

# Li (Na) insertion in TiO<sub>2</sub> polymorphs and their composites with graphene for battery applications

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## Abstract

Both TiO<sub>2</sub> polymorphs (anatase and TiO<sub>2</sub> (B)) and TiO<sub>2</sub> based 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[1, 2]. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (spinel, LTO) has attracted attention as a promising candidate for Li-ion battery anode material due to its excellent Li-ion insertion/extraction reversibility with zero structural change[3]. Due to limited size of reserves and higher cost to obtain Li, Na-based compounds have made a comeback and several reports on Na storage in LTO and TiO<sub>2</sub> have been published recently as well[4]. The reversible reaction,  $\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3\text{e}^- = \text{Li}_7\text{Ti}_5\text{O}_{12}$ , takes place at a relatively high potential of 1.55 V vs. Li<sup>+</sup>/Li, hence one can avoid the dendrite problem, differently from carbon-based materials, though at the expense of the lower working potential difference in resultant batteries. This character of LTO should also prevent the Na-dendrite deposition, and LTO should be a promising candidate of a negative electrode material for Na-ion batteries. However, there are still issues to be addressed; poor electrical conductivity and sluggish Li/Na ion diffusion resulting in poor rate capability. Efforts to improve the rate capability of TiO<sub>2</sub> and LTO include a synthesis of nanosized particles to shorten the Li<sup>+</sup>/Na<sup>+</sup> diffusion path and coating with conductive species. The maximal Li-insertion coefficient  $x$  (in Li <sub>$x$</sub> TiO<sub>2</sub>) is usually close to 0.5 for anatase, but larger reversible capacities,  $x = 0.8$  were also reported in certain anatase nanostructures[2]. Similar or even larger insertion coefficients were obtained for TiO<sub>2</sub> (B). An opened channel structure of this metastable monoclinic modification of titanium dioxide is particularly suitable for Na storage.

Graphene has superior electronic conductivity and is an ideal conductive additive for hybrid nanostructured electrodes. Electrochemical tests reveal that the presence of reduced graphene oxide can increase the capacity and cycling stability of LTO anodes, especially at higher C rate[5].

In our work we carried out systematical screening of morphology-dependent and particle size-dependent electrochemical performance of different TiO<sub>2</sub> polymorphs, LTO and their composites with graphene prepared by both dry and wet coating with graphene oxide during cyclic voltammetry of Li insertion and chronopotentiometry. The LTO-graphene composite containing 5% of graphene made by wet coating exhibited improved specific capacity of 169mAh/g as compared to that of pure LTO (143 mAh/g). Li insertion in TiO<sub>2</sub>(B) was considerably facilitated by reduced graphene oxide coating (Figure 1). The specific capacity calculated from cathodic branch of cyclic voltammogram increased from 105 mAh/g (TiO<sub>2</sub>(B)) to 188mAh/g for TiO<sub>2</sub>(B) composite with graphene. In addition to this an influence of coating procedure on properties of final composite was studied as well. Electrochemical behavior of composites made by wet coating was superior to dry coated or non-coated TiO<sub>2</sub> and LTO.

This work was supported by the Grant Agency of the Czech Republic (contract No. 15-06511S).

## References

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**Figure 1**

Cyclic voltammograms of Li insertion into  $\text{TiO}_2(\text{B})$  and  $\text{TiO}_2(\text{B})$ -graphene composite. Scan rate: 01mV/s, electrolyte: M LiPF<sub>6</sub> in EC/DMC (1:1).

