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The effect of ceramic synthesis conditions on the electrochemical properties of $\text{Li}_2\text{Ti}_3\text{O}_7$

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ABSTRACT. Different ceramic synthesis conditions of ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ have been investigated in order to determine the influence on the electrochemical performances as the negative electrode of lithium ion batteries. Lithium source, thermal pretreatment, synthesis temperature and time of reactions were the analyzed conditions. A convenient and cheap reagent like Li_2CO_3 treated with TiO_2 at high temperature (1250 °C) for very short time (2 h) provides a reliable active material. When tested versus lithium, the initial specific capacity (150 mAh g^{-1}) is lower than that of ceramic samples prepared at lower temperature or for longer treatment times (ca. 170 mAh g^{-1}). The lower initial capacity is attributed to the large particle size obtained at high temperature. However, advantageously the capacity retention of the former is superior. Thus, 115 mAh g^{-1} at C/20 rate are fairly kept (77% retention) after 100 cycles. The better cyclability of samples prepared at high temperature (with large particle size) is likely due to lower surface reactivity that compensates the lower initial discharge capacity when cycling. A compromise between high initial capacity and capacity retention must be reached when using $\text{Li}_2\text{Ti}_3\text{O}_7$ as a battery electrode. The good behavior of the optimized material is shown by testing it against commercial LiCoO_2 as the positive electrode. The high capacity (ca. 135 mAh g^{-1}) and outstanding cyclability observed proves that optimized ramsdellite may be effectively used as a long life negative electrode material.

Introduction

Titanium oxides and lithium titanates have been widely investigated as candidates to negative electrode materials for lithium ion batteries due to the good electrochemical performances regarding lithium intercalation [1-6]. These oxides contain Ti^{4+} which is partially reduced to Ti^{3+} upon lithium intercalation at ca. 1.5 V. This voltage is higher than in other negative electrode materials, but still low enough to be considered interesting for such applications; the decrease of energy, owing to the smaller potential difference between a given positive electrode and titanium oxides, is compensated by additional safety compared to other lithium-ion battery technologies at present. Replacing graphite by titanates eliminates the risks of metallic lithium dendrite formation observed during overcharge of graphite-based lithium-ion batteries [4,7,8], because the intercalation potential of titanates is far from 0 V vs Li^+/Li . Additionally, operative voltage of titanates lies within the stability window of common electrolytes, preventing electrolyte decomposition and gas emission involved. Thus, safety is perhaps one of the most determining issues to enable a wider commercialization as for instance in modern airplanes, in which hydraulic systems have been replaced by electric systems, in electrical vehicles or in small electronic devices for final consumers. The high abundance of titanium is a further important advantage when availability assessments are considered and therefore, no likely bottle-neck can be foreseen in the future. Moreover, in terms of durability many of the titanium oxides and titanates are denominated zero-strain materials, because they exhibit very low structural stress (i.e. small volume change) upon successive intercalation-deintercalation reactions, ensuring an optimum cycling behavior ideal for long-life rechargeable batteries [3]. Contrarily, the volume expansion and shrinkage occurring upon intercalation in the case of graphite and other carbonaceous anodes results in cracking and loss of electrical contact [9,10]. Thus, titanium

oxides and lithium titanates provide a wide selection of safe and long life anodes for lithium-ion batteries. In fact, the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO hereafter) [3] has been already commercialized as competitive negative electrode for lithium-ion technology.

