

Nanomaterials Meet Li-ion Batteries

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Abstract: Li-ion batteries are used in many applications in everyday life: cell phones, laser pointers, laptops, cordless drills or saws, bikes and even cars. Yet, there is room for improvement in order to make the batteries smaller and last longer. The Fromm group contributes to this research focusing mainly on nanoscale lithium ion cathode materials. This contribution gives an overview over our current activities in the field of batteries. After an introduction on the nano-materials of LiCoO_2 and LiMnPO_4 , the studies of our cathode composition and preparation will be presented.

Keywords: Cathode · Composite structure · Li-ion batteries · Nano- LiCoO_2 · Nano- LiMnPO_4

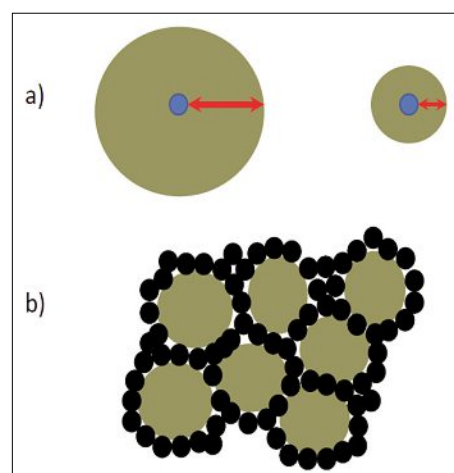
Nano- LiCoO_2

Today's commercial Li-ion batteries are typically based on the layered structure of the high-temperature (HT) phase of LiCoO_2 as active material in the form of a micron-sized powder, using a carbon additive as well as a binder to increase the electronic conductivity and to process the so-obtained paste into a cathode.^[1] Commercial HT- LiCoO_2 is produced *via* a solid-state synthesis operating under oxygen at very high temperature (600–900 °C) and over long times (2–3 days).^[2,3] Using the precursor method, the Fromm group was able to simplify the reaction conditions and to reduce i) the production time, ii) the reaction temperature as well as iii) the grain size. Indeed, by reacting dry CoCl_2 with different ratios of LiOR in dry THF (R = Ph, tBu, Et, Me), we were able to obtain Li-Co alkoxides and aryloxides which combined the two metal ions. Compounds such as $[(\text{thf})_2\text{Li}(\mu\text{-OR})_2\text{Co}(\mu\text{-OR})_2\text{Li}(\text{thf})_2]$ (for R = Ph) and $[(\text{thf})_2\text{Li}(\mu\text{-OR})_2\text{Co}(\mu\text{-OR}')_2\text{Co}(\mu\text{-OR})_2\text{Li}(\text{thf})_2]$ (R = Ph, R' = tBu) could be identified.^[4] While the second compound has the correct stoichiometric ratio between the metal ions and solely yields HT- LiCoO_2 as combus-

tion product, the first compound yields also Li_2CO_3 upon heating in air. This byproduct can be eliminated by a short washing step with water.^[4] Optimizing the alkoxide and aryloxide ligands, it was possible to generate the desired high-temperature phase of LiCoO_2 at as low as 350 °C and within two hours. The so-obtained nano-powders of different sizes, depending on the precursor and the temperature gradients used during combustion, are now being studied by us for their electrochemical performance in Swagelok and coin cells. In comparison with the commercial micron-scale material, the nano-sized LiCoO_2 is expected to possess a higher Li-ion diffusivity as the grains are smaller and the Li-ions should be able to migrate in and out of the grains much easier. Therefore, the reversible capacities of nano-sized LiCoO_2 are higher at high C-rates (>1 C) compared to the micron-sized LiCoO_2 .^[5,6] We will soon report on these results.

Nano- LiMnPO_4

In parallel to this research on LiCoO_2 , we are also developing the technology around nano-scale LiMnPO_4 , an olivine-type material with high structural stability.^[7] Compared to the commercially used LiFePO_4 , the Mn-analogue has a 20% higher energy density based on its higher potential versus Li^+/Li . On the other hand, it has a lower ionic and electronic conductivity resulting in a poor capacity and rate capability.^[8] One way to overcome these drawbacks is to generate nano-scale LiMnPO_4 and to add conductive carbon additives.^[9–13] Indeed, smaller particles reduce the Li-ion diffusion pathway and improve hence the ionic conductivity, while carbonaceous material such as graphite or carbon black improves the electronic conductivity (Scheme 1).^[12]



Scheme 1. a) Comparison of the maximum Li-ion (blue) diffusion pathway (red) as a function of particle size of active material (valid for LiCoO_2 as well as LiMnPO_4); b) ideal mixing of active material LiMnPO_4 (olive green) with carbon black (black) as conductive additive for the improvement of electronic conductivity.

