Enhanced rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes with bridged grain boundaries

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Abstract

Excellent rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) electrodes results from mixed Li site occupancy and facile Li ion exchange at 8a and 16c sites in structures with intermediate composition $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ($0 < x < 3$). In this paper, we reveal that inter-particle connectivity within LTO electrodes significantly affects 8a and 16c site occupancies upon discharge and greatly impacts Li ion diffusion. LTO electrodes of the same primary crystal structure but of different grain boundary structures were prepared and they showed significantly different electrochemical performance. LTO electrodes with a percolated 3D structural network and bridged grain boundaries offered balanced 8a-16c occupancy with Li ion exchange at 8a and 16c sites upon discharge, high ionic conductivities, and good rate performance. While LTO electrodes with isolated clusters of particles showed strong rate dependence of 8a-16c occupancy upon discharge and a lack of Li ion exchange at 8a and 16c sites, large over-potential, and significant capacity decay upon fast charging. Bridged grain

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1 boundaries in LTO secondary particles facilitate apparent solid-solution process
2 during electrochemical cycling by maintaining Li site exchange in LTO electrodes and
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4 thus enhance the rate performance of LTO electrodes.
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8 **Keywords:** Lithium-ion battery, lithium titanium oxide, solid-state NMR, grain
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1. Introduction

High rate performance of rechargeable Li ion batteries (LIBs) is highly desirable in high-power energy storage applications.[1–5] The formation of phase boundaries in battery electrode materials is often associated with poor rate performance. However, two exceptions are $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4 , which despite showing a first-order phase transition, offer excellent rate performance and stable long-term cycling.[5–11] Debates regarding these two exceptional systems center around the fundamental nature of the structural change, whether it is a solid solution, a phase separation on different length scales, or a combination of the two depending on the particle size of electrodes and battery cycling conditions.[7, 12–17] For the two-phase reaction mechanism, it has been proposed that the grain boundary, in the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, facilitates ion and electron transport instead of impeding it, which explains the low activation energy for fast ion transport in the intermediate region of discharge with $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ($0 < x < 3$).[18] The effects of grain boundaries on charge carrier transport and the rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have been extensively investigated. Both computational and experimental effort have been investigated to resolve the contradiction of phase separation vs. solid solution contradiction.[7,18]

Experimental studies[19–21] on Li ion dynamics and diffusion pathways in $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 3$) have provided the following insights: i) spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a poor Li ion conductor with the following site occupancy $[\text{Li}]_{8a}[\text{Ti}_{5/3}\text{Li}_{1/3}]_{16d}[\text{O}_4]_{32e}$, ii) early-stage lithiation with $x \leq 0.3$ dramatically increases Li ion diffusivity, followed by continuous decrease in Li ion diffusivity with $x > 0.3$, and iii) fully lithiated $\text{Li}_7\text{Ti}_5\text{O}_{12}$ has a rock salt structure with a site occupancy of $[\text{Li}_2]_{16c}[\text{Ti}_{5/3}\text{Li}_{1/3}]_{16d}[\text{O}_4]_{32e}$. $\text{Li}_7\text{Ti}_5\text{O}_{12}$ is a mixed conductor, with higher Li ion diffusivity than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ but lower than $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ($0 < x < 3$). Diffraction measurements reveal that $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ stays as a single phase at equilibrium, and fast lithiation or de-lithiation promotes the two-phase reaction but relax to a solid-solution state with time.[7] Mixed 8a and 16c Li occupancy is credited for the formation of apparent solid solution, and thus for the excellent rate performance of $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ($0 < x < 3$).