The diversity of structures and polymorphs exhibited by titanium oxides and titanates increases their possibilities as negative electrodes [11]. All TiO_2 polymorphs are known to intercalate lithium at relatively low potential at room temperature although their electrochemical performances differ considerably. Rutile inserts a small amount (0.13 Li per formula unit -/f.u., hereafter- [12]), whereas anatase and $\text{TiO}_2(\text{B})$ reach a considerable amount (0.5 Li per formula unit, Li/f.u. hereafter) providing an interesting specific capacity (168 mAh g^{-1}) [13,14]. Moreover, the hollandite and ramsdellite polymorphs of TiO_2 provide higher quantity of intercalated lithium (ca. 0.8 Li/f.u.) and hence larger specific capacity (ca. 280 mAh g^{-1}) [15-17]. Interestingly, binary titanium oxide polymorphs obtained with controlled morphology are being considered as alternative to LTO in view of their improved performances [2,18]. Unfortunately, in most cases, complicated or expensive methods based on titanium alkoxides [19-21], titanium halides [22] or even metallic titanium [23] as reagents are used that will likely inhibit its use in cost-effective industrial fabrication processes and batteries. This is not the case for $\text{TiO}_2(\text{B})$ that can be easily synthesized as a needle-like powder from a Li/H^+ ion exchange of precursor $\text{K}_2\text{Ti}_4\text{O}_9$ followed by dehydration [24-26]; reversible capacities in the $200 - 250 \text{ mAh g}^{-1}$ range at 1.6 V have been found for this material which make it a promising candidate as negative electrode [27]. Even more, higher capacities has been reached by proper optimization of synthesis, composite preparation, etc. [28].

Among further titanates such as $\text{Li}_2\text{Ti}_3\text{O}_7$ [29], $\text{Li}_2\text{Ti}_6\text{O}_{13}$ [30] and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ [31] $\text{Li}_2\text{Ti}_3\text{O}_7$ ramsdellite has received much attention in view of the large capacity of 175 mAh g^{-1} at C/20

rate. Furthermore, it also exhibits one of the highest capacities under equilibrium ever reported for 1.5 V negative electrode materials (ca. 200 mAh g⁻¹) due to the intercalation of almost 2 Li/f.u. [29]. Whether this capacity can be effectively achieved or not under practical constant current discharge conditions used in electrochemical cells is not known and it is one of the objectives of this work. In this connection the need of full-cell studies on negatives electrode beyond carbonaceous anodes for practical Li-ion batteries was evidenced in a recent review [6]. Lithium intercalation in Li₂Ti₃O₇ ramsdellite proceeds with very good reversibility, being related to little volume change during the intercalation reaction [32]. A further advantage is that Li₂Ti₃O₇ can be prepared by a cost-effective ceramic procedure. Most of reported methods comprise a two-step reaction with an initial pretreatment of the reactant mixture consisting of Li₂CO₃ and TiO₂ (anatase or rutile) at 800-900 °C followed by further heating at higher temperature [33]. Different temperature treatments ranging from 1050 to 1200 °C for several days are reported [34-36]. However, this persistent synthesis procedure tends to produce loss of lithium at high temperature and the subsequent formation of secondary rutile phase. Therefore use of excess lithium has been reported to obtain a single phase product [37-40]. Synthetic approaches using other methods such as sol-gel or spray pyrolysis are also possible yielding also very good results, though more expensive reagents like Ti(OCH(CH₃)₂)₄ are required [41],[42].

In the present paper we have investigated the effect of different experimental ceramic synthesis conditions on the electrochemical properties of Li₂Ti₃O₇. The influence of lithium source, thermal pretreatment of the starting mixture of reactants, final heating temperature and heating time are the variables that were explored in this work to decrease fabrication costs and facilitate its later commercialization as anode material for Li-ion batteries. All products were tested

electrochemically and the performances of an optimized $\text{Li}_2\text{Ti}_3\text{O}_7$ as the anode in a lithium-ion cell bearing LiCoO_2 as the cathode.

Experimental

Synthesis of materials was carried out by a ceramic procedure using different reagents and reaction steps. Following the most reported method, Li_2CO_3 was used as lithium source. However, we have also investigated $\text{LiOH}\cdot\text{H}_2\text{O}$ as an alternative reagent. Either Li_2CO_3 (99% Aldrich) or $\text{LiOH}\cdot\text{H}_2\text{O}$ (98% Aldrich) were mixed with TiO_2 (anatase) in the stoichiometric ratio (1:3 and 2:3, respectively) and pelletized. In some cases these initial mixtures were firstly subjected to a thermal pretreatment at 800 or 900 °C to decompose the lithium containing reagent. After grinding and new pelletizing the mixtures were heated at two different temperatures, 1100 and 1250 °C, and quenched at room temperature afterward. In some other cases thermal pretreatment was skipped to check whether a more straightforward synthesis is possible and to determine its influence on the electrochemical behavior. Final heating time was 2 h independent of the thermal procedure selected.

