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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 $\text{Li}(\text{CF}_3\text{SO}_2)_2$ 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.

Introduction

The insertion of Li^+ into titanium dioxide (anatase) is a process with considerable theoretical and practical interest. From the theoretical point of view, this reaction may be used to characterise the TiO_2 band energetics—e.g. the flat band potential [1, 2]. From the practical point of view, because of its ability to act as a host for Li^+ , the TiO_2 may be considered as a material for lithium [3] or rocking-chair batteries [4]. Despite the attention paid to this process so far, the published results are still rather contradictory.

The injection of an electron into the conduction band of TiO_2 in accumulation regime creates a negative charge in the solid state, which must be compensated either by adsorption or insertion of a cation. Since the insertion reactions are generally topotactic [5], the essential criterion that decides whether the compensation process will be adsorption or insertion can be derived from the crystallographic data. According to neutron diffraction data, there are channels in the anatase lattice the diameter of which is ca. 0.07 nm [6]. This fact restricts the insertion process to cations of a diameter smaller than 0.07 nm. This is the case only for Li^+ (ionic diameter 0.068 nm) (and for Be^{2+} , though the reaction has not yet been studied in Be^{2+} containing solutions). There are several reports that the Li^+ may be inserted/extracted into/from a TiO_2 (anatase) electrode; the overall process may be described by the following equation



where the x may be 0.5 [7], 0.6 [3], 0.8 [8] or 1 [9]. The values of x were obtained using various methods e.g. galvanostatic charge/discharge [7–9], but the insertion levels up to 0.5 can also be achieved by slow cyclic voltammetry [10].

Additional information about the process may be gathered by exploiting the fact that the electrode reaction should always change the electrode mass (reduction

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should lead to mass increase, and oxidation to mass decrease). In this paper we present the data obtained by the study of Li^+ insertion into mesoscopic TiO_2 (anatase) electrodes using an EQCM (electrochemical quartz crystal microbalance) coupled with cyclic voltammetry. The obtained electrochemical (I and Q) and mass change (ΔM) transients are used to analyse the overall process and to separate the contributions of ionic and neutral species.

Experimental

Propylene carbonate (PC) (Fluka) was vacuum distilled and dried over a 4-Å molecular sieve before use. LiClO_4 and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (both Fluka) were dried at 120 °C at 0.1 mPa. All solutions were prepared and stored in an Ar-filled glove box (water content < 10 ppm); the electrolyte solutions were purged with argon and dried over a molecular sieve. The typical trace water content was between 50 and 90 ppm as measured by Karl Fischer titration using the WTK 891 titrator (Diram, Czech Republic).

All experiments were performed on the anatase electrodes prepared on the AT cut 10-MHz quartz crystals (International Crystal Manufacturing, Okla., USA) with deposited "key-hole" shaped gold contacts (1000 Å of Au on 100 Å of Cr). TiO_2 (anatase) electrodes were prepared by sintering colloidal TiO_2 particles at 450 °C for 45 min directly at one of the crystal contacts. The anatase colloid was prepared by a method described elsewhere [11, 12]. The sintered films were less than 10- μm thick and were composed of spherical particles of average diameter 14 nm [12]. The porosity of the sintered films was ca. 49%; no pores greater than 14 nm were found (A. Zukal, unpublished results). All electrochemical experiments were performed in a three-electrode arrangement with a Pt foil auxiliary electrode using the PAR 263 potentiostat. Working electrode potentials were measured and are quoted with respect to the $\text{Li}/0.5 \text{ M Li}^+$ reference electrode. The mass transients were measured using an EQCM apparatus based on the microbalance circuitry described by Bruckenstein et al. [13].

Results and discussion

Typical cyclic voltammograms of the anatase electrode in 0.5 M LiClO_4/PC and 0.5 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{PC}$ solutions are shown in Fig. 1. There is a reduction process during the cathodic scan with potential onset at ca. 2.0 V showing a current peak at ca. 1.5 V. The corresponding anodic process is characterised by a peak at ca. 2.05 V in the case of perchlorate solutions and ca. 2.25 V in the case of $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ -containing solutions. The cathodic peak may be assigned to the insertion and the anodic peak to the extraction of Li^+ into/from anatase electrode. However, the requirement of the 100% coulombic reversibility predicted by Eq. 1 is not usually fulfilled in real experiments because of cathodic side reactions [10]. The trace water and, presumably, also the propylene carbonate itself are involved in a rather complex cathodic process, which takes place at ca. 1.3–1.4 V [10], i.e. simultaneously with Li^+ insertion. The identification of the products of this breakdown process has been subject of various studies, and several compounds were detected, namely LiOH

