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Comparative study of carbon free and carbon containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes

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Abstract

Traditionally electrodes for lithium ion batteries are manufactured using carbon additives to increase the conductivity. However, in case of lithium titanate, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), carbon free electrodes have gathered some interest lately. Therefore two LTO materials synthesized using the same synthesis but different end milling process resulting in materials with different particle size and surface area are compared here using electrodes manufactured with and without carbon additives. Both LTO samples (LTO-SP with small primary particle size and high surface area, and LTO-LP with larger primary particle size and small surface area) produce similar capacities and voltages with or without carbon additives at low C-rates at the room temperature. However, at high C-rates and/or sub-zero temperatures electrodes with carbon additives produce higher capacities and smaller ohmic losses and this behavior is more pronounced for the LTO electrodes with smaller primary particle size and larger surface area. These results show that the feasibility of carbon free LTO electrodes depends on the properties of LTO affecting the morphology of the electrode and consequently, the transport properties. This is most pronounced under conditions where electron and Li^+ ion transfer become limiting (high C-rates and low temperature).

Keywords: $\text{Li}_4\text{Ti}_5\text{O}_{12}$, carbon content, conductivity, low temperature, lithium ion battery

Introduction

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been intensively investigated since 1990's as an alternative negative electrode material for lithium ion batteries. It has a spinel structure with theoretical capacity of 175 mAh/g and high lithium insertion/extraction potential of 1.55 V (vs. Li/Li^+). Since the lithium insertion potential of LTO is well above the deposition potential of metallic lithium, no lithium plating is likely to occur even at high C-rates and/or at low operation temperatures as in the case of graphite negative electrodes. This together with the minimal volume change of the structure (less than 0.2%) during cycling makes LTO very durable and safe predicting long cycle life. Indeed very long cycle lives of over 20 000 cycles have been reported with for example $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells using high charging and discharging rates [1]. Consequently, LTO has been adopted for commercial batteries manufactured by for example Altairnano and Toshiba.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an insulating material and traditionally electrical conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is considered as one of the main problems of LTO electrodes as conductivity of pure LTO is only $10^{-8} \dots 10^{-13}$ S/cm [2,3]. Several approaches to increase the conductivity of LTO by substituting different atoms for Li^+ , Ti^{4+} or O^{2-} sites in order to generate $\text{Ti}^{3+}/\text{Ti}^{4+}$ mixed state have been introduced [4]. For example doping with small amounts of Mg [2,5], Ag [6], and Zn [7] atoms has been reported to increase the conductivity and thus performance of LTO. Common methods to increase the conductivity also include carbon coating of LTO [8-11], and formation of composite materials of LTO and some highly conductive carbonaceous materials such as carbon nanotubes (CNT) [12]. Small amount of carbon black is routinely used in commercial electrode manufacturing with all electrode materials for enhancing electron transport in the composite electrodes [13].

Recently carbon free LTO electrodes have gathered some interest as it has been reported that LTO electrodes manufactured without any carbon additives or carbon coating show capacities similar to carbon containing LTO electrodes even at high C-rates [14,15]. This has been explained by the high conductivity of the lithiated $\text{Li}_7\text{Ti}_5\text{O}_{12}$ phase. As lithium ions are inserted into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structure, Ti 3d orbitals are filled as Ti^{4+} is partially reduced to Ti^{3+} . This is also seen in the color of the material when white $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder gradually turns into dark blue $\text{Li}_7\text{Ti}_5\text{O}_{12}$ and at the same time the conductivity of the material increases up to 10^{-2} S/cm [16]. Thus it has been suggested that unlike other electrode materials for lithium ion batteries such as graphite, LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LTO could be used without any conductive additives in electrodes [15].

Electrode manufacturing without carbon additives would be industrially very desirable as it would simplify the electrode processing and reduce the manufacturing costs. However, the published information of the necessity of carbon additives or carbon coating in LTO electrodes is inconsistent as for some LTO materials carbon free electrodes have shown worse rate capabilities when compared to carbon containing electrodes [17,18]. Here we study the performance of carbon free $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes using two different LTO powders manufactured by a pilot scale process with different particle size and specific surface area. Effect of carbon content on the electrochemical performance at high C-rates and low temperatures is evaluated based on these results.