Purity of the samples was determined by powder X-ray diffraction (XRD) on a Bruker D8 high-resolution diffractometer using monochromatic $\text{CuK}\alpha_1$ radiation ($\lambda = 0.15406$ nm) obtained with a germanium primary monochromator, and equipped with a solid-state rapid LynxEye detector.

High resolution neutron diffraction (ND) data were collected at the neutron source FRM II - MLZ (Garching, Germany) on the high resolution SPODI powder diffractometer. A Ge(551) monochromator was used to select a wavelength of $\lambda = 1.54831$ Å. A cylindrical vanadium can of 8 mm diameter was filled with 4 g of $\text{Li}_2\text{Ti}_3\text{O}_7$ powder sample. ND patterns were collected for 4 h over the 5-160° 2θ range with a step size of 0.05 ° at 298 K.

The diffraction patterns were analyzed using the Rietveld method [43] as implemented in the Fullprof program [44]. A pseudo-Voigt function was chosen to reproduce the line-shape of diffraction peaks. The coherent neutron scattering lengths used were: Li: -1.90 fm; Ti: -3.30 fm and O: $+5.80$ fm [45]. Structural models were drawn using the Vesta software (version 3.0.2) [46].

On the other hand, the morphology of crystallites obtained was determined by Scanning Electron Microscopy (SEM) with a FEI XL30®.

Electrochemical lithium insertion/de-insertion experiments into/from the ramsdellite were performed using lithium CR2032 cells with the following general configuration:

(-) Li // LiPF₆ in EC+DMC // Li₂Ti₃O₇+C+PVDF (+)

with abbreviations EC, DMC and PVDF for ethylene carbonate, dimethyl carbonate and Polyvinylidene Fluoride, respectively.

The composite positive electrode was made by mixing 85% Li₂Ti₃O₇ (active material), 10% Super C65 conductive carbon black (Imerys, Timcal) to enhance the electronic conductivity of composite and 5% PVDF as binder (Kynarflex of Elf Atochem) in weight percentage. After grinding the mixture was pressed to 8 mm diameter pellets having ca. 20 mg active material. A lithium metal disk (5 mm diameter) was used as the negative electrode. A solution of 1 M LiPF₆ in a 50:50 by volume mixture of EC and DMC was used as the electrolyte (Selectylite BASF). All cells were assembled in an argon-filled glove box and tested by using a multichannel system VMP3 (BioLogic). Galvanostatic experiments were carried out under different C/n rates with n ranged from 0.1 to 20, where n stands for the time needed (in hours) to insert 1 lithium per formula unit of titanate. Experiments close to equilibrium were carried out using the galvanostatic intermittent titration technique, GITT, with current density pulses of 0.1 mA cm^{-2}

applied for 30 minutes; after each pulse the system was allowed to relax for 12 h in order to reach equilibrium.

Lithium-ion cells were assembled using $\text{Li}_2\text{Ti}_3\text{O}_7$ as the negative electrode and LiCoO_2 (99.8%, Aldrich) as the positive one. LiCoO_2 -based electrodes were prepared by mixing it with Super C65 carbon black and PDVF Kynarfex (85:10:5) following the same procedure above detailed for $\text{Li}_2\text{Ti}_3\text{O}_7$ electrodes. Based on the results obtained in half-cells at C/55 the balanced mass ratio was determined to be $m^+/m^- = 1.1$ by mole. This mass ratio was used for all cells cycled in the 1.0 V to 3.0 V voltage range.

Results and discussion

The effect that the pretreatment temperature has on phase purity can be clearly observed from the XRD patterns of two $\text{Li}_2\text{Ti}_3\text{O}_7$ ramsdellites (1100 °C as synthesis temperature) with previous treatments at 800°C and 900 °C (Figure 1a and 1b, respectively). Pure ramsdellite samples are obtained for low temperature pretreatment (800 °C), whereas pretreatment at **higher** 900 °C produces a minor secondary phase identified as TiO_2 rutile, regardless the origin of the lithium source ($\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_2CO_3). Partial lithium loss occurring at 900 °C may be the origin of the residual rutile phase. The amount of rutile in mixtures subjected to pretreatment at 900 °C did not vary significantly even after prolonged heating at higher temperatures. Regarding the effect of time of reaction, pure ramsdellite can be obtained using short reaction times of only 8 h or even 2 h. On the other hand prolonged heating of reaction mixtures for 24 h resulted in the appearance of rutile as secondary phase even using a lower synthesis temperature of 1100 °C, which is again very likely due to partial lithia loss. The other two variables studied were the influence of lithium source ($\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_2CO_3) and the final synthesis temperature (1100 or 1250 °C). Neither of them seems to be decisive in the phase purity of the final $\text{Li}_2\text{Ti}_3\text{O}_7$ product obtained as there is no