We therefore studied i) different syntheses to obtain nanoscale LiMnPO_4 in order to gain control over grain size and shape, ii) the influence of the particle size, and iii) the amount of carbon additive necessary to obtain full capacity.

In a previous publication,^[12] it was shown that for sample sizes ranging from 410 nm to 140 nm, the smaller the particle size, the better the reversible capacity (Fig. 1).

We therefore fine-tuned and improved the synthesis pathway using the polyol direct precipitation method (Scheme 2) in order to obtain yet smaller particles with different shapes.

In particular, we added a ligand exchange step to eliminate remaining surfactant from the surface of the particles, reducing thus the amount of remaining carbon residue after the final heating step.^[15]

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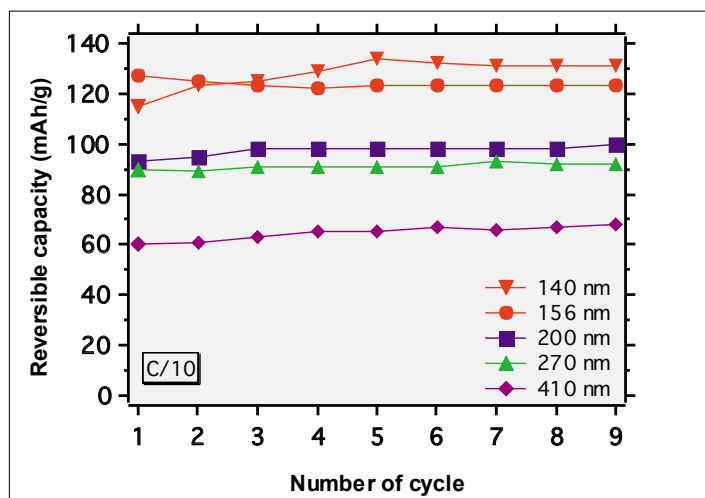


Fig. 1. The reversible capacities of LiMnPO_4 consisting of different particle sizes. The smallest particle size showed the highest reversible capacity.^[12,14]

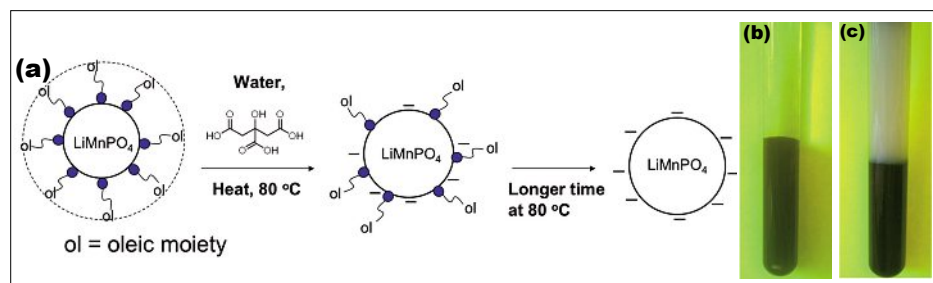
Carbon Additives and Cathode Preparation Methods

Since many different carbon additives are available on the market, and since the generation of homogeneous nanocomposites is non-trivial, we decided to study both aspects. In a first test, four different commercial carbon additives, two graphitic and two carbon black materials, were tested under similar conditions with commercial micron-scale LiCoO_2 .^[16] The platelet-shaped graphite material has a lower specific surface area compared to the nano-sized carbon black with spherical particles. We expected that carbon black would thus perform better than graphite, as it would mix better with the LiCoO_2 -particles. In parallel, we also investigated the influence of the ball-milling on the formation of the composites.^[17] For this study, we expected a longer ball-milling to lead to a more ho-

Indeed, we succeeded in controlling the reaction conditions such that we could reduce the particle sizes below 30 nm obtaining different shapes, from spherical to rod-like (Fig. 2), and, more importantly, in very high yield.^[15]

The nanoscale LiMnPO_4 shown in Fig. 2 (c) was used to study the best composition of a cathode in terms of carbon additive content. The higher percentage of active material versus carbon additive required to improve the electronic conductivity, the better is the capacity per weight of an electrode. While in the literature, amounts of 20–40% of carbon are reported, we could show that as little as 10% of carbon black could give rise to the full theoretical capacity of 170 mAh/g

at a charging rate of C/40 (Fig. 3).^[15] This brings LiMnPO_4 into the game as potential commercial product for cathode materials of future Li-ion batteries.



Scheme 2. a) A schematic of the process of LiMnPO_4 surface modification from oleic acid to citric acid. Chloroform (bottom) and water (above) solution before b) and after c) ligand exchange.^[15] Reprinted from ref. [15] with permission from Elsevier.

