

## Electrochemical performance of granulated titania nanoparticles

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### Abstract

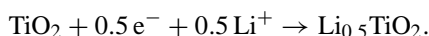
The electrochemical performance of Li-ion insertion into electrodes made of various sizes of anatase titania nanoparticles embedded in larger granulated entities (1–10 μm) is investigated. The granules are formed by spray drying of a suspension containing titania nanoparticles made by hydrolyzing titanium tetraisopropoxide (TTIP). Depending on the three process steps, i.e. hydrolysis–condensation, hydrothermal processing and spray drying, different properties for the electrode made from these granules can be achieved in terms of phase composition, specific surface area (SSA) and specific charge capacity. Hydrothermally processed (HP) particles are more resistant to calcination than sol–gel precipitated (SGP) ones and have a higher SSA which leads to a better performance with respect to specific charge capacity. Electrodes made from granulated nanoparticles have superior specific charge capacity than from non-granulated ones as the former have more inter-particle contacts.

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**Keywords:** Sol–gel; Nanocrystalline titania; Electrochemical lithium insertion; Granulation; Structured electrode

### 1. Introduction

Titania (TiO<sub>2</sub>) electrodes are used in solar cells [1], electrochromic devices [2] and lithium-ion batteries [3]. By replacing the carbon at the negative electrode with titanium based oxide materials working at more than 1 V, the thermodynamic stability of the electrolyte is guaranteed, which saves 15% energy loss during the first cycles and is expected to improve safety. In order to maintain the cell energy, positive electrode materials with working voltage 1 V higher than LiCoO<sub>2</sub> can be used. Anatase TiO<sub>2</sub> is a prospective interesting negative electrode material for 2 V lithium ion batteries due to its convenient formal potential around 1.8 V (versus Li/Li<sup>+</sup>). Although there are eight polymorphs of TiO<sub>2</sub> [4] only the anatase and rutile phase are examined more closely for their electrochemical performance. Rutile shows only a weak intercalation of Li-ions into the TiO<sub>2</sub> crystal at room temperature [5]. Anatase phase accommodates the charged Li-ions by a first-order phase transformation [6]:



Many authors report the existence of the orthorhombic Li<sub>0.5</sub>TiO<sub>2</sub> phase [7]. Others report maximum electrochemical insertion for Li<sub>x</sub>TiO<sub>2</sub> with  $x = 0.7$ –1 (e.g. [8]). The ability of the anatase phase to intercalate a large number of Li-ions together with relatively fast kinetics makes it a good candidate for an application in high density lithium-ion batteries [6].

Especially the morphology plays an important role in the kinetics of the charge/discharge process. Several authors report the influence of organised or ordered mesoporous films [7] on the electrochemical performance. Other works mention the importance of the dimension of the crystals in porous electrodes for the intercalation kinetics [9]. Supposing that the intercalation time  $t$  can be estimated based on the effective diffusion  $D$  we get  $t = R^2/\pi D$  [9]. The square root dependence of the intercalation time from the radius  $R$  of the crystals makes the use of nanostructured mesoporous electrodes for Li-ion batteries evident.

This is a new approach to organise the electrode in nanoparticles embedded in larger granulated entities in order to increase their interconnectivity. The influence of titania phase, specific surface area (SSA) and granule morphology on the electrochemical behaviour of the powder is examined. The nanoparticles are derived from a sol–gel

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process and granulated in a spray drier. The particle size is influenced by hydrothermal treatment and calcination.

## 2. Experimental procedure

The sol–gel and spray drying processes for production of the colloid suspension and the packaged nanoparticles were described in an earlier paper [10] and are only summarized here. A titania suspension is synthesised by hydrolysis and condensation of titanium tetraisopropoxide (TTIP;  $\text{Ti}(\text{OC}_3\text{H}_7)_4$  97% Aldrich) in ethanol and water as solvent liquids. In order to form granules out of the sol–gel precipitate (SGP) the suspension is fed into a co-current spray drier. After spray drying, the powders are annealed at 300, 450 and 600 °C, respectively, for 2 h in an oven at ambient pressure. Hydrothermally processed (HP) granules are produced by aging the SGP slurry in an autoclave for 12 h at 80 °C and spray drying the resulting suspension [11]. As well the HP granules are annealed at 300, 450 and 600 °C.