significant difference in their XRD patterns. Thus, though widely used conditions for ceramic synthesis of pure ramsdellite include the use of lithium excess [37-40] to compensate lithia loss we have found that this problem is avoided using short reaction times (2-8 h) while still pure product is obtained. Interestingly enough, we have found that the commonly used thermal pretreatment can be completely skipped enabling single-step synthesis of pure $\text{Li}_2\text{Ti}_3\text{O}_7$, which contributes further to production costs optimization.

We have characterized electrochemically samples prepared by annealing Li_2CO_3 or $\text{LiOH}\cdot\text{H}_2\text{O}$ with TiO_2 at 1100 or 1250 °C for 2 h or 8 h. Temperature of the final heating and reaction time are variables that may have an influence on electrochemical properties due to both particle size and cation distribution differences. In fact, the controversy between several authors [35,47-50] on the different lithium ion distribution between the channel and the framework sites of the ramsdellite crystal structure may be due to different thermal treatment of the different samples. It is worth mentioning that the synthesis at elevated temperature may trigger lithia loss or at least have an effect changing lithium site distribution. This could enable changes in the electrochemical lithium insertion behavior owing to altered lithium site occupancy in the ramsdellite structure (channel and framework sites).

The structure formula of $\text{Li}_2\text{Ti}_3\text{O}_7$ is generally expressed with models taking into account that in this titanate containing Ti^{4+} the Ti/O ratio is smaller than $\frac{1}{2}$. Thus a distribution of lithium ion and vacancies between channel and framework sites has to be considered. When referred to the formula unit, $\text{A}_4\text{B}_4\text{O}_8$, the two limit models are : a) the more widely used formula $[\text{Li}_{1.72}\square_{2.28}][(\text{Ti}_{3.43}\text{Li}_{0.57})\text{O}_8]$, where the non-channel octahedra are filled with statistically distributed Li and Ti and partially filled channel sites with Li, or alternatively b) $(\text{Li}_{2.29}\square_{1.71})(\text{Ti}_{3.43}\square_{0.57}\text{O}_8)$ with all the Li in the channel and defective $(\text{Ti},\square)\text{O}_6$ octahedra. ^7Li MAS NMR spectra recorded (not

shown) reveals only one sharp signal for all the $\text{Li}_2\text{Ti}_3\text{O}_7$ samples analyzed instead of two expected signals if lithium atoms were in both tetrahedral (channel) and octahedral (framework) environments. This finding is in agreement with earlier reports [37,47]. Therefore we decided in favor of the second model to address the structural refinement of neutron powder diffraction data, which were performed on samples synthesized using LiOH and Li_2CO_3 as lithium source, heated at 1100 and 1250 °C and subjected to heating periods of 2 h and 8 h. As a main conclusion no noticeable changes are observed in the powder neutron diffraction profile of all the samples studied. The experimental and calculated powder ND pattern of a typical sample synthesized at 1100 °C for 8 h is given in Figure 2. Rietveld refinement converged to the following conventional reliability parameters $R_{\text{wp}} = 3.66\%$, $R_{\text{Bragg}} = 3.63\%$ and $\chi^2 = 4.49$. The main structural parameters of the refinement are summarized in Table 1. Refined Li site occupancies of all samples agreed to within error. The structural results allowed us to rule out the possibility of lithia loss or altered Li site distributions while the structural homogeneity of all the samples is confirmed.