In this paper, we report observations regarding the effects of bridged grain boundaries on maintaining the occupancy balance between 8a and 16c sites in LTO structures, and the subsequent impact on rate performance and over-potentials of LIBs using LTO electrodes. Pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been prepared with two different Li-containing precursors (Li_2CO_3 and CH_3COOLi) or in a different way (with or without high-temperature $\geq 900^\circ\text{C}$ treatment), which exhibit the same crystal structure as characterized by X-ray diffraction and high-resolution solid-state Li NMR, but show different morphologies, as revealed by scanning electron microscopy (SEM). The 3D bridged network of LTO particles results in a relatively constant 8a and 16c occupancy, variable rate discharging and minimal over-potential upon fast charging. In contrast, isolated small clusters of LTO particles lead to changes in the 8a/16c occupancy ratio when discharged at different rates, due to the lack of 8a-16c Li exchange observed by NMR. As a result, the low ionic conductivities of LTO electrodes with isolated particles yield significant over-potential for fast-rate electrochemical cycling. In summary, this paper investigates the impact of grain boundaries in LTO electrodes on altering the crystal structure, site occupancy, and Li ion transport properties upon battery cycling.

2. Experimental

2.1 Material preparation

Two different LTO samples were synthesized using TiO_2 and different lithium sources (Li_2CO_3 and LiAc) with the same calcining temperature. A mixture of TiO_2 and Li_2CO_3 (LiAc) was hand ground for 30 min to be homogeneous, with the molar ratio of Li to Ti being 4.2 to 5. The mixture was then calcined at 500°C for 5 h and 800°C for 10 h to ensure complete reaction. For convenience, LTO/ Li_2CO_3 and LTO/ LiAc were used to denote the samples synthesized with Li_2CO_3 and CH_3COOLi , respectively.

2.2 Electrochemistry

$\text{Li}_4\text{Ti}_5\text{O}_{12}$, acetylene black, and polyvinylidene fluoride (pvdf) dissolved in

1 N-methyl-2-pyrrolidinone were mixed together to form a homogenous slurry, then the
2 slurry cast on a piece of carbon coated copper foil. After drying at 100°C, the
3 electrode film was punched into discs with a diameter of 12.5 mm. The prepared
4 electrode contains 80 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$, 10 wt.% acetylene black, and 10 wt.% pvdf.
5 Loading of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ on each disc was 2-3 mg. The electrochemical performance of
6 LTO electrodes was measured using CR2032 coin cells with Li metal as the counter
7 electrode. The cells were assembled in an argon-filled dry-box (MBraun) with a
8 microporous membrane (Celgard, K2045) as the separator, and 1 M LiPF_6 in
9 EC/DMC/DEC (w/w=1:1:1) as the electrolyte. They were cycled on a multi-channel
10 battery test system (LAND) within a voltage range of 1.0 V to 2.5 V. Cyclic
11 voltammetry (CV) on these batteries was measured at room temperature on a
12 Reference 600 (Gamry Instruments), with the voltage range from 1.0 V to 2.5 V.
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25 **2.3 X-ray diffraction, scanning electron microscopy, and electrode surface area** 26 **measurement.**

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29 The crystal structures of these $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were determined by X-ray
30 diffraction (XRD) (X'PERT Pro MPD, Cu $K\alpha$ radiation, $\lambda=0.15406$ nm). The
31 diffraction patterns were recorded at room temperature in the 2θ range from 10° to
32 80°, with a scan rate of 7°/min. The morphology and particle size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$
33 samples were characterized with scanning electron microscopy (SEM, Nova 400
34 Nano, FEI). Electrode surface area measurements were performed on a Micromeritics
35 TriStar 3000 surface area and porosity analyzer using nitrogen adsorption method.
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44 **2.4 NMR spectroscopy.**

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46 Pristine LTO samples were packed into 1.3-mm rotors inside an Argon glovebox
47 before acquiring NMR spectra. The ^7Li magic angle spinning (MAS) spectra were
48 acquired on an Avance III Bruker spectrometer using a 1.3-mm MAS probe in a 14.7
49 T magnetic field, with a ^7Li Larmor frequency of 233.1 MHz. ^7Li spectra were
50 obtained using a rotor-synchronized spin-echo sequence at a MAS rate of 50 kHz. The
51 90° pulse length was 1 μs and the recycle delay was 15 s. ^7Li shifts were referenced to
52 LiF at -1 ppm.
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The cycled LTO electrodes were washed with dimethyl carbonate (DMC) 3 times to ensure the removal of residual electrolytes. DMC was removed by vacuum drying before NMR characterizations. As the discharge voltage was limited to 1 V, no significant solide-electrolyte-interphase (SEI) formation is expected on the surface of LTO electrodes