The specific surface area of the powder is obtained by nitrogen gas adsorption/desorption at 77 K by the multipoint Brunauer–Emmett–Teller (BET) method. X-ray diffraction

(XRD, Model D5000, Siemens) was used to evaluate the crystallite structure of the powder samples with Ni-filtered  $\text{Cu K}\alpha$  radiation. The software tool TOPAS was used to evaluate crystallite sizes and crystallite fractions. Scanning electron microscopy is used to get information about the granule morphology (Hitachi, H-900).

The electrochemical analysis is done in a cell with one lithium electrode. For electrochemical measurements, the synthesized samples are mixed with 10% carbon black and 5% PVDF are coated on Al foil using the doctor blade technique. The foils were pressed at 2000  $\text{kg}/\text{cm}^2$  and dried at 150 °C for 24 h under vacuum. The electrochemical test is performed versus Li-metal in a two electrode cell using EC/DEC 1 M  $\text{LiPF}_6$  electrolyte in a Arbin battery test system.

## 3. Results

Fig. 1 shows SEM micrographs of HP (a and b) and SGP (c and d) granules after spray drying. The SGP granules consist of hard agglomerates of nanoparticles which can be seen in Fig. 1d. This kind of granule substructure cannot be

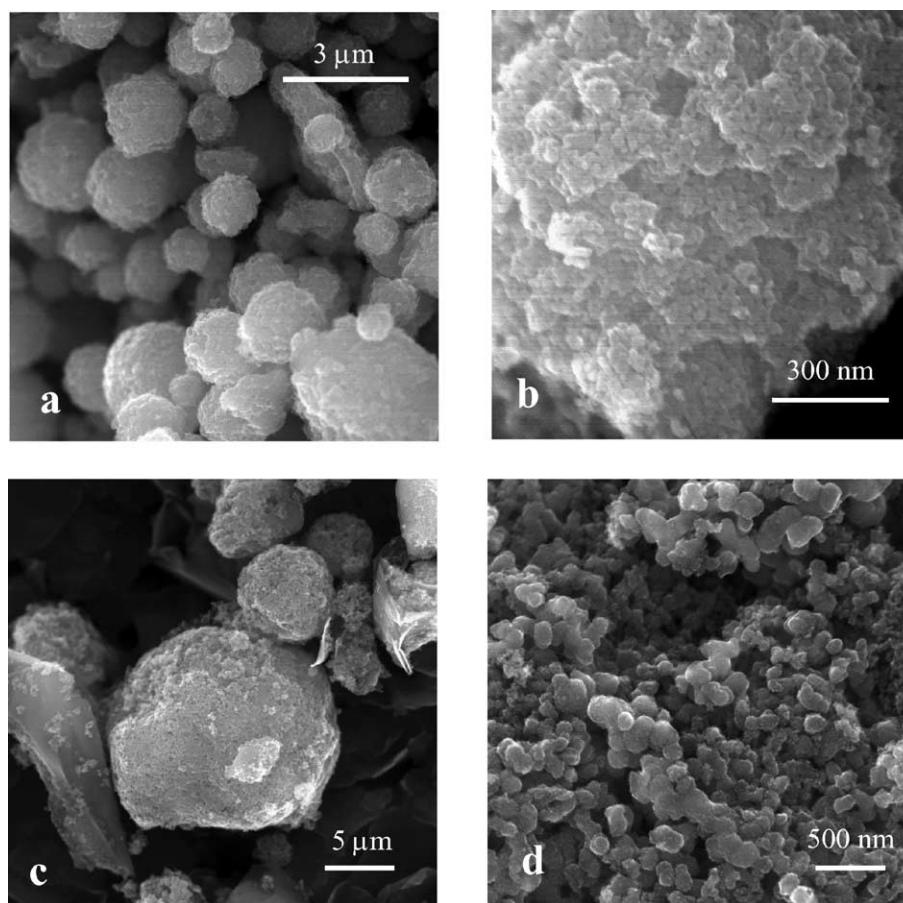


Fig. 1. SEM micrographs of spray-dried granules from (a and b) hydrothermally processed (HP) and (c and d) sol–gel precipitated (SGP) granules. The SGP granules consist of numerous hard aggregates whereas the substructure of HP granules appears less compact.

