SHORT COMMUNICATION

Insertion of cations into WO$_3$ investigated by QCM techniques

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Abstract The electrochemical insertion of Li$^+$, Na$^+$, and hydrogen ions into thin layers of WO$_3$ was investigated with the help of an electrochemical quartz crystal microbalance. Solutions of perchlorates in propylene carbonate were used as electrolytes, and the first cycle of coloration/discoloration cycles was studied. In both cases, insertion of cations was accompanied by a massive and partly irreversible uptake of the solvent in a molar ratio from 1:1 to 1:2 (ion vs solvent). The insertion of Na was observed for the first time. Molecules of water coinserted with H$^+$ indicated that the inserted species is H$_3$O$^+$ rather than merely a proton H$^+$. Very small but observable insertion of Mg^{2+} from perchlorate/PC solution proceeded in a marginal but observable extent from ClO$_4^-$/PC solution.

Keywords Tungsten trioxide · Insertion of cations · Quartz crystal microbalance · Coinsertion of solvent

Introduction

The electrochemical insertion or intercalation of ions into various solid bodies is the fundamental principle of many processes such as lithium ion batteries and electrochromic devices. It is based on the incorporation of these ions into the voids in the crystal structure of a solid body compound while the corresponding charge enters free energy levels in the solid from the outer electric circuit. Some of the materials used in these reactions can be prepared as thin layers, preferably by vacuum deposition. Among them, the tungsten trioxide WO$_3$ is rather interesting as an active material for electrochromic systems. The mass of inserted ions can be detected using the techniques of quartz crystal microbalance (QCM).

The status of inserted ions is not quite a solved problem at present. In water, one can hardly expect insertion of a bare H$^+$ ion (i.e., a free proton). A question has arisen if the insertion proceeds via insertion of H$_3$O$^+$ species or if any hopping of hydrogen in the form of OH groups in the oxide occurs. The mass increase in the electrode material during the ion insertion could answer this.

Similarly, the solvent somehow influences insertion of lithium ions. An entirely new question is the probable insertion of sodium under the condition of an electrochromic process. Moreover, also other small ions (magnesium) should undergo this process in a very small and slow degree.

The aim of this paper was to find an answer to these questions by means of the QCM techniques.

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Theory

The electrochemical QCM method is based on the observation of resonance frequency. As a sensor, the substance under investigation was deposited by vacuum evaporation on a quartz crystal element (resonator). This thin layer is in contact with electrolytes [1]. Any change in mass of the layer changes the resonance frequency in a simple manner.

Therefore, we can perform any electrochemical measurement and observe the changes of mass simultaneously.

Usually, we have to calibrate the sensor. The electrodepositon of copper or silver and its dissolution is the most common method suitable for it.

Tungsten trioxide WO_3 is one of the most important substances used in working electrodes in electrochromic devices. The color change from almost colorless to deep blue is caused by electrochemical insertion of cations into the solid substance and undoubtedly is accompanied by the change of mass. As in many other electrochemical processes, the insertion of cation into a solid substance is influenced by the presence of a solvent. A survey of intercalation processes in WO_3 in connection to its use in electrochromic devices is given by Granqvist [2].

Several papers can be found on the use of QCM. For example, insertion of hydrogen in rf-sputtered WO_3 film was investigated by Dong-Jim Kim et al. [3] who pointed out the irreversible uptake of water followed by qacceleration of hydrogen insertion and simultaneous degradation of the film. Another investigation was performed by Bohnke et al. [4] who used impedance spectroscopy together with a QCM and found a mass uptake of the films because of ion intercalation. Moreover, they compared the reversible increase in mass and the change of optical parameters of the electrode.

The irreversibility of mass increase in the first cycling of an electrochromic electrode by lithium insertion was studied by Bueno et al. [5] in the case of an electrochromic Nb_2O_5 electrode and insertion of lithium. In addition, this work was conducted using a QCM device.