Experimental

Two $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders (Sachtleben Pigments) were used as active materials. Samples are labeled hereafter as LTO-SP and LTO-LP according to the primary particle size (SP for smaller primary particle size and LP for larger primary particle size). These materials have been synthesized using the same pilot scale method and the difference in the particle size results from different milling processes.

Morphology of the particles was observed by scanning electron microscopy (SEM, JEOL JSM-7500FA). Particle sizes were calculated from the SEM images measuring 212 LTO-SP and 455 LTO-LP particles. BET measurements were done using Nova 3200 surface area analyzer (Quantachrome Instruments).

Electrode slurries were prepared by mixing LTO, carbon black (C65, Timcal), and PVDF (polyvinylidene fluoride) in *N*-methyl-2-pyrrolidone (Ashland) in weight ratios 92:3:5 for carbon containing electrodes and 95:0:5 for carbon free electrodes. Electrode slurries were then coated on an aluminum foil and dried at 80 °C overnight. 14 mm electrodes were cut from the dried electrode foils and calendered with a pressure of 3300 kg cm⁻².

Electrodes were dried overnight at 110 °C under vacuum before assembling 2016 coin cells in an argon filled glove box (oxygen and water vapour levels below 1 ppm). Lithium metal foil (0.38 mm in thickness, Aldrich) was used as a counter electrode, and 1M LiPF₆ in ethylene carbonate:dimethyl carbonate 1:1 w/w (LP30, Merck) as an electrolyte. 260 µm thick glass micro fiber filter (GF/A, Whatman) was used as a separator. Charging/discharging experiments were conducted using a Neware battery cycler. Galvanostatic charging and discharging was done between 1.1 and 2.5 V vs. Li/Li⁺ using C-rates from 0.1 C to 10 C. C-rates were calculated using the theoretical capacity of Li₄Ti₅O₁₂ (175 mAh g⁻¹) and 1 C corresponds to complete charging or discharging in 1 hour. Low temperature measurements were done at 0 °C and -20 °C in temperature chamber (Vötsch). Temperature was let to stabilize for 1h before the measurements.

Electrochemical impedance spectroscopy (EIS) was conducted with an Autolab potentiostat (PGSTAT302N) using 3-electrode set up (Hohsen HS-3E test cell) with a lithium metal foil counter and reference electrode. Frequency range of 100 kHz – 0.01 Hz and voltage amplitude of 10 mV were used.

Results and Discussion

Two Li₄Ti₅O₁₂ samples synthesized with the same process were chosen for electrode manufacturing. The only difference in the synthesis of these materials was a different end milling process resulting in different particle sizes and morphologies. XRD diffractograms published elsewhere [20] verified that both the samples have well defined crystalline structure of Li₄Ti₅O₁₂. However, the intensities of the diffraction peaks are clearly lower for LTO-SP than for LTO-LP which is attributed to particle size effect as the slight broadening of the LTO-SP peaks suggests presence of smaller particles in this sample. This observation is verified by SEM spectroscopy showing LTO-SP powder consisting of smaller primary particles with the mean size of 79 nm and standard deviation of 50 % (Figure 1a) which form large spherical aggregates of 10-50 µm (Figure 1b). LTO-LP has larger primary particles with size with the mean size of 150 nm and standard deviation of 36 % (Figure 1c) forming smaller aggregates of 1-5 µm (Figure 1d). The BET surface areas and the tap densities of the Li₄Ti₅O₁₂ particles are 22 m² g⁻¹ and 970 g dm⁻³ for LTO-SP and 7 m² g⁻¹ and 670 g dm⁻³ for LTO-LP. The secondary aggregate structure of LTO-SP is also preserved during the mixing of the slurry and the electrode preparation process as flattened spherical aggregates are observed in the electrode surface images of the LTO-SP electrodes.

Figure 1. SEM images of the LTO-SP (a-b) and LTO-LP samples (c-d). Scale bar in Figures a and c is 1 μm , and in Figures b and d 10 μm .