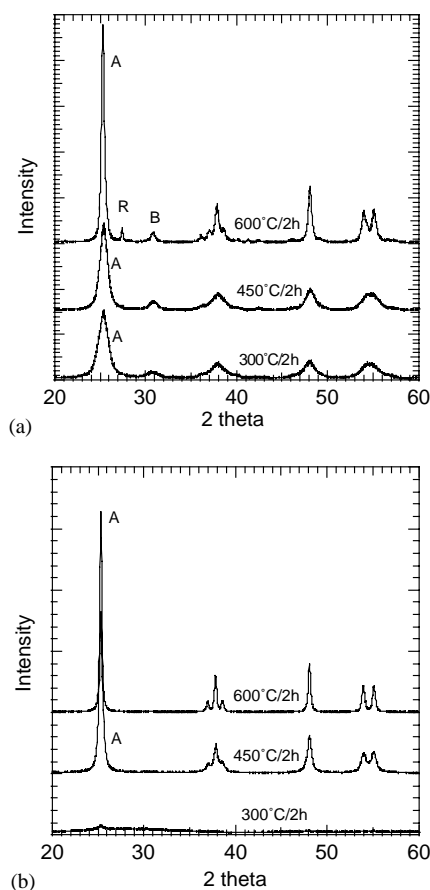


Fig. 2. XRD spectra at different calcination temperatures of the granulated HP (a) and SGP powder (b) (A stands for anatase phase, R for rutile and B for brookite).

seen for the HP granules. The granule size distribution is between 1 and 10  $\mu\text{m}$  consistent with Kim et al. [12].

Fig. 2 shows the XRD patterns of HP (a) and SGP (b) granules at different calcination temperatures. Most samples show clearly the anatase peak at  $2\theta = 25.3^\circ$ . Only the sample of SGP granules at 300 °C calcination temperature appears to be largely amorphous but it is transformed to anatase at higher calcination temperatures [13]. The HP granules which were calcined at 300 °C show already a distinct anatase peak. At 600 °C the HP granules contain small fractions of rutile and brookite phase. Fig. 3a illustrates the dependence of the specific surface area with respect to calcination temperature of SGP (full symbols) and HP (open symbols) titania granules. Increasing the calcination temperature is decreasing the SSA for all investigated powders. The SSA results are within about 10% for the SGP [12] and HP [11] granules. For calcination temperatures above 300 °C the SGP powders show a distinctly smaller SSA and bigger particle size than the HP granules. This indicates the higher thermal stability of HP granules. The anatase crystallite size is comparable to the BET primary particle size of the HP granules for calcination temperatures at 300, 450 and 600 °C (Fig. 3b) and in agreement with Kim et al. [11]. The fraction

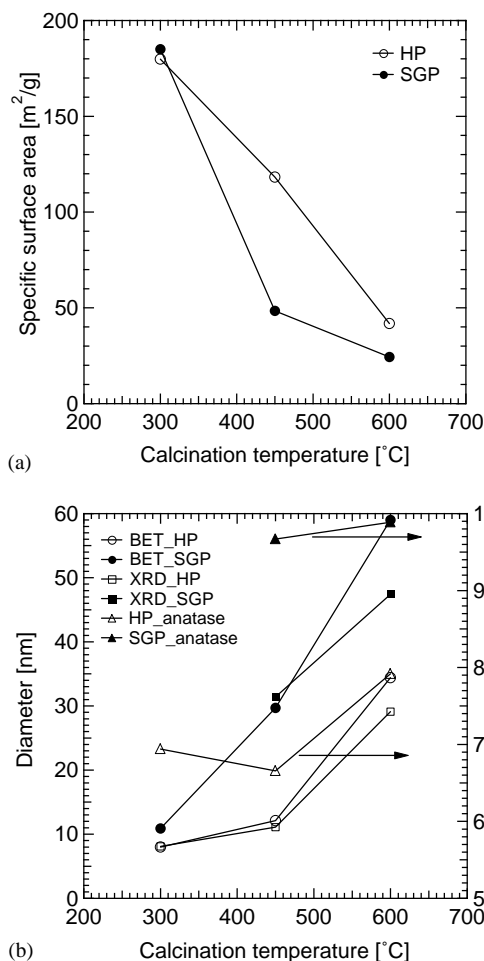


Fig. 3. (a) Specific surface area (SSA) and (b) BET diameter (circles), anatase size (squares) and fraction (triangles) of SGP (filled symbols) and HP (open symbols) granules after calcination at 300, 450 and 600 °C for 2 h. There is no value for the crystallite size of the SGP granule at 300 °C because it is mostly amorphous.

of anatase phase is around 70% for all three calcinations temperatures. The other 30% are brookite phase. The brookite crystals have about the same size (7.8, 10.0 and 20.2 nm at 300, 450 and 600 °C, respectively) as the anatase crystallites. This suggests that the primary particles are single crystals, either anatase or brookite. The sample at 600 °C also shows a small rutile peak, 3.7% by weight. There is no value given for the anatase crystallite size of the SGP granules at 300 °C where titania is still largely amorphous. At 450 and 600 °C the anatase phase dominates with 95% by weight. Also here the crystallite size is close to the primary particle size calculated from BET indicating single crystallites.

