

^6Li MAS NMR investigations of the Li insertion into nanocrystalline Li-Ti-O spinels - the influence of the coherent domain size on the reaction mechanism

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The nanocrystalline oxide materials form a group of highly prospective electrode material for use in advanced Li ion batteries or electrochromics. It is generally expected that these materials will allow for better control of the interface quality and active area¹. It was shown that by convenient selection of low temperature synthetic routes one can obtain material with improved characteristics like the attainable capacity², electron transfer kinetics or tendency to phase transitions³. Despite the growing interest in practical application of these materials some of the fundamental aspects of the insertion behaviour of these materials connected with the particle and/or coherent domain size are not fully understood.

This paper will demonstrate the influence of the coherent domain size on the insertion activity of the Li-Ti-O spinels. As will be shown using electrochemical, TEM and ^6Li MAS NMR data the coherent domain size can effectively alter the mechanism of the Li insertion reaction. The materials with sufficiently big coherent domain size tend to accommodate the inserted Li in octahedral coordination (16c - ^6Li NMR signal at ca -0.7 ppm) (see Figure 1). In order to reduce the electrostatic repulsions the material undergoes a phase transition in which the tetrahedrally coordinated Li (8a ^6Li NMR signal at ca 0.3 ppm) moves into octahedrally coordinated site to reduce the electrostatic repulsions. The Knight shift type signal observed in NMR spectra indicates formation of metal-like conductivity due to the filling of the conduction band.

The materials with small coherent domain size (coherent domain size ca 5-10 smaller than characteristic particle size) show different behavior. The inserted lithium is preferentially stored in tetrahedrally coordinated positions (8b ^6Li NMR signal at ca 0.7 ppm). (see Fig. 2). This behavior indicates that small coherent domain size suppresses the tendency of the oxide host to undergo the phase transition probably due to the high number of the boundaries between different domains which represent additional energy stabilizing the arrangement with tetrahedrally coordinated Li in reduced spinel. This phase transition suppression also improves kinetics of the Li insertion process, the attainable specific capacity, remains, however, unaffected.

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References

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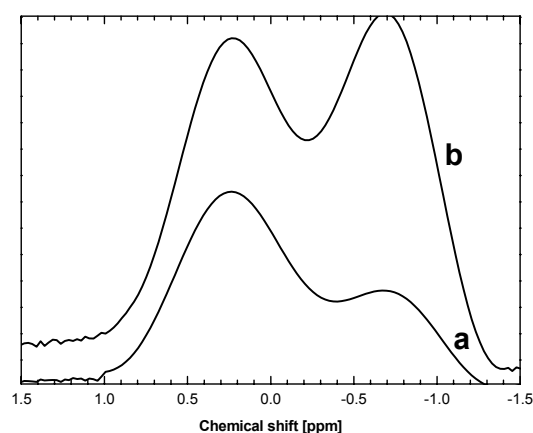


Figure 1. ^6Li MAS NMR spectra of the Li-Ti-O spinel samples, prepared by solid state reaction at 800°C, after reduction by bytillithium. The spectrum a) corresponds to material reduced from 20%, the spectrum b) to the material reduced from 80%.

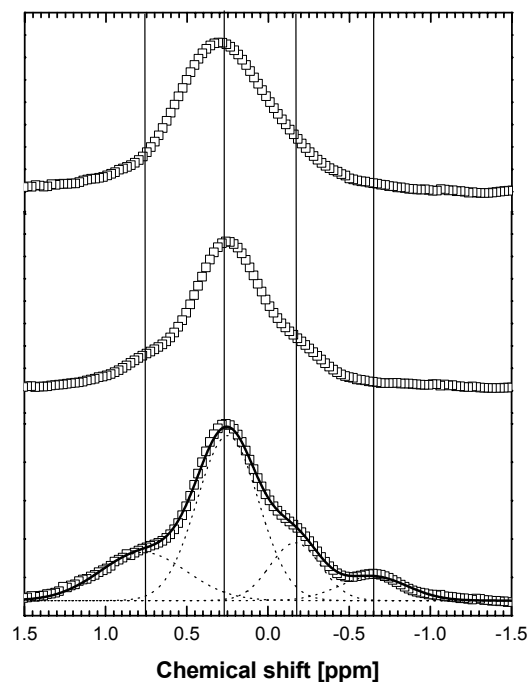


Figure 2. ^6Li MAS NMR spectra of the Li-Ti-O spinel samples, prepared by solvothermal reaction with subsequent annealing at 450°C. The spectra correspond to completely oxidized material (top spectrum), to material reduced from 20% (middle spectrum) and to material reduced from 80% (bottom spectrum).