

Li and Na insertion into TiO₂ polymorphs and Li.Ti ternary oxides

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Both TiO₂ polymorphs (anatase and TiO₂ (B)) and Li-Ti ternary oxides are attractive candidates for anodes in rechargeable Li-ion batteries, due to their low cost, non-toxicity, cycling stability at high charging rate and reasonable capacity. Li insertion into anatase proceeds as a diffusion controlled process, where the peak current scales with square root of the scan rate, whereas Li-insertion electrochemistry of TiO₂(B) is basically different. Zukalova et al found that Li-insertion into TiO₂(B) is characterized by unusually large faradaic pseudocapacitance[1]. The predominant pseudocapacitive process in TiO₂(B) was related to accommodation of Li inside the TiO₂(B) open channels in monoclinic lattice.

In parallel with an employment of Li-ion batteries as prominent power sources for many portable devices and their perspectives in large-scale applications more and more research teams realize limited sources of lithium and transition metals. In search for possible alternative a substitution of Li with Na seems to be a feasible solution. Na resources as NaCl in seawater are practically unlimited. However, due to larger radius of Na ion (Na: 1.02 Å, Li: 0.76 Å) there is only limited number of possible Na-ion host materials in contrary to relatively broad variety of materials inserting Li. Recently, lithium titanate spinel (Li₄Ti₅O₁₂, LTO), used as the negative electrode material in Li-ion batteries, has also been examined for the Na-ion battery. LTO is known as a "high potential" negative electrode material with a formal potential of 1.55 V vs. Li/Li⁺, whereby one can avoid the dendrite problem. This character should also prevent the Na-dendrite deposition. Na insertion in LTO is accompanied with development of extra phase with an about 4-5% larger unit cell volume which co-exists with LTO in a single particle and is identified as a Na-substituted LTO phase[2].

In our work we studied Li and Na insertion into TiO₂(B) and LTO spinel of different particle size and synthetic history, either commercial or laboratory made. The highest capacity and charging rate both for Li and Na insertion exhibited nanocrystalline LTO prepared by sol-gel process pioneered in our laboratory[3]. During testing of Li insertion/extraction by galvanostatic chronopotentiometry at 1C this material exhibited excellent stability over tens of cycles with almost 100% of theoretical capacity (175 mAh/g). In contrary, commercial materials exhibited a capacity drop of about 30% after 50 cycles. In case of Na insertion, the charge capacity of nanocrystalline LTO prepared by sol-gel process was 158mAh/g in the first cycle, however considerable capacity drop of about 40% was observed during cycling. This is obviously the consequence of irreversible structural changes induced by Na accommodation in the Li₄Ti₅O₁₂ lattice. The best cycling stability for Na insertion exhibited commercial LTO from Altair. After 50 cycles at 1C the charge capacity of this material (with 20% Super P additive) decreased from initial 105 mAh/g to 85 mAh/g, i. e. of about 20%.

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References

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