Fig. 4a and b show the specific charge capacity of granulated hydrothermally processed and SGP titania electrodes at different C-rates. 1C corresponds to complete charging of the electrode within 1 h. The specific capacity shows good values for charging rates up to C for all electrodes except the SGP which was calcined at 300 °C. As a large fraction of this powder is amorphous, it is not active for Li-ion interca-

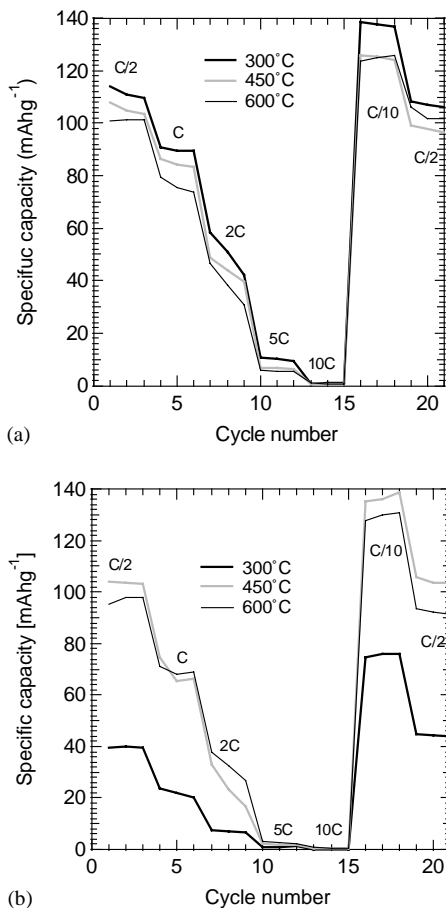


Fig. 4. Specific charge capacity at different calcination temperatures for 2 h of the electrode made from granulated HP (a) and SGP (b) powders.

lation and therefore lost for charging. At low charging rates (C/10—charging of electrode in 10 h) the specific capacity can be up to 140 mAh/g (HP granules at 300 °C calcination temperature) which corresponds to  $x = 0.42$  being close to the value of a completely filled octahedral lattice where  $x = 0.5$ . All powders show good cycling stability. After 20 cycles, the capacity at C/2 (corresponding to charging in 2 h) is still more than 90% of the original specific capacity. Higher charge/discharge rates lead to lower specific capacities. The HP granules show in general a better performance compared to the SGP powder at the same charging rate. Only at very low charging rates (C/10) the specific capacity is comparable. The primary particle size of HP primary particles is smaller than the one of SGP primary particles, so a faster Li-exchange is possible between titania lattice and surrounding electrolyte. The best performance is given by the HP granules calcined at 300 °C which also have the smallest primary particle size of all powders ( $d_{\text{BET}} = 8$  nm). Increasing the particle size by calcination lowers the specific charge capacity. Exnar et al. [9] found that the optimal anatase particle size in practical  $\text{TiO}_2/\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  button cells is about 10–15 nm. Kavan et al. [14] investigated Li insertion into  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  spinel structures and observed a significant decrease of charge capacity with decreasing SSA

