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 TiO2 (anatase) electrodes was studied using cyclic voltammetry combined with the in situ gravimetric monitoring of the electrode mass in LiClO4 and Li(CF3SO2)2 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 of neutral species in solutions containing CIO4 - and (CF3SO2)2N- respectively.