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Lithium insertion into mesoscopic and single-crystal TiO₂ (rutile) electrodes

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Abstract

Electrochemical behavior of single-crystal and mesoscopic TiO₂ (rutile) was studied in propylene carbonate solutions at potentials negative to the flatband potential. In electrolytic solutions containing sodium or tetrabutylammonium (Bu₄N⁺), the injected charge is compensated by protonization of the surface and/or by adsorption of cations in the double layer. In electrolytic solutions containing Li⁺, the insertion into the rutile lattice occurs at potentials below 1.5 V (Li/Li⁺). At higher potentials, the charge is compensated mainly by a nonfaradaic process. Lithium insertion into rutile proceeds at a potential ca. 0.4 V more negative than the insertion potential into anatase. The maximum insertion capacity of rutile is also lower than that of anatase. The insertion of lithium into rutile is accompanied by an increase of the electrode mass, while the mass/charge relations show hystereses between anodic and cathodic potential sweeps. This behavior is explained in terms of a free convection in the electrode vicinity.

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