Electrochemical performance of the carbon free LTO electrodes was compared to that of the carbon containing LTO electrodes by charge/discharge measurements using different C-rates at the room temperature. Charge/discharge curves of the 3% carbon and 0% carbon containing LTO-SP electrodes at the room temperature are presented in Figure 2a and those of the corresponding LTO-LP electrodes in Figure 2b. At low C-rates capacities close to the theoretical capacity of 175 mAh/g are obtained with all the electrodes of the LTO-SP and LTO-LP samples containing either 3% or 0% carbon. The charge/discharge curves of LTO-SP and LTO-LP have different shape regardless of the carbon content such that LTO-LP has more flat charge/discharge curves over wide capacity range and very steep slopes near the beginning and end of charge/discharge whereas LTO-SP has more curved charge/discharge profiles. This behavior is typical for the LTO material with small particle size and large surface area [19,20]. Difference in the charging/discharging profiles between the carbon containing LTO-SP and LTO-LP electrodes is discussed in detail elsewhere [20]. Shortly, it is attributed to the available LTO surface sites and crystal planes inducing different activity for (de)lithiation processes and overlithiation of the near surface region of LTO-SP. LTO-SP with a larger fraction of near surface sites and presence of (400) planes appears to have a higher affinity for lithium during the (de)lithiation process than LTO-LP with (111) planes.

Figure 2. Charge/discharge curves of a) the LTO-SP and b) LTO-LP half cells at 0.1C, 1C and 10C and room temperature, and specific discharge capacities of c) the LTO-SP and d) LTO-LP half cells at C-rates 0.1-10. Active material loadings of the electrodes are 4.5-4.9 mg cm⁻².

From Figure 2 it is also evident that both the carbon containing and carbon free LTO-SP electrodes show higher capacities in comparison to LTO-LP and this difference is more pronounced at the high C-rates. It is also observed that the 3% carbon and 0% carbon containing electrodes have similar performance at low C-rates up to 1C but when C-rate is further increased, 3% carbon electrodes show higher capacities and at 10C the difference is almost 10%. It should be noted that no significant difference in the electric conductivity of carbon containing LTO-SP and LTO-LP electrodes is observed in electrochemical impedance measurements (not shown) as the obtained semicircles are similar in size as well as R_s describing the ohmic resistance of the electrolyte and electrode. For the 0 % carbon containing LTO electrodes semicircles are clearly higher in comparison to the 3 % containing ones suggesting that the reaction kinetics is slower because of deficiency of electrons resulting from their slower transport in the carbon free electrodes. On the other hand, effect of the morphology of the electrodes cannot be excluded as the carbon free electrodes can be less porous (*cf.* carbon containing ones) hindering also Li^+ transport. However, difference in capacity and ohmic resistance between the carbon free and carbon containing electrodes is observed only at the high C-rate of 10C (Fig 2a) so that lower capacity and higher ohmic losses are observed for the former ones. As the slower kinetics of the carbon free electrodes does not affect significantly the LTO

electrode performances, these results suggest that the lithium (de)intercalation process is not limited by kinetics but mass transfer.

These observations are partly in conflict with previously published results of carbon free LTO electrodes where no difference was observed with carbon containing and carbon free electrodes even at high C-rates up to 10C [14,15]. However, these studies are made with LTO materials with different particle size. Song *et al* [14] and Kim *et al* [15] both used LTO particles from simple solid state synthesis of TiO_2 and Li_2CO_3 starting materials producing relatively large particle size up to 1 μm . On the other hand, carbon additives or carbon coating has been earlier found to improve the performance of LTO electrodes when particle size has been close to our LTO particles (100-300 nm) [18] or surface area very large ($68.7 \text{ m}^2 \text{ g}^{-1}$) [17].