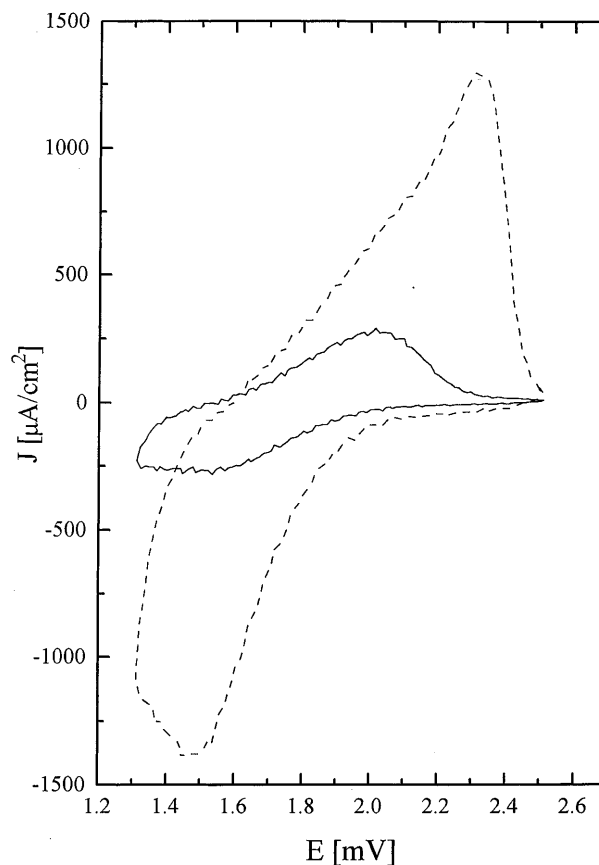


Fig. 1 Cyclic voltammograms of a mesoscopic TiO_2 (anatase) film ($\Gamma = 1.25 \mu\text{mol cm}^{-2}$) in 0.5 M $\text{LiClO}_4/\text{propylene carbonate}$ (full curve) and in 0.5 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{propylene carbonate}$ (dashed curve) solutions. Scan rate 20 mV/s

[14, 15], LiHCO_3 [15], Li_2CO_3 [16, 17], $\text{Li}_2\text{CH}_3\text{CH}(\text{CO}_3)\text{CH}_2(\text{CO}_3)$ [17], $\text{LiR}(\text{CO}_3)$ ($\text{R} = \text{alkyl}$) [17].

The observed coulombic reversibility (Q_A/Q_C), which is ca. 81% in both solutions, can be therefore accounted for by these cathodic side-reactions proceeding either on the anatase-electrolyte solution or on the Au-electrolyte solution interfaces (note relatively high porosity of the TiO_2 films). Because of the low solubility of the products of breakdown side reactions we can also expect an incomplete mass recovery during the CV experiments (see below). The charge determined from the cyclic voltammograms corresponds to the x ranging from 0 to 0.1 (note the surface coverage of the crystal on figure captions).

The change of the electrode mass, ΔM , observed to occur with CV, is shown in Fig. 2. The dependence of the mass change transient, however, differs in ClO_4^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ -containing solutions. During the reduction in the perchlorate solution, the mass of the electrode practically does not change until the electrode potential reaches ca. 2.0 V. In the subsequent anodic scan, the electrode mass starts to decrease at potentials greater than 1.7 V. In the $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ -containing solution, the ΔM vs E curve is much broader than in the case of ClO_4^- solution. Both the electrode mass increase

