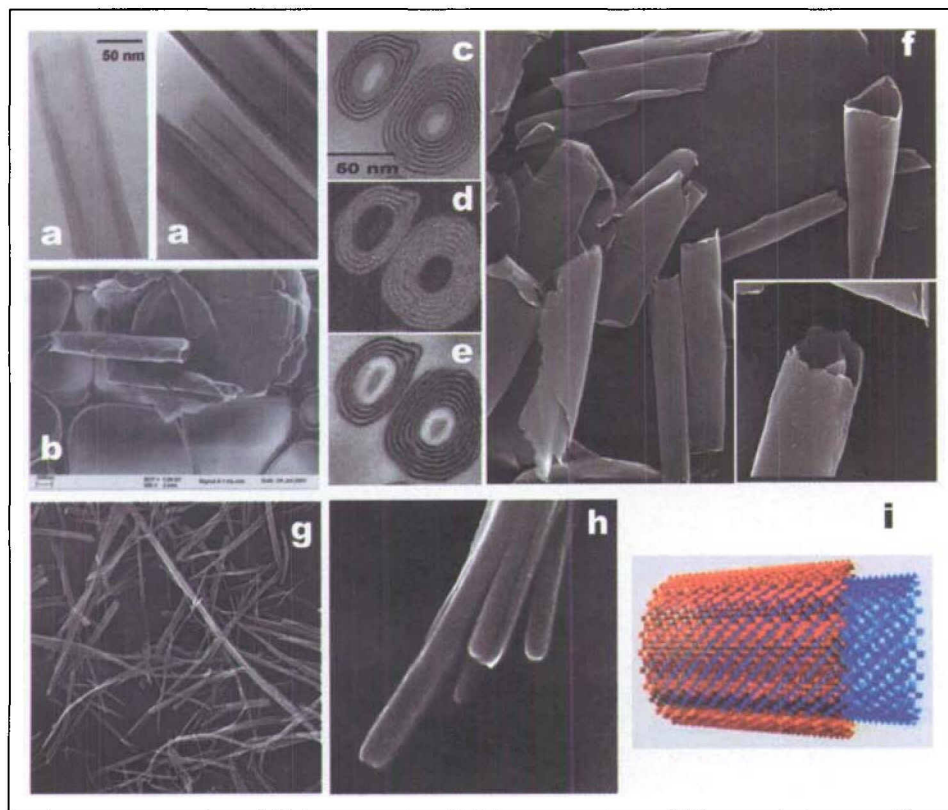

Fig. 3. Anisotropic nanoparticles: (a) transmission electron micrographs of vanadium oxide nanotubes; (b) high-resolution scanning electron micrograph of VO_x nanotubes displaying clearly their scrolled nature; (c) cross sections of VO_x nanotubes, (d) with vanadium mapping (light areas), (e) with carbon mapping (light areas); (f) high-resolution scanning electron micrograph of TiO_2 nanotubes displaying their scrolled and sometimes cone-like morphology; (g) the novel MoO_3 fiber material, (h) MoO_3 fiber end split into smaller constituting fibers; (i) schematic display of the tube-in-tube situation.
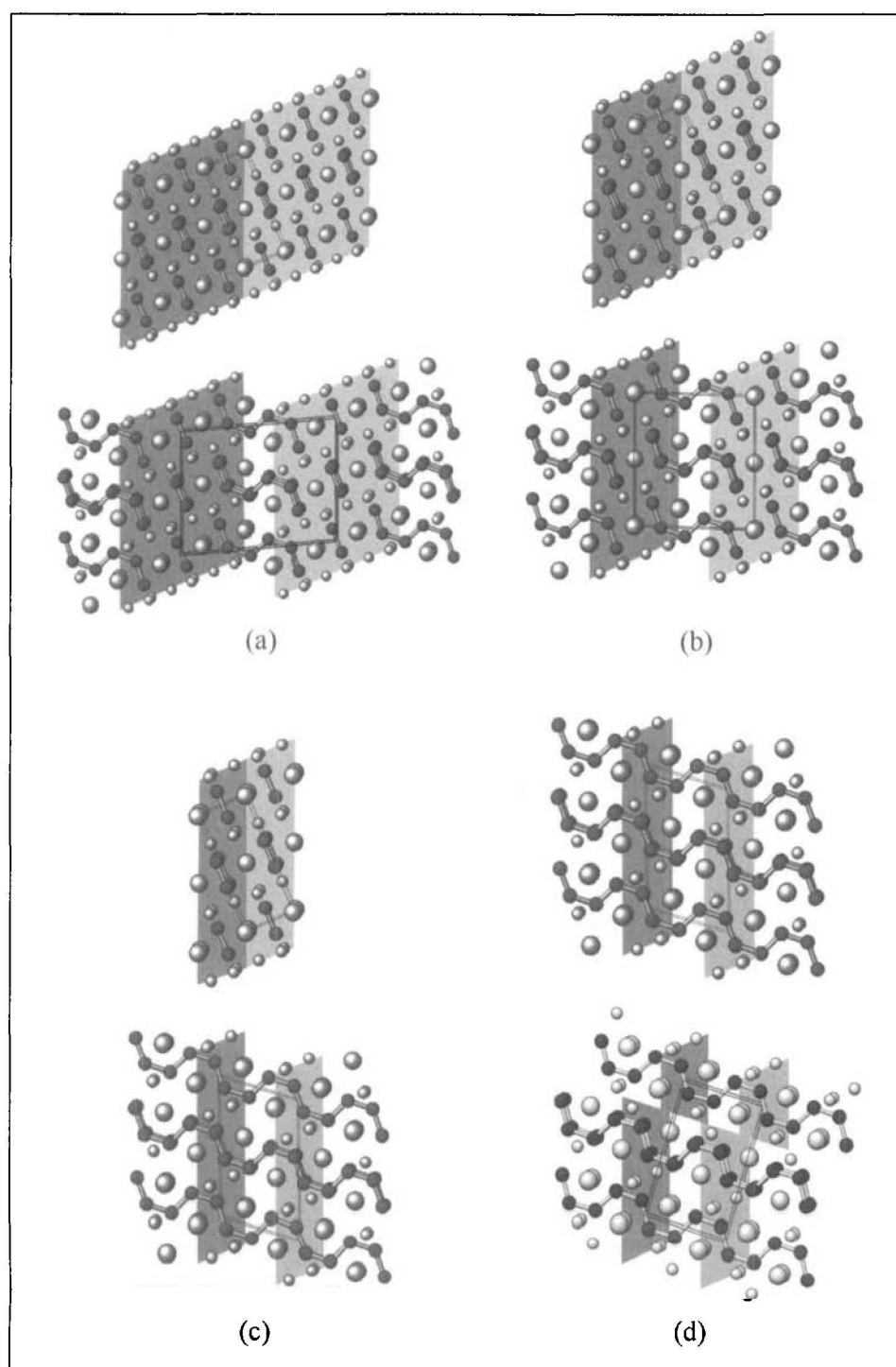
(a)　　　　　(b)

(c)　　　　　(d)

Fig. 4. Topological building block relationships between the ternary dumb-bell aristotype $BaMg_2Si_2$ and (a) the ternary six chain compound $Ba_2Mg_3Si_4$ which may be written as $[BaMg_2Si_2]$ $[BaMg1Si_2]$ where ı stands for a missing Mg atom; (b) the quaternary six-chain compound $Ba_6Mg_{5.3}Li_{2.7}Si_{12}$, which may also be written as $[BaMg_2Si_2]$ $[BaMg_{0.3}Li_{0.7}ıSi_2]_4$ $[BaMg_2Si_2]$ or $[BaMg_2Si_2]$ $[BaMıSi_2]_4$ $[BaMg_2Si_2]$, respectively, and (c) the quaternary infinite chain compound $Ba_2M_2Si_4$ (M = Mg, Li) which may be formulated as $[BaMıSi_2]$ $[BaMg_ıSi_2]$, respectively. (d) Comparison of the structures of the quaternary infinite chain compound $Ba_2M_2Si_4$ (M = Mg, Li) and the hypothetical infinite chain compound $M'_2M_2Si_4$ (M' = large divalent cation; M = small mono or divalent cations).