Kim *et al* [15] explained progress of the lithium insertion reaction in carbon free LTO electrodes during charging by propagation of a conductive LTO front, i.e. partly lithiated LTO, from the electrode surface toward the surface facing the separator during the charging process. This conductive LTO front would transfer electrons to adjacent LTO particles enabling further lithium insertion reactions and intruding the conductive front towards the center of the battery. Hence, conductive carbon would not be needed because of the high conductivity of the partly or fully lithiated LTO. Our results show that the ability of this partly or fully lithiated LTO to transfer electrons, and Li^+ , depends on LTO particle size and morphology, and consequently electrode morphology, affecting notably the functioning of carbon free LTO electrodes.

Active material particle size affects notably the performance of lithium ion battery as the relative number of the available sites at surface region increases and lithium diffusion length inside the solid active material decrease (diffusion is slow and often limits the performance) with the decreasing particle size. Our LTO materials originate from the same batch and hence, have the same bulk properties though the surface areas, available surface sites and diffusion lengths for lithium differ. No difference in the performance is observed between the 0 and 3 % containing LTO-SP and LTO-LP electrodes at low C rates (Fig 2) suggesting that electronic conductivity is not limiting the performance under these conditions. Hence, it is plausible that the observed difference in the performance of carbon containing and carbon free electrodes arises from differences in the electric conductivity *i.e.* different mobility of electrons and/or Li^+ ions during high rate discharging/charging (Fig 2). Adding 3% carbon in the electrode affects more the performance of the LTO-SP electrode showing higher capacities. LTO-SP has larger surface area and is more densely packed (*cf.* LTO-LP), suggesting better connectivity between LTO particles and hence, faster propagation of electrons and conducting LTO front. Still adding conductive carbon improves more the performance of this electrode at the high C rates (*cf.* LTO-LP). Transport both inside (for freeing reaction sites at the surface) and outside (transport of reactants to active sites) of the active material becomes more important with the increasing C rate as the mass transfer controlled lithium (de)insertion process [20] proceeds faster. Of the studied materials the solid state diffusion lengths are shorter and active area larger for the LTO-SP particles (*cf.* LTO-LP) suggesting that the limiting phenomenon is the reactant transport outside the active material particles. This can be explained tentatively by introduction of conductive carbon into the LTO electrodes besides enhancing electron transport also other effects arising from the different morphology of the LTO-SP and LTO-LP electrodes affect the performance: Adding carbon can increase the porosity of the more densely packed LTO-SP electrode enhancing Li^+ transport.

In addition to the difference in primary particle size and surface area, different secondary particle structure might affect the electrode morphology. It is also well known that electrode preparation, *e.g.* active mass loading and ratio of the electrode components, affects the electrode performance. As a conclusion, it is difficult to compare results obtained with LTO materials manufactured using different synthesis and electrode processing methods. Nevertheless, so far it seems that the difference in carbon free and carbon containing electrodes is observed only with small particle size/large surface area both in this study as well as in literature [17,18] suggesting that need for conductive carbon depends on LTO particle size. It is possible that morphology of the electrodes has a major role as they differ affecting the transport phenomena as contacts between the particles and consequently, electric conductivity and contact resistance differ. This is very plausible also for our electrodes as the secondary structure of the LTO-SP and LTO-LP particles as well as their tap densities are very different.

Figure 3. Charge/discharge curves of the LTO-SP (a and c) and LTO-LP (b and d) half cells at different temperatures. Active material loadings of the electrodes are 4.6-4.7 mg cm⁻².

As difference in the obtained capacities between 3% carbon and 0% carbon containing electrodes was observed at the high C-rates at the room temperature we also performed measurements at lower temperatures to study more in detail the effect of electrode conductivity in different conditions. Charge/discharge profiles for the 3% carbon and 0% carbon containing electrodes at the

temperatures of 20 °C, 0 °C, and -20 °C are presented in Figure 3a and 3c (LTO-SP) and 3b and 3d (LTO-LP). Similar capacities are obtained for the 3% carbon and 0% carbon electrodes at the low C-rate (0.1C) for both LTO-SP and LTO-LP. However, when current is increased to 1C and the temperature lowered to -20 °C there is clear difference in the measured capacities so that 3% carbon containing electrodes produce 10 mAh/g (LTO-LP) or 20 mAh/g (LTO-SP) higher capacity than 0% carbon containing electrodes. Similarly as in Figure 2a and b, the lower capacities of the carbon free LTO-SP and LTO-LP electrodes at -20 °C and 1C originate from transport effects rather than differences in phase coexistence i.e. carbon additives facilitate the sluggish kinetics at low operating temperature (-20 °C) by affecting the electrode morphology and thus enhancing the lithium transport. Therefore, it seems that carbon additives are not needed to enhance the conductivity at moderate conditions but when high currents or low temperatures are used the lower conductivity and limited ion transport of the carbon free electrodes begins to affect the performance obtained with this type of LTO particles.