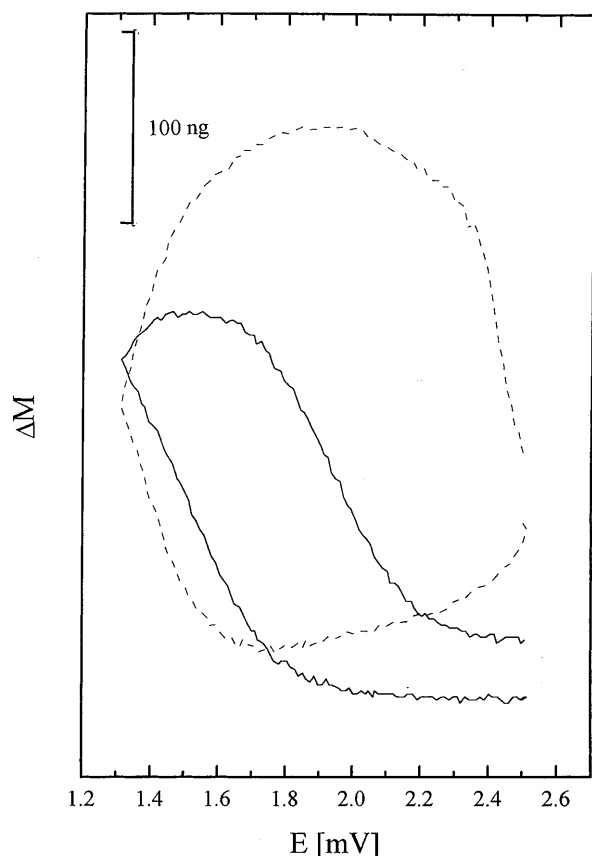


Fig. 2 ΔM vs E plot for a TiO_2 (anatase) film ($\Gamma = 1.25 \mu\text{mol cm}^{-2}$) in 0.5 M LiClO_4 /propylene carbonate (full curve) and in 0.5 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ /propylene carbonate (dashed curve) solutions. Data acquired simultaneously with CV experiment. Scan rate 20 mV/s

and the electrode mass decrease exhibit a “momentum” with respect to the applied potential. While in the ClO_4^- -containing solutions the ΔM signal starts to change at the same potentials as those at which the current starts to change in the cyclic voltammogram, in the $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ -containing solution the mass change onsets are shifted by ca. 200 mV with respect to those of the current in the cyclic voltammogram. It is necessary to note that in both cases the ΔM vs E dependence is an open curve, i.e. the mass change in the cathodic scan is greater than that of the anodic scan. The mass change reversibility ($\Delta M_A/\Delta M_C$) was about 85% in both cases. These values are in good accordance with relatively low coulombic reversibility (see above) caused by cathodic side reactions. Nevertheless, an incomplete charge and mass recovery of a kinetic nature cannot be fully excluded under given experimental conditions.

Quantitative characterisation of the mass change data using the calculation of the apparent molar mass M_{ap} of the inserted/extracted species according to the equation

$$M_{\text{ap}} = \Delta M_{\text{tot}} F / Q \quad (2)$$

where ΔM_{tot} is the overall mass change in the anodic or cathodic process, F is the Faraday constant and Q is the

charge equivalent to the total mass change upon oxidation or reduction yields the value of the apparent molar mass $12.0 \pm 0.4 \text{ g/mol}$ of electrons in ClO_4^- -containing solution and $4.8 \pm 0.1 \text{ g/mol}$ of electrons in $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ -containing solution. The apparent molar mass observed for the perchlorate solution is larger by ca. 60% than the value expected according Faraday’s law and Eq. 1; in the case of $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ -containing solution, the M_{ap} is, however, lower by 30% than the expected value. The difference between the insertion process in LiClO_4 and $\text{Li}(\text{CF}_3\text{SO}_3)_2\text{N}$ is evident also from the ΔM vs Q curves (see Fig. 3). The dashed line in both graphs indicates the mass transient corresponding to the Li^+ insertion according Faraday’s law. The value of ΔM observed during cyclic voltammetry in ClO_4^- -containing solution is always larger than the calculated value; also, the anodic and cathodic mass transients track each other. On the other hand, the mass change transient observed in $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ -containing solution is always lower than the calculated value. This curve also shows evident hysteresis between the anodic and cathodic branches.

Since there is no chance for any other species but Li^+ to enter the channels of the anatase structure (i.e. the solid phase of the electrode), the only possible explanation of the deviations between experimental and theoretical values of M_{ap} is that EQCM measurements reflect a more complex process than the insertion of Li^+ and the influence of the anion on the electrode process should also be considered.