^7Li MAS NMR experiments were performed on a Bruker AVANCE III spectrometer with a 2.5-mm MAS probe in a magnetic field of 11.75 T. The Larmor frequency of ^7Li was 194.3 MHz. A rotor-synchronized spin-echo pulse was employed at a MAS rate of 25 kHz. The 90° pulse length was 5 μs and the recycle delay was 2 s. Solid LiCl with a ^7Li shift at 1.1 ppm was used as a reference. The ^7Li NMR spectra were simulated using the dmfit software.[22]

3. Results and discussions

Fig. 1 SEM images of LTO/Li₂CO₃ (a) and LTO/LiAc (b) with a scale bar of 100 nm. ^7Li NMR of LTO/Li₂CO₃ (c) and LTO/LiAc (d). Blue plots represent experimental spectra, while the purple/green plots represent simulated spectra. The sums of the simulated spectra are shown in red. The fraction of each subcomponent in the total spectra is indicated.

SEM images of LTO/Li₂CO₃ and LTO/LiAc in Fig. 1a and 1b show that primary

LTO/LiAc particles aggregate to loosely packed small clusters while LTO/Li₂CO₃ particles of submicron size are connected to form a percolated network. When using Li₂CO₃ as the lithium source, it starts to melt at 723°C, which helps the growth of grain boundaries (red circle in Fig. 1a) between Li₄Ti₅O₁₂ particles. LiAc decomposes to lithium oxides with a very high melting point before converting to Li₄Ti₅O₁₂. At 800 °C, the lack of intermediate liquid phase yields loose particles aggregates. Further examination on the crystal structures of LTO/LiAc and LTO/Li₂CO₃ was carried out using solid-state ⁷Li NMR and X-ray diffraction. ⁷Li NMR of both LTO/LiAc and LTO/Li₂CO₃ revealed a major resonance at 0.08 ppm with a shoulder on the left at -0.26 ppm. Based on the spectral simulation and previous NMR studies of LTO [19,20], the 0.08-ppm resonance was assigned to Li at 8a sites and the -0.26 ppm resonance was assigned to Li at 16d sites. The ratio of [Li]_{8a} : [Li]_{16d} is 3:1 in both LTO/LiAc and LTO/Li₂CO₃, consistent with the stoichiometry of Li₄Ti₅O₁₂, *i.e.*, [Li]_{8a}[Ti_{5/3}Li_{1/3}]_{16d}[O₄]_{32e}. The XRD patterns of LTO/LiAc and LTO/Li₂CO₃ were near identical (Fig. S1). SEM, NMR, and XRD results revealed the same crystal structure but different morphologies of LTO/LiAc and LTO/Li₂CO₃ pristine electrodes.

Fig. 2 a) Electrochemical profile of a typical LTO/Li half-cell battery, b) *ex situ* high-resolution ⁷Li NMR of cycled LTO electrodes at different states of charge as indicated in a). P represents pristine electrode.

Ex situ ⁷Li NMR was performed to follow structural and phase transitions of LTO used in half-cell batteries at different states of charge. The electrochemical profile of an LTO/Li half-cell battery cycled at a rate of C/16 (11 mA/g) is shown in Fig. 2a. A

major plateau occurs around 1.55 V for both charge and discharge with very small hysteresis. ^7Li NMR spectra at different states of (dis)charge indicated as P, D1, D2, C1, and C2 in Fig. 2a are displayed in Fig. 2b. The ^7Li NMR spectrum of pristine LTO (P at the bottom of Fig. 2b) shows two partially overlapped peaks around 0 ppm from Li at 8a and 16d sites. Upon discharge, a broad low-lying resonance centered at -10 ppm emerges, assigned to Li at 16c sites. The broad 16c resonance grows stronger as the discharge process proceeds until the end at 1.0 V. This indicates the gradual insertion of Li ions into 16c sites of LTO. In addition, the intensity of the 8a resonance decreases, suggesting Li migration from 8a to 16c. These two processes, direct Li insertion into 16c sites and Li migration from 8a to 16c, lead to the eventual phase transformation of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to rock salt $\text{Li}_7\text{Ti}_5\text{O}_{12}$ at the end of discharge. The charging process is the reverse of the discharge process, manifested in Fig. 2b as the decrease and disappearance of the 16c resonance at -10 ppm and the return of the 8a NMR peak around 0 ppm.

