SPECTROSCOPIC INVESTIGATION OF LITHIUM INTERCALATION IN THIN FILMS OF ANATASE TITANIUM DIOXIDE

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ABSTRACT

Thin films of anatase TiO_2 have been deposited on tin-doped indium oxide (ITO) and Sb-doped tin oxide using electron beam evaporation. Subsequently these samples have been mounted into an electrochemical cell. Assuming a composition of Li_xTiO_2 with x being 0.5 or 1, voltammetric measurements show that all lithium is present within the first 15 or 7.5 nm of the TiO_2 film, respectively. Stepped potential experiments in combination with optical transmission measurements show that de-intercalation is much faster than intercalation. Differential absorption spectra as a function of intercalation potential suggest that the observed dark coloring of intercalated anatase can be attributed to electron traps at Li^+ sites. This contradicts assumptions made in literature that the coloring mechanism of anatase is based on intervalence charge transfer from Ti^{4+} to Ti^{3+} .

INTRODUCTION

Anatase TiO_2 is a promising candidate for devices based on lithium intercalation, such as electrochromic windows¹⁻⁴ and rocking-chair lithium-ion batteries.^{5,6} Porous nanostructured films can be used to increase the specific surface area of the electrode, thereby decreasing the diffusion path length for the lithium ions. This results in a large enhancement of the efficiency and speed of the device.¹

Though a considerable amount of research has already been dedicated to lithium intercalation in titanium dioxide,¹⁻⁹ some fundamental questions remain unanswered. The mechanism of lithium intercalation has not yet been fully resolved. Another point of discussion is the rate-determining step of the intercalation process, for which both diffusion limited^{2,9} as well as surface-adsorption limited⁷ processes have been suggested. There is also the question what will happen to the electrons once lithium is intercalated into the titanium dioxide. These electrons can be donated to the conduction band, or be trapped at Li^+ , Ti^{4+} , or positively charged oxygen vacancies.

In this work lithium intercalation in electron-beam evaporated thin films of anatase TiO_2 is studied. Films deposited with electron beam evaporation are extremely smooth, which enables a more accurate interpretation of the results than is possible with sputtered films.² Evaporated films can be made with approximately the same donor density as porous films, i.e. in the order of $\approx 10^{17} \text{ cm}^{-3}$. Several aspects of the intercalation process are described using voltammetric, stepped-potential and spectroscopic techniques. Results are related to electronic properties of the intercalated material.

EXPERIMENTAL

Electron beam evaporation of reduced TiO_2 was used to deposit thin films of anatase TiO_2 on both ITO coated glass (80 nm ITO on glass, Glastron, $30 \Omega/\square$) and Sb: SnO_2 coated quartz substrates. The Sb: SnO_2 films, having a thickness of 100 nm, were made by electron beam

evaporation of a mixture of Sb_2O_3 and SnO_2 powders. The target material for TiO_2 deposition was anatase powder (Acros Chimica, 99.95+%) reduced in a hydrogen atmosphere at 1000°C for 6 hours. Deposition took place under a controlled O_2 atmosphere of 1×10^{-4} mbar, with an argon background pressure smaller than 2×10^{-6} mbar. During deposition the substrates were heated to 375°C . Typical growth rates, monitored with a quartz microbalance, were 2 nm/min. After deposition a heat treatment of 12 hours at 450°C in air was carried out to restore stoichiometry. The TiO_2 film thickness is 80 nm in all experiments.

Electrochemical and spectroscopic measurements were carried out in a conventional three-electrode electrochemical cell. Glassy carbon was used as a counter electrode, while a saturated calomel electrode (SCE) served as a reference electrode. All potentials mentioned will be referred to as versus SCE. As an electrolyte a 1 M LiClO_4 solution in propylenecarbonate was used. Since water absorption by the electrolyte could in our case not completely be avoided, 1% water was added deliberately in order to get a constant water concentration.

RESULTS AND DISCUSSION

A convenient method to follow the Li-intercalation in titanium dioxide is by standard voltammetric and optical transmission measurements, shown in Figure 1. The peaks at -1.35 V and -0.78 V can be attributed to lithium intercalation and de-intercalation respectively, since these peaks are not observed if the same measurement is performed in an electrolyte not containing LiClO_4 . The intercalation process shows a good reversibility after several scans.

Figure 1. Current (Δ), charge ($\square$), and optical transmission ($\circ$) curves recorded as function of potential during lithium intercalation and de-intercalation of thin film anatase TiO_2 . The surface area under the de-intercalation peak at -0.78 V corresponds to a charge of $3.4 \times 10^{-3} \text{ Ccm}^{-2}$.

When monitoring the transmission with 650 nm light, coloring and bleaching of the electrode occurs at the same potentials as where the peaks are located. At cathodic potentials

side-reactions are present, which are probably caused by the reduction of water. To determine the amount of lithium that has been intercalated, the current has been integrated to yield the total charge passed through the system (Figure 1). Due to the occurrence of side-reactions at very negative potentials, only the de-intercalation peak should be integrated, yielding a total charge of $3.4 \times 10^{-3} \text{ C cm}^{-2}$, corresponding with $3.5 \times 10^{-8} \text{ mol cm}^{-3}$. If one assumes a constant stoichiometry of $\text{Li}_{0.5}\text{TiO}_2$,⁷ this corresponds to a diffusion length of 15 nm. A stoichiometry of $\text{Li}_{1.0}\text{TiO}_2$ has also been suggested,⁹ which in our case would yield a diffusion length of 7.5 nm. These results are in good agreement with values found in literature.^{7,9} It should be noted, however, that no conclusive data concerning the actual composition of Li_xTiO_2 has yet been presented in literature.