The presented paper describes some experiments focused on quantitative relation between charge and mass increase. Moreover, the attempt to observe electrochemical insertion of other ions into WO_3 was done and is described here.

Experimental

Instrumentation

Potentiostat EcoChemie-Autolab model PGSTAT-12 and the QCM unit PM-710 (product of Maxtek) were the main instruments used for the investigations. This arrangement made it possible to follow both the voltammogram and the gravimetric curve.

The calibration followed the recommendations and was conducted by electrodeposition and dissolution of copper from $CuSO_4$ aqueous solution. The calibration factor equal to 5.921 ± 0.013 mV μg^{-1} was found in our case.

Saturated calomel electrode and cadmium perchlorate gel electrode [6] were used for experiments in aqueous and aprotic electrolytes, respectively.

Preparation of the electrodes

The crystal elements (Maxtek) were washed by ethanol and a layer (200 to 400 nm thick) was deposited onto it from a WO_3 source in vacuum. Then, the electrode was put into the crystal holder and submerged into the electrolyte. The layer was amorphous as checked by X-ray diffraction. After each experimental run, the electrode was washed in water and dried at 120 °C.

Electrolytes

Insertion of Li^+, Na^+, and Mg^{2+} ions was tested in 0.1-M solutions of perchlorates in propylene carbonate (PC). All these chemicals were dried carefully before use. Insertion of hydrogen was observed using a 0.1-M solution of H_2SO_4.

Evaluation of results

The mass W_{QCM} was evaluated directly from the output signal of the QCM.

The total charge passed through the electrode was evaluated by simple numeric integration of the current using a simple numerical procedure. Then the mass increase was estimated from the expected molecular weight M, Faraday constant F, and a correction factor α:

$$W_q(t) = \frac{M\alpha}{F} \int_0^t \mathrm{j} \mathrm{d}t$$

In this paper, the correction factor α indicates real (effective) molecular weight $M_{eff} = M \alpha$ of particles that enter the WO_3 lattice. It can be explained either as a solvatation of the ion or just as a parallel process in which the insertion of an ion is accompanied by penetration of the solvent in the solid body. The value of the coefficient correction factor α was estimated according to criterions given below so that the overlapping of both values (W_{QCM} and W_q) was reasonable. Details are given below. Voltage step 1 mV offered low error because of the stepwise change of potential, and the result of integration was assumed as undistorted by it.

