Mechanism of alkali metal insertion into TiO_2 polymorphs

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TiO_2 (anatase) and TiO_2(B) (monoclinic polymorph of TiO_2) are attractive candidates for anodes in rechargeable Li-ion batteries, due to their cycling stability, reasonable capacity and operating potential. Li insertion into TiO_2 polymorphs proceeds as a diffusion controlled process, where the peak current in cyclic voltammogram scales with square root of the scan rate. Excess Li can be accommodated either at the surface of the nanometer-sized particles or at the open channels in the structure of particular polymorphs by a pseudocapacitive faradaic process, which is not controlled by diffusion. In this case, currents in the peaks of cyclic voltammograms of Li scale with the first power of scan rate.

Li-insertion electrochemistry of TiO_2(B) is basically different from that of anatase. Accommodation of Li in the TiO_2(B) lattice manifests itself by two pairs of peaks in cyclic voltammogram with formal potentials of ca. 1.5 and 1.6 V. Zukalova et al[1] found that Li-insertion into TiO_2(B) is characterized by unusually large faradaic pseudocapacitance. This peculiar effect was ascribed to Li^+ accommodation in open channels of TiO_2(B) structure allowing fast Li-transport in TiO_2(B) lattice along the b-axis (perpendicular to (010) face). Deeper insight into differences between charging mechanisms of TiO_2(B) and anatase during Li^+ insertion provides analysis of cyclic voltammograms of Li insertion. The ratio of capacitive contributions to overall charge of Li-storage was found to be over 30% higher in TiO_2(B) compared to that in anatase nanocrystals[2]. The predominant pseudocapacitive process in TiO_2(B) was related to accommodation of Li inside the TiO_2(B) open channels in monoclinic lattice.

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References

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