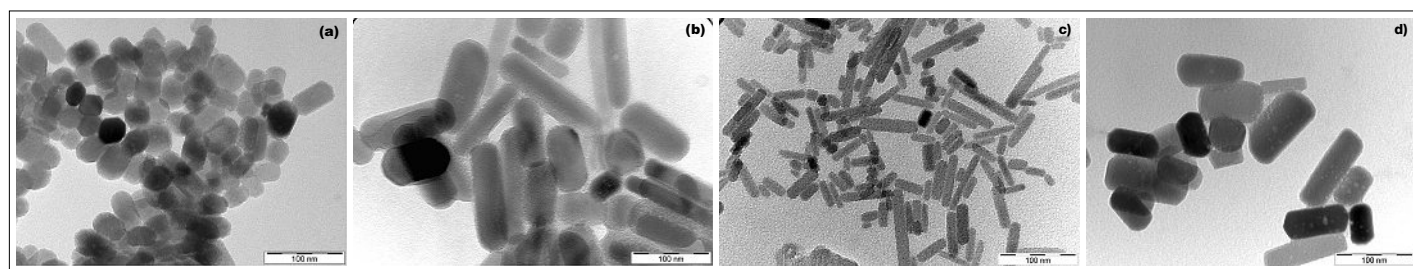


Fig. 2. TEM morphologies of LiMnPO_4 controlled by the concentration of oleic acid, the reaction temperature and time. a) and b) are 9:1 and 3:1 in the molar ratio of oleic acid and precursors at 280 °C, respectively. c) is obtained at the reaction temperature of 265 °C. d) is obtained by the reaction time of 1 h. The molar ratio of 3:1 = oleic acid and precursors in (c) and (d). The scale bar is 100 nm.

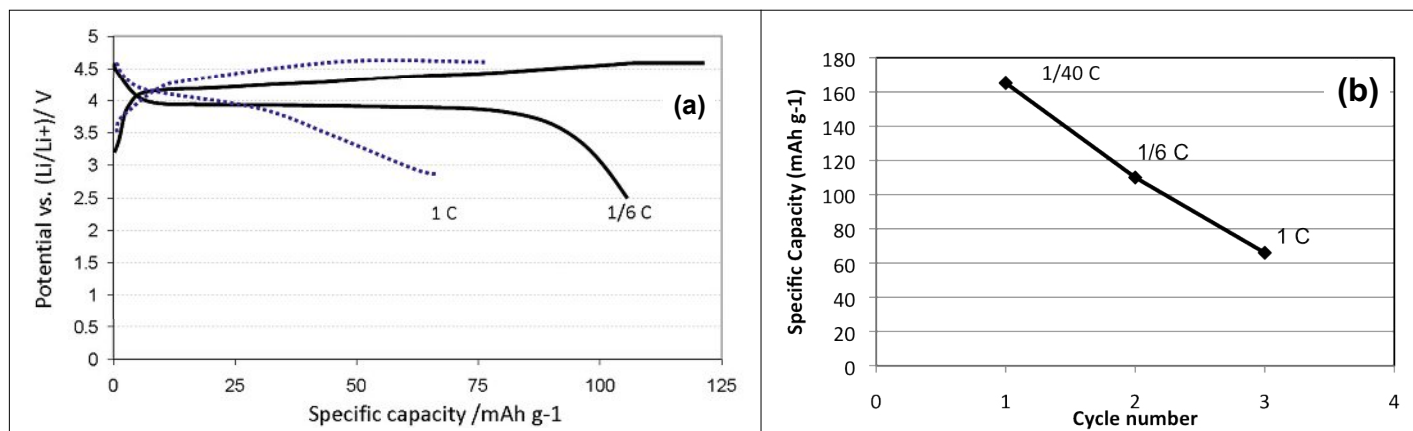


Fig. 3. a) The charge and discharge curves of 10 wt% carbon added nano- LiMnPO_4 cathode. b) The rate capability of the same cathode.

mogenous composite and hence to better electrochemical properties.

For the generation of the composite, SEM and TEM analyses surprisingly showed that the platelet-shaped graphite assembles homogeneously with micron-sized LiCoO_2 using the ball-milling method. Furthermore, a 5-min ball-milling process provided better results and smaller particles than a 30-min or 60-min ball milling or no ball-milling at all. Graphite thus turned out to provide a superior quality of the composite cathode material with a still high specific surface area. It also gives better quality cyclic voltammograms (Fig. 4, top) and leads to higher specific capacities (Fig. 4, bottom) of the LiCoO_2 electrodes compared to nano-sized spherical carbon black.