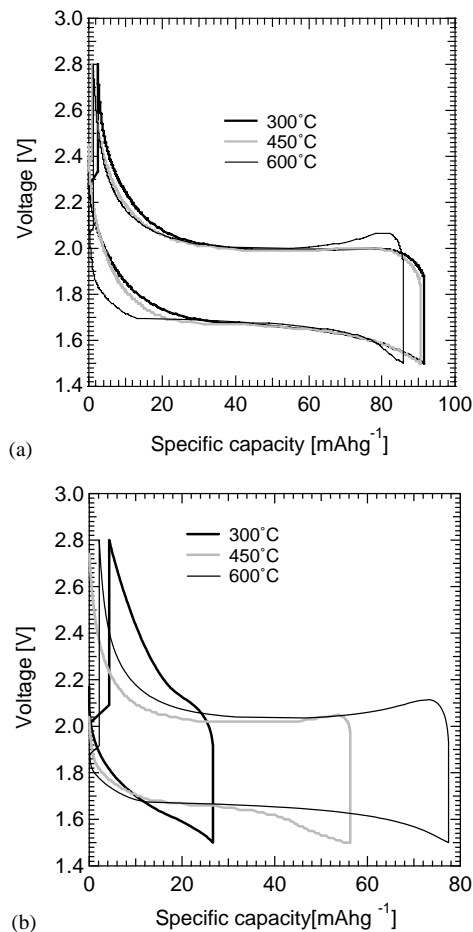


Fig. 5. Galvanostatic chronopotentiometry at different calcination temperatures for 2 h of the granulated HP (a) and SGP (b) electrode.

(meaning increasing particle size). This experiment was performed on thin film electrodes in absence of any supporting additives.

Fig. 5a and b show the galvanostatic charge/discharge characteristics of the HP and SGP titania electrodes against lithium metal at 1C rate charge and discharge. The examples were chosen to demonstrate behaviour of electrode with thickness and composition usual in conventional electrodes. Hence, the polarization of electrodes is relatively high and the maximum reversible capacity is in expected range (ca. 90 mAh/g) as shown in Fig. 4. Despite of high polarization of electrodes due to high ohmic losses can we observe significant difference between HP and SGP electrode.

The performance of an ordered electrode consisting of HP granules concerning the specific capacity is compared to an unstructured (ungranulated) nanoparticle electrode in Fig. 6. The comparison of SSA of granulated and ungranulated powders show a difference in the range of 10% or less. Fig. 6a and b show the specific capacity of granulated and ungranulated electrode for calcination temperature 300 °C (a) and 450 °C (b) at different charging and discharging rates. The specific capacity is about 20% higher for the granulated nanoparticle electrode at charging rates higher than C for

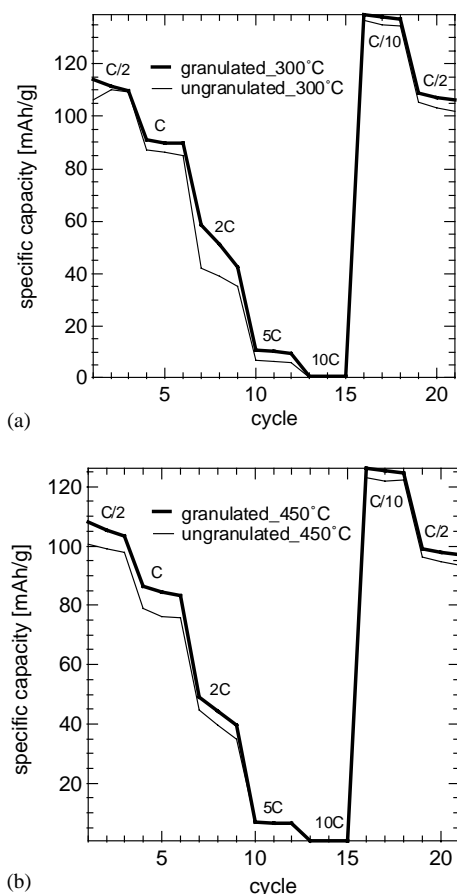


Fig. 6. Specific charge capacity at different charging rates of granulated and ungranulated HP powders at calcination temperatures 300 °C (a) and 450 °C (b).

both calcination temperatures. At low charging rate (C/10) the specific capacity has the same value for granulated and ungranulated electrodes. This effect cannot be attributed to the negligible difference in SSA. Presumably it is the increased number of contacts in the granules which facilitates current flow resulting in higher charging capacity. Again at low charging rates the electrode structure has less influence on the intercalation kinetics.

#### 4. Conclusions

The electrochemical performance of nanosized, granulated anatase titania was investigated. The influence of the

primary particle size on the ability of the titania electrode to intercalate Li-ions was clearly shown. With decreasing size of the primary particles down to 8 nm an increase in charge capacity at different charging rate could be found. The maximum charge capacity is 140 mAh/g (at C/10 charging rate) which is close to the value in the orthorhombic structure [7]. Ordering the primary nanoparticles to larger entities by granulation enhanced the charge capacity of the electrodes as a higher number of bonds or contacts were formed between the nanoparticles during spray drying.

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