Figure 2. Optical transmission at 650 nm after potential steps to intercalation and de-intercalation conditions. Intercalation at -1.8 V vs. SCE results in a transmission decrease of approximately 30% after 1 hour. De-intercalation is a much faster process, a return to the bleached state is accomplished in less than 15 minutes.

To determine the rate of intercalation, stepped-potential measurements have been performed while measuring the optical transmission at 650 nm. Potential steps from +1.0 V to -1.8 V vs. SCE and vice versa have been made to start intercalation and de-intercalation, respectively. The results are presented in Figure 2, showing that intercalation is a much slower process than de-intercalation. This phenomenon has also been observed by other authors,^{3,7} and can be explained in terms of lattice relaxation and expansion effects, and/or energy barriers due to ionic solvation energies of the lithium ions in the electrolyte.⁷ It is interesting to note that for porous nanostructured films both processes are reported to occur with the same rate.¹ The nature of this discrepancy is unclear and calls for further investigation.

Figure 3 shows the differential absorption spectra of the intercalated TiO_2 at various intercalation potentials. All spectra shown are calculated with respect to the absorption spectrum recorded at 0 V vs. SCE, i.e. under de-intercalation conditions. Under intercalation conditions, a bleaching at 320 nm is observed, while at 750 nm a dark coloring occurs. The bleaching at 320 nm can be attributed to a Moss-Burstein shift, i.e. an apparent increase of the bandgap

caused by free electrons filling up the energy levels at the bottom of the conduction band. These free electrons compensate the positive charge carried by the intercalated lithium ions. At potentials between -1.2 V and -1.3 V vs. SCE, a sudden decrease in absorption at 320 nm is observed, accompanied by a increase in absorption at 750 nm. This is shown in Figure 4, where

Figure 3. Differential absorption spectra at various intercalation potentials. All spectra are calculated with respect to the de-intercalated state at 0 V vs. SCE. The spectrum of the sample reduced in argon was recorded using a Cary 2400 spectrophotometer. Measurements on the lithium intercalated samples were performed in a wet electrochemical setup, using a photomultiplier to measure the transmission.

the peak maximum of the differential absorption at 320 nm is plotted as a function of intercalation potential. A possible explanation may be found in a decrease of the density of states around a specific energy in the conduction band, giving rise to a local sharpening of the absorption band edge. Figure 4 also shows the position of the peak maxima, and the peak widths at half height as a function of intercalation potential. The peak maximum shifts to higher energies at stronger intercalation potentials, as would be expected. The peak width, however, does not change significantly. This contrasts with the results of Enright et al.¹⁰, who calculated the effective hole mass for nanocrystalline anatase from the broadening of the peak. So far no satisfactory explanation has been found for this discrepancy, though it points to a difference in electronic structure between porous nanostructured anatase and thin film anatase. Specifically, a higher density of states from some point in the conduction band of thin film anatase is expected to sharpen the absorption band edge, which can lead to a increase in peak height without additional broadening.

The darkening of the intercalated TiO_2 observed at 750 nm indicates the presence of trapped electrons. Possible trap sites are Ti^{4+} , Li^+ and oxygen vacancies. To determine the nature of the sites at which the electrons are trapped, absorption spectra of anatase TiO_2 before and after

reduction at 450°C in argon were recorded. The resulting differential absorption spectrum is shown in Figure 3. An almost identical spectrum is obtained when the reduction is carried out in a hydrogen atmosphere. Comparing reduced TiO_2 to lithium intercalated TiO_2 , a much larger Moss-Burstein shift is present, while no trapped electrons are observed at 750 nm. This suggests that in the case of lithium insertion a significant fraction of the free conduction band electrons is trapped at Li^+ sites. This contradicts previous assumptions made in literature that the absorption band in the near-infrared region can be attributed to intervalence charge transfer between Ti^{4+} and Ti^{3+} species.^{8,9}

Figure 4. Data for the peaks centered around 320 nm in the differential absorption spectrum from Figure 3. Under stronger intercalation conditions the peak position shifts to higher energies, and the peak height increases. Both the peak position (filled circles) as well as the peak height (open squares) show a large change at intercalation potentials around -1.25 V vs. SCE. No significant peak broadening was found as a function of potential.

CONCLUSIONS

Lithium intercalation in thin films of anatase TiO_2 is studied. Assuming a composition of Li_xTiO_2 with x between 0.5 and 1.0, the lithium intercalates over a distance of 7.5 to 15 nm into the TiO_2 . However, since the actual composition across the film cannot be measured directly, assumptions on the composition should be treated with caution. Stepped-potential experiments show the intercalation process to be much slower than the de-intercalation of lithium, which contrasts with the results reported for porous nanostructured anatase. Differential absorption spectra suggest that the coloring of anatase observed on intercalation should be attributed to electron trapping at Li^+ instead of intervalence charge transfer from Ti^{4+} to Ti^{3+} . Furthermore, the spectra for thin film anatase are different from those reported for porous nanostructured anatase. Further investigations are necessary to clarify these interesting discrepancies between thin film and porous anatase TiO_2 .

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