Values of the apparent molar mass greater than 7 g/mol of electrons (the theoretical value) were reported by Lyon and Hupp [18], who observed the M_{ap} values ranging from 7 to 22 g/mol of electrons by cyclic voltammetry of a TiO_2 in 0.1 M LiClO_4 solution in acetonitrile. They explained such a high value by the presence of dissolved oxygen, which leads to the incorporation of O^{2-} and formation of the Li_2TiO_3 in the electrode [18]. Nevertheless, the highly irreversible character of such a process (which should finally lead also to the suppression of the electrochromism) does not accord with our observations. Besides, the process proposed in [18] would explain only deviation towards greater values of M_{ap} and not to lower ones [$(\text{CF}_3\text{SO}_3)_2\text{N}^-$ -containing solutions] and, therefore, should not be used in our case.

An alternative approach can, however, be adopted if we take into account the following features of our anatase electrodes: (1) the anatase electrodes in completely oxidised state are practically insulating, (2) the faradaic process directly involves the electrode material, forming a charge excess in it which must be compensated by an ionic process, and (3) there might generally be a volume change of the electrode upon the redox switching, although in the case of the anatase electrode this volume change is negligible [19]. All these features are also common to electrodes modified by an electroactive polymer. Therefore, we can similarly describe our system as a polymer-modified electrode [20]. The redox

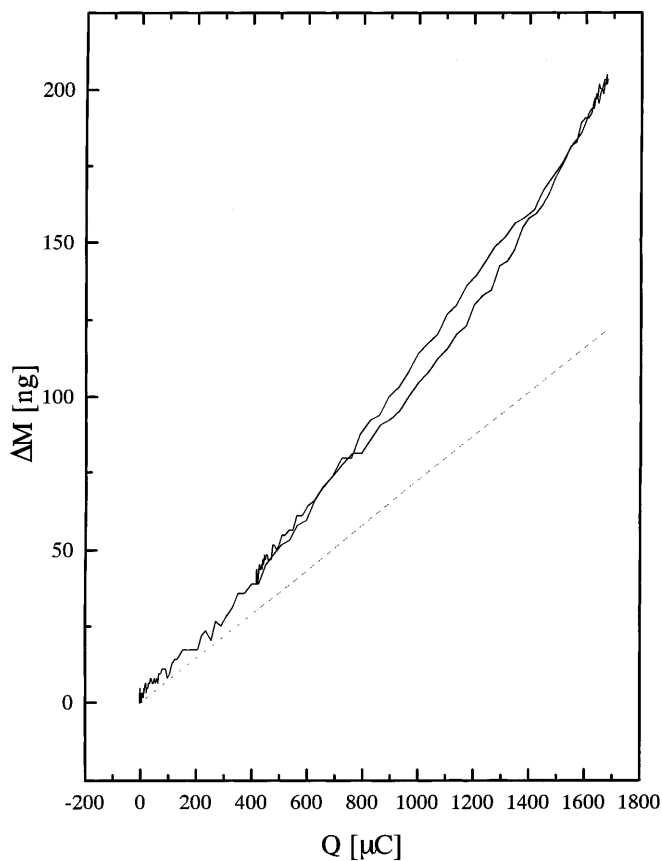
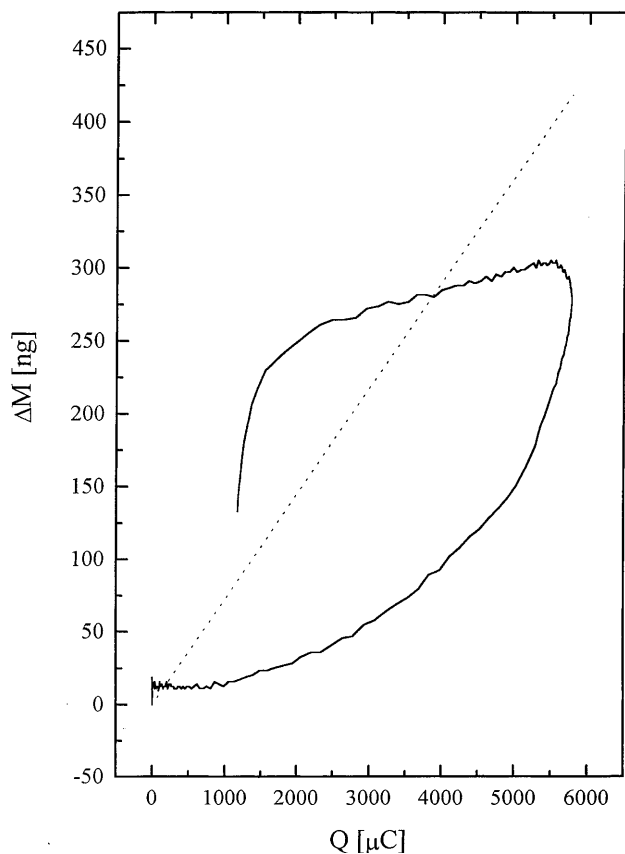