Results

Insertion of hydrogen

A typical example is shown in Fig. 1. In this study, the mass changes that took place during the voltammetric sweep (scan rate 5 mV s^{-1} was used in this case) are plotted vs the electrode potential. The solid line represents the mass
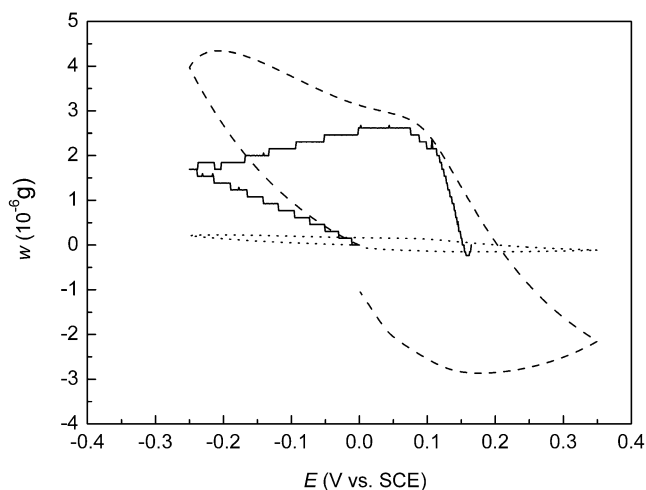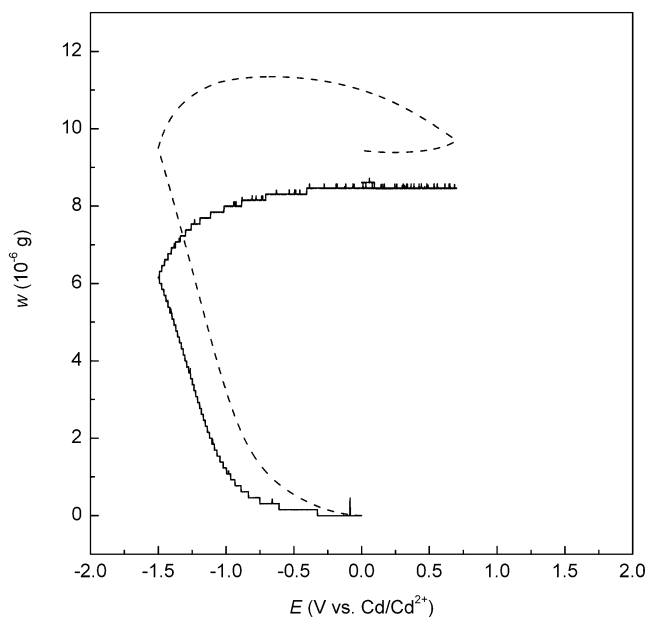
Fig. 1 Mass change of a WO$_3$ deposited on a QCM probe in a 0.1-M solution of H$_2$SO$_4$ in water. *Solid line*, mass changes evaluated from the output of the QCM. *Punctuated line*, mass changes calculated from the charge (obtained by integration of voltammograms) using the Faraday law and assuming a molecular weight of the inserted species equal to 1 g mol^{-1}. *Broken line*, mass estimated under the assumption of molecular weight equal to 19 g mol^{-1}. *Horizontal axis*, potential vs SCE. Scan rate, 5 mV s^{-1}

changes estimated from the output of the QCM device using the calibration factor given above. It is stepwise distorted because of the digital principle of the QCM device and the rather small increment of weight. The change of charge absorbed by the electrode was converted in a mass change by the Faraday law on the assumption that the molecular weight (i.e., factor α) is equal to 1. This is plotted as a punctuated line in Fig. 1. We can easily see that the mass evaluated from the QCM output is by an order of magnitude higher than that from the evaluation of charge. Therefore, we suggest the hypothesis that one H$^+$ ion is inserted together with one molecule of water. This means that H$_3$O$^+$ ions are inserted, and it follows that α will be 19. The mass changes calculated in this manner are plotted in Fig. 1 by the broken line. These values are at least qualitatively similar to the values obtained from the QCM. The value α=19 corresponds to the maximum of the charge at potential E=0 V on the reverse curve of the cyclic voltammogram. Hence, the incorporation of H$_3$O$^+$ ion instead of just a proton should be considered.

The process is almost reversible if the potential does not exceed +0.18 V.

Insertion of lithium and sodium

The values W_q and W_{QCM} for lithium are plotted in Fig. 2 in the same manner (at san rate 2 mV s^{-1}). Apparently, the mass increase is much higher, and the stepwise distortion because of digitization by the digital to analog conversion in the QCM device is not so markedly visible. In this case, the factor apparent molecular weight equal to 125 was taken as

Fig. 2 Mass changes of a WO$_3$ deposited on a QCM probe in a 0.1-mol l^{-1} solution of LiClO$_4$ in PC. *Solid line*, mass changes were evaluated from the output of the QCM; *broken line*, mass estimated under the assumption of molecular weight of inserted species equal to 125. Reference electrode Cd/Cd^{2+} in PC. Scan rate, 2 mV s^{-1}

the best approximation. T number corresponds to one molecule of PC for one lithium ion entering the WO$_3$ layer. The values obtained using α=1 are not plotted in this figure.