Figure 3a shows the cycling behavior of different $\text{Li}_2\text{Ti}_3\text{O}_7$ ramsdellite samples prepared in a single step under different conditions. For a better comparison Fig. 3b shows the first discharge capacity together with the reversible capacities achieved after 5 and 40 cycles for five samples obtained under different experimental conditions (labeled A-E). A comparison of samples B and C (prepared using different lithium sources, identical final synthesis temperature of 1100 °C and heating time of 8 h) shows that higher initial capacities are obtained for sample B (lithium source was Li_2CO_3). In addition capacity retention is better when the carbonate precursor is used instead of hydroxide as lithium source. Fig. 3b also indicates that shorter heating times (2 h) slightly

improve the initial capacity as well as capacity retention, though not significantly (compare for example (C and D). However, the most important difference is to be noted related to the synthesis temperature. For a $\text{Li}_2\text{Ti}_3\text{O}_7$ sample synthesized at ~~higher~~ 1250 °C (sample E) the initial capacity largely decreases (from 175 to 150 mAh g^{-1}). However capacity retention is significantly better than in samples prepared at 1100 °C (Fig. 3b), and a capacity of 120 mAh g^{-1} are kept at a C/20 current rate after 75 cycles (see Fig 3a). The differences in initial capacities are not related to structural changes that might have an effect on the amount of insertable lithium; thermal treatment of compounds at 1100 or 1250 °C did not produce noticeable structural differences, as deduced from neutron diffraction data analysis. Accordingly, these samples intercalate the expected amount of 2 Li/f.u. when analyzed by GITT (see Fig. 4). The powders used for electrode fabrication of these two samples were investigated by SEM to get to the bottom of such differences. According to SEM micrographs shown in Fig. 5a and Fig. 5b morphology and particle size of $\text{Li}_2\text{Ti}_3\text{O}_7$ ramsdellite obtained at 1100 °C with LiOH and Li_2CO_3 as the lithium source are very similar, which explains the just subtle differences found in the electrochemical behavior of both samples (those labeled as C: $\text{Li}_2\text{CO}_3/1100\text{ °C}/8\text{h}$ and B: $\text{LiOH}\cdot\text{H}_2\text{O}/1100\text{ °C}/8\text{h}$ in Fig. 3b).

Different heating temperatures, on the other hand, have significant influence on morphology of samples as revealed by SEM. The SEM images, recorded after manual grinding prior to electrode fabrication and depicted in Fig. 5b and 5c (recorded at the same magnification), correspond to powders prepared at 1250 °C and 1100 °C for 2h, respectively, with Li_2CO_3 as lithium source for both. SEM images show that morphology in the sample synthesized at 1100 °C is that typical of a product formed after decomposition and gas evolution without sintering phenomena of adjacent particles. Small particles of ca. 1-2 microns are agglomerated and holes

through which gas escaped are clearly seen. In the sample synthesized at 1250 °C temperature was high enough to develop growth of the grains and yields well defined polyhedral crystals in the 20-50 microns range. Similar results are found when using LiOH·H₂O as lithium source (not shown). Different morphology and grain size of ramsdellite particles, obtained under different synthesis temperature conditions, partially explain the influence on the electrochemical properties as shown in Fig. 3.

Attending to kinetic limitations it is expectable that the sample with the largest crystallite size would exhibit the lowest initial capacity under constant current as observed for the first two cycles; at the same time this sample with larger particle size exhibits the best capacity retention. This apparently contradictory behavior may be explained by a surface-related reactivity of electrode materials with the electrolyte. According to this a pronounced capacity loss can be expected for Li₂Ti₃O₇ with smaller particle size because of increased surface reactivity. To confirm this assumption a sample prepared from LiOH·H₂O at 1100 °C for 8 h was subjected to different milling times in order to reduce and optimize the particle size. It is seen that mild milling (max. 1 h) slightly reduces the average grain size and breaks initial particle agglomerates, ≈ 5 - 10 μm (see Figure 6a and 6b), leading to an increase of total capacity without further capacity retention effect (Fig. 7). Longer milling times (up to 4 h), by contrast, result in a substantial decrease of particle size, ≈ 1 - 5 μm (Fig. 6c). As a consequence the fast capacity fading, likely due to enhanced surface reactivity, translates into a detrimental effect on electrochemical performance (Fig. 7), despite the large increase of initial capacity. The material processed in this way is practically useless as anode material. Note that capacity of the sample milled for 4 h drops by more than 75% after 40 cycles (to 40 mAh g⁻¹) whereas the non-milled or 1 h-milled sample yields a capacity of ca. 120 mAh g⁻¹ after 40 cycles.