Fig. 3 Electrochemical profiles of LTO/Li batteries discharged at 1C and charged at different rates of 1C, 4C, 8C, and 16C with LTO electrodes made from precursors of a) Li_2CO_3 , b) LiAc , average charge voltage (c) and rate performance (d) of LTO/Li batteries.

The first-order $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - $\text{Li}_7\text{Ti}_5\text{O}_{12}$ phase transition occurs at 1.55 V with a very small over-potential at a relatively slow cycling rate. Over-potentials for both

discharge and charge increase with increasing (dis)charge rates. LTO/Li₂CO₃ and LTO/LiAc electrodes display different behaviors (Fig. 3), regarding over-potentials at fast charging. These half-cell batteries were discharged at a rate of 1C and charged at 1C, 4C, 8C, and 16C. Fig. 3a shows very small over-potential even at a fast charging rate of 16C, and minimal capacity decay is observed for batteries using LTO/Li₂CO₃ electrodes. In contrast, Fig. 3b shows a gradual increase in over-potential when the charging rate was increased from 1C to 16C, and noticeable capacity decay occurs at 16C. For clearer comparison, the plots of average charge voltage vs. C rate for batteries using LTO/Li₂CO₃ and LTO/LiAc electrodes are shown in Fig. 3c. A linear increase of the average charge potential (vs. Li/Li⁺) with increasing C rate is seen for both LTO/Li₂CO₃ and LTO/LiAc electrodes, and the slope is much larger for LTO/LiAc than for LTO/Li₂CO₃. In addition to over-potential, rate performance of electrodes can also be gauged based on capacity variation upon cycling with different rates. As seen in Fig. 3d, the specific capacity for LTO/Li₂CO₃ electrodes stayed almost constant with increasing charge rate, however, substantial reduction in specific capacity is correlated with fast charging for LTO/LiAc electrodes. Overall, LTO/Li₂CO₃ electrodes exhibit significantly better rate performance compared with LTO/LiAc electrodes.

Fig. 4 Cyclic voltammetry of half-cell batteries employing a) LTO/Li₂CO₃ and b) LTO/LiAc electrodes. Only the charge process with varying voltage-scanning rate is shown, the discharge scanning rate was fixed at 0.2 mV/s. c) a plot of the peak current

i_p vs. the square root of voltage scanning rate. Two distinct processes P1 and P2 were identified for the LTO/Li₂CO₃ electrodes, and one process P3 for the LTO/LiAc electrodes.

The difference between LTO/Li₂CO₃ and LTO/LiAc electrodes in terms of electrochemical performance can be further probed with cyclic voltammetry (CV). Fig. 4a and b show the CV profiles with increased scanning rate from 0.2 mV/s to 10 mV/s in the positive direction for half-cell batteries employing LTO/Li₂CO₃ and LTO/LiAc electrodes. The scanning rate in the negative direction is kept constant at 0.2 mV/s. Two distinct processes are seen for the LTO/Li₂CO₃ electrode, while only one is resolved for LTO/LiAc. To more clearly illustrate this difference, the peak current i_p (mA) is plotted against the square root of voltage scanning rate (V/s) and the plot is presented in Fig. 4c. For Faradaic processes, i_p and $v^{1/2}$ are linearly correlated [23],

$$i_p = (2.69 \times 10^5) n^{3/2} A D_{Li^+}^{1/2} C_{Li} v^{1/2} \quad (1)$$

n : number of electrons on each charge carrier, $n=1$ for Li⁺.

A (cm²): surface area of the electrode material.

C_{Li} (moles/cm³): bulk concentration of Li⁺ in electrodes (0.03).

