Abstract

Titanium dioxide (TiO_2) and spinel $Li_4Ti_5O_{12}$ belong to widely studied semiconducting metal oxides. Nanocrystalline TiO_2 and $Li_4Ti_5O_{12}$ are attractive materials for applications in Li-ion batteries and the former also for photoelectrochemical solar cells. Moreover, spinel $Li_4Ti_5O_{12}$ could be a promising material for Na-ion batteries too, because of possible accommodation of larger Na^+ ions (compared to Li^+). The nanocrystalline TiO_2 anatase with a predominant {001} facet was studied electrochemically by cyclic voltammetry of Li^+ insertion and by chronoamperometry and compared with anatase materials with dominating {101} facet. Both voltammetric and chronoamperometric diffusion coefficients and activation energies proved higher activity of anatase {001} nanosheets toward Li^+ insertion than that of the usual anatase nanoparticles exposing the {101} facet. Subsequently, the flatband potential and electron kinetics of TiO_2 anatase nanocrystals with mostly exposed facet {101} or {001} were compared. The anatase {001} nanoplatelets exhibited more negative flatband potential, higher chemical capacitance and longer electron lifetime than anatase {101} nanoparticles. The Li^+ insertion into TiO_2 anatase nanoparticles was studied by Raman spectroscopy and by in situ Raman spectroelectrochemistry. Four combinations of isotopologues, namely $^{6/7}Li_xTi^{16/18}O_2$ (x is the insertion coefficient), were prepared and studied. The combination of experimental and theoretical Raman frequencies with the corresponding isotopic shifts brings new inputs for still open questions about the Li-insertion into TiO_2 (anatase). The cyclic voltammograms of Li^+ insertion into TiO_2 (B) and anatase provided information about capacitive contributions to the overall charge of Li-storage. The enhancement by 30% is found in capacitive charges (normalized to the total voltammetric charges) in TiO_2 (B) compared to those in anatase. Facilitated Li-insertion in TiO_2 (B) is explained by different charging mechanism caused by pseudocapacitive Li-storage in the bulk TiO_2 (B). Sodium insertion into nanocrystalline spinel, $Li_4Ti_5O_{12}$ (nanoLTS) was investigated by cyclic voltammetry. Changes in the cyclic voltammograms of nanoLTS were observed during long-term cycling. Raman spectroscopy of nanoLTS after Na-insertion reveals a formation of orthorhombic $Li_{0.5}TiO_2$ phase. The occurrence of this phase is ascribed to induced Li^+ redistribution into trace anatase impurities.