Fig. 3 a ΔM vs Q plot for a TiO_2 (anatase) film ($\Gamma = 1.25 \mu\text{mol cm}^{-2}$) in 0.5 M LiClO_4 /propylene carbonate. Data extracted from the CV experiment. Experimental conditions as Figs. 1 and 2, **b** ΔM vs Q plot for a TiO_2 (anatase) film ($\Gamma = 1.25 \mu\text{mol cm}^{-2}$) in 0.5 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ /propylene carbonate solution. Data extracted from the CV experiment. Experimental conditions as Figs. 1 and 2

switching of such an electrode can be viewed as a consequence of a coupled electron/ion transfer, neutral species transfer and a “reconfiguration” [20]. The neutral species transfer may then be divided into solvent transfer and salt (ion pairs) transfer. The mass fluxes corresponding to these fundamental steps may cause either increase or decrease of the electrode mass, depending on experimental conditions. Since the contribution of the coupled electron/ion transfer can be precisely determined from the charge passed, the only processes which can cause deviations from the behaviour predicted by Faraday’s law must be the transfer of neutral species and/or “reconfiguration”. Since in the case of redox switching of TiO_2 we observe a negligible volume change [19], we can also neglect the reconfigurational processes. Therefore, in view of this model [20], we may conclude that the remarkable deviations in M_{ap} must be caused by a transfer of neutral species.

The concept of neutral species transfer seems to oppose the previously mentioned statement that no other species but Li^+ may enter the anatase structure for steric reasons. However, as is generally known from EQCM theory [21], the EQCM signal does not just reflect the mass change of the crystal and the oxide layer itself, but it is also affected by the mass changes in a thin adjacent layer of the electrolyte solution, which oscillates together with the crystal (see [21] and references therein). The thickness of this layer depends on the viscosity of the solution, and, in the case of propylene carbonate based solutions, it would be of the order of 10^{-7} m (see the scheme in Fig. 4). The total mass change thus has to be viewed as a sum of various mass fluxes crossing the plane at a distance L_0 . Even if the neutral species do not enter the anatase structure, there are some processes which may be proposed to explain the neutral species transfer. One such process is a rearrangement of the double layer in the mesopores of the sintered anatase film upon oxidation/reduction. In such a case, the overall neutral species transfer may flow either to or from the electrode. The actual value and orientation of this flux then should depend on various factors, e.g. on electrolyte concentration, anion size, electrode microstructure etc.

The above approach [20] can also be used to identify the rate-limiting process in the redox switching employing the CV and EQCM data. Applying this formalism [20] to our data, we find that the insertion process is far from ‘equilibrium’ on the timescale of our experiment (it is questionable whether an anatase film prepared by this procedure would reach equilibrium on a reasonable timescale at all). As shown by analysis of the ΔM vs Q curves, the controlling step in the case of



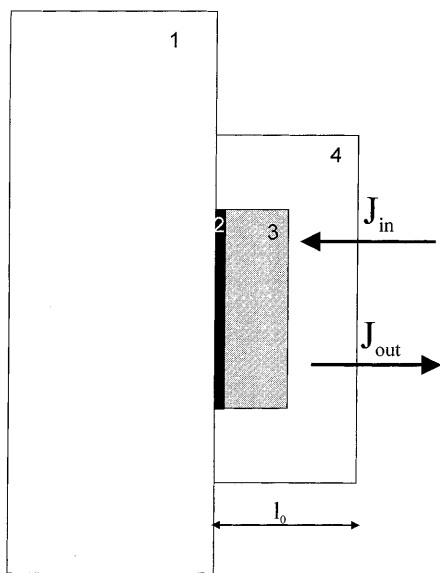


Fig. 4 Schematic representation of the situation at the TiO_2 /electrolyte solution interface during an EQCM experiment. Quartz crystal (1), Au contact (2), TiO_2 layer (3), electrolyte solution (4) oscillating simultaneously with the crystal

LiClO_4^- -containing solution is probably the coupled electron/ion process; in the case of $\text{Li}(\text{CF}_3\text{SO}_3)_2\text{N}^-$ -containing solution some neutral species transfer process seems to be the rate-determining step.

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