D_{Li^+} (cm²/s): Li⁺ diffusivity.

Fig. 5 ⁷Li NMR of a) LTO/Li₂CO₃ and b) LTO/LiAc electrodes discharged to 1 V at

0.1C, 1C, 2C, and 4C rates, c) the ratio of Li at 8a and 16d sites vs. 16c sites for electrodes discharged to 1 V against Li metal with different rates, and d) ^7Li spectra recorded at 0.5 h, 1 h, and 17 h after disassembling a fully discharged LTO/ Li_2CO_3 electrode against Li metal at a rate of 4C.

The specific surface area was determined, based on N_2 absorption, to be $2.46 \text{ m}^2/\text{g}$ for LTO/ Li_2CO_3 and $4.80 \text{ m}^2/\text{g}$ for LTO/LiAc. The relatively larger specific surface area for LTO/LiAc is consistent with the observation with SEM that the particle sizes for LTO/ Li_2CO_3 and LTO/LiAc electrodes are similar but LTO/ Li_2CO_3 exhibits more grain boundaries thus reduced specific surface area. The mass of both LTO/ Li_2CO_3 and LTO/LiAc electrodes are 2.12 mg. Therefore, according to equation (1), one of the two processes (P1) shown for LTO/ Li_2CO_3 electrodes has a slightly higher Li^+ diffusivity of $3.32 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ than the other process (P2), $2.52 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. Li^+ diffusivity in LTO/LiAc (P3) is calculated to be $5.62 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. It is worth mentioning that closer examination of the CV profile for LTO/LiAc electrodes also reveals two processes. However, due to relatively sluggish ion and electron transport at high scanning rates, only one linear $i_p-v^{1/2}$ correlation curve is resolved. In addition, the Li^+ diffusivity was also measured with the Ac impedance at different charge depth and the LTO/ Li_2CO_3 also shows ~ 5 times higher average Li^+ diffusivity (Tab. S1) compared with LTO/LiAc.

Factors accounting for the difference in Li ion conduction LTO/ Li_2CO_3 and LTO/LiAc electrodes upon charge can be traced back to the characteristics of $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ structures and Li occupancies. ^7Li NMR spectra of LTO/ Li_2CO_3 and LTO/LiAc electrodes cycled with different rates were used to show Li occupancy variation (Fig. 5a and 5b) at the end of discharge. As the discharge rate was increased, 16c site occupancy decreases for both LTO/ Li_2CO_3 and LTO/LiAc electrodes, but larger variation in the 8a site occupancy was observed for LTO/LiAc electrodes compared with LTO/ Li_2CO_3 electrodes. For quantitative process, the ratio of Li at 8a and 16d sites vs. Li at 16c site is calculated for both types of electrodes based on the area integral of ^7Li NMR spectra of electrodes at the end of discharge. The occupancy

ratio plotted against discharge rate is presented in Fig. 5c. For LTO/Li₂CO₃ electrodes, the ratio of (8a+16d)/16c remains within a small range with different discharge rates of 0.1C, 1C, 2C, and 4C. At a low discharging rate of 0.1C, the (8a+16d)/16c ratio is 0.78, and with increasing discharge rates from 0.1C to 4C, the (8a+16d)/16c ratio only slightly increases and levels off around 1.00. In contrast, for LTO/LiAc electrodes, the (8a+16d)/16c ratio continuously increases from 0.6 at 0.1C to > 1.2 at 4C. The relatively un-regulated (8a+16d)/16c ratio in LTO/LiAc electrodes is likely from the lack of Li exchange between 8a and 16c sites. To test this hypothesis and to further explore Li ion exchange dynamics at 8a and 16c sites, LTO/Li₂CO₃ electrodes were prepared and cycled against Li metal at a rate of 4C until the end of discharge, the exchange between 8a and 16c was monitored with time-resolved ⁷Li NMR. Selective ⁷Li spectra at the time of 0.5, 17, and 33 hours after disassembling the discharged battery are shown in Fig. 5d. The spectra reveal continuous decrease in the intensity of the 16c Li resonance and increase in intensity of the 8a resonance with time, suggesting Li migration from 16c to 8a sites, consistent with previous neutron diffraction measurements.[7] On the other hand, similar migration from 16c to 8a was not observed in LTO/LiAc electrodes. Previous studies have concluded that Li exchange between 8a and 16c sites helps to reach apparent solid-solution state of LTO electrodes and prevent phase segregation on a macroscopic scale during fast charging. [7] Solid-solution state often exhibits much higher ionic and electronic conductivities compared with phase-segregated composites. Therefore, the observation of 8a-16c Li exchange contributes to the better rate performance of LTO/Li₂CO₃ electrodes compared to LTO/LiAc.