4B

4A

Figure 4. Cycle life data of the LTO/Li half cells at a) 60 °C and b) at the room temperature.

Carbon black as conductive additive is required for most type of lithium ion battery electrodes. Even though the active material itself does not suffer from poor conductivity, as for example in case of graphite negative electrodes, large volume changes of the active material during cycling requires carbon additives to maintain electrical contacts when cycled for a long time. Extremely small change in the lattice size upon cycling distinguish LTO from other electrode materials with clearly larger volume changes [21,22] possibly allowing long cycle lives without carbon additives. Another factor affecting the cycle life is the formation of surface films which is dependent on the surface morphology. For example He *et al.* investigated two LTO materials, one with small particle size and high surface area, and the other with large particle size and small surface area [23]. It was found out that the high surface area LTO has high reactivity towards electrolyte and forms smooth SEI layer within few cycles whereas the small surface area LTO forms porous SEI layer and therefore, shows slightly poorer cyclic performance. It has also been reported by Song *et*

al. that carbon additives in LTO electrodes affect SEI formation and the reactivity towards electrolyte was increased at high temperatures in the presence carbon additives in the electrodes [24]. Therefore, we compared the cyclability of LTO-SP and LTO-LP in the 3% and 0% carbon containing electrodes at different temperatures. In contrast to the results of Song *et al.* [24] the cyclability of the carbon free and carbon containing LTO electrodes had no significant difference at 60 °C as seen in Figure 4a. The capacity of both the carbon free and carbon containing electrodes started to decrease very fast around 50 or 60 cycles and there was also no difference between the LTO-SP and LTO-LP electrodes. The particle size of LTO in our experiments is considerably smaller than in [24] and larger surface area might increase the reactivity of LTO towards electrolyte and thus explain the poorer high temperature cyclability results of our carbon free electrodes. Room temperature performance of LTO-SP and LTO-LP electrodes with and without carbon additives are presented in Figure 4b and cycle life behavior was similar with other samples except LTO-SP containing 0% carbon which showed slightly poorer cycle life behavior. It is possible that the larger surface area of LTO-SP increase gas evolution affecting cycle life performance of LTO-SP electrodes negatively [25,26], however, this phenomenon is difficult to observe in coin cell measurements.

Conclusions

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is an excellent electrode material for high power applications and sub-zero temperatures. Here, two LTO materials, LTO-SP with small primary particle size of 79 nm and surface area of $22 \text{ m}^2 \text{ g}^{-1}$ and LTO-LP with 150 nm primary particle size and surface area of $7 \text{ m}^2 \text{ g}^{-1}$, were investigated in electrodes containing 3% or 0% carbon additives using different C-rates and temperatures. As a result, capacities close to the theoretical capacity 175 mAh/g were achieved at low C-rates and at the room temperature with both the carbon containing and carbon free electrodes. Thus, carbon additives are not needed at moderate conditions and carbon free LTO electrodes can be used at the room temperature with low currents. However, at high C-rates and low temperature 3% carbon electrodes show higher capacities and the difference was more pronounced with the high surface area LTO-SP indicating that carbon additives are needed in more demanding conditions when LTO particles have small particle size and large surface area. These results show that the feasibility of carbon free LTO electrodes depends on the properties of LTO (particle size and surface area) affecting the morphology of the electrode and consequently, the transport properties. This is most pronounced under conditions where electron and Li^+ ion transfer become limiting (high C-rates and low temperature). This brings new knowledge to the recent discussion on the carbon free LTO electrodes.

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