The nano-sized carbon black on the other hand aggregates during the ball-milling process and forms isolated clusters for which the specific surface area is dramatically reduced. Furthermore, the thick coating of nano-carbon black on the LiCoO_2 particles renders the contact with the liquid electrolyte difficult. We further assume that a long ball-milling process leads to a heating of the material and hence formation of aggregates and particle/crystallite growth. Our two studies thus lead to the conclusion that a 5-min ball milling process of micron-scale LiCoO_2 with graphitic carbon provides the best composite cathodes. We are currently studying these effects also for our above-mentioned nanoscale LiCoO_2 and LiMnPO_4 in order to

determine the best conditions for high-quality electrodes.

Conclusions, Ongoing Work, and Outlook

We are now able to provide nano-scale LiCoO_2 and LiMnPO_4 in a multi-gram scale to partners who wish to test battery packs. Furthermore, the Fromm group has considerable expertise in the encapsulation of nanoparticles into porous inorganic shells.^[18–21] We have thus started to investigate the use of encapsulated Sn-nanoparticles as anode material for Li-ion batteries. Within the framework of the NRP-70 of the Swiss National Science Foundation, research on the next generation batteries, such as Li–air and Li–water are ongoing in order to provide new membranes in collaboration with the group of H.G. Park at ETHZ, as well as electrolytes, which can also serve in classical Li-ion batteries.

Within the framework of the SCCER ‘Heat and Electricity Storage’, we contribute to the work package WP1 by providing our nanoscale cathode materials, assembling half cells against Li-metal and full cells against anode material provided by e.g. the group of M. Kovalenko from ETHZ. *In situ* and *in operando* studies of our composite materials are ongoing in collaboration with the group of P. Novak and C. Villeville at the PSI. The Fromm group also collaborates with the Peter

Broekmann group of WP4 of the SCCER, and we have worked here on the synthesis and electrochemical analysis of pseudo-capacitor multilayer thin films.^[22]

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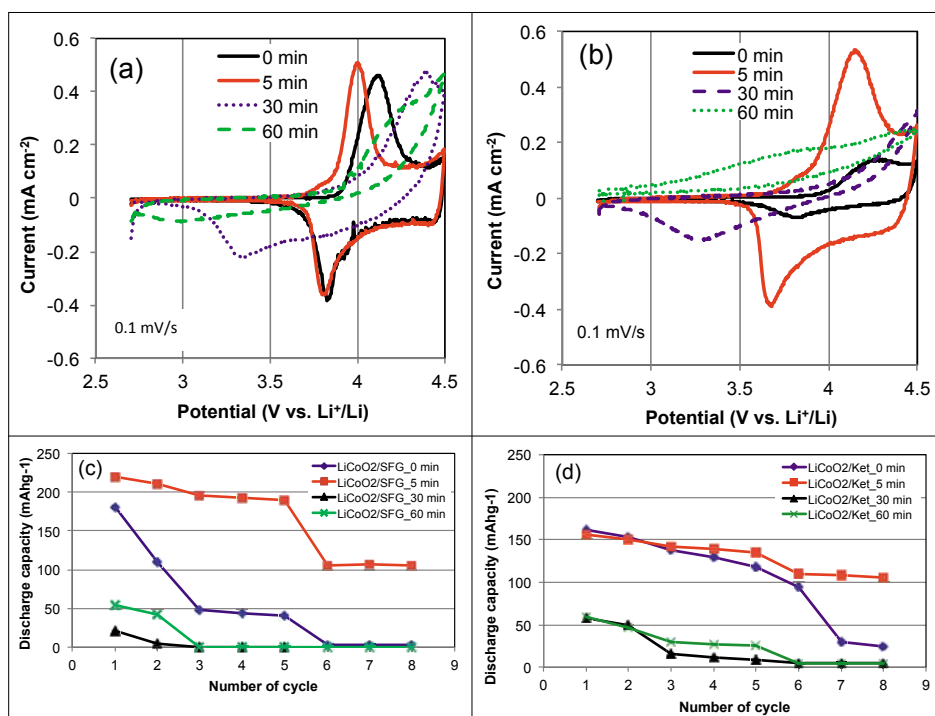


Fig. 4. Top: Cyclic voltammograms of a) SFG/ LiCoO_2 and b) Ket/ LiCoO_2 composite electrodes. The composites were prepared by ball milling for various milling time.^[17] Bottom: Specific capacities of LiCoO_2 electrodes containing the composites with either (c) SFG or (d) Ket by various ball milling times.^[17] Reprinted from ref. [17] with permission from Elsevier.

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