From these results we deduce that kinetics limitations of $\text{Li}_2\text{Ti}_3\text{O}_7$ cannot be alleviated just by reducing particle size due to increased surface reactivity with the electrolyte and loss of performance. Supporting our interpretation of capacity fading in connection to surface increase, interfacial reaction between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and alkyl carbonate solvents has been recently reported as being the origin of gassing and swelling of LTO batteries [51]. The destructive gas generation including H_2 , CO_2 , and CO has been signaled as major challenge for implementation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at large scale. This may be also the case of $\text{Li}_2\text{Ti}_3\text{O}_7$ ramsdellite for which further studies will be needed to suppress or at least to minimize this surface reaction.

From the data herein presented we conclude that an optimized $\text{Li}_2\text{Ti}_3\text{O}_7$ ramsdellite combining both relatively high capacity and cyclability can be obtained by using Li_2CO_3 and TiO_2 anatase as reagents, heated at $1250\text{ }^\circ\text{C}$ for 2 h and quenched to room temperature. The general discharge-charge behavior of the corresponding electrode is shown in Fig. 8a, where variation of voltage and specific capacity for the first 90 cycles are shown. The response of this ramsdellite electrode to different current rates (Fig. 8b) shows that acceptable capacities are retained up to a 0.5 C rate, while a 73% of capacity is developed at slower rate (0.05 C). Capacity drops very fast (1 C rate) in agreement with kinetic limitations expected at high rates due to the big particle size.

Nevertheless the electrode recovers pretty well the initial capacity under low current rate conditions. Being large crystal size morphology a main characteristic of this material, further optimization (carbon coating, particle surface passivation by means of non-active protective layer...) would be necessary for high power application, which is far from the objectives of this research.

As a proof of the optimized ramsdellite performances and its interest as negative electrode, a complete lithium-ion cell using LiCoO_2 as the positive electrode is shown in Fig. 9. The capacity

of the positive electrode was limited to 0.5 lithium ions to avoid the irreversible behavior to over-delithiation ($\approx 150 \text{ mAh g}^{-1}$) [52-55]. This cell provides an average output voltage of 2.5 V and keeps a capacity $> 120 \text{ mAh g}^{-1}$ after 90 cycles. The use of LiFePO_4 as the cathode may also be considered, though that cell would yield a lower output voltage of ca. 2.0 V.

Concluding Remarks

Although the ceramic synthesis method of $\text{Li}_2\text{Ti}_3\text{O}_7$ ramsdellite is well known, optimization process focused on industrial applications and characterization of full lithium-ion cells using $\text{Li}_2\text{Ti}_3\text{O}_7$ as the anode has not been done up to now. Different synthesis conditions can be used to obtain pure ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$. We have investigated several synthesis variables (thermal pretreatment, lithium sources, time of reactions and temperature). We have found that pretreatment can be skipped. A combination of high temperature and short reaction times (1250 °C for 2 h) followed by final quenching are found to be the most suitable synthesis conditions providing single phase ramsdellite, as short reaction times suppress lithia loss and consequently formation of secondary phases. Shortening of reaction time to two hours is a very convenient characteristic for industrial purposes and cheaper production.

Among all variables investigated in this work the synthesis temperature has a significant effect on the electrochemical properties of $\text{Li}_2\text{Ti}_3\text{O}_7$. Compounds prepared at high temperature (1250 °C) provide lower initial discharge capacities, but advantageously exhibit a better long life behavior. Samples synthesized at 1100 °C develop considerably higher initial capacities under same discharging conditions, but capacity of these drops below the one of samples prepared at higher temperature after 40 cycles. On the other hand, samples synthesized at 1100 and 1250 °C do not exhibit any significant structural difference, especially related to the lithium ion distribution among octahedral and tetrahedral sites. Temperature, by contrast, has a direct