Fig. 6 a) SEM image of LTO/LiAc electrode sintered at 900°C for 30 min., b) Electrochemical profile of LTO/LiAc electrodes sintered at 900°C for 30 min. cycled against Li metal at a constant discharge rate of 1C and different charging rates of 1C, 4C, 8C, and 16C, and c) rate performance of LTO/LiAc electrodes without high-temperature sintering, and sintered at 900°C for 30 min.

The crystal structures of pristine LTO/Li₂CO₃ and LTO/LiAc electrodes do not exhibit significant difference, as evidenced by similar ⁷Li NMR (Fig.1c and 1d) and XRD patterns (Fig. S1). Simulation of the ⁷Li NMR spectra reveals the stoichiometric composition, 25% Li at 16d sites and 75% at 8a sites, in both LTO/Li₂CO₃ and LTO/LiAc pristine electrodes. LTO/Li₂CO₃ and LTO/LiAc show very different morphologies, as observed with SEM. The SEM images in Fig. 1a and 1b show that LTO/LiAc particles clustered in small groups while LTO/Li₂CO₃ particles form connected 3D structures with grain boundaries. The difference in grain boundaries affects the crystal structures of cycled LTO/Li₂CO₃ and LTO/LiAc electrodes significantly. In LTO/Li₂CO₃ electrodes, Li ion exchange between 8a and 16c sites helps to maintain a balance of Li occupancies at these two sites, which prevents phase separation and also proves to be beneficial for fast ion conduction. In LTO/LiAc electrodes, the lack of Li exchange between 8a and 16c sites leads to imbalanced 8a and 16c site occupancies and results in early phase segregation. Higher Li diffusivity found in cycled LTO/Li₂CO₃ electrodes contributes to the observed lower

over-potential at fast charging rates, compared with cycled LTO/LiAc electrodes.

Employing LiAc precursors for synthesizing LTO leads to the formation of small clusters of particles, likely due to the pyrolysis process of acetate groups. The secondary particles of LTO/LiAc electrodes can be improved by sintering at temperatures $\geq 900^{\circ}\text{C}$. High-temperature sintering over a short period of time promotes the aggregation of smaller particle clusters and the establishment of a 3D structural network (Fig. 6a). As shown in Fig. 6b, sintering the LTO/LiAc electrode at 900°C for 30 min significantly reduces the over-potential at fast charging and improves the rate performance of LTO/LiAc electrodes.

4. Conclusion

Two types of LTO electrodes with the same crystal structure but different grain boundary structures were studied to examine the effects of inter-particle connectivity on Li site occupancy and rate performance of cycled LTO electrodes used in rechargeable LIBs. The LTO electrodes with significant presence of grain boundaries demonstrated very small over-potential upon fast charging, while significant over-potential and capacity decay were observed for LTO electrodes made of isolated particles. The measured Li diffusivity in $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ is higher for LTO electrodes with connected particles compared with those with isolated LTO particles. High-resolution ^7Li NMR results have shown a larger extent of Li exchange between 8a and 16c sites in cycled LTO electrodes with connected particles compared with those of isolated particles. 8a-16c Li exchange in LTO electrodes prevents phase separation and supports good rate performance. It has been shown with this work that morphologies such as bridged grain boundaries and percolated structural networks induce changes on the crystal structure of cycled electrodes, which in turn affects the electrochemical performance of LTO anodes.

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