(M' = large divalent cation; M = small mono or divalent cations). In other building-block families other non-linear Zintl anions (Si, Ge clusters) can be build up in a similar way.

Acknowledgment

[1] M.E. Spahr, P. Novák, O. Haas, R. Nesper, *J. Power Sources* 1997, *68*, 629.

[2] M.E. Spahr, P. Novák, B. Schnyder, O. Haas, R. Nesper, *J. Electrochem. Soc.* 1998, *145*, 1113.

[3] P. Novák, M. Coluccia, R. Nesper, 'Elektrodenmaterial für positive Elektroden wiederaufladbarer Lithium Batterien', Patent applications No. CH 2215/99, 1999 and PCT/CH 00/ 00641, 2000.

[4] M. Coluccia, Dissertation, ETH no. 13751, Zürich, 2000.

[5] P. Novák, J.-C. Panitz, F. Joho, M. Lanz, R. Imhof, M. Coluccia, *J. Power Sources* 2000, *90*, 52.

[6] P. Novák, F. Joho, M. Lanz, B. Rykart, J.-C. Panitz, D. Alliata, R. Kötz, O. Haas, *J. Power Sources*, 2001, in press.

[7] R. Nesper, G. Patzke, *Nachrichten aus Chemie* 2001, *491*, 886.

[8] M. Wörle, J. de Onate, H.-J. Muhr, F. Bieri, R. Nesper, *Chimia* 1999, *53*, 336.

[9] R. Nesper, M.E. Spahr, M. Niederberger, P. Bitterli, *Int. Patent Appl. PCT/CH97/ 00470*, Bundesamt für Geistiges Eigentum, Bern, 1997.

[10] M.E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, H.-U. Nissen, *Angew. Chem.* 1998, *110*, 1339; *Angew. Chem. Int. Ed.* 1998, *37*, 1263; F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, R. Nesper, *J. Am. Chem. Soc.* 1999, *121*, 8324;

[11] H.-J. Muhr, F. Krumeich, U.P. Schönholzer, F. Bieri, M. Niederberger, L.J. Gauckler, R. Nesper, *Adv. Mater.* 2000, *12*, 231;

[12] F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, M. Reinoso, R. Nesper, 'Nanophase and Nanocomposite Materials III', Eds. S. Komareni, J.C. Parker, H. Hahn, MRS Symp. Proc. 581, Warrendale, 2000, p. 393–398.

[13] M. Niederberger, H.-J. Muhr, F. Krumeich, F. Bieri, D. Günther, R. Nesper, *Chem. Mater.* 2000, *12*, 1995.

[14] F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, R. Nesper, *Z. Allg. Anorg. Chem.* 2000, *626*, 2208.

[15] X. Wang, L. Liu, R. Bontchev, A.J. Jacobson, *Chem. Commun.* 1998, 1009.

[16] J. M. Reinoso, H.-J. Muhr, F. Krumeich, F. Bieri, R. Nesper, *Helv. Chim. Acta.* 2000, *83*, 1724.

[17] K.S. Pillai, F. Krumeich, H.-J. Muhr, M. Niederberger, R. Nesper, *Solid State Ionics* 2001, *141–142*, 185.

[18] T. Kasuga, M. Hiramutsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir*, 1998, *14*, 3160; T. Kasuga, M. Hiramutsu, A. Hoson, T. Sekino, K. Niihara, *Adv. Mater.* 1999, *11*, 1307.

[19] F. Zürcher, Dissertation, ETH, no 12546; Zürich, 1998.

[20] S. Wengert, Dissertation ETH, no. 12070, Zürich, 1997.

[21] S. Wengert, R. Nesper, *Inorg. Chem.* 2000, *39*, 2861.