influence on the particle size of materials. High temperature produces larger particles that very likely minimize surface reaction typical of titanates [51] and favor capacity retention; therefore, milling process must be limited to the rupture of the obtained agglomerates after synthesis and size homogenization in the 10 μm range. To sum up an optimized ramsdellite is produced in a single step at a temperature of 1250 °C for 2h. It exhibits an initial discharge capacity of 150 mAh g^{-1} and is able to sustain a reversible capacity of ca. 115 mAh g^{-1} (77 % retention) after 100 cycles at C/20. Although initial capacity is lower than that obtained for samples prepared at 1100 °C (ca. 170 mAh g^{-1}), capacity retention is better and will improve the durability of any related device. When optimized $\text{Li}_2\text{Ti}_3\text{O}_7$ as negative electrode is used in combination with LiCoO_2 as positive electrode in a lithium-ion cell, a capacity of 135 mAh g^{-1} is delivered with fairly good capacity retention after 90 cycles. We show that optimized ramsdellite may be a competitive anode material for so called LTO lithium-ion batteries. Nevertheless large crystallite size unfavorably affects electrochemical performance at high current rates. Decrease of particle size combined with passivation of these smaller particles to avoid possible reactivity with the electrolyte would be needed for high power application.

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Compliance with Ethical Standards:

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Figure Captions.

Fig. 1 Experimental (red points) and profile fitting (continuous black line) and their difference (blue line at the bottom) for a product obtained from LiOH·H₂O and TiO₂ (anatase) pre-treated at a) 900 °C and b) 800°C followed by reaction at 1100 ° C; the vertical bars (green) indicate the positions of the Bragg peaks. Secondary TiO₂ (rutile) Bragg peaks position are also indicated and the most intense peak of this common impurity is highlighted by a red circle

Fig. 2 Final observed (points) and calculated (solid line) powder neutron diffraction profile ($\lambda = 1.54831 \text{ \AA}$) for Li₂Ti₃O₇ with $a = 5.01634(4) \text{ \AA}$, $b = 9.54908(8) \text{ \AA}$ and $c = 2.94500(3) \text{ \AA}$, space group Pbnm (#62). Conventional agreement factors of the Rietveld refinement: $R_p = 2.94\%$, $R_{wp} = 3.66\%$; $R_{exp} = 1.73\%$; $R_{Bragg} = 3.63\%$; $\chi^2 = 4.49$

Fig. 3 a) Discharge capacity variation at C/20 rate with cycle number for selected Li₂Ti₃O₇ samples prepared in one step synthesis procedure as a function of the reagents (Li₂CO₃ or LiOH·H₂O), the temperature (1100 or 1250°C) and the heating time (2 or 8 h); b) bar graph showing a comparison of 1st discharge capacity an capacity after 4 and 40 cycles of different ramsdellites samples synthesized using indicated conditions.

Fig. 4 Voltage-composition curve recorded under equilibrium condition (GITT) on a selected Li₂Ti₃O₇ sample prepared in one step synthesis at 1250°C for 2 h

Fig. 5 Back-scattered SEM images of samples used for electrochemical investigations prepared at a) 1250 °C using LiOH·H₂O as lithium source; b) 1250°C and b) 1100 °C for 2h using Li₂CO₃ as lithium source.

Fig. 6 Back-scattered SEM images showing a) the starting size and morphology of the electrode powder prepared from $\text{LiOH}\cdot\text{H}_2\text{O}$ as lithium source at $1100\text{ }^\circ\text{C}/8\text{h}$, and after milling times of b) 1 h and c) 4h

Fig. 7 Variation of discharge capacity with number of cycles for a sample prepared from $\text{LiOH}\cdot\text{H}_2\text{O}$ as lithium source at $1100\text{ }^\circ\text{C}$ for 8h and processed to reduce particle size for different milling times.

Fig. 8 Electrochemical performances of a $\text{Li}_2\text{Ti}_3\text{O}_7$ -based electrode prepared at $1250\text{ }^\circ\text{C}$ for 2 h using Li_2CO_3 as lithium source: a) Specific capacity variation at C/20 rate (1st -90th cycle) and b) rate performance.

Fig. 9 a) Voltage profile for selected cycles up to the 90th of a lithium ion battery bearing the optimized $\text{Li}_2\text{Ti}_3\text{O}_7$ as the negative electrode and commercial LiCoO_2 as the positive; b) variation of discharge capacity with cycle number and efficiency.

