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Insertion of lithium into mesoscopic anatase electrodes - An electrochemical and in-situ EQCM study

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Abstract

The insertion of Li^+ into mesoscopic TiO_2 (anatase) electrodes was studied using cyclic voltammetry combined with the in situ gravimetric monitoring of the electrode mass in LiClO_4 and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ /propylene carbonate (PC)-based solutions. The insertion of Li^+ takes place at potentials less than 2.0 V vs Li/Li^+ . The cathodic process is associated with a mass uptake; the subsequent oxidation process is associated with a mass decrease. The apparent molar mass of the inserted/extracted material is, however, remarkably different from that expected for the simple insertion/extraction of unsolvated Li^+ ions. For a more accurate description of the behaviour of the mesoscopic anatase electrodes, we consider them as gold electrodes modified with a porous film. Thus, the mesoscopic anatase electrode behaves similarly to a polymer-modified electrode, i.e. the overall process includes coupled electron/ion transfer (insertion of Li^+) and a transfer of neutral species. Analysing the EQCM (electrochemical quartz crystal microbalance) data, one can conclude that the controlling step of the insertion/extraction of Li^+ into/from anatase electrodes is a coupled electron/ ion transfer or the transfer of neutral species in solutions containing ClO_4^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ respectively.
