

Small change — great effect: Steep increase of Li ion dynamics in $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ at the early stages of chemical Li insertion ($x = 0.1, x = 0.3$)

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Polycrystalline $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ (LTO, $0 < x \leq 3$) is a well-known negative electrode material for lithium-ion batteries. It shows a flat Li insertion plateau of about 1.5 V vs. Li/Li^+ ; its theoretical specific capacity is approximately 175 mAh/g. The increased use of LTO, which is also commercially available, is due to various properties such as low cost, satisfactory safety and easy preparation. Most importantly, upon Li insertion, the expansion of the material is almost negligible favoring a long cycle life. In samples with $x = 0$, Li self-diffusion, which can be microscopically probed via Li nuclear magnetic resonance (NMR), is rather low. With increasing Li insertion, however, the diffusivity increases significantly. This is accompanied by a redistribution of Li ions across the 8a and 16c sites in the spinel structure [1].

While earlier ^7Li NMR studies put emphasis on samples with Li contents of $x > 1$ [2], there are, however, no information available from NMR answering the question of how Li self-diffusion changes when x is only slightly increased. The present study shows that even at $x = 0.1$ ^7Li NMR relaxometry, when performed in the so-called rotating frame of reference, reveals a drastic enhancement of Li diffusivity [3]. This enhancement, which points to the 8a – 16c – 8a migration pathway, is associated with a considerable reduction of the local hopping barrier. Thus, the largest increase in Li diffusivity is observed at the early stages of Li insertion [3]. Strong Coulomb repulsions caused by the simultaneous occupation of neighboring 8a and 16c sites might be considered to explain the enhanced Li diffusivity observed.

High resolution NMR was helpful to corroborate the findings from time-domain NMR. Via ^6Li MAS NMR it was possible to reveal the magnetically different Li sites in LTO (8a, 16c, 16d) and to calculate the site occupancies by evaluating the areas under the NMR lines. This enabled us to follow the change in site occupancy as a function of x . Site-specific (MAS) NMR spin-lattice relaxation times and ^6Li 2D NMR experiments point to rapid Li ion change between the 8a and 16c sites. This is in contrast to the Li ions residing in the 16d voids; obviously, they do not participate in the fast Li diffusion process that is relevant for battery applications.

[1] M. Wagemaker *et al.*, *Adv. Mater.* 2006, 18, 3169.

[2] M. Wilkening *et al.*, *Phys Chem. Chem. Phys.*, 2007, 9, 6199.

[3] W. Schmidt *et al.*, *Chem. Mater.*, 2015, 27, 1740.