Insertion of sodium was tested analogically. The results are plotted in Fig. 3 (obtained at san rate 2 mV s^{-1}). The
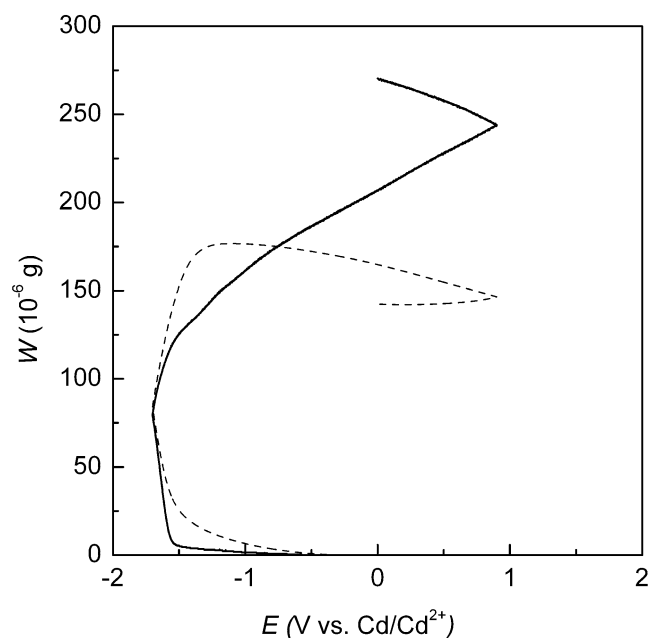
Fig. 3 Mass changes of a WO$_3$ deposited on a QCM probe in a 0.1-mol l^{-1} solution of NaClO$_4$ in PC. *Solid line*, mass changes were evaluated from the output of QCM; *broken line*, mass estimated under the assumption of molecular weight of inserted species equal to 273. Reference electrode Cd/Cd^{2+} in PC. Scan rate, 2 mV s^{-1}

similarity of both curves is not as obvious as in previous cases. As we can see, the similarity of W_q and W_{QCM} was obtained using the apparent molecular weight 273, which suggests two molecules of PC per one Na ion. However, the similarity is apparent on the first (descending) branch of the voltammogram from the starting value to the first vertex point. Even if the potential increased backwards (the ascending part of the curve), the mass increased continuously. The electrode was bleached at the same time. Apparently, it is some incorporation of PC or its reduction products into the layer or deposited on its surface.

Hence, we may consider coinsertion of the solvent and ions in a ratio close to one or two molecules of solvent to one ion of sodium.

The system WO_3—Mg^{2+}

An attempt to observe the electrochemical insertion of magnesium ions into WO_3 was performed. The results are qualitative only because the changes of the QCM output voltage were very close to the limit of its sensitivity just within three or four steps caused by the output signal in the range of the lowest bites of the frequency counter in the Maxtek control unit. A very low scanning equal to 0.1 mV s^{-1} rate had to be used. Therefore, roughly estimated magnesium diffusion coefficient should be by three to four orders lower than those of Li$^+$ and/or Na$^+$. The process needed some time to start on the descending part of the voltammetric curve despite the low scanning rate. The electrode underwent a slight greenish-blue coloration. The results are difficult to quantify, but they clearly showed that the insertion did proceed, to a small extent at least. The low diffusivity of magnesium ions is undoubtedly caused by their higher charge yielding stronger interactions with the lattice.

Conclusions

The quantitative comparison of charge absorbed by an electrochromic WO_3 electrode and of the mass increment has indicated clearly that ions do not enter the space lattice alone but accompanied by molecules of the solvent. In the case of hydrogen ion, we can consider the entering of hydroxonium ion H_3O^+. Slightly more difficult is the explanation of PC entering the lattice.

The electrochemical insertion of sodium ion seems quite a new observation; so is the qualitative observation of Mg^{2+} insertion into WO_3.

According to our results, the coinsertion of propylene carbonate seems well evidenced, qualitatively at least.

Further investigations will focus on the status of propylene carbonate and the behavior of